View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: S. Nilforoushan, M. Ghiaci, S. M. Hosseini, S. Laurent and R. Muller, *New J. Chem.*, 2019, DOI: 10.1039/C8NJ06469E.



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 **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, 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.



rsc.li/njc

Selective Liquid Phase Oxidation of Ethyl Benzene to Acetophenone by Palladium Nanoparticles Immobilized on g-C₃N₄-rGO Composite as Recyclable Catalyst

Sheyda Nilforoushan^a, Mehran Ghiaci^{a,*}, Sayyed Mahdi Hosseini^a, Sophie Laurent^b, Robert N. Muller^b

^aIsfahan University of Technology, Department of Chemistry, Isfahan 8415683111, Iran

^bUniversity Mons, NMR & Mol Imaging Lab, Department Gen Organic& Biomedical Chemistry, B-7000 Mons (Belgium)

*Corresponding author: Mehran Ghiaci

Email address: mghiaci@cc.iut.ac.ir, Tel: +983133913254

Abstract

In this study, synthesis of acetophenone as a widely used industrial compound was investigated by liquid phase oxidation of ethylbenzene with TBHP as an oxidant in acetonitrile over Pd/g-C₃N₄-rGO as a recyclable catalyst. The hybrid composite of graphitic carbon nitride $(g-C_3N_4)$ and reduced graphene oxide (rGO) was synthesized by a simple wet impregnation method and was used as support for palladium nanoparticles. The characterization of the Pd/g-C₃N₄-rGO composite was done by different techniques such as XPS, FT-IR, X-ray Diffraction, FESEM-EDS and Mapping, TEM, TGA, ICP-OES, and BET-Surface area. The Pd nanoparticles were homogeneously distributed on the hybrid support with reasonable surface area. Moreover, this system revealed a good performance in the production of acetophenone as the main product of oxidation of ethylbenzene in mild conditions with 67% and 97% conversion and selectivity, respectively. In addition, the proposed catalyst also retained its activity and selectivity for acetophenone after 5 runs.

Keywords: Acetophenone; Heterogeneous catalysis; Oxidation; Palladium nanoparticles.

New Journal of Chemistry Accepted Manuscript

1. Introduction

Recently, carbon materials with nano porous structures are mostly considered as a support in heterogeneous catalysts due to superior thermal and chemical stabilities [1, 2]. Among carbon allotropes, graphene, which includes thick carbon planes with sp² hybrid, has been used in different fields because of its prominent optical [3], electrical [4] and mechanical [5] properties. Graphene has different applications in super capacitors [6], Li-ion batteries [7], catalysts [8, 9], and biological fields [10]. Nowadays, because of the simplicity of synthesis and economic benefits, different derivatives of graphene-like graphene oxide (GO) and reduced graphene oxide (rGO) have attracted more attention in comparison with pure graphene [11, 12]. Catalytic systems which contain metal on nitrogen-doped carbon attracted the attention of researchers because of their chemical, electrical and structural properties for manufacturing of chemicals with high activity and selectivity in catalytic oxidation, reduction processes and glucose sensing [13-18]. The use of inexpensive materials as well as reproducible resources for producing nitrogen-doped carbon materials have been favored in recent years [13, 14]. In general, pyrolysis of rich nitrogen and carbon-containing materials with a metal salt leads to the formation of metal carbon-nitrogen doped structures, which can be used as a general route for producing nanoparticles-based carbon nitride catalysts [14, 19].

Graphitic carbon nitride (g-C₃N₄) is a carbonaceous material with high nitrogen content that can be used as N-substituted graphite [20, 21]. In addition, the presence of structural and surface defects, as well as high content of nitrogen atoms with their coordination capability, has converted it to a good candidate for application in catalytic applications. In other words, it is the active support that could increase the catalytic performance and has the capability for use in surface modification, photocatalysis, and optical sensors [22-28]. In order to synthesize bulky g-C₃N₄ using thermal treatment of nitrogen-rich precursors by a pyrolysis technique, various compounds such as cyanamide, dicyandiamide, urea, thiourea as well as melamine are used [22, 29-33]. All of these materials are carcinogenic and expensive except melamine. Thermal synthesis of g-C₃N₄ based on melamine as the precursor, depending on the reaction conditions, leads to crystalline structures with different condensation, and is generally done through heating melamine at high pressures or low-vacuum systems [22, 34-36]. In addition, achieving a honeycomb arrangement of the g-C₃N₄ structure with s-triazine rings is more probable when

New Journal of Chemistry Accepted Manuscript

starting with melamine as the precursor and gradually increasing temperature with low rate [30, 31, 37]. During the process of carbon nitride condensation, when using urea or thiourea; ammonia and H₂X gases will be produced. Therefore, on a large scale process for g-C₃N₄ synthesis using these materials as the precursor is highly toxic and inappropriate environmentally and economically. However, melamine has a high tendency to sublimate above 290 °C [38]. To solve this problem, melamine condensation is carried out in a closed or a semi-closed system [36-39]. G-C₃N₄ samples prepared through thermal annealing of melamine show irregular big particles with very low specific surface area (less than 10 m².g⁻¹) [39, 40]. Hence, many efforts have been done to modify g-C₃N₄ synthesis for achieving more active sites and increasing the surface area. One way of modifying the process is to protonate the melamine by strong mineral acids [41-43].

The coupling of $g-C_3N_4$ with carbon materials such as graphene and its derivatives has been practiced for producing compatible composites because both materials have twodimensional carbon networks [22, 44, 45, 47]. In a study by Quan et al. GO/g-C₃N₄ composite prepared by sonication technique, showed acceptable performance in the degradation of rhodamine B and 2, 4-dichlorophenol under visible light irradiation conditions [22]. Recently, a hybrid composite of g-C₃N₄-rGO or in combination with various metals has attracted more attention by improving the catalytic performance of g-C₃N₄ [45-50]. Wang et al. used g-C₃N₄rGO composite to support Pd nanoparticles for the investigation of electro-oxidation of formic acid and methanol [51].

Acetophenone is a valuable intermediate in pharmaceuticals and resins industry. It can be used as the solvent, tear gas, and can also be used as flavors. Furthermore, hydrogenation of acetophenone to 1-phenyl ethanol is carried out with the purpose of producing aromatic ester fragrances [52, 53]. Industrially, acetophenone is obtained as a byproduct of the Hock process which is performed for the production of phenol. Also, selective decomposition of cummen hydroperoxide is performed in the presence of copper catalysts at 50-150 °C to obtain acetophenone [54]. Another process for producing acetophenone is Friedel-Crafts acylation of benzene with acetyl chloride in the presence of stoichiometric amounts of AlCl₃ [55], which is not an eco-friendly process. Interest in the development of chemical material synthesis through green and economic processes has led to extensive research to achieve fine products like phenyl

4 5

6

7 8

38 39

40 41

42

43 44 45

46 47

48

49 50

51 52

53

54 55

ketones from selective oxidation of alkyl arenes. Oxidation of ethylbenzene using heterogeneous catalytic systems and environmentally-friendly oxidizing reagents such as O₂, H₂O₂, and tertbutyl hydroperoxide (TBHP) is considered an appropriate method for synthesis of acetophenone, which has none of the above problems and limitations [56-58]. This process has byproducts such as 1-phenyl ethanol, 2-phenyl ethanol, benzaldehyde, styrene and benzoic acid [56, 59, 60]. Therefore, designing a catalytic system to achieve acetophenone with high selectivity is important because of the purification process as one of the most important and expensive processes for obtaining pure products among industrial processes. In this case, catalytic systems such as M-MCM-41 (M=Ti, V, Cr) [61], Ag/SiO₂ [52], Co(II) porphyrin complex [62], Mn-Ti/SBA-15 [56], Ni-Al/hydrotalcite [63], Flower-like Co-Cu microspheres [64], VO_x/HZSM-22 [57], Mn/MCM-41 [65], and Zeolite-Y encapsulating Zn(II), Cu(II) and Ru(III) complexes of imidazole [60] have been reported. Although acetophenone with high conversion and selectivity is obtained in industrial processes, they are not desirable due to the use of hazardous starting materials and reagents in large scales as well as harsh reaction conditions. In addition, many of these systems significantly lose their activity after several runs. In this respect, for manufacturing acetophenone by catalytic oxidation, Pd-based catalysts mainly focus on Wacker oxidation, oxidative coupling, alcohol oxidation, reduction of nitroarenes and C-C cross-coupling reactions [66-71]. One of the related works in this area is our previous work which focused on the modification of bentonite surface with a designed surfactant, i.e. 3.3'-(dodecyl-azanediyl)bis(N-(2-(2-aminoethyl amino)ethyl) propanamide (DAEP), which provided the possibility of homogeneous and nano metric distribution of palladium particles. Although this process led to very high conversion and selectivity of acetophenone, there was no possibility for this process to be carried out in industrial scales due to the complexity of the process, time-consuming synthesis of catalyst, and the use of expensive materials [72].

In the present study, after the modification of the synthetic route of melamine-based graphitized carbon nitride using H₂SO₄, a hybrid composite of g-C₃N₄ and rGO was formed using a thermal annealing process that finally led to the g-C₃N₄-rGO structure using a simple, short time, and cast-effecting and green synthetic method. In fact, by modifying the GO surface with g-C₃N₄ through increasing π - π interactions, the restacking of GO plates was prevented. In the optimized conditions, g-C₃N₄-rGO composite with a ratio of 1:2 is chosen as support for immobilizing Pd nanoparticles. This combination played an important role in changing the

behavior of the nucleation growth of Pd particles without any agglomeration in accordance with our characterization analysis, and finally the formation of a very ordered structure with honeycomb units. In the end, the catalytic performance of ternary composite $Pd/g-C_3N_4$ -rGO was investigated through the oxidation reaction of ethylbenzene in the presence of TBHP as an oxidizing agent and acetonitrile as solvent. Probably, high activity of the hybrid g-C₃N₄-rGO composite and the lack of agglomeration and proper distribution of Pd nanoparticles played an important role in achieving the acetophenone product with high selectivity and minimum related by-products.

2. Experimental

2.1 Materials

All chemical materials and solvents were purchased from Merck and Aldrich companies and were used without any purification.

2.2 Preparation of GO

GO was synthesized by a modified Hummer's method from graphite powder [73]. In the first step, 2 g of graphite powder, 2 g of sodium nitrate and 92 mL concentrated sulfuric acid were added to a three neck round bottom flask equipped with a mechanical stirrer at 0 °C. In the next step, 12 g of KMnO₄ was slowly added to the flask and stirred vigorously at 35 °C for 1 h. Then, the reaction flask was placed into an ice bath and 100 mL of DI water was slowly added to it. In this step, the above composite was put in an oil bath with a temperature of 98 °C for 15 minutes. After that, the flask was put into an ice bath while 100 mL of DI water and 20 mL of H₂O₂ (30%) were added to it. Subsequently, it was put in an ultrasound bath for 3 h under stirring. In the last step, the prepared samples were centrifuged and washed with 5% HCl solution and DI water to neutral pH. The obtained brown powder was dried under vacuum at 80 °C for 24 h, which resulted in the GO powder.

2.3 Preparation of g-C₃N₄

5 g melamine and 1 g Pluronic P123 co-polymer were dissolved in 100 mL of DI water and the solution was refluxed for 1 h. After cooling the mixture to room temperature, 3 mL H_2O/H_2SO_4 (1.5 mL H_2O and 1.5 mL H_2SO_4) was added. The white precipitate was separated and

washed thoroughly with water and then dried at 80 °C. Finally, the dried precipitate was pyrolyzed at 600 °C with a rate of 50 °C/h for 4 h under argon atmosphere.

2.4 Preparation of g-C₃N₄-rGO composite

In the first stage, 1 g of $g-C_3N_4$ and 2 g of GO were dispersed in 50 mL ethanol and the mixture was put under continuous ultra-sonication. The prepared mixture was maintained at room temperature for 24 h under stirring, and then after 2x15 min ultra-sonication, the solvent was removed and the solid was pyrolyzed under argon atmosphere at 700 °C for 1 h.

2.5 Synthesis of Pd (4 wt%)/g-C₃N₄-rGO catalyst

At first, 1 g of the g-C₃N₄-rGO composite was distributed in 25 mL ethanol, and then a solution of 40 mg of palladium acetate in 5 mL THF was added to it during 2 h under stirring. The mixture was put under continuous ultra-sonication (4x15 min). The solvent was removed using rotary evaporator. In the last stage, the obtained powder was washed with DI water and dried in an oven at room temperature; the prepared catalyst was designated as Pd (4 wt%)/g-C₃N₄-rGO. For comparison, Pd nanoparticles supported on rGO (Pd/rGO) and g-C₃N₄ (Pd/g-C₃N₄) were also prepared using the same procedure.

2.6 Catalyst characterization

The structure and morphology of the catalysts were characterized as follows: FT-IR spectra of the samples were studied by JASCO, FT-IR (680 plus) spectrophotometer. X-Ray diffraction analyses were performed using a Philips 87, Netherland with Cu anode (40 kV, 30 mA) connected to a DACO-MP microprocessor using the Diffract-AT software. X-ray photoelectron spectroscopy (XPS) measurement was performed by a VG ESCALAB 3 MK II. The analysis chamber pressure was <10-9 Torr. The sample was excited using Mg K α (1253.6 eV) radiation (operated at 300 W), having an instrument resolution of 0.7 eV. The component peaks were separated by the VG Avantage software. Field emission scanning electron microscopy (FESEM) with energy dispersive X-ray spectrometer and mapping were obtained using the TESCAN MIRA3. BET surface area was used through N₂ adsorption/desorption isotherms at 77.3 K using a micro metrics PHS-1020 (PHSCHINA). TEM images were taken using a Philips CM-120 microscopy with an accelerating voltage of 150 kV. TGA analysis was obtained using a STA503 TA (Germany) under argon flow with a scan range from 25 to 800 °C under the constant heating

rate of 10 °C/min. The palladium content in samples was determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES) using a Shimadzu ARL 34000 instrument. The reaction products were analyzed by GC-Ms (Fisons Instruments 8060, USA) and an Agilent gas chromatography equipped with HP5 5% phenyl methyl siloxane capillary column and FID detector was used for determination of the types and amounts of the products, respectively (bromobenzene as internal standard).

2.7 Typical oxidation procedure

Liquid phase oxidation of ethylbenzene to acetophenone was done in a round bottom flask in reflux conditions. Therefore, 10 mg catalyst, 1 mmol ethylbenzene (122 μ l) and 480 μ l of TBHP (80%) were put into a 10 mL flask including 5 mL acetonitrile as solvent, and the system was refluxed at 80 °C for 24 h. After the completion of the reaction, the reaction mixture was centrifuged to separate the catalyst and after preparing standard solutions containing an internal standard (bromobenzene), the amount and type of products were analyzed by GC and GC-MS, respectively.

3. Results and discussion

3.1 Characterization of catalysts

3.1.1 XPS analysis

Surface chemical composition and oxidation states of Pd in the Pd/g-C₃N₄-rGO were studied using X-ray photoelectron spectroscopy (XPS). The survey XPS spectrum revealed the presence of C, N, O and Pd elements in the sample (Fig. 1a). The precise amount of C, N, O and Pd elements (at %) of the sample according to XPS analysis, is equal to 63.1, 17.4, 17.4 and 2.2%, respectively. Fig. S1 shows the spectra of carbon (C 1s), nitrogen (N 1s) and oxygen (O 1s) separately and as can be seen, the peak at about 400.1 eV is attributed to pyrrolic-type nitrogen [74, 75]. The Pd XPS spectrum always appears in a doublet ($3d_{3/2}$ and $3d_{5/2}$) due to spin-orbit coupling and is separated by 5.26 eV [76]. Fig. 1b shows the Pd XPS spectrum of the Pd/g-C₃N₄-rGO fresh catalyst. The peaks at 335.0 and 337.3 eV were attributed to $3d_{5/2}$ and $3d_{5/2}$ of Pd° and Pd⁺² (palladium oxide), respectively. Also, the peak at 339.6 eV is representative of the Pd (IV) (Pd $3d_{5/2}$) that indicates the presence of PdO₂ [77-80]. By calculating the surface area of

the peaks of different palladium species, clearly, Pd^{+2} was distinguished as the major phase on the surface of the catalyst (about 45%). According to previously reported data [81], the amine groups on the carbon support increases Pd° stability and makes them resistant to re-oxidation in environmental conditions. It seems that the presence of 19.4% of palladium in the form of metallic palladium is due to the presence of nitrogen groups of the g-C₃N₄-rGO composite. Herein, the nitrogen atoms as metal-anchoring sites lead to a homogeneous, fine dispersion of metal nanoparticles and increase their stability on the support surface, and as we will see later, a strong coupling between Pd NPs and g-C₃N₄-rGO leads to creating a stable catalyst with high reusability.



Figure 1. XPS scan survey for Pd/g-C₃N₄-rGO (a), Deconvoluted high resolution spectrum of Pd 3d (b)

3.1.2 FT-IR spectra

Fig. 2 shows the FTIR spectra of g-C₃N₄, GO, rGO, g-C₃N₄-rGO and Pd (4 wt%)/g-C₃N₄-rGO. The stretching vibrations of C-N bonds in the g-C₃N₄ structure appear at 1200-1650 cm⁻¹ (Fig. 2a). The wide peak at 3428 cm⁻¹ is ascribed to stretching vibration of the N-H bond and the peak at 806 cm⁻¹ is related to tri-s-triazine unit in g-C₃N₄ [29]. In the GO spectrum (Fig. 2b), a wide peak at 3416 cm⁻¹ shows stretching vibrations of the hydroxyl groups and the peaks at 1721, 1621 and 1056 cm⁻¹ were due to stretching vibrations of C=O, C=C and C-O bonds, respectively [82]. Because of decrease in oxygen functional groups at the surface of GO through pyrolysis, almost all peaks attributed to oxygen-containing functional groups in rGO (Fig. 2c)

 Rublished on 04.4 Roil 2018. Downloadedby Ruger Name University of London on 44.2019 5:32-33.2 Mo

 2
 9
 5
 4
 8
 7
 0
 5
 7
 0

 2
 9
 5
 4
 8
 7
 0
 5
 7
 0

and $g-C_3N_4$ -rGO (Fig. 2d) were declined [50, 51, 83]. In addition, the peaks at 808 and 1245 cm⁻¹ in $g-C_3N_4$ -rGO were ascribed to the tri-s-triazine units and the stretching vibration of the C-N bond in the $g-C_3N_4$ structure.



Figure 2. FTIR spectra of g-C₃N₄ (a), GO (b), rGO (c), g-C₃N₄-rGO (d) and Pd/g-C₃N₄-rGO

3.1.3 XRD and TGA analysis

X-ray Diffraction patterns of g-C₃N₄, GO, g-C₃N₄-rGO composite and Pd (4 wt%)/g-C₃N₄rGO catalyst are shown in Fig. 3. In the XRD pattern of g-C₃N₄, the strongest peak at $2\theta = 27.4^{\circ}$ is related to (002) plane and the peak at $2\theta = 13.0^{\circ}$ is assigned to (100) planes of tri-s-triazine unit based on JCPDS-87-1526 pattern [84]. Furthermore, in the GO structure the peak related to (001) planes has appeared at $2\theta = 12.3^{\circ}$ [85]. The wide peak observed at $2\theta = 26.1^{\circ}$ in the structure of $g-C_3N_4$ -rGO is possibly related to covalent interactions between rGO planes and $g-C_3N_4$, where the graphene planes are separated because of in situ growth of $g-C_3N_4$ planes [86]. Furthermore, the diffraction peaks corresponding to Pd nanoparticles are not observed in the Pd/g-C₃N₄-rGO catalyst because of its good dispersion and very small amounts based on ICP analysis.



Figure 3. XRD patterns of g-C₃N₄, GO, g-C₃N₄-rGO and Pd/g-C₃N₄-rGO

To investigate the thermal stability of the Pd (4 wt%)/g-C₃N₄-rGO catalyst, thermal gravimetric analysis (TGA) was performed in the scanning range of 25 to 800 °C with a rate of 10 °C/min where it shows about 40% weight loss up to 800 °C (Fig. 4). The gentle slope observed until 400 °C is probably related to the loss of surface water, CO, CO₂, and other oxygen functional groups of the catalyst that resulted in 10.4% loss of the mass [87]. The 25% loss of weight in a range of 400-600 °C arises from the destruction of the g-C₃N₄-rGO planes. The minor mass-loss between 600-800 °C could be related to the loss of oxygen from palladium oxide present in the char yield. Finally, the overall weight loss of 40% from the fresh catalyst was observed from 25 to 800 °C.



Figure 4. TGA curve for Pd/g-C₃N₄-rGO nanocatalyst

3.1.4 FESEM-EDS and TEM images

Fig. 5 shows the FESEM images of the g-C₃N₄, g-C₃N₄-rGO and Pd (4 wt%)/g-C₃N₄-rGO samples. The lamellar structure of g-C₃N₄ can clearly be seen in Figs 5a, and 5b where after pyrolysis and formation of the g-C₃N₄-rGO sample, the surface morphology of the composite had completely changed (Figs 5c, and 5d), and the sample has the two-dimensional sheet-like structure with many wrinkles. In addition, the images of (e, and f) in this figure show the planar structure of the Pd (4 wt%)/g-C₃N₄-rGO catalyst.

New Journal of Chemistry Accepted Manuscript





Energy dispersive X-ray Mapping analysis was also performed to study whether palladium nanoparticles were homogeneously distributed in the support (Fig. 6a-h). The EDS data showed the amount of 1.87 wt% of palladium on the surface of the g-C₃N₄-rGO composite. In addition, in mapping images of this catalyst, different elements such as C, O, N, and Pd are shown under different colors in which Pd NPs are dispersed quite homogeneously on the surface of the g-C₃N₄-rGO support.



Figure 6. EDS mapping analysis result for the Pd/g-C₃N₄-rGO

TEM images of the Pd (4 wt%)/g-C₃N₄-rGO were obtained to observe particle size distributions of palladium nanoparticles (Fig. 7). The particle size distributions were obtained using the software that counted approximately 100-150 particles. The Pd nanoparticles were uniformly dispersed in the g-C₃N₄-rGO network, and the statistical analysis showed that the mean diameters of the spherical shape palladium nanoparticles were 9 nm.



Figure 7. TEM images of $Pd/g-C_3N_4$ -rGO and histogram of the size distribution of the Pd NPs.

3.1.5 N₂ sorption studies and ICP-OES measurements

The specific surface area (S_{BET}), Barrett-Joyner-Halenda desorption average pore diameter (d_{BJH}), total pore volume (V_{tot}), average pore size ($d_{average}$) and Langmuir surface area are summarized in Table 1. According to the IUPAC definitions (Fig. 8b), the Pd (4 wt%)/g-C₃N₄-rGO catalyst should be categorized as a Type III solid with macro-mesoporous pores (Fig. 8a) [88].

Table 1. The pore parameters of the Pd (4 wt.%)/g-C₃N₄-rGO nanocatalyst

Sample	$S_{BET}(m^2g^{\text{-}1})^{a}$	$d_{\rm BJH}(nm)^{b}$	V_{tot} (cm ³ g ⁻¹) ^c	d _{average} (nm) ^d	S _{Langmuir} (m ² g ⁻¹)
Pd/g-C ₃ N ₄ -rGO	77.3	1.2	0.3	2.2	120.5

^a Brunauer–Emmet–Teller (BET) surface area. ^b Pore diameter calculated by the Barrett–Joyner–Halenda (BJH) method utilizing the adsorption branches. ^c Total pore volume calculated as the amount of nitrogen adsorbed at relative pressure. ^d Average pore diameter. ^e Langmuir surface area.



Figure 8. N₂ adsorption-desorption isotherm of Pd/g-C₃N₄-rGO catalyst (a), IUPAC isotherms for gas physisorption

The precise amount of loaded Pd metal in the Pd (4 wt%)/g-C₃N₄-rGO catalyst was measured using ICP analysis, where the fresh catalyst had 0.11 mmol.g⁻¹, and the catalyst after 5 runs had 0.09 mmol.g⁻¹. As will be discussed, this catalyst has retained its activity without significant loss of its activity after five runs.

Page 15 of 28

3.2 Catalytic performance



Scheme 1. Oxidation reaction of ethyl benzene catalyzed by Pd/g-C₃N₄-rGO in the presence of TBHP

Catalyst activity of the Pd/g-C₃N₄-rGO catalyst was investigated through ethylbenzene oxidation in acetonitrile in the presence of TBHP as the oxidizing reagent. The oxidation of the benzylic C-H bond in ethylbenzene using TBHP through a radical chain resulted in acetophenone as the main product and benzaldehyde as a byproduct (Scheme1). Effect of the amount of catalyst on reaction progress is depicted in Fig. S2. As displayed, the amount of 10 mg of the Pd (4 wt%)/g-C₃N₄-rGO catalyst leads to maximum conversion and selectivity to acetophenone. By increasing the amount of catalyst to larger amounts, the selectivity and conversion did not change appreciably. Therefore, in all subsequent experiments, 10 mg of the catalyst was used.

As shown in Table 2, the time of the reaction has a considerable influence on the reactivity and selectivity of the reaction. By enhancing the time from 6 to 24 h, not only the conversion of ethylbenzene to acetophenone was increased, but also the selectivity was improved to some extent. **Based on the data reported in this work, we cannot calculate the TOF [89, 90], and only the TON was reported which might be sufficient from an economic point of view**. Therefore, 24 h was chosen as the optimal time.

Entry	Time(h)	Conversion	TON ^a	Selectivity (%)	
-		(%)			ОН
1	6	30	4545	90	10
2	12	41	3106	95	5
3	24	67	2538	97	3
4	36	67	1692	97	3

Table 2. The effect of reaction time on the conversion and selectivity of EB oxidation

Reaction conditions: EB: TBHP (mol ratio) = 1:4, temperature = reflux, 5 ml CH₃CN, 10 mg Pd (4 wt.%)/g-C₃N₄-rGO ^a Turnover Number = [moles of ethyl benzene consumed]/(total mole metal)

The effect of temperature on the oxidation of ethylbenzene over the Pd (4 wt%)/g-C₃N₄rGO catalyst was also studied in the temperature range of 40 to 80 °C (CH₃CN as solvent) (Table 3). The results show that by increasing the temperature, a high conversion of 67% with a selectivity of 97% for acetophenone was achieved at 80 °C.

Table 3.	The influence	of reaction	temperature o	n the	conversion	and	selectivity	of EB	oxidation
----------	---------------	-------------	---------------	-------	------------	-----	-------------	-------	-----------

Entry	Temperature	Conversion	TON ^a		Selectiv (%)	vity	
2	(°C)	(%)			о н	OH	ОН
1	40	22	833	64	19	4	13
2	60	36	1364	89	5	6	-
3	80	67	2538	97	3	-	-

Reaction conditions: EB: TBHP (mol ratio) = 1:4, 24h, 5 mL CH₃CN, 10 mg Pd (4 wt.%)/g-C₃N₄-rGO

^a Turnover number = [moles of ethyl benzene consumed]/(total mole metal).

After optimizing the amount of catalyst, reaction time and temperature, the amount of Pd loaded on the g-C₃N₄-rGO composite was also optimized (Figure S3). By increasing the amount

 Rublished on 04.4 Roil 2018. Downloadedby Ruger Name University of London on 44.2019 5:32-33.2 Mo

 2
 9
 5
 4
 8
 7
 0
 5
 7
 0

 2
 9
 5
 4
 8
 7
 0
 5
 7
 0

of palladium loaded on the support to 6 wt%, a decrease in the conversion of ethylbenzene was observed that could be related to more aggregation of palladium nanoparticles and decreasing the active sites due to the constant amount of the g- C_3N_4 -rGO support.

Tables 4 and 5 show catalytic oxidation of ethylbenzene over $g-C_3N_4$, $g-C_3N_4$ -rGO, Pd/rGO, and Pd/g-C₃N₄ as catalysts. These catalysts have shown a lower conversion in comparison with Pd (4 wt%)/g-C₃N₄-rGO. Reactivity of $g-C_3N_4$ without metal could be related to electron-deficient defects existing on its surface, and there should be much fewer defects on the surface of the $g-C_3N_4$ -rGO sample. It seems that the presence of nitrogen atoms in the graphitized carbon nitride structure have an important role in improving the stability of palladium nanoparticles with a high disparity in the Pd (4 wt%)/g-C₃N₄-rGO catalyst [91]. Hence, Pd/g-C₃N₄-rGO nanostructure with the highest efficiency of ethylbenzene conversion and selectivity toward acetophenone was selected as the best catalyst for the reaction.

Entry	Catalysts	Conversion	TON ^a	Sele	ctivity %)
ŗ	-	(%)		o ↓	о н
1	g-C ₃ N ₄	58	-	96	4
2	g-C ₃ N ₄ -rGO	30	-	92	8
3	Pd/g-C ₃ N ₄ -rGO	67	60912	97	3
4	$Pd/g-C_3N_4$	39	-	93	7

Table 4. Results of EB oxidation catalyzed by different catalysts

Reaction conditions: EB: TBHP (mol ratio) = 1:4, 24 h, temperature = reflux, 5 mL CH₃CN, 10 mg cat

^a Turnover number = [moles of ethyl benzene consumed]/[total mole metal]

New Journal of Chemistry Accepted Manu



Table 5. Nitrogen doping effect on the conversion and selectivity of EB oxidation

Reaction conditions: EB: TBHP (mol ratio) = 1:4, 24 h, temperature = reflux, 5 mL CH₃CN, 10 mg cat

^a Turnover number = [moles of ethyl benzene consumed]/[total mole metal]

Based on the results shown in Table 6, it seems that TBHP 80% as oxidizing reagent should be chosen as the best oxidant compared to H_2O_2 and O_2 because of its more intrinsic activity and solubility in the mentioned reactions. Furthermore, according to literature, TBHP with the generation of active oxygen species on redox sites prevents removal of O_2 from the reaction mixture, and as a result, high conversion of ethylbenzene is obtained [56]. On the other hand, when O_2 is used as the oxidant, the reaction conversion is very low because of its easy expulsion from the reaction mixture, and more importantly activation energy of breaking the C-H bond by molecular oxygen. Decomposition of H_2O_2 in the reaction conditions explains its low reactivity. Therefore, TBHP was selected as the best oxidant in a molar ratio of 1:4 for ethylbenzene oxidation to acetophenone (Table 7). Moreover, the reaction was conducted in different solvents and in agreement with previously reported data, acetonitrile was applied as the medium for the ethylbenzene oxidation reaction. Probably, the polar nature of this solvent resulted in partial decomposition of TBHP at the beginning of the reaction.

Moreover, it is clearly documented that oxidation of ethyl benzene using TBHP as oxidant follows the free-radical mechanism and goes through formation of ethyl benzene hydroperoxide as intermediate. This intermediate could be activated by the catalyst in two different routes for producing acetophenone or benzaldehyde where benzoic acid is obtained from oxidation of benzaldehyde. If we accept that oxidation of ethyl benzene hydroperoxide was occurred on the active sites of the catalyst, then for producing benzaldehyde or acetophenone, a C-C or a C-H bond must be broken, respectively (Scheme 2). Therefore, it might be reasonable to say that at

lower temperatures, the conformational arrangement shown in route a, has more chance to be formed.



Scheme 2. Proposed mechanism for conversion of ethyl benzene hydroperoxide for producing benzaldehyde (route a), and acetophenone (route b).

	Table 6. The result	s of EB oxidatio	n with different	oxidant
--	---------------------	------------------	------------------	---------

Entry	Oxidant effect	Conversion	TON ^e	Selectivity (%)			
-		(%)		● ●	ОН		
1	TBHP ^a	67	2538	97	3		
2	$H_2O_2^a$	5	189	90	10		
3	$O_2{}^b$	1	38	100	-		
4	O ₂ /TBHP ^c	31	1174	95	5		
5	TBHP ^d	21	795	87	13		

Reaction conditions: ^a EB:TBHP (mol ratio) = 1:4, 24 h, temperature = reflux, 5 mL CH₃CN, 10 mg Pd (4 wt.%)/g-C₃N₄-rGO ^b 1mmol EB, 24 h, 80 °C, 5 mL CH₃CN, 20 bar O₂, The reaction was carried out inside the reactor, 10 mg Pd (4 wt.%)/g-C₃N₄-rGO rGO

^c 1 mmol EB, 19 μl TBHP, 24 h, 110 °C, 5 mL CH₃CN, 20 bar O₂, The reaction was carried out in an auto pressure reactor, 10 mg of Pd (4 wt.%)/g-C₃N₄-rGO

^d 1 mmol EB, 19 µl TBHP, 24 h, 110 °C, 5 mL CH₃CN, The reaction was carried out in an auto pressure reactor, 10 mg Pd (4 wt.%)/g-C₃N₄-rGO

^e Turnover number = [moles of ethyl benzene consumed]/(total mole metal)

Entry	EB:TBHP	Conversion	TON ^a	(%	ctivity %)
-	(mol)	(%)			ОН
1	1:1	45	1704	96	4
2	1:2	47	1780	93	7
3	1:3	60	2273	97	3
4	1:4	67	2538	97	3
5	1:5	67	2538	97	3

Table 7. The effect of molar ratio of EB: TBHP on conversion and selectivity to products

Reaction conditions: 1 mmol EB, 24 h, temperature = reflux, 5 mL CH₃CN, 10 mg Pd (4 wt.%)/g-C₃N₄-rGO

^a Turnover number = [moles of ethyl benzene consumed]/(total mole metal)

3.2.1 Reusability of catalyst

After the optimization of parameters affecting the activity of Pd (4 wt%)/g-C₃N₄-rGO catalyst in selective ethylbenzene oxidation to acetophenone, reusability of the prepared catalyst was examined under obtained optimized conditions. To this end, the catalyst was simply separated by filtration after the first run, washed with acetone, dried at 80 °C, and used again in the sequential runs. Reusability of catalyst was examined for 5 runs in a similar manner. The results of Table S1 indicate high stability of Pd (4 wt%)/g-C₃N₄-rGO catalyst during the reaction without considerable loss of its activity. In addition, the results of ICP analysis of the catalyst reached to 0.09 mmol) was leached from g-C₃N₄-rGO support. Based on the observed data, we can conclude that g-C₃N₄-rGO is a good and effective support for dispersing and immobilizing Pd nanoparticles.

3.2.2 Comparison with the other researches on oxidation of ethylbenzene

Table S2 shows the results obtained by catalytic oxidation of ethylbenzene with TBHP as the oxidant in the presence of Pd/g-C₃N₄-rGO catalyst as compared to other catalytic systems previously reported in the literature. In our previous work [92], we used supercritical CO₂ for performing this reaction where we reached excellent conversion and selectivity. But comparing the operational difficulties for performing such reaction in supercritical conditions makes this work acceptable. This is quite obvious that the Pd/g-C₃N₄-rGO catalyst used in the present study has a reasonable catalytic activity and performance selectivity, and also has more appropriate and milder conditions in comparison to other catalysts.

4. Conclusion

Since selective oxidation of ethylbenzene is hardly performed because of the lack of electron active groups in aromatic rings, more active, economic and green catalysts with reusability properties are of importance. Therefore, in this study, the hybrid structure with honeycomb units was formed for immobilizing Pd nanoparticles through the modification of GO surface with g-C₃N₄ by simple wet impregnation method that led to more active sites or in other words, increasing the number of defects which enhancing the reactivity of the catalyst. The catalyst was characterized by TEM, XPS, FESEM-EDS & Mapping, X-ray Diffraction, BET–

Surface area, FT-IR, TGA, and ICP-OES techniques and tested in the ethylbenzene oxidation reaction by TBHP as oxidant reagent, and the result showed 67% conversion and 97% selectivity toward acetophenone under optimized conditions. Moreover, this catalyst retained its activity and selectivity to the desired product and remained approximately constant after 5 runs.

Acknowledgments

We gratefully acknowledge financial supports from the Isfahan University of Technology and technical support from Mons University.

References

1 2 3

4 5

6

7 8

versity of London on 4/4/2019 0 6 8 2 9 5 5

Nark (Nark)

38

39 40

41 42

43 44

45 46

47

48 49

50

51 52

53

54 55

- (1) Y. Wan, H. Wang, Q. Zhao, M. Klingstedt, O. Terasaki and D. Zhao, J. Am. Chem. Soc., 2009, **131**, 4541-4550.
- (2) Y. Hao, G-P. Hao, D-C. Guo, C-Z. Guo, W-C. Li, M-R. Li and A-H. Lu, Chem.Cat.Chem., 2012, 4, 1595-1602.
- (3) F. Bonaccorso, Z. Sun, T. Hasan and A. C. Ferrari, Nuture photonics., 2010, 4, 611-622.
- (4) K. I. Bolotin, K. J. Sikes, Z. Jiang, M. Klima, G. Fudenberg, J. Hone, P. Kim and H. L. Stormer, Solid State Commun., 2008, **146**, 351-355.
- (5) C. Lee, X. Wei, J. W. Kysar and J. Hone, Sci., 2008, **321**, 385-388.
- (6) M. D. Stoller, S. Park, Y. Zhu, J. An and R. S. Ruoff, Nano Lett., 2008, 8, 3498-3502.
- (7) D. Wang, D. Choi, J. Li, Z. Yang, Z. Nie, R. Kou, D. Hu, C. Wang, L. V. Saraf, J. Zhang, L. A. Aksay and J. Liu, ACS Nano., 2009, 3, 907-914.
- (8) X. Li, R. Shen, S. Ma, X. Chen and J. Xie, Appl. Surf. Sci., 2018, 430, 53-107.
- (9) X. Li, J. Yu, S. Wageh, A. A. Al-Ghamdi and J. Xie, Small., 2016, 12, 6640-6696.
- (10) P. T. Yin, S. Shah, M. Chhowalla and K. Lee, Chem. Rev., 2015, 115, 2483-2531.
- (11) O. C. Compton and S. T. Nguyen, Small., 2010, 6, 711-723.
- (12) G. Eda, G. Fanchini and M. Chhowalla, Nat Nanotechnol., 2008, 3, 270-274.
- (13) R. J. White, N. Yoshizawa, M. Antonietti, M-M. Titirici, Green Chem., 2011, 13, 2428ss2434.
- (14) T. C. Nagaiah, A. Bordoloi, M. D. Sanchez, M. Muhler and W. Schuhmann, Chem. Sus. Chem., 2012, 5, 637-641.
- (15) G. Wu, R. Swaidan, D. Li and N. Li, Electrochim. Acta., 2008, 53, 7622-7629.
- (16) R. Atchudan, N. Muthuchamy, T. Edison, S. Perumal, R. Vinodh, K. H. Park and Y. R. Lee, Biosens. Bioelectron., 2019, **126**, 160-169.
- 58 59
- 60

4

5 6

7

8

ີ່ ອີຊ ຊີ25

1 market on the state

38

39

40 41

42

43 44

45 46

47

48 49

50

51 52

53

54 55

56 57

- (17) N. Muthuchamy, R. Atchudan, T. Edison, S. Perumal and Y. R. Lee, J. Electroanal. Chem., 2018, 816, 195-204.
- (18) A-I. Gopalan, S. Komathi, N. Muthuchamy, K. P. Lee, M. J. Whitcombe, L. Dhana and G. Sai-Anand, Prog. Polym. Sci., 2019, **88**, 1-129.
- (19) X. Lin, S. Zhao, Y. Chen, L. Fu, R. Zhu and Z. Liu, J Mol. Catal. A Chem., 2016, **420**, 11-17.
- (20) S. Yang, Y. Gong, J. Zhang, L. Zhan, L. Ma, Z. Fang, R. Vajtai, Z. Wang and P. M. Ajayan, Adv. Mater., 2013, 25, 2452-2456.
- (21) Y. Zhang, T. Mori, L. Niu and J. Le, Energy Environ. Sci., 2011, 4, 4517-4521.
- (22) G. Liao, S. Chen, X. Quan, H. Yu and H. Zhao, J. Mater. Chem., 2012, 22, 2721-2726.
- (23) J. Liu, Y. Yang, N. Liu, Y. Liu, H. Huang and Z. Kang, Green Chem., 2014, 16, 4559-4565.
- (24) E. Z. Lee, Y. Jun, W. H. Hong, A. Thomas and M. M. Jin, Angew. Chem. Int., 2010, **49**, 9706-9710.
- (25) X. Li, J. Xie, C. Jiang, J. Yu and P. Zhang, Front. Environ. Sci. Eng., 2018, 12, 14.
- (26) D. Xu, B. Cheng, W. Wang, C. Jiang and J. Yu, Appl. Catal., B., 2018, 231, 368-380.
- (27) J. Wen, J. Xie, X. Chen and X. Li, Appl. Surf. Sci., 2017, **391**, 72-123.
- (28) A. Nikokavoura and C. Trapalis, Appl. Surf. Sci., 2018, **430**, 18-52.
- (29) Y. Yu, Q. Zhoua and J. Wang, Chem. Commun., 2016, **52**, 3396-3399.
- (30) Y. Zhang, J. Liu, G. Wu and W. Chen, Nanoscale., 2012, 4, 5300-5303.
- (31) Q. Su, J. Sun, J. Wang, Z. Yang, W. Cheng and S. Zhang, Catal. Sci. Technol., 2014, 4, 1556-1562.
- (32) L. Shi, L. Liang, F. Wang, M. Liu, S. Zhong and J. Sun, Catal. Commun., 2015, **59**, 131-135.
- (33) J. Xiao, Y. Xie, F. Nawaz, S. Jin, F. Duan, M. Li and H. Cao, Appl. Catal., B., 2016, **181**, 420-428.
- (34) S. Kumar, S. Tonda, A. Baruah and V. Shanker, J. Mater. Chem. A., 2013, 1, 5333-5340.
- (35) Y. C. Zhao, D. L. Yu, O. Yanagisawa, K. Matsugi and Y. J. Tian, Diamond Relat. Mater., 2005, **14**, 1700-1704.
- (36) H. A. Ma, X. P. Jia, L. X. Chen, P. W. Zhu, W. L. Guo, X. B. Guo, Y. D. Wang, S. Q. Li, G. T. Zou, G. Zhang and P. Bex, J. Phys.: Condens. Matter., 2002, 14, 11269-11273.
- (37) C. Li, C-B. Cao, H-S. Zhu, Q. Lv, J-T. Zhang and X. Xiang, Mater. Sci. Eng., B., 2004, 106, 308-312.
- (38) A. Thomas, A. Fischer, F. Goettmann, M. Antonietti, J-O. Muller, R. Schlogl and J-M.

Carlsson, J. Mater. Chem., 2008, 18, 4893-4908.

- (39) S. C. Yan, Z. S. Li and Z. G. Zou, Langmuir., 2009, 25, 10397-10401.
- (40) Z. Mo, X. She, Y. Li, L. Liu, L. Huang, Z. Chen, Q. Zhang, H. Xu and H. Li, RSC Adv., 2015, 5, 101552-101562.
- (41) X-S. Zhang, J-Y. Hu and H. Jiang, Chem. Eng. J., 2014, 256, 230-237.
- (42) H. Yan, Y. Chen and S. Xu, Int. J. Hydrogen Energy., 2012, 37, 125-133.
- (43) J. Zhang, M. Zhang, G. Zhang and X. Wang, ACS Catal., 2012, 2, 940-948.
- (44) Q. Xiang, J. Yu and M. Jaroniec, J. Phys. Chem. C., 2011, 115, 7355-7363.
- (45) Y. Li, H. Zhang, P. Liu, D. Wang, Y. Li and H. Zhao, Small., 2013, 9, 3336-3344.
- (46) Y. Min, X. Feng Qi, Q. Xu and Y. Chen, Cryst. Eng. Comm., 2014, 16, 1287-1295.
- (47) Y. Bao and K. Chen, Appl. Surf. Sci., 2018, 437, 51-61.
- (48) J. Yin, G. Liao, D. Zhu, P. Lu, L. Li, J. Photochem. Photobiol., A., 2016, 315, 138-144.
- (49) Q. Liu and J. Zhang, Langmuir., 2013, 29, 3821-3828.
- (50) Q. Hao, S. Hao, X. Niu, X. Li, D. Chen and H. Ding, Chin. J. Catal., 2017, 38, 278-286.
- (51) W. Zhang, H. Huang, F. Li, K. Deng and X. Wang, J. Mater. Chem. A., 2014, **2**, 19084-19094.
- (52) Raji, Vadakkekara, M. Chakraborty and P. A. Parikh, Ind. Eng. Chem. Res., 2012, **51**, 5691-5698.
- (53) K. Bauer, D. Garbe and H. Surburg, Commen fragrance and flavor materials; Wiley: New York, 1960.
- (54) G. Lartigau and P-E. Bost, Patent No. 3968162, 1976.
- (55) M. Arshadi and M. Ghiaci, Appl. Catal., A., 2011, 399, 75-86.
- (56) P. Visuvamithiran, K. Shanthi, M. Palanichamy and V. Murugesan, Catal. Sci. Technol., 2013, **3**, 2340-2348.
- (57) L. Luo, H. Liu, G. Li and C. Hu, RSC Adv., 2016, 6, 55463-55471.
- (58) Y. Chen, S. Zhao and Z. Liu, Phys. Chem. Chem. Phys., 2015, 17, 14012-14020.
- (59) M. Nandi and A. K. Talukdar, Arabian J. Chem., 2016.
- (60) K. N. Bhagya and V. Gayathri, J Porous Mater., 2012, 19, 1037-1045.
- (61) R. K. Jha, S. Shylesh, S. S. Bhoware and A. P. Singh, Microporous Mesoporous Mater., 2006, **95**, 154-163.
- (62) Y-X. Du, Z-Q. Zhang, Y-H. Yao and J. Li, Inorg. Chem. Commun., 2016, 64, 19-22.
- (63) S. K. Jana, P. Wu and T. Tatsumi, J. Catal., 2006, 240, 268-274.

59 60

1 2 3

4 5

6

7

8

194 25

38

39 40

41

42 43

44 45

46 47

48 49

50

51 52

53

54 55

4 5

6

7

8

0 1 232:33.BMG

194 25

18 Downloaded by

ົສ1

38

39

40 41

42

43 44

45

46 47

48 49

50

51

New Journal of Chemistry Accepted Manuscript

- (64) R. Xie, G. Fan, L. Yang and F. Li, Chem. Eng. J., 2016, **288**, 169-178.
- (65) K. M. Parida and S. S. Dash, J. Mol. Catal. A: Chem., 2009, 306, 54-61.
- (66) A. C. Bueno, A. O. de Souza and E. V. Gusevskaya, Adv. Synth. Catal., 2009, 351, 2491-2495.
- (67) Y. Liu, X. Wang, X. Cai, G. Chen, J. Li, Y. Zhou and J. Wang, Chem. Cat. Chem., 2016, 8, 448-454.
- (68) D. Sun, B. Li, J. Lan, Q. Huang and J. You, Chem. Commun., 2016, 52, 3635-3638.
- (69) D. I. Enache, J. K. Edwards, P. Landon, B. Solsona-Espriu, A. F. Carley, A. A. Herzing, M. Watanabe, C. J. Kiely, D. W. Knight and G. J. Hutchings, Sci., 2006, 311, 362-365.
- (70) J. Kim, A. Kim, N. Muthuchamy and K. H. Park, Catal., 2018, 8, 280.
- (71) S. Jang, T. Kim and K. H. Park, Catal., 2017, 7, 247.
- (72) M. Ghiaci, Z. Sadeghi, M. E. Sedaghat, H. Karimi-Maleh, J. Safaei-Ghomi and A. Gil, Appl. Catal., A., 2010, **381**, 121-131.
- (73) W. S. Hummer and R. E. Offeman, J. Am. Chem. Soc., 1958, 80, 1339.
- (74) R. Arrigo, M. Hävecker, R. Schlögl and D. Sheng Su, Chem. Comm., 2008, 4891-4893.
- (75) D. Wei, Y. Liu, Y. Wang, H. Zhang and L. Huang, Nano Lett., 2009, 9, 1752-1758.
- (76) C. D. Wagner and G. E. Muilenberg, Handbook of x-ray photoelectron spectroscopy: a reference book of standard data for use in x-ray photoelectron spectroscopy. Physical Electronics Division; Perkin-Elmer Corp., 1979.
- (77) J. Chang, X. Sun, L. Feng, W. Xing, X. Qin and G. Shao, J. Power Sources., 2013, 239, 94-102.
- (78) S-H. Oh and G. B. Hoflund, J. Phys. Chem. A., 2006, 110, 7609-7613.
- (79) L. Meng, A-P. Jia, J-Q. Lu, L-F. Luo, W-X. Huang and M-F. Luo, J. Phys. Chem. C., 2011, **115**, 19789-19796.
- (80) K. R. Priolkar, P. Bera, P. R. Sarode, M. S. Hegde, S. Emura, R. Kumashiro and N. P. Lalla, Chem. Mater., 2002, 14, 2120-2128.
- (81) W. Wang, J. Yao, H. Li, D. Su and M. Antonietti, J. Am. Chem. Soc., 2011, **133**, 2362-2365.
- (82) M. Ghiaci and M. Ghazaie, Catal. Commun., 2016, 87, 70-73.
- (83) A. Kumar Das, M. Srivastav, R. K. Layek, M. E. Uddin, D. Jung, N. H. Kim and J. H. Lee, J. Mater. Chem. A., 2014, **2**, 1332-1340.
- (84) M. Sierra, E. Borges, P. Esparza, J. Méndez-Ramo, J. Martín-Gil and P. Martín-Ramos, Sci. Technol. Adv. Mater., 2016, **17**, 659-668.
- (85) Y. Fu and X. Wang, Ind. Eng. Chem. Res., 2011, **50**, 7210-7218.

- 58
- 59 60

New Journal of Chemistry Accepted Manuscript

- (86) Y. Sun, C. Li, Y. Xu, H. Bai, Z. Yao and G. Shi, Chem. Commun., 2010, 46, 4740-4742.
- (87) J. Zhang, J. Ding, C. Li, B. Li, D. Li, Z. Liu, Q. Cai, J. Zhang and Y. Liu, ACS Sustainable Chem. Eng., 2017, **5**, 4982-4991.
- (88) K. A. Cychosz and M. Thommes, Engineering., 2018, 4, 559-566.
- (89) S. Kozuch and J. M. L. Martin, ACS Catal., 2012, 2, 2787-2794.
- (90) A. P. Umpierre, E. de Jesffls and J. Dupont, Chem.Cat.Chem., 2011, 3, 1413-1418.
- (91) D. Deng, Y. Yang, Y. Gong, Y. Li, X. Xu and Y. Wang, Green Chem., 2013, **15**, 2525-2531.
- (92) M. Arshadi, M. Ghiaci, A. Rahmanian, H. Ghaziaskar and A. Gil, Appl. Catal., B., 2012, **119-120**, 81-90.
- (93) M. Ghiaci, F. Molaie, M. E. Sedaghat and N. Dorostkar, Catal. Commun., 2010, 11, 694-699.

New Journal of Chemistry Accepted Manuscript

Table of contents

A hybrid structure $g-C_3N_4$ -rGO with honeycomb units was prepared for immobilizing Pd nanoparticles by simple wet impregnation method.

Table of contents

