

Catalysis Science & Technology

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Efficient tandem aqueous room temperature oxidative amidations catalysed by supported Pd nanoparticles on graphene oxide

Sadegh Rostamnia,^{a,*} Esmail Doustkhah,^{a,b} Habib Golchin-Hosseini,^a Behzad Zeynizadeh,^{b,*} Hongchuan Xin,^{c,*} Rafael Luque^d

^a *Organic and Nano Group (ONG), Department of Chemistry, Faculty of Science, University of Maragheh, PO Box 55181-83111, Maragheh, Iran. Email: rostamnia@maragheh.ac.ir; srostamnia@gmail.com*

^b *Department of Chemistry, Faculty of Science, Urmia University, Urmia 57159-165, Iran. Email: bzeynizadeh@gmail.com*

^c *Key Laboratory of Biofuels, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China. Email: xinhc@qibebt.ac.cn*

^d *Departamento de Química Organica, Universidad de Cordoba, Edificio Marie Curie, Ctra Nnal IV, Km 396, E-14014, Cordoba, Spain. E-mail: q62alsor@uco.es; Fax: +34 957212066; Tel: +34 957211050*

Abstract: Pd nanoparticles deposited onto graphene oxide nanosheets (SE-GO/Pd_{NPs}) were found to successfully promote two oxidative processes for the synthesis of amides, providing alternative possibilities to these important compounds. SE-GO/Pd_{NPs} exhibited excellent activities with an optimum efficiency in tandem one-pot conversion of alcohol to amides in the presence of various amines.

Keywords: Oxidative amidations; tandem oxidation; SE-GO/Pd_{NPs}; graphene oxide (GO); surfactant exfoliated GO.

Introduction

Heterogeneous catalysts possess inherent advantages as compared to homogeneous catalysts including recyclability, easy work-up and consequently cleaner and often also greener reaction workup [1]. Importantly, the use of recyclable heterogeneous catalytic systems may be easier implemented in industrial scale, especially in continuous flow processes [2]. The stability and activity of certain heterogeneous catalysts can be however compromised by reaction conditions (i.e. temperature, pressure, acidic media) for which these critical parameters needs to be carefully designed/controlled in a catalytic process [3]. Nanotechnology and nanocatalysis opened up a new concept in heterogeneous catalysis in which the design of nanomaterials/nanocatalysts based on nanoparticles is able to provide highly active and stable catalysts for a number of chemistries due to the excelling properties of some of the catalyst active sites in the nanoscale (i.e. enhanced selectivity and activities) [4].

Amide functionalities are ubiquitously present in a large number of organic compounds, polymers, natural and pharmaceutical compounds. Synthesis of amides using conventional protocols (i.e. reactions of acyl halides or anhydrides with and amines) could be inconvenient especially in larger scales or in a total synthetic approach. While alternative methods have been considered in recent years [5], oxidative amidations have provided considerable advances in the field in recent years. Advantages of these protocols include a simple and cost-competitive method based on cheap and available starting materials [6]. A range of homogeneous catalysts for efficient syntheses of amides have been recently developed [7-10]. However, these catalysts are generally not heterogeneous and recyclable. A recent copper grafted SBA-15 was reported as an efficient catalyst for synthesis of primary amides via a Beckmann-type rearrangement of oximes [11]. Due to the fact that basic media is not suitable for SBA-15-type materials, we

aimed to turn our attention to the synthesis of secondary and tertiary amides via a tandem green oxidative-amidation using Pd nanoparticles supported on graphene oxide as a robust and stable carbon-based nanosheet support (surfactant exfoliated Pd-supported graphene oxide, SE-GO/Pd_{NPs}).

Tandem methods for oxidative amidation reactions directly from alcohols can be appealing pathways to decrease the consumption of organic compounds, synthetic costs as well as avoiding tedious and complex synthetic methods. In this regard, Milstone and co-workers found that the reaction of primary amine and alcohols generates amide and molecular hydrogen with the use of ruthenium based complexes [12]. Also, Kobayashi and co-workers reported Au nanoparticles and Au-supported systems as heterogeneous catalysts for the tandem synthesis of various types of aliphatic, aromatic and cyclic (lactame) amides directly from alcohols under aerobic conditions [13-15]. The same group also found that the gold nanoparticle size possessed different catalytic effects while most interestingly appropriate particle sizes could directly convert alcohols to amides in the presence of amines under aerobic conditions [16].

The design new or develop Pd decorated heterogeneous nanocatalysts has been one of the major interests from our groups [17-21]. Pd based nanocatalysts are generally used in coupling chemistries [22-24]. However, there are few reports on oxidative amidations catalyzed by palladium-based catalysts which generally suffer from nanoparticle aggregation and catalyst deactivation in each run [25-27]. Recently palladium supported graphene oxide (Pd/GO) synthesized by reduction of Pd ions on the surface of GO was reported to be an efficient, recyclable and convenient catalytic system for a range of heterogeneously catalysed reactions [28-31]. This is due to suitable interaction of Pd species with carbon based structures [32, 33]. However, GO and Pd/GO nanosheets tend to self-assembly in relatively higher concentrations

and temperatures especially in aqueous media. Recently, we have established the study of GO and Pd/GO exfoliation by surfactant and catalytic activity in the presence of surfactants. The addition of a surfactant during Pd/GO catalysed reaction can provide remarkable improvements and activation of catalytic sites by exfoliation of the GO sheets [34].

In this work, we aim to report the excellent catalytic activity of Pd/GO in the presence of different surfactants for various types of oxidative amidation reactions, namely two approaches. Secondary and tertiary amides were produced from oxidative reactions of aldehydes and various amines (Figure 1, Method A) as compared to a tandem method from *in situ* production of aromatic aldehydes from benzylic alcohols followed by reaction with amines (Figure 1, Method B). Method B is a promising strategy to directly convert alcohols to amides in a one-pot approach [27, 35, 36]. In spite of previous reports employing homogeneous palladium catalysts and/or Pd-containing homogeneous metal mixtures, this is the first report of Pd supported NPs in oxidative amidation reactions.

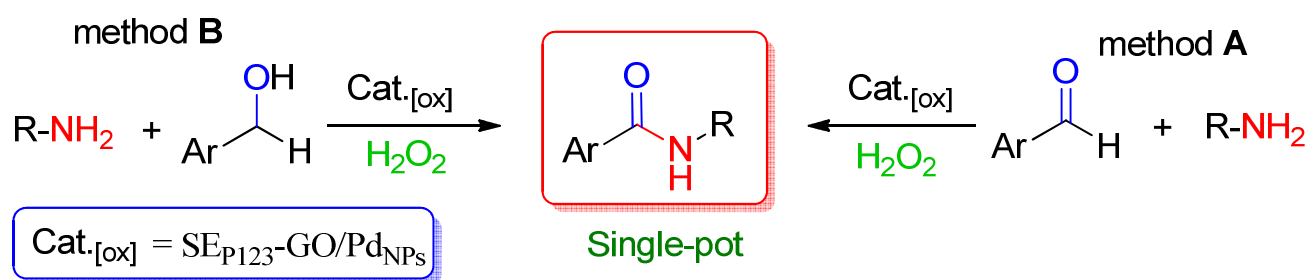


Figure 1. Schematic illustration of our work.

Results and discussion

SEM and TEM images of the synthesized GO/Pd_{NPs} showed that Pd nanoparticles are uniformly dispersed on the surface of GO nanosheets. The estimated average particle size of deposited Pd_{NPs} by SEM and TEM is around 21-22.5 nm (Fig. 2 and Fig. 3). The particle size histogram of GO/Pd_{NPs} shows that particle size ranged from 18 nm to 34 nm (Fig. 2b and Fig. 3b).

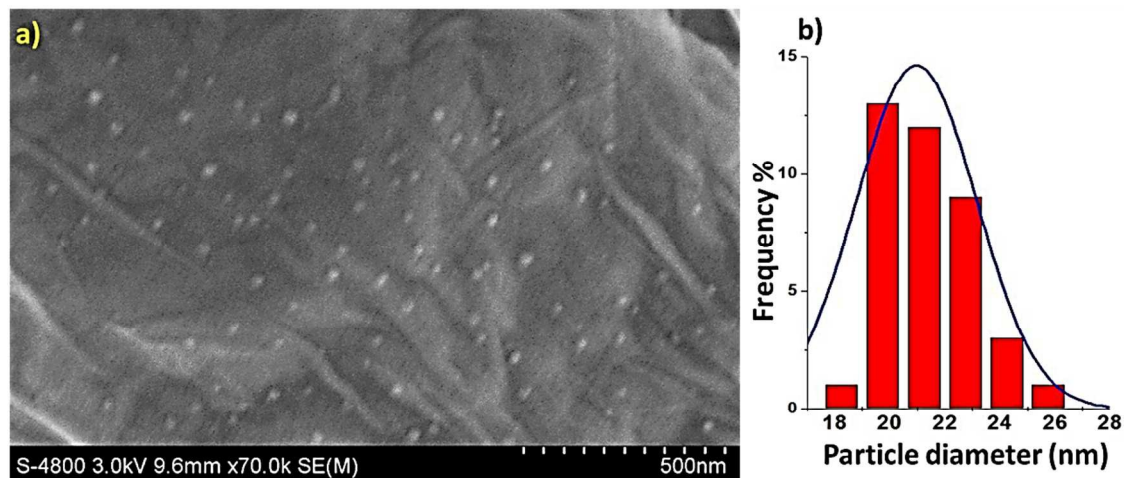


Figure 1. SEM images of (a) Pd_{NPs}-GO and (b) particle size histogram.

FT-IR spectra of GO shows two distinct peaks at 598 and 1637 cm^{-1} , and a broad band ranging in 3300-3600 cm^{-1} (related to -OH of surface). After reduction of Pd²⁺ ions on the surface of rGO, relative functional groups for both GO and rGO can be seen. However, the XRD analysis proves that the final structure of graphene is GO (supporting information).

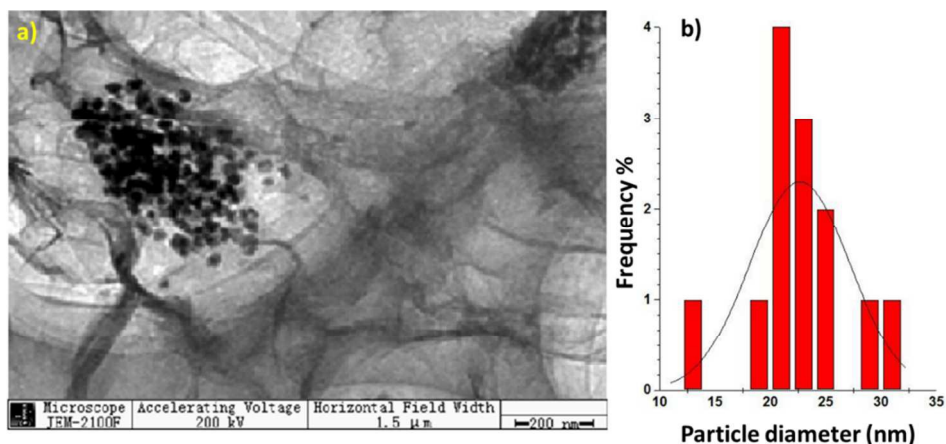


Figure 2. TEM images of (a) Pd_{NPs}-GO and (b) particle size histogram.

Fig. 4 shows the XRD patterns of rGO, 7th reused Pd_{NPs}-GO and EDX of Pd_{NPs}-GO (see also Fig. 1). In Fig 4a a wide peak at $2\theta = 24^\circ$ could be assigned to rGO sheets [37] and for Pd_{NPs}-GO, a peak around $2\theta = 11^\circ$ assigned to GO sheets in Fig 4a, which in that the well-defined peaks around 39° , 44° can be assigned to (111) and (200) crystal planes of Pd-nanoparticle. EDX analysis was performed to confirm the composition of the as-prepared products (Fig. 4b). The EDX analysis, the elemental analysis, confirms the existence of elements Pd, C and O in Pd_{NPs}-GO.

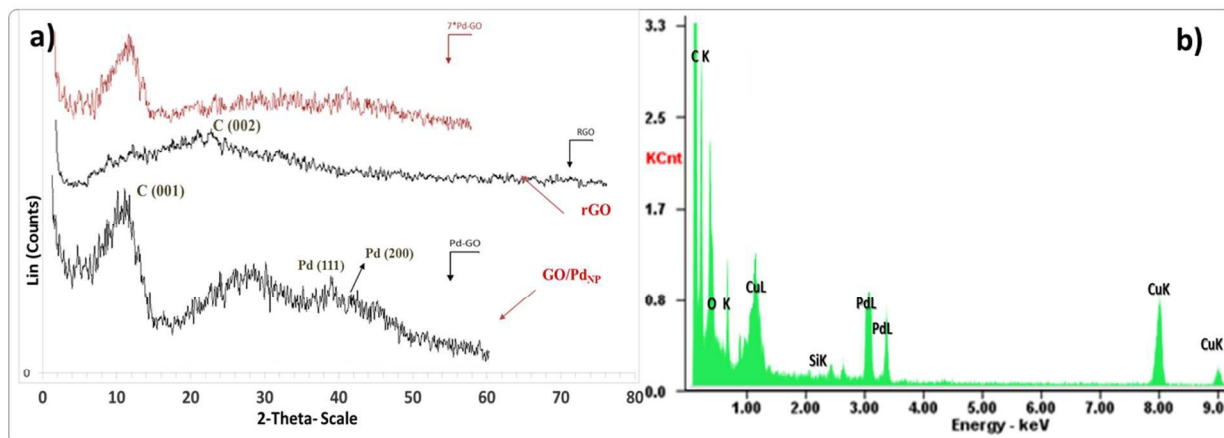


Figure 3. XRD patterns of (a) rGO, Pd_{NPs}-GO and 7th reused of Pd_{NPs}-GO. SEM-EDX of Pd_{NPs}-GO.

Catalysts were then explored in the oxidative amidation reactions in the presence of H_2O_2 (30%). All reactions were optimized using benzaldehyde and aniline as model reaction (Table 1). In method A, we attempted to engage our catalytic system to synthesize benzanilide. Various conditions were taken to account to find out optimized conditions. Several parameters including surfactant, base, solvent and reaction time and temperature were examined in this optimization. For this catalyst, we chose four types of surfactants to exfoliate Pd_{NPs} -GO sheets during the catalysis, which includes cetyltrimethylammonium bromide (CTAB), sodium dodecylsulfate (SDS), and a triblock copolymer of P123 and F127. The only difference between P123 and F127 is in the number of monomers, ethylene oxide-propylene oxide-ethylene oxide (EO-PO-EO). The number of each monomers are higher than P123. In our prediction, F127 due to longer chain, better exfoliation could be seen for both exfoliation and reaction catalysis. However in spite of a better exfoliation from F127, a lower catalytic activity was observed towards production of amide. It seems that, well-exfoliation of GO/Pd is not the mere reason for higher catalytic activity in the presence of P123. These three surfactants were compared in the oxidative amidation of benzaldehyde and aniline under the similar conditions. Based on this study, P123 was a suitable agent for exfoliation of GO/ Pd_{NPs} (Fig. 5).

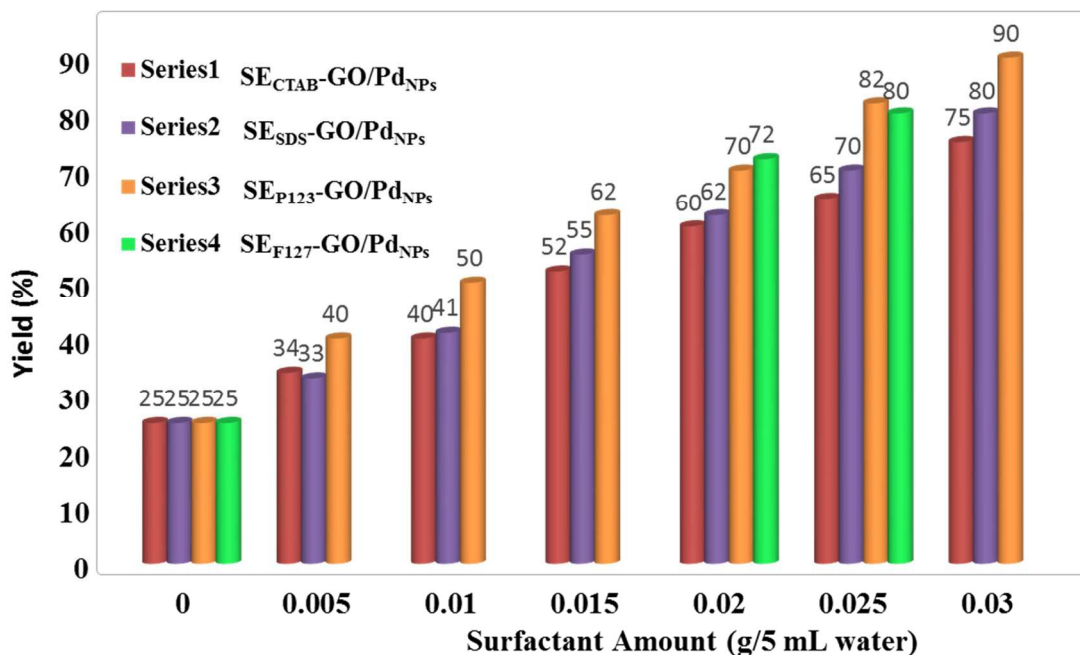


Figure 4. Effect of surfactant type and amount on the catalytic activity of GO/Pd_{NPs} in oxidative amidation: benzaldehyde (1 mmol), aniline (1.5 mmol), H₂O₂ (4 mmol) in 3 mL of Pd/GO suspension (1 mol% of Pd, 2 g/100 mL of solution) at room temperature during 15 h.

After selection of a suitable P123, we extended our catalytic (SE_{P123}-GO/Pd_{NPs}) system to two types of oxidative amidation reactions. Scheme 1 indicates a general route to manufacture and use of catalyst in the amidation syntheses. In recent method, as shown in Table 1, we attempted to extend the catalytic capability of SE_{P123}-GO/Pd_{NPs} for the synthesis of benzanilide from benzaldehyde and aniline in the presence of oxidant. Several bases including sodium carbonate, potassium carbonate, potassium phosphate and triethylamine were also selected to investigate the base effect on the reaction. Accordingly, a better result was matched with potassium carbonate. Among various oxidants such as H₂O₂, SeO₂, MnO₂, etc., the H₂O₂ was selected thanks to its availability, lower price and lower side products of H₂O₂ (Table 1).

Table 1. Investigation of SE-GO/Pd_{NPs} in the presence of various types of oxidants and surfactants. ^a

[Pd] = SE-GO/Pd_{NPs}

Entry	Surfactant	Cat. suspension ^b	Time (h)	oxidant	T (°C)	Yield (%)
1	CTAB	3 mL	15	H ₂ O ₂	25	75
2	CTAB	3 mL	15	SeO ₂	25	62
3	SDS	3 mL	15	MnO ₂	25	76
4	SDS	6 mL	15	H ₂ O ₂	25	74
5	F127	3 mL	15	H ₂ O ₂	25	81
6	F127	6 mL	15	DDQ	25	40
7	P123	9 mL	15	NaClO	25	30
8	P123	1 mL	15	H ₂ O ₂	25	80
9	P123	3 mL	18	H ₂ O ₂	25	90

^a Reaction conditions: benzaldehyde (1 mmol), aniline (1.5 mmol), oxidant (4 mmol) and GO/Pd_{NPs} (variant mol% of Pd) in 3 mL H₂O at room temperature in specific time. ^b mL of as-prepared SE-GO/Pd_{NPs} suspension and 0.03 g surfactant at room temperature.

Solvent studies for oxidative amidation from benzaldehyde and aniline were also conducted (Fig. 6). The use of water as solvent provided improved product yields which can be attributed to a good exfoliation of Pd/GO in the water/P123 system. Another reason can be related to polymeric nature of P123 which acts as a spectator species during the reaction which cause to produce an excellent media for reactants. Therefore, this examination led to disclose water as a good solvent for P123 to exfoliate the Pd/GO/P123 and interconnect aqueous and organic phases.

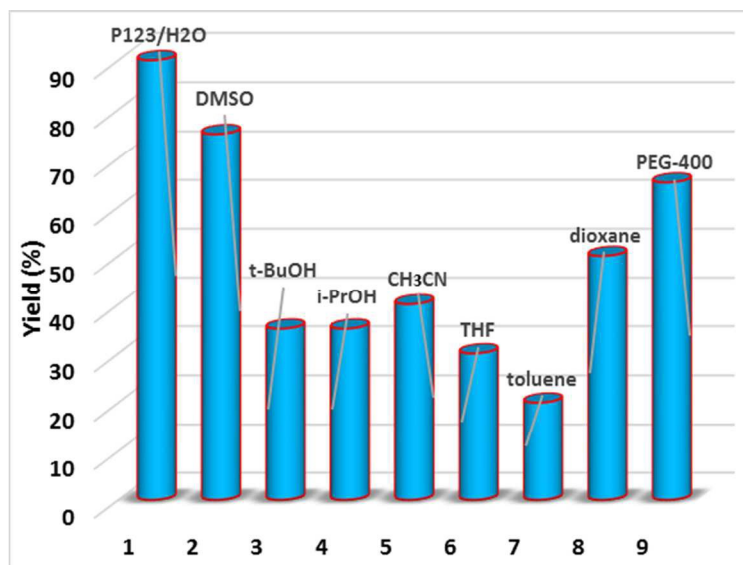


Figure 5. Study of solvent effect; reaction conditions: benzaldehyde (1 mmol), aniline (1.5 mmol), H₂O₂ (4 mmol) and 3 mL of as-prepared SE_{P123}-GO/Pd_{NPs} suspension (1 mol% of Pd) in 5 mL solvent at room temperature during 15 h.

In this investigation, the reaction at room temperature during 18-20 h proceeded with convenient results. These conditions were chosen as an optimized pathway to synthesize other derivatives of amides (Table 2).

Table 2. Scope of amines.^a

yrtnE ^a	enimA	imAde	T (h)	deiY ^b (%)	Conversion (%)
1			18	90	97
2			24	74	95

3			18	92	97
4			24	84	95
5			18	82	97
6			24	76	86

^a Reaction conditions: reactions were performed by benzaldehyde (2 mmol), amine (3 mmol), H₂O₂ (4 mmol), 3 mL of as-prepared SE_{P123}-GO/Pd_{NPs} (1 mol% of Pd) suspension at room temperature in aqueous conditions; ^b isolated yields.

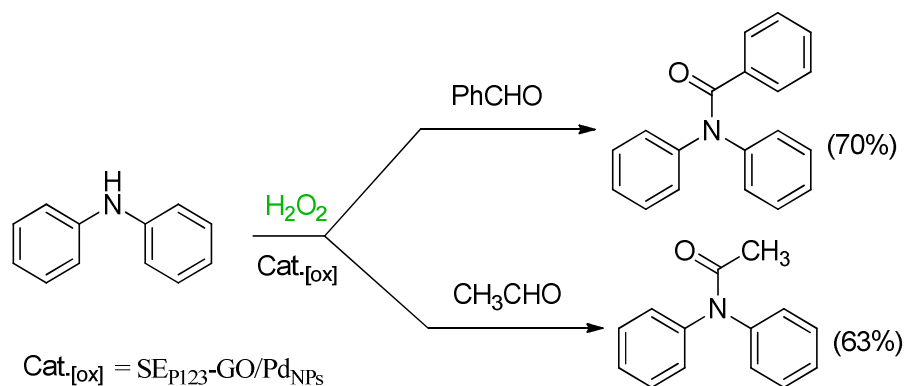
After testing this catalytic system under the optimized conditions in the oxidative amidation of benzaldehyde with various types of aromatic amines, other kinds of aldehyde including aromatic and aliphatic ones were reacted with different types of amines even with secondary aliphatic amine (Table 3). All products were obtained in good yields with high selectivity. This study revealed that electron donating substituents on the aromatic ring of amine lead to higher yields of amide. On the other side, aliphatic aldehyde showed relatively lower activity towards oxidative amidation.

Table 3. Synthesis of amides with various types of aldehydes through oxidative amidation.^a

yrtnE	R	enimA	T (h)	deiY ^b (%)	Conversion
1	CH ₃		20	62	84
2	CH ₃		18	66	85
3	Ph-		18	84	93
4	p-Ph-NO ₂		18	76	95
5	p-Ph-NO ₂		18	81	90
6	Ph-		20	77	87

^a Reactions were performed by benzaldehyde (1 mmol), amine (1.5 mmol), H₂O₂ (4 mmol), 3 mL of as-prepared SE_{P123}-GO/Pd_{NPs} suspension (1 mol% of Pd) at room temperature; ^b isolated yields.

The reactivity of less active amines (e.g. diphenylamine) with aliphatic and aromatic aldehydes (i.e. acetaldehyde and benzaldehyde, respectively) under identical reaction conditions was studied. Aromatic aldehydes were observed for be more active as compared to aliphatic aldehydes (Scheme 1).



Scheme 1. Reactivity comparison of aromatic and aliphatic aldehyde in the amidation with diphenylamine.

In the optimization of reaction conditions for tandem synthesis of amides from benzyl alcohol, we also substituted some other solvents both for studying exfoliation effect and solvent effect on reaction of reactants under the similar conditions. Likewise, it was found that water/P123 was a good pair for the reaction progress at room temperature. Once, we found that $\text{SE}_{\text{P123}}\text{-GO/Pd}_{\text{NPs}}$ is good catalytic system, and following to our previous experience on the oxidative activity of $\text{SE}_{\text{P123}}\text{-GO/Pd}_{\text{NPs}}$ in the oxidation of alcohols [33], we promoted this system to a tandem synthesis of amides starting from alcohols in one-pot conditions (Table 4). This investigation led to formation of amide from a consecutive oxidation of alcohol to aldehyde and then oxidation to amide formation via amine in one-pot conditions. In the first oxidation step, aromatic aldehydes, specifically those have electron withdrawing groups, were more active to be oxidized.

Recyclability studies of $\text{SE}_{\text{P123}}\text{-GO/Pd}_{\text{NPs}}$ were subsequently investigated. Reuse studies demonstrated an extraordinary recyclability of the catalyst up to 9 reaction runs (Figure 7) with an almost unchanged catalytic activity (<20% activity loss) as compared to the fresh catalyst. Based on atomic absorption spectroscopy (AAS) results, there was no evidence to confirm that significant Pd leaching happened after 9 runs for each method. However, continued reaction runs demonstrated that the catalyst exhibited a continuous loss of catalytic activity after 9 reuses.

Table 4. Tandem oxidative amidation of benzylic alcohols. ^a

yrtnE	R	enimA	T ₁ (h)	T (h)	Yield ^b (%)	Conversion (%)
1	Ph-		2	18	82	90
2	Ph-		2	18	70	87
3	Ph-		2	18	84	92
4	CH ₃		2	20	64	80
5	Ph-		2	18	73	77
6	Ph-		2	18	74	87
7	Ph-		2	18	77	92
8	Ph-		2	18	62	94
9	p-Ph-NO ₂		1.5	18	71	91
10	p-Ph-NO ₂		1.5	18	74	94
11	Ph-		2	20	69	77

^a Reaction conditions: benzaldehyde (1 mmol), amine (1.5 mmol), 5 mL of as-prepared SE_{P123}-GO/Pd_{NPs} suspension (1.7 mol% of Pd); ^b isolated yields.

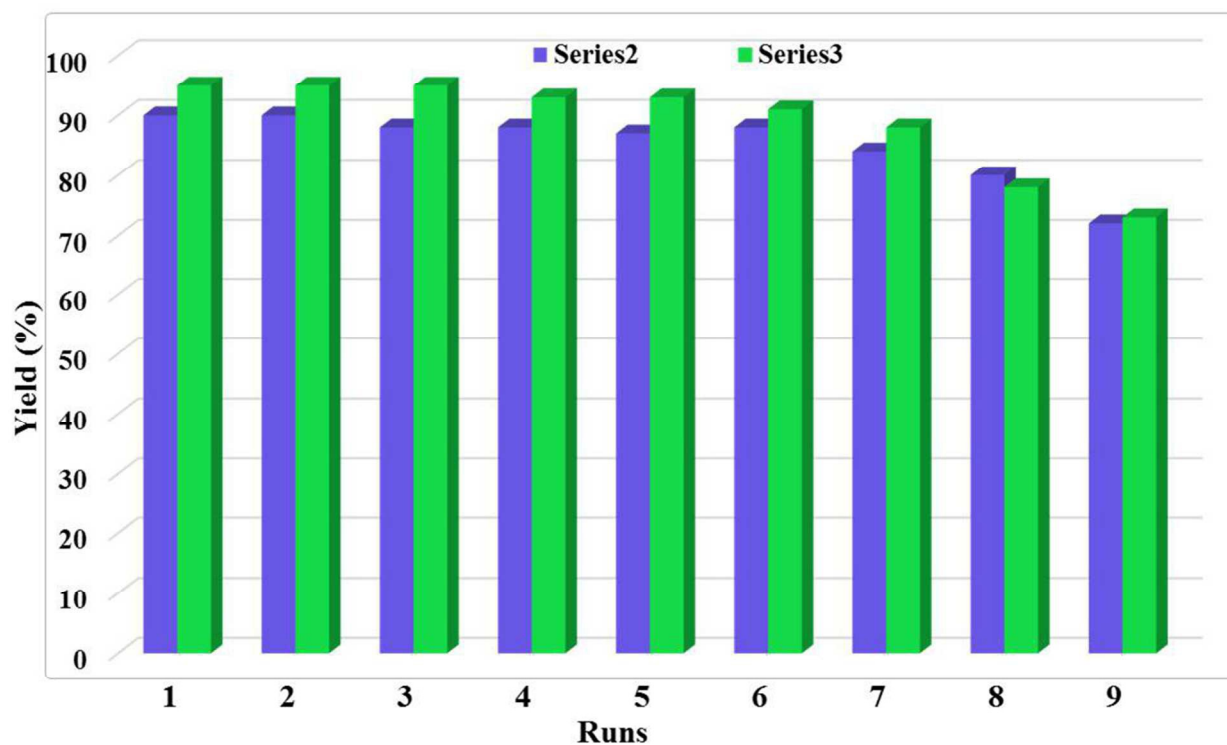
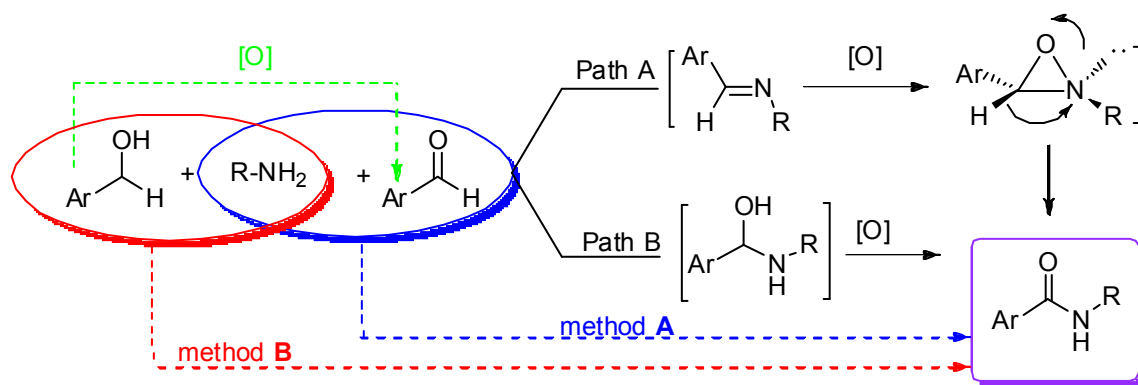


Figure 6. Recyclability of both methods under their optimized conditions.

Due to the fact that there are few reports for these reactions with palladium and we have not investigated the exact mechanism of amidations, we can also speculate two types of possible mechanism for these processes. On the other hand, there are some similar reports that can reinforce our proposed mechanisms [25, 34, 38]. Scheme 2 indicates the possible pathways to amide production. The presence of imine formation as an intermediate during the reaction (and the fact that the reaction also seems to work with imines as substrates) seems to point out the pathway A as main reaction mechanism. However, Path B and the reaction taking place from carboxylic acids (not mentioned in Scheme 2) cannot be ruled out in the formation of the final products.



Scheme 2. Proposed mechanisms for oxidative amidations [41].

Our proposed approach was finally compared with other previously reported strategies of oxidative amidations either from alcohol or benzaldehyde, in which the catalysts are Pd-based, Cu- and Ru-base or even metal-free (Table 5). The main advantages of our method rather to others are the recyclability of the catalyst, the use of no ligand, green chemical procedure, and low mol percent of Pd in each reaction which have made the presence method superior to others [39-44].

Table 5. Comparison of the presence method in oxidative amidation with previously published methods.

Metal	Ligand	Oxidant	Conditions	%Yield ^[Ref]
PdCl ₂ (2.5 mol%)	Xantphos (2.5 eq)	H ₂ O ₂ -Urea	20 h/ MeOH/CH ₃ CN/50 °C	> 86 ^[25]
Au/Pd/resin	-	O ₂	NaOH/ 25-40 °C/	49-99 ^[27]
CuI (2-20 mol%)	2-pyrimidonate (4 mol%)	Open air	Toluene/reflux/20 h	61-88 ^[40]
CuSO ₄ ·5H ₂ O (5 mol%)	-	TBHP	CaCO ₃ /MeCN/rt-60 °C/6-24 h	> 96 ^[41]
CuI/AgIO ₃	T-HYDRO [®]	t-BuOOH	CaCO ₃ /MeCN/40 °C/6h	39-91 ^[42]
[Ru(p-cymene)Cl ₂] ₂ (2.5 mol%), [Ru(benzene)Cl ₂] ₂ (2.5 mol%)	NHC carbene precursor (5 mol%)	-	NaH (15 mol%), and pyridine (5 mol%) in toluene at reflux for 36 h	19-99 ^[43]
RuH ₂ (PPh ₃) ₄ (5 mol%)	Imidazolium ionic liquid/MeCN	-	NaH/toluene/reflux/24 h	29-96 ^[44]
Supported AuNPs (1.5 mol%)	-	O ₂	THF/water/12 h/40 °C	10-97% ^[13]
SE _{P123} -GO/Pd _{NPs} suspension (1 mol%)	-	H ₂ O ₂	r.t./ 18h/H ₂ O	62-90 ^[This work]

Conclusion

A highly active, stable and reusable SE_{P123}-GO/Pd_{NPs} was synthesized using a straightforward methodology and tested as efficient catalytic system in oxidative amidation reactions, providing excellent yields to products for a wide range of substrates and two different methodologies including a one-pot alcohols conversion to amides. The catalytic system in this work was able to oxidize aliphatic and aromatic alcohols for *in situ* production of aldehydes and then a further oxidative amidation with various amines including electron withdrawing and releasing functions, and even with secondary aliphatic amine. The proposed methodology has the potential to pave the way to the utilisation of highly active and reusable supported Pd catalysts for more challenging oxidative/dehydrogenation reactions that will be reported in due course.

Experimental

Catalyst synthesis and characterization

A novel strategy was devised to synthesize Pd_{NPs} supported on the surface of GO (Figure 8). Firstly, graphite oxide powder was obtained via chemical oxidation of graphite according to the method by Hummer *et al.* method and based on our previous experiences [45]. Briefly, graphite was oxidized by treating with KMnO₄ and NaNO₃ in concentrated H₂SO₄ to form graphite oxide. 2 g of the obtained graphite oxide was then exfoliated to graphene oxide (GO) in 400 mL of water under sonication for 2 h. The extent of exfoliation after sonication was measured by conductivity (5900 S.cm⁻¹). NaBH₄ (0.1 g in 4 mL methanol) was subsequently added to the dispersion of GO under sonication and the mixture was further stirred for 15 min. The reductive

behaviour of reduced GO (rGO) in the presence of Pd ions was then investigated. A solution of PdCl₂ (0.004 g in 10 mL water, 5 mL methanol and 3 drops of HCl) was added to dispersed rGO (0.2 g in 10 mL water) under ultrasonic irradiation. The solution was centrifuged and washed with methanol several times before analysis. The obtained TEM images indicate that Pd ions were reduced to Pd_{NPs} by rGO while rGO itself was partially converted to GO (see supporting information). The obtained Pd supported GO (Pd_{NP}-GO) was subsequently exfoliated using Pluronic P123, a non-ionic surfactant, to generate the final SE_{P123}-GO/Pd_{NPs}. (Fig. 8) to be used as catalyst [2 g PdNP-GO in 100 mL of related solution in the presence of P123 (0.6 g)], with a palladium content of 1.86 wt% as measured by ICP-AES.

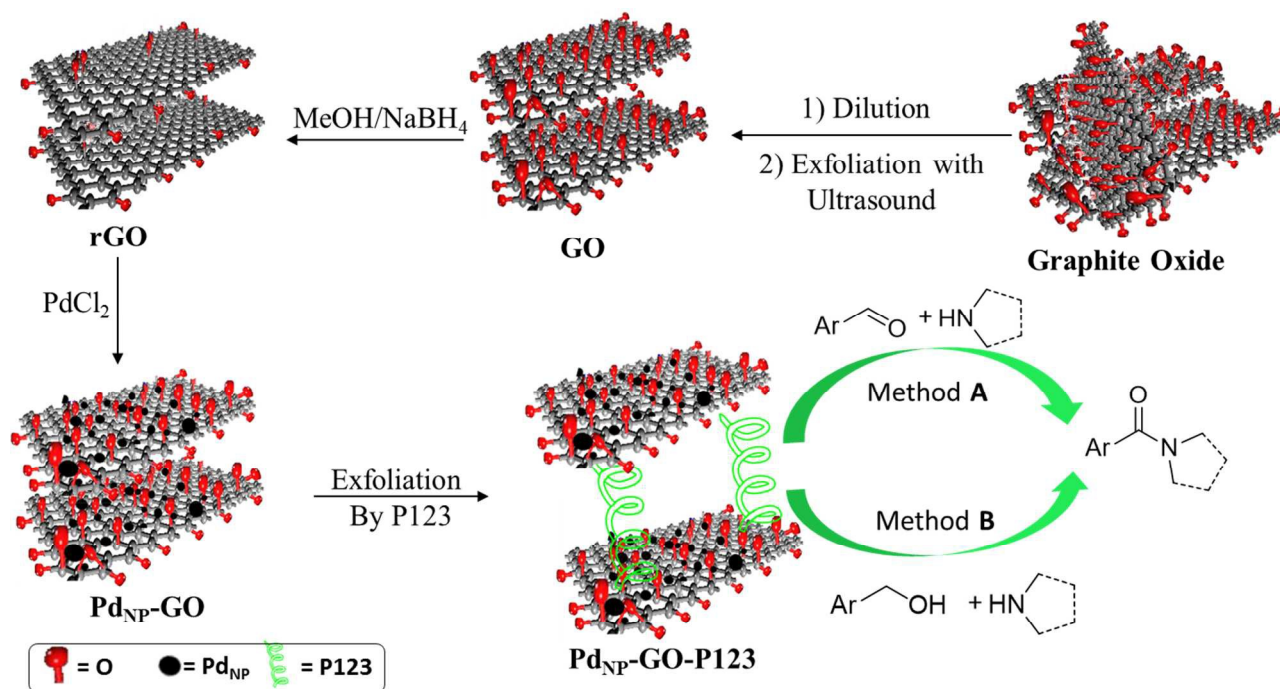


Figure 8. Preparation and application of SE_{P123}-GO/Pd_{NPs}.

All reagents were purchased from Fluka, Sigma-aldrich and Merck and used without further purification. The physicochemical properties of Pd_{NPs}/GO nanomaterials were characterized using FTIR spectroscopy (Shimadzu IR-460 spectrometer), X-ray diffraction (XRD) (Philips-

PW1800 diffractometer), scanning electron microscopy (SEM) (Zeiss-DSM 960A microscope), transmission electron microscopy (TEM) (Zeiss EM 900 electron microscope), and X-ray analysis (EDX). A multiwave ultrasonic generator (Sonicator_3000; Misonix Inc., Farmingdale, NY, USA), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, was operated as continuous irradiation with a maximum power output of 600 W. Frequencies below 50 kHz are usually suitable for the heterogeneous systems due to the more intense mechanical effects. Hence, we selected 19.6 kHz as optimum for sonication.

Oxidative amidation catalytic experiments

General procedure for the synthesis of secondary amides from aldehydes

In a typical reaction, benzaldehyde (1.0 mmol), aniline (1.5 mmol), H₂O₂ (4 mmol, 30%) and a dispersion of as-prepared SE_{P123}-GO/Pd_{NPs} (5 mL) were added to a 25 mL round bottomed flask. The reaction was allowed to stir at room temperature for 18 h. Upon reaction completion, the catalyst was separated by centrifugation and the organic residue was extracted with ethyl acetate and evaporated under reduced pressure. The final product was purified by column chromatography.

General procedure for the one-pot synthesis of secondary amides

In a typical experiment, benzyl alcohol (1.1 mmol), 2 mmol of aqueous H₂O₂ (30%) and 5 mL of as-prepared SE_{P123}-GO/Pd_{NPs} in water were added to a 25 mL round bottomed flask and allowed to react at room temperature for 2 h, followed by the addition of 1.5 mmol of aniline and 4 extra mmol of H₂O₂. The reaction was monitored during 18 h at room temperature. Upon reaction

completion, the catalyst was separated by centrifugation and the organic residue was extracted with ethyl acetate and evaporated under reduced pressure.

All synthesized amides in both methods are known and they were identified and characterized by FTIR, ^1H and ^{13}C NMR spectroscopy. Some key spectral data have been included below:

Spectral data

***N*-Phenylbenzamide.** White solid, Mp: 162-163 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 7.98 (s, 1 H), 7.80-7.06 (m, 10 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 165.71, 137.96, 135.09, 131.80, 129.09, 128.78, 127.00, 124.57, 120.21.

***N,N*-Diphenylbenzamide.** ^1H NMR (CDCl_3 , 400 MHz) δ : 7.494-7.172 (m, 15 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 170.572, 143.985, 136.227, 130.090, 129.148, 129.059, 127.820, 127.497, 126.291.

***N*-(3-Chlorophenyl)-4-nitrobenzamide.** ^1H NMR (CDCl_3 , 400 MHz) δ : 8.30-7.19 (m, 9 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 161.08, 142.96, 136.803, 129.309, 128.259, 125.369, 124.100, 120.362, 116.894, 116.804, 116.520.

4-Nitro-*N*-phenylbenzamide. White solid, Mp: 214-216 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.30-7.109 (m, 10 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 163.66, 154.68, 140.04, 138.31, 130.24, 128.27, 125.42, 124.12, 120.54.

***N*-(3-Chlorophenyl)benzamide.** ^1H NMR (CDCl_3 , 400 MHz) δ : 8.138 (s, 1 H), 7.75-7.13 (m, 9 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 166.11, 139.11, 134.66, 134.48, 132.07, 130.01, 128.78, 127.11, 124.61, 120.51, 118.40.

Phenyl(pyrrolidin-1-yl)methanone. Colorless liquid. ^1H NMR (CDCl_3 , 400 MHz) δ : 7.44-7.301 (m, 5 H), 3.57 (t, J = 6.6 Hz, 2 H), 3.33 (t, J = 6.2 Hz, 2 H), 1.87 (t, J = 6.5 Hz, 2 H), 1.79 (t, J =

6.2 Hz, 2 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 168.71, 136.30, 128.72, 127.21, 126.07, 45.13, 25.37.

Ethyl-2-(benzamido)benzoate. ^1H NMR (CDCl_3 , 400 MHz) δ : 12.10 (s, 1 H), 8.97-7.14 (m, 9 H), 4.45 (q, $J = 1.8$ Hz, 2 H), 1.45 (t, $J = 1.8$ Hz, 3 H) ^{13}C NMR (CDCl_3 , 100 MHz) δ : 168.62, 165.70, 141.93, 135.02, 134.64, 131.84, 130.90, 128.76, 127.39, 122.51, 120.50, 115.54, 61.47, 14.18.

***N*-(4-Bromophenyl)acetamide.** ^1H NMR (CDCl_3 , 400 MHz) δ : 8.00 (s, 1 H), 7.461-7.281 (m, 4 H), 2.185 (s, 3 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 168.97, 138.34, 131.97, 121.35, 114.95, 24.47.

***N*-(4-Bromophenyl)benzamide.** White solid, Mp: 198-200 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 7.97 (s, 1H), 7.189-7.797 (m, 9H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 168.14, 137.01, 134.86, 132.08, 128.88, 126.99, 121.69, 114.51.

***N*-(4-Hydroxyphenyl)benzamide.** ^1H NMR (CDCl_3 , 400 MHz) δ : 8.06 (s, 1 H), 8.04-7.18 (m, 9 H), 5.08 (s, 1 H) ^{13}C NMR (CDCl_3 , 100 MHz) δ : 171.59, 158.62, 133.77, 130.21, 129.26, 129.04, 128.86, 128.59, 128.493.

***N*-(Pyridin-2-yl)benzamide.** White solid, Mp: 80-82 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 9.23 (br, 1 H), 8.47-7.09 (m, 9 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 173.04, 151.75, 149.30, 147.36, 138.79, 132.47, 129.31, 127.44, 119.87, 114.60. FT-IR (KBr, cm^{-1}) 1458, 1528, 1579, 1598, 3173.

***N*-Benzylbenzamide.** White solid, Mp: 102-103 °C. ^1H NMR (CDCl_3 , 400 MHz) δ : 8.11 (s, 1 H), 7.82-7.28 (m, 10 H), 4.64 (d, $J = 5.63$ Hz, 2 H). ^{13}C NMR (CDCl_3 , 100 MHz) δ : 167.485, 138.28, 134.39, 131.533, 128.758, 128.572, 127.883, 127.565, 127.039, 44.097.

N-Phenylacetamide. White solid, Mp: 113-115 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 7.592-7.11 (m, 5 H), 2.18 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz) δ: 168.43, 137.97, 128.95, 124.29, 119.97, 24.49.

N,N-Diphenylacetamide .White solid, Mp: 102-103 °C. ¹H NMR (CDCl₃, 400 MHz) δ: 6.93-7.31 (m, 10 H), 2.08 (s, 3 H). ¹³C NMR (CDCl₃, 100 MHz) δ: 169.93, 143.13, 129.34, 121.00, 117.82, 23.83.

References

- [1] S. Rostamnia, E. Doustkhah, *RSC Adv.* 2014, **4**, 28238-28248.
- [2] K. Hii, K. Hellgardt, *Catalysis in Flow: Why Leaching Matters*, in, Springer Berlin Heidelberg, 2015, pp. 1-14.
- [3] B. Karimi, A. Zamani, *Org. Biomol. Chem.* 2012, **10**, 4531-4536.
- [4] J. Hu, Y. Wang, M. Han, Y. Zhou, X. Jiang, P. Sun, *Catal. Sci. Technol.* 2012, **2**, 2332-2340.
- [5] C.L. Allen, J.M.J. Williams, *Chem. Soc. Rev.* 2011, **40**, 3405-3415.
- [6] H.P.L. Gemoets, Y. Su, M. Shang, V. Hessel, R. Luque, T. Noel, *Liquid phase oxidation chemistry in continuous-flow microreactors*, *Chem. Soc. Rev.* 2015, in press
- [7] X.-F. Wu, M. Sharif, A. Pews-Davtyan, P. Langer, K. Ayub, M. Beller, *Eur. J. Org. Chem.* 2013, 2783-2787.
- [8] X. Liu, K.F. Jensen, *Green Chem.* 2012, **14**, 1471-1474.
- [9] S. Gaspa, A. Porcheddu, L. De Luca, *Org. Biomol. Chem.* 2013, **11**, 3803-3807.
- [10] R. Deshidi, M. Kumar, S. Devari, B.A. Shah, *Chem. Commun.* 2014, **50**, 9533-9535.
- [11] S. Rostamnia, E. Doustkhah, *Synlett* 2015, **26**, 1345-1347.
- [12] C. Gunanathan, Y. Ben-David, D. Milstein, *Science* 2007, **317**, 790-792.
- [13] J.-F. Soulé, H. Miyamura, S. Kobayashi, *J. Am. Chem. Soc.* 2011, **133**, 18550-18553.

- [14] J.-F. Soulé, H. Miyamura, S. Kobayashi, *Asian J. Org. Chem.* 2012, **1**, 286.
- [15] J.-F. Soulé, H. Miyamura, S. Kobayashi, *Chem. Asian J.* 2013, **8**, 2614-2626.
- [16] H. Miyamura, H. Min, J.F. Soulé, S. Kobayashi, *Angew. Chem. Int. Ed.* 2015, **54**, 7564-7567.
- [17] S. Rostamnia, X. Liu, D. Zheng, *J. Colloid Interf. Sci.* 2014, **432**, 86-91.
- [18] S. Rostamnia, H. Xin, *Appl. Organometallic Chem.* 2013, **27**, 348-352.
- [19] S. Rostamnia, K. Lamei, F. Pourhassan, *RSC Adv.* 2015, **4**, 59626-59631.
- [20] J.M. Campelo, T.D. Conesa, M.J. Gracia, M.J. Jurado, R. Luque, J.M. Marinas, A.A. Romero, *Green Chem.* 2008, **10**, 853-858.
- [21] C. Gonzalez-Arellano, R. Luque, D.J. Macquarrie, *Chem. Commun.* 2009, 1410-1412.
- [22] S. Rostamnia, E. Doustkhah, B. Zeynizadeh, *Micropor. Mesopor. Mater.* 2015, in press.
- [23] R.A.D. Arancon, C. S.K. Lin, C. Vargas, R. Luque, *Org. Biomol. Chem.* 2014, **12**, 10-35.
- [24] S. Rostamnia, H. Golchin Hossieni, E. Doustkhah, *J. Organometallic Chem.* 2015, **791**, 18-23.
- [25] Y. Suto, N. Yamagiwa, Y. Torisawa, *Tetrahedron Lett.* 2008, **49**, 5732-5735.
- [26] X. Liu, K.K. Hii, *Eur. J. Org. Chem.* 2010, 5181-5189.
- [27] L. Zhang, W. Wang, A. Wang, Y. Cui, X. Yang, Y. Huang, X. Liu, W. Liu, J.-Y. Son, H. Oji, T. Zhang, *Green Chem.* 2013, **15**, 2680-2684.
- [28] S.-I. Yamamoto, H. Kinoshita, H. Hashimoto, Y. Nishina, *Nanoscale* 2014, **6**, 6501-6505.
- [29] S.J. Hoseini, V. Heidari, H. Nasrabadi, *J. Mol. Catal. A* 2015, **396**, 90-95.
- [30] S.S. Shendage, J.M. Nagarkar, *Colloids Interf. Sci. Commun.* 2014, **1**, 47-49.
- [31] S.S. Shendage, A.S. Singh, J.M. Nagarkar, *Tetrahedron Lett.* 2014, **55**, 857-860.
- [32] S. Rostamnia, B. Zeynizadeh, E. Doustkhah, H.G. Hosseini, *J. Colloid Interf. Sci.* 2015, **451**, 46-52.
- [33] S. Rostamnia, E. Doustkhah, Z. Karimi, S. Amini, R. Luque, *ChemCatChem* 2015, **7**, 1678-1683.
- [34] S. Rostamnia, N. Nouruzi, H. Xin, R. Luque, *Catal. Sci. Technol.* 2015, **5**, 199-205.
- [35] C. Chen, S.H. Hong, *Org. Biomol. Chem.* 2011, **9**, 20-26.

- [36] B. Kang, Z. Fu, S.H. Hong, *J. Am. Chem. Soc.* 2013, **135**, 11704-11707.
- [37] B.F. Machado, P. Serp, *Catal. Sci. Technol.* 2012, **2**, 54-75.
- [38] S. Yang, H. Yan, X. Ren, X. Shi, J. Li, Y. Wang, G. Huang, *Tetrahedron* 2013, **69**, 6431-6435.
- [39] J. Gao, G.-W. Wang, *J. Org. Chem.* 2008, **73**, 2955-2958.
- [40] M. Zhu, K.-I. Fujita, R. Yamaguchi, *J. Org. Chem.* 2012, **77**, 9102-9109.
- [41] S.C. Ghosh, J.S.Y. Ngiam, A.M. Seayad, D.T. Tuan, C.L.L. Chai, A. Chen, *J. Org. Chem.* 2012, **77**, 8007-8015.
- [42] W.-J. Yoo, C.-J. Li, *J. Am. Chem. Soc.* 2006, **128**, 13064-13065.
- [43] S.C. Ghosh, S. Muthaiah, Y. Zhang, X. Xu, S.H. Hong, *Adv. Synth. Catal.* 2009, **351**, 2643-2649.
- [44] S. Muthaiah, S.C. Ghosh, J.-E. Jee, C. Chen, J. Zhang, S.H. Hong, *J. Org. Chem.* 2010, **75**, 3002-3006.
- [45] W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.* 1958, **80**, 1339-1339.

Efficient tandem aqueous room temperature oxidative amidations catalysed by supported palladium nanoparticles on graphene oxide

Sadegh Rostamnia, Esmail Doustkhah, Habib Golchin-Hosseini, Behzad Zeynizadeh, Hongchuan Xin, Rafael Luque

