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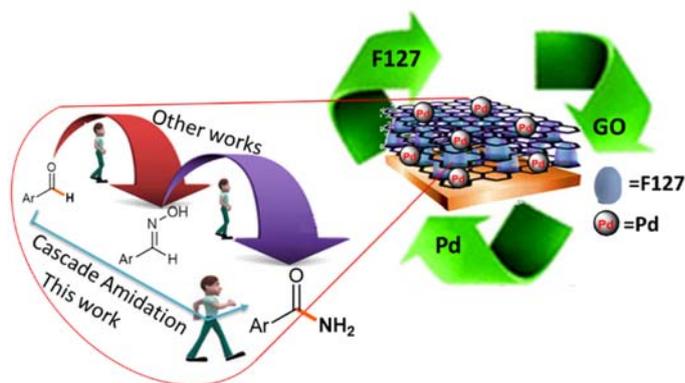
**Exfoliation effect of PEG-type surfactant on Pd supported GO (SE-Pd(nanoparticle)/GO) in cascade synthesis of amides; a comparison with Pd(nanoparticle)/rGO**

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Graphical abstract



**Research highlights**

- Exfoliation of Pd supported GO (SE-Pd<sub>NP</sub>/GO).
- Graphene oxide as advanced support for Pd.
- A cascade method for the synthesis of primary amides.

**Abstract**

In the present investigation, a cascade method for the synthesis of primary amides is discussed by the catalysis of Pd supported onto graphene oxide (Pd/GO) nanosheets. Also, the effect of different polyethyleneglycol-type (PEG-type) polyethers including PEG-300, P123 and F127 on the catalytic activity of Pd/rGO is studied in the reaction of aldehyde and hydroxylamine hydrochloride to give benzamide. Addition of PEG-type polyethers played an important role in raising the catalytic power of Pd(nanoparticle)/GO by exfoliation of GO sheets. The present paper introduces Pd(nanoparticle)/GO as first Pd supported GO for the synthesis of primary amides through this method. This catalyst was highly active, efficient, tolerant, and environmentally benign in one-pot conditions with recyclability at least for 8 runs. Also, this study suggests the prevailing catalytic activity of Pd(nanoparticle)/GO rather than Pd(nanoparticle)/rGO in a comparative experiment.

**Keywords:** Cascade amidation; Pd(nanoparticle)/GO; reduced graphene oxide; polyethers; exfoliation.

**Introduction**

Amide functional groups are placed within a vast range of crucial organic materials including polymers, peptides, protein, and pharmaceutical compounds [1]. Synthesis of amides by traditional procedures through the reaction of carboxylic acids (or their activated derivatives such as chlorides, anhydrides or esters) and amine, could be inconvenient and unselective in a total synthesis or a densely functionalized compounds. Hence, many other methods are developed [2-4]. Among them and based on “green chemistry” desire, cascade-type and tandem amidation processes are the considerable part of recent developments. Their easier economical processing,

costly-reasonable and available starting materials are the advantages to others. Some catalysts are developed for efficient synthesis of amides [5-8]. However, most of the catalysts could not be recovered and reused for next times. Recently we developed copper grafted SBA-15 as a recyclable catalyst in amidation reaction using aldehydes, hydroxylamine hydrochloride in a basic condition [9]. Now, due to the fact that basic condition is not suitable for silica structure of SBA-15 support, we aimed to extend our research area to new types of catalytic systems based on Pd which can be produced and stabilized by efficient carbon-based materials such as graphene oxide (GO) and reduced graphene oxide (rGO) nanosheets.

Pd-based heterogeneous nanocatalysts [10] is of our interests which are previously developed by our group [11-15]. Pd based nanocatalysts are generally used in C-C and X-C (X = N, S, O) coupling reactions such as C-N bond coupling (e.g. primary amide and arylhalide) [16]. However, there are few reports that a Pd-based material has catalyzed the synthesis of primary amides through the condensation of hydroxylamine hydrochloride and benzaldehyde in a cascade method. On the other side, Pd-based catalysts suffer from aggregation and deactivation in each run [17-19]. Necessity of Pd species engagement with a suitable ligand or support is inevitable in order to obtain an efficient, recyclable, and atom efficient catalyst [20-24].

Pd/carbon based materials are promising catalysts in Pd-catalyzed reaction from the point view of their recyclability, high yield of production and stability of the catalyst in harsh acid/base conditions [25]. Due to suitable interaction of Pd species with carbon based structures, Pd deposition happens on the surface of carbon based materials. Bulkier types of Pd/carbon catalysts may suffer from higher catalytic amount of Pd/carbon and their lower recyclability and therefore earlier aggregation of Pd species [26-28]. Deposition of Pd on graphene oxide (Pd/GO) and reduced graphene oxide (Pd/rGO) are of efficient methods rather to other Pd/carbon based catalysts

[29-32]. However in comparison, rGO and Pd/rGO nanosheets exhibit more tendency to self-assembly rather to GO and Pd/GO in relatively higher concentrations and temperatures especially in H<sub>2</sub>O. This may restrict the efficiency of Pd/rGO in some cases by decreasing the catalytic surface area. Recently in our group, we have established the study of Pd/GO and Pd/rGO exfoliation by surfactant and their catalytic activity in the presence of various surfactants. In this work, we found that addition of poly ethyleneglycol-type (PEG-type) polyetheric surfactant during the catalysis of Pd(nanoparticle)/rGO makes a remarkable change in the catalytic activity.

Transition metal-catalysed rearrangement of aldoxime to amide, which is usually catalyzed by transition metal ions such as Cu [33], Zn [34], Ru [35], Rh [36], and Au [37], is a strategy of primary amide synthesis. In the present paper, we have studied the catalytic activity of Pd supported GO in the presence of different PEG-type polyethers. In this cascade method, synthesis of primary amides from simple aromatic aldehydes and hydroxyl amine were accomplished. To the best of our knowledge, this is the first report of a Pd supported catalyst in the synthesis of primary amides through this reaction pathway. Homogeneous Pd(OAc)<sub>2</sub> salt is the only Pd-based catalyst for the direct conversion of benzaldehyde to benzamide [38]. Hence, we applied PEG-type polyethers for intense exfoliation of Pd/GO to acquire homogeneous behaviour on this catalyst while keeping itself a recoverable and reusable catalyst.

## **Results and Discussion**

### *Catalyst synthesis and characterization*

Synthesis of the catalyst, Pd(nanoparticle)/GO, was achieved by oxidizing the graphitic carbon to graphene oxide following our method [13, 15]. Then, in the presence of ultrasonic irradiation (for exfoliation of GO), Pd species were supported onto GO sheets. For the synthesis of

Pd(nanoparticle)/rGO, the reduction of GO and Pd ions were performed through addition of NaBH<sub>4</sub> as a reductant. However after reduction, tendency towards aggregation of graphene sheets was high. Sonication of the solution before addition of Pd source has a drastic effect on the uniform distribution of Pd particles onto surface of well exfoliated graphene sheets. On the other hand, using ultrasonic irradiation during the reaction for long-time reactions is restricted and is not suitable. Therefore to keep the Pd(nanoparticle)/GO and Pd(nanoparticle)/rGO sheets exfoliated, we used polyethers to stabilize the exfoliation state of these sheets. For example, the obtained Pd(nanoparticle)/GO was kept exfoliated by surfactant of F127, to produce SE<sub>F127</sub>-Pd(nanoparticle)/GO. A general synthetic pathway for the synthesis of SE<sub>F127</sub>-Pd(nanoparticle)/GO is illustrated in Scheme 1.

To characterize the physicochemical properties of the Pd(nanoparticle)/GO, FTIR spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray analysis (SEM-EDS) and atomic absorption spectroscopy (AAS) were applied. To our surprise, supporting Pd<sup>2+</sup> leads to reduction and supporting of Pd nanoparticles on the surface of GO as observed by SEM and TEM images. Accordingly, in this material, Pd nanoparticles are dispersed on the surface of GO nanosheets. The estimated average particle size of deposited Pd nanoparticles by SEM and TEM is around 15-22 nm (Figure 1 and Figure 2). The particle size histogram of Pd(nanoparticle)/rGO shows that particle size ranged from 14 nm to 23 nm (Fig. 1b and Fig. 2b).

Fig. 3a shows the XRD patterns of Pd(nanoparticle)/rGO and Pd(nanoparticle)/GO. SEM-EDS of Pd(nanoparticle)/GO is also shown in this figure. SEM-EDS analysis was performed to confirm the composition of the as-prepared products (Figure 3b). Accordingly, a wide peak around  $2\theta =$

$24^\circ$  could be assigned to rGO sheets [39], which in the case of Pd(nanoparticle)/GO, the wide peak can be observed around  $2\theta = 10^\circ$ . A peak around  $2\theta = 10^\circ$  can be also assigned to GO sheets in Fig 3a. The EDS analysis, the elemental analysis, confirms the existence of elements Pd, C and O in Pd(nanoparticle)/GO.

Comparison of FTIR spectrum of Pd(nanoparticle)/rGO and Pd(nanoparticle)/GO exhibits the formation and preservation of rGO chemical structure after Pd supporting. In FTIR of Pd(nanoparticle)/rGO, a broad band at  $3431\text{ cm}^{-1}$  may be attributed to the hydroxyl and carboxylic groups. A peak at  $1108\text{ cm}^{-1}$  can be assigned to C-O bonds. A peak at  $1574\text{ cm}^{-1}$  is owing to C=O bonds. Some peaks in the range of  $2870\text{-}2969\text{ cm}^{-1}$  relates to the existence of aliphatic C-H bonds which are generated following to reduction of some groups in GO (Figure 4).

#### *Catalyst tests*

For cascade amidation, as expected, we needed for well-exfoliation of Pd(nanoparticle)/GO sheets followed by excellent catalysis. Thus, we chose three types of PEG-type polyethers to exfoliate Pd(nanoparticle)/GO sheets during the catalysis, which includes triblock copolymers of PEO-PPO-PEO (P123 and F127) and pure polyethylene glycol (PEG-300). The only difference between P123 and F127 is in their number of monomers, in which F127 (average number of monomers = 265) has a longer chain compared to P123 (average number of monomers = 110). And the main difference between PEG-300 with two of P123 and F127 is that the later ones have propylene at the middle and ethylene at both sides while in the case of PEG-300, a homopolymer of ethylene oxide with 300 monomers can be found.

The presence of propylene causes to produce a hydrophobicity at the middle (propylene motif) of P123 and F127 and different micellar behaviours in aqueous phase while PEG-300 doesn't have

such property [40]. Regarding to these differences, they were added to solution of Pd(nanoparticle)/GO to monitor their impact on exfoliation and catalytic behaviour of Pd(nanoparticle)/GO sheets in the amidation of benzaldehyde under the similar conditions. Pd(nanoparticle)/GO sheets tend to aggregate and self-assemble in the absence of ultrasonic (US) or any additive. These three polyethers can well-exfoliate the Pd(nanoparticle)/GO sheets in the absence of any reactants which are similar, while in the presence of reactants and other additives, F127 acted well both in exfoliation and catalytic activity. This result shows that the higher number of monomers rather to P123 has a drastic effect on the obtained results. Also in the case of PEG-300, which their number are near, in spite of well-exfoliation of Pd(nanoparticle)/GO sheets it shows that the middle hydrophobic block of F127 and side blocks' hydrophilicity have made a balance in hydrophobicity and hydrophilicity of the reaction media which indeed both are indispensable (Fig. 5).

In the presence of these three selected exfoliating agents, Pd(nanoparticle)/rGO was also put into examination. To our surprise, these polyethers had no remarkable exfoliating effect on the Pd supported reduced graphene oxide sheets at higher temperature. We observed that the higher temperature enhances the interactions of rGO sheets and polyethers are not capable of dominating these interactions. Therefore, we set aside the further study of Pd(nanoparticle)/rGO catalytic behaviours in the amidation reaction.

Once investigation on the exfoliation effect of Pd(nanoparticle)/GO was accomplished, we studied the other effective parameters on the catalytic behaviour of Pd(nanoparticle)/GO in the presence of F127 (F127 surfactant exfoliated Pd(nanoparticle)/GO = SE<sub>F127</sub>-Pd(nanoparticle)/GO). Scheme 1 indicates a general route to manufacture and use of catalyst in the amidation syntheses. The

amidation reaction in this work is a cascade-type method for converting the benzaldehyde to benzamide. In this case, hydroxylamine hydrochloride is added to aldehyde and oxime forms initially. Then after a required reaction time, it converts to benzamide. And hence, we have developed the chemistry of primary amide synthesis by the catalysis of Pd nanoparticles which are supported onto GO sheets.

All reactions were optimized by benzaldehyde and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  as model reaction. Our attempt was to engage our catalytic system ( $\text{SE}_{\text{F127}}\text{-Pd(nanoparticle)/GO}$ ) for the synthesis of primary amides. Several parameters including base, solvent, and reaction time and temperature were carefully examined on this reaction. Some of them are represented in Table 1. In this optimization, DMSO indicates excellent results compared to other solvents during 48 h.  $\text{K}_2\text{CO}_3$  and  $\text{Cs}_2\text{CO}_3$  had mutual effect on the reaction yield. Therefore owing to economical reason,  $\text{K}_2\text{CO}_3$  was preferred. Once investigation of this matter, we studied the other effective parameters on the catalytic behavior of  $\text{Pd(nanoparticle)/GO}$  in the presence of F127 (F127 surfactant exfoliated  $\text{Pd/GO} = \text{SE}_{\text{F127}}\text{-Pd(nanoparticle)/GO}$ ). Scheme 1 indicates a general route to manufacture and use of catalyst in the amidation syntheses. The amidation reaction in this work is a cascade-type method for converting the benzaldehyde to benzamide. In this case, hydroxylamine hydrochloride is added to aldehyde and oxime forms initially. Then after a required reaction time, it converts to benzamide. And hence, we have developed the chemistry of primary amide synthesis by the catalysis of Pd nanoparticles which are supported onto GO sheets.

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After finding the optimized conditions, other derivatives of primary amides were synthesized according to the optimized conditions. Accordingly, DMSO was selected as optimized solvent, F127 as a superior exfoliating agent and  $K_2CO_3$  as the suitable base. Thus, other derivatives of benzamide were synthesized at 120 °C during 48-54 h (Table 2). Good to excellent yields of products were obtained using aromatic aldehydes bearing electron-donating (Table 2, entry 2-5) or electron-withdrawing (Table 2, entry 6-10) functional groups. Ortho-substituted aryl aldehydes (Table 2, entry 11) gave comparably lower isolated yields than those of para-substituted compounds, which can be attributed to steric effects. Similar results were obtained with the reactions of heteroaromatic aldehydes including thiophene-2-carbaldehyde (Table 2, 12).

F127 was found to be more versatile and efficient for this system and therefore, all Pd(nanoparticle)/rGO exfoliations during the amidation reactions were performed by F127. The yields were comparable with that of homogenous  $Pd^{2+}$  which is previously reported [38]. This comparison indicate a competitable results of the heterogeneous catalyst against homogeneous Pd species.

It is to be noted here that for iodine derivative of benzaldehyde, when we performed the reaction with p-iodobenzaldehyde under the optimized conditions, the main product was homo-coupled biaryl compound (Scheme 3).

Recyclability study of Pd(nanoparticle)/GO in amidation with benzaldehyde and  $NH_2OH$  as representative for other derivatives were investigated in further step. This investigation

demonstrated that the catalyst except F127 has ability to be recovered and reused at least for 8 runs. Figure 6 exhibits obtained yields in each run for each method and 8th run TEM image in which the major ratio of Pd<sup>2+</sup> ions has been reduced converted to aggregated Pd nanoparticles. As a result, the related decrease in yields after several runs can be attributed to aggregation of Pd nanoparticles and subsequently, its catalytic deactivation. Atomic absorptions spectroscopy (AAS) results also reveals no significant leaching of Pd (less than 10 wt% from total amount of Pd in Pd/GO) from the surface of graphene oxide.

Due to the fact that there are few reports for these reactions with palladium and we haven't investigated the exact mechanism of amidations, we have speculate a possible mechanism for this process. On the other hand, there are some mechanistic studies and reports that can reinforce our proposed mechanisms [17, 41, 42]. The mechanism (see SI) indicate two possible pathways to amide products. In the previous reports, it is claimed that because the labeled oxygen atom on hydroxyl amine finally appears at carbonyl oxygen of the product, amide, the pathway of mechanism is majorly pass through path 2, where a cyclic intermediate forms [43]. This proposed mechanism is mostly for transition metal catalyzed conversion of aldoxime to primary amide.

Also, the catalytic system was compared by other catalysts in this cascade amidation of benzaldehyde with hydroxylamine hydrochloride (Table 3). This study demonstrated that SE<sub>F127</sub>-Pd(nanoparticle)/GO has superior activity rather to other types of Pd supported catalysts. Based on this test, Pd(nanoparticle)/GO was more active than Pd(nanoparticle)/rGO which can be due to the fast aggregation of rGO sheets at higher temperature in the presence of reactants. Aggregation cause to entrapment of Pd between rGO sheets. In this study, there was 94% of the reactant

conversion in which the only 4% of it stopped in aldoxime which shows a higher selectivity towards the product.

## Conclusion

Pd(nanoparticle)/GO as a first Pd-supported nanocatalyst was applied in the cascade synthesis of amides through the reaction of aromatic aldehyde and  $\text{NH}_2\text{OH}\cdot\text{HCl}$  in oxime formation and then beckman rearrangement in one-pot conditions. GO sheets were highly exfoliated during the catalysis through various polyethers and converted to a highly dispersive heterogeneous nanocatalysts. Among polyethers, F127 acted better in the results and exfoliation behaviour. This catalytic system was successfully applied as a relatively green, recyclable, and efficient system in cascade primary amide synthesis and single-pot amidation. Cascade reactions were advantageous to their non-cascade corresponding reactions. Some possible mechanisms were proposed for cascade amidation of aromatic aldehydes.

## Experimental

### *Experimental and Catalyst Characterization*

All reagents were purchased from Merck (Germany), Fluka (Switzerland) and Sigma-Aldrich and used without further purification. A multi-wave ultrasonic generator (Sonicator-3000; Misonix Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn). GC analyses was recorded on GC Chrom (Teif Gostar Faraz Co., Iran)

*Preparation of SE- Pd(nanoparticle)/GO*

Graphite oxide was prepared from graphite according to the Hummers method [45]. Briefly, graphite was oxidized by treating with  $\text{KMnO}_4$  and  $\text{NaNO}_3$  in concentrated  $\text{H}_2\text{SO}_4$  to form graphite oxide, and 2 g of the obtained graphite oxide was exfoliated into graphene oxide (GO) by 400 mL of water under sonication for 2 h. The conductivity of GO sheets after sonication was  $5700 \text{ S}\cdot\text{cm}^{-1}$ . After sonication, a solution of  $\text{PdCl}_2$  (0.12 g in 5 mL saline solution) was added to mixture in the presence of ultrasonic irradiation for 2h. The purified Pd(nanoparticle)/GO (2 g) was quickly dispersed in F127/DMSO solution for further use as the catalyst [2 g Pd(nanoparticle)/GO in 50 mL pure DMSO in the presence of polyether (6 wt%)]. The amount of Pd loaded on GO sheets was measured by AAS which was 3.8 wt%.

*Preparation of SE-Pd(nanoparticle)/rGO*

Synthesis of SE-Pd(nanoparticle)/rGO was achieved according to SE-Pd(nanoparticle)/GO procedure except GO was first reduced to rGO by required amount of  $\text{NaBH}_4$ . After separation and washing rGO, it was applied for Pd supporting and the dispersion was prepared according to procedure of SE-Pd(nanoparticle)/GO.

*General procedure for synthesis of primary amides from aldehyde*

In a typical method, benzaldehyde (1.0 mmol), hydroxylamine hydrochloride (1.5 mmol), potassium carbonate (2.5 mmol) and 0.5 mL of as-prepared  $\text{SE}_{\text{F127}}$ - Pd(nanoparticle)/GO in DMSO were added to reaction media in the presence of 1.5 mL DMSO. The reaction was allowed to stir at  $120^\circ\text{C}$ . Upon reaction completion, the catalyst was separated by centrifuge and the organic residue was extracted with dichloromethane and evaporated under reduced pressure. The organic

residue was purified by column chromatography. All yields were reported based on isolated amount. All products are known and identified by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  spectrum and physical properties.

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### Supplementary data

Supplementary Information (SI) of this article can be found, in the online version, at [www.elsevier.com](http://www.elsevier.com).

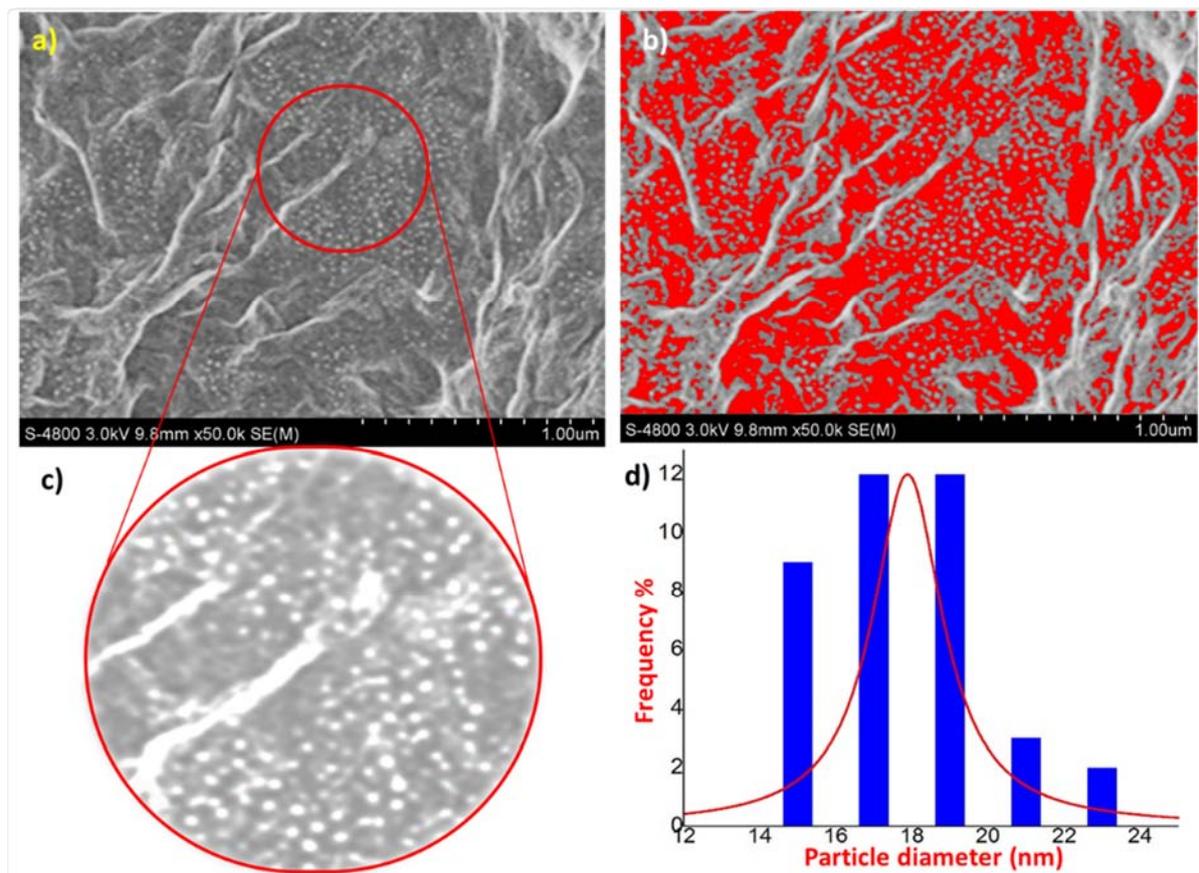
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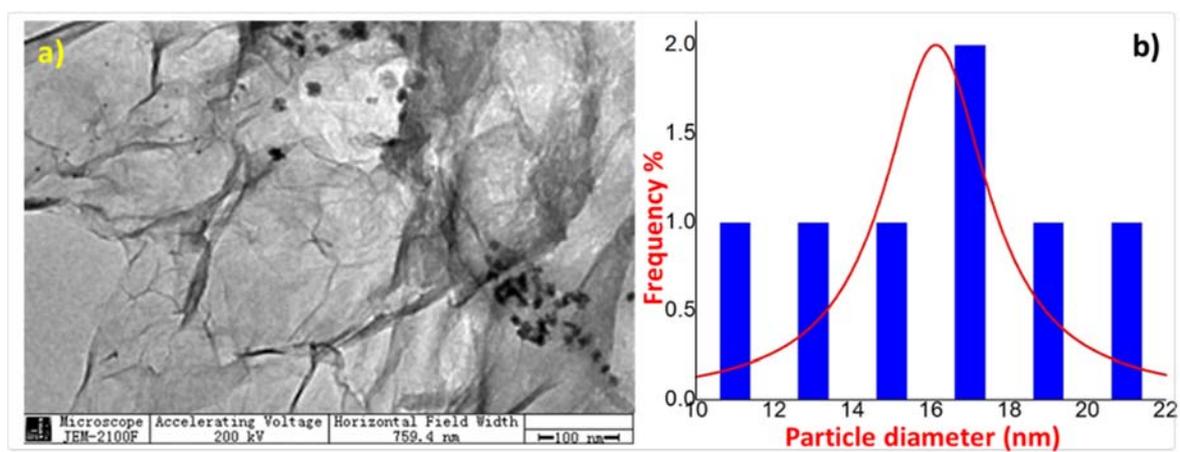
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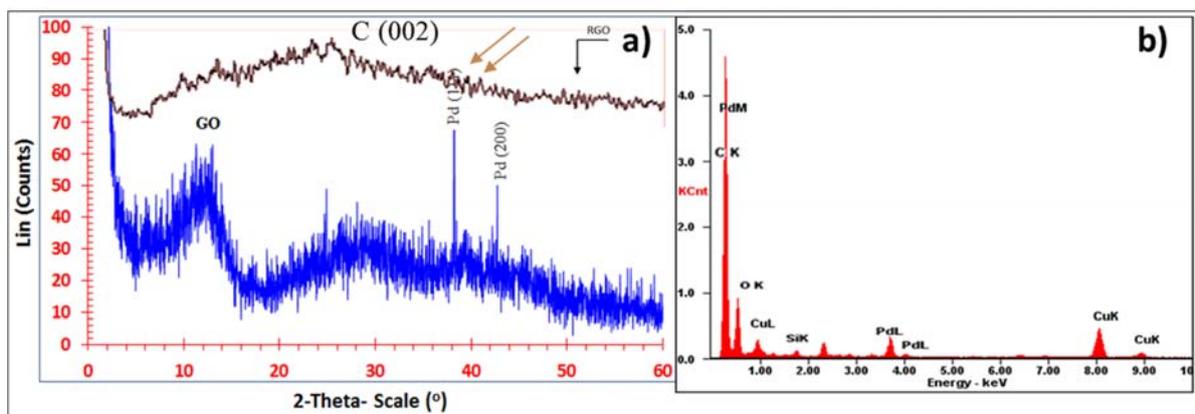
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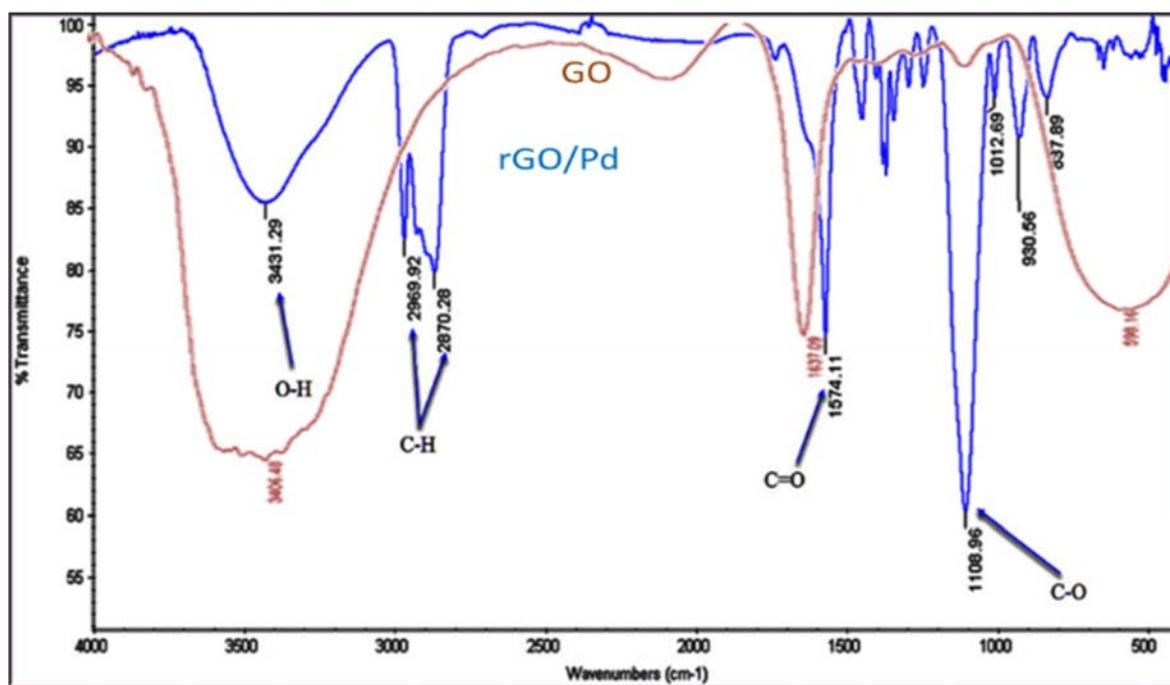
**Fig. 1.** SEM image (a), Binary-SEM (b) and reflected/zoomed SEM Pd(nanoparticle)/GO and its (d) particle size histogram.



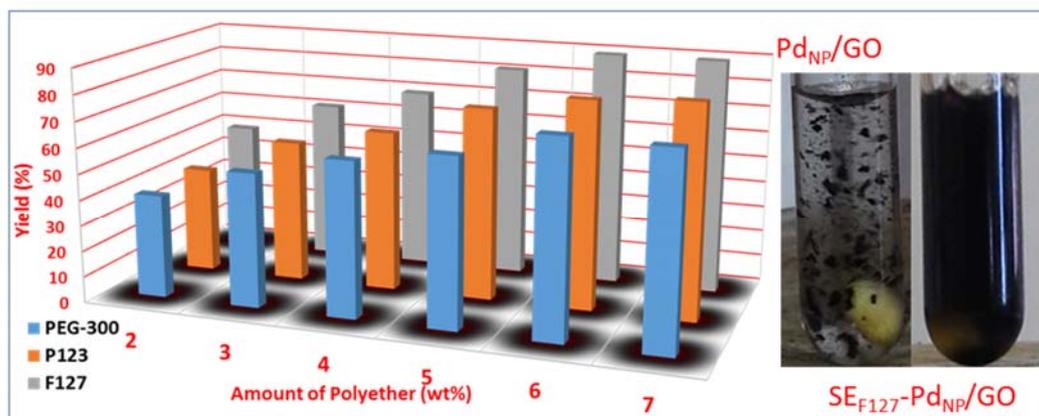
**Fig. 2.** TEM image (a) and its particle size histogram (b).



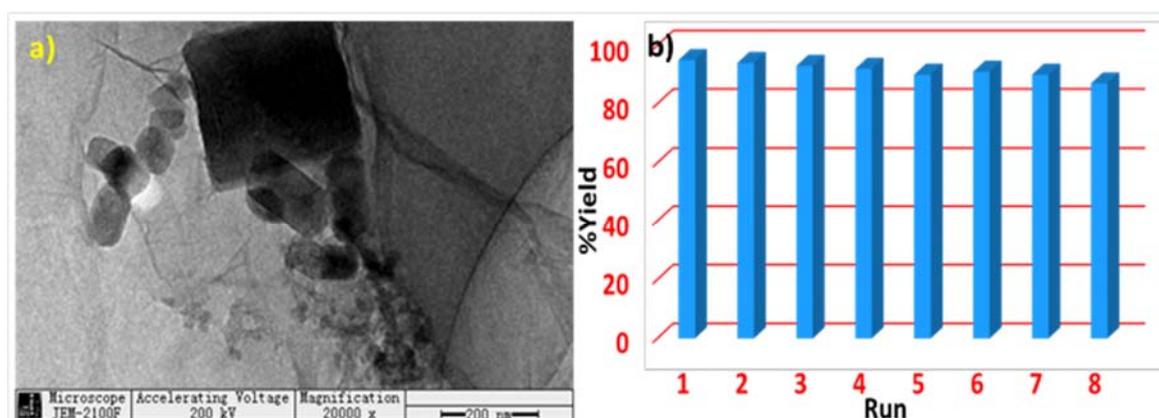
**Fig. 3.** XRD patterns of Pd(nanoparticle)/GO and Pd(nanoparticle)/rGO (a). SEM-EDX of Pd(nanoparticle)/GO (b).



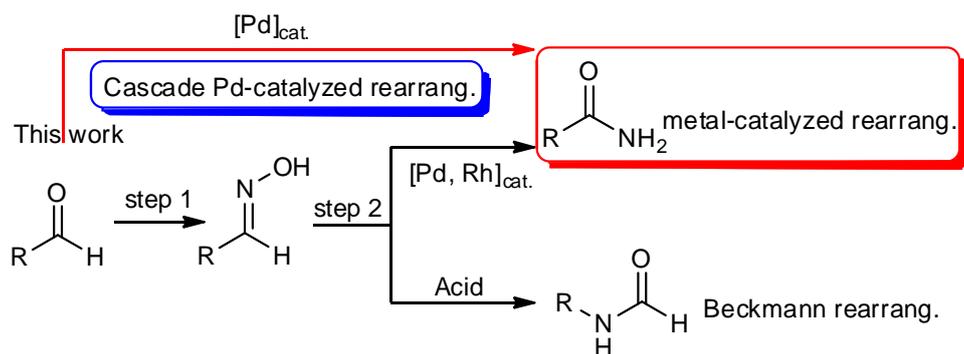
**Fig. 4.** FTIR spectra of Pd(nanoparticle)/GO and Pd(nanoparticle)/rGO.



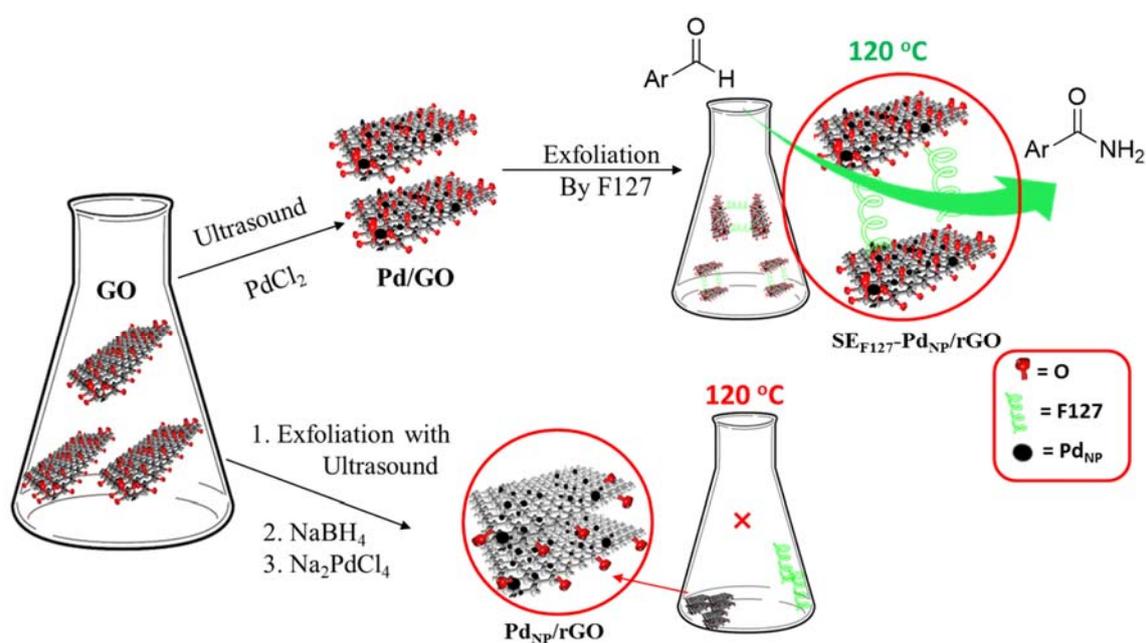
**Fig. 5.** Effect of surfactant type and amount on the catalytic activity of Pd(nanoparticle)/GO in amidation of benzaldehyde (1 mmol) and hydroxylamine hydrochloride (1.5 mmol), potassium carbonate (2.5 mmol) and 0.7 mol% Pd at 100 °C during 48 h in 2 mL DMSO mixture.



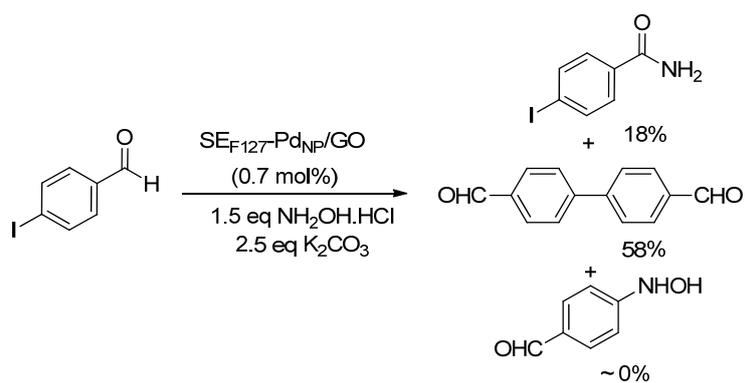
**Fig. 6.** a) TEM image of Pd(nanoparticle)/GO after 8<sup>th</sup> run. b) Recyclability study of Pd(nanoparticle)/GO in amidation with benzaldehyde (5 mmol) and NH<sub>2</sub>OH.HCl (7.5 mmol) and K<sub>2</sub>CO<sub>3</sub> (12.5 mmol) in the presence of Pd(nanoparticle)/GO /F127 [Pd (0.7 mol%) and F127 (6 wt%)] during 48 h at 120 °C.



**Scheme 1.** Rearrangements of oximes to amides and cascade amidation.



**Scheme 2.** Preparation and application of SE<sub>F127</sub>-Pd(nanoparticle)/GO.



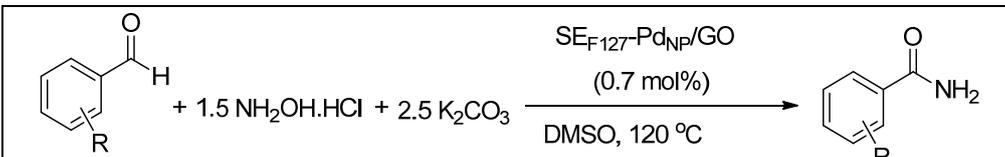
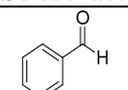
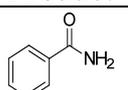
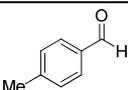
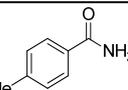
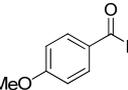
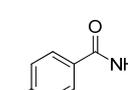
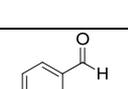
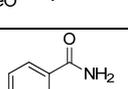
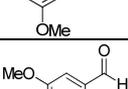
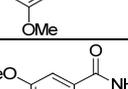
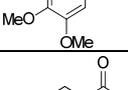
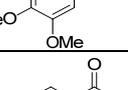
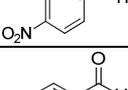
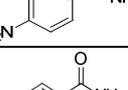
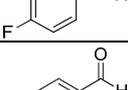
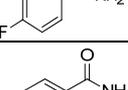
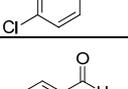
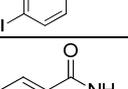
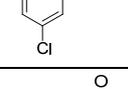
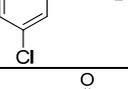
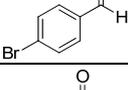
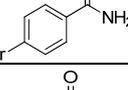
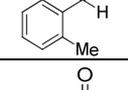
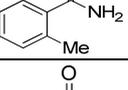
**Scheme 3.** Application of *p*-iodobenzaldehyde for amidation test.

**Table 1.** Investigation of SE<sub>F127</sub>- Pd(nanoparticle)/GO for optimizations.

Entry	Base	Solvent <sup>a</sup>	Time (h)	T (°C)	Yield (%) <sup>b</sup>
1	K <sub>2</sub> CO <sub>3</sub>	DMSO	44	80	83
2	K <sub>2</sub> CO <sub>3</sub>	Toluene	48	130	Trace
3	K <sub>2</sub> CO <sub>3</sub>	H <sub>2</sub> O	100	100	70
4	Na <sub>2</sub> CO <sub>3</sub>	DMSO	100	130	82
5	K <sub>2</sub> CO <sub>3</sub>	DMSO	48	120	90
6	Cs <sub>2</sub> CO <sub>3</sub>	DMSO	48	100	91
7	KOH	DMSO/H <sub>2</sub> O	72	100	34
8	Cs <sub>2</sub> CO <sub>3</sub>	DMSO/H <sub>2</sub> O	72	120	74
9	K <sub>2</sub> CO <sub>3</sub>	DMSO/H <sub>2</sub> O <sup>c</sup>	72	120	71

<sup>a</sup>) The solvents in this section were first used in the dispersion of Pd/GO and then used in the reactions. <sup>b</sup>) Isolated yields. <sup>c</sup>) 0.5 mL of dispersed SE<sub>F127</sub>- Pd(nanoparticle)/GO (containing 0.7 mol% of Pd and 6 wt% of F127) was used per 1 mmol of benzaldehyde, 1.5 mL DMSO was added in entry 9 (Other conditions include 1 mmol of benzaldehyde, 1.5 mmol of NH<sub>2</sub>OH.HCl, and the amount of base for each reaction test is 2.5 mmol).

**Table 2.** Synthesis of primary benzamides under the catalysis of SE<sub>F127</sub>-Pd(nanoparticle)/GO.<sup>a</sup>

				
Entry	Substrate	Product	Time (h)	Yield (%)
1			48	90
2			48	80
3			48	85
4			48	87
5			54	85
6			48	92
7			48	90
8			48	84
9			48	86
10			48	61
11			50	74
12			48	81

<sup>a</sup> Reaction conditions include 1 mmol of benzaldehyde, 1.5 mmol of NH<sub>2</sub>OH.HCl, 2.5 mmol of K<sub>2</sub>CO<sub>3</sub>, 0.5 mL water dispersed SE<sub>F127</sub>-Pd(nanoparticle)/GO (Pd, 0.7 mol% and F127, 6 wt%) in the presence of 1.5 mL DMSO at 120 °C.

**Table 3.** Catalytic comparison of Pd species in the amidation.<sup>a</sup>

Entry	Catalyst	Time (h)	Conv. (%)	Yield (%) <sup>b</sup>	Ref.
1	Pd/C (10 wt%)	10	70	50	[44]
2	SBA-15/PrEn-Cu	10	90	70	[44]
3	SE <sub>F127</sub> -Pd/GO	72	94	90	This work <sup>c</sup>
4	SE <sub>F127</sub> -Pd/rGO	72	92	35	This work

<sup>a</sup> Reaction is under optimum conditions. <sup>b</sup> Isolated yields. <sup>c</sup> Similar to preparation procedure of SE<sub>F127</sub>-Pd/rGO.