Ru supported on N-doped reduced graphene oxide aerogels with different N-type for
alcohol selective oxidation

Joel Sanchez-Garcia, Ana M. Benito, Wolfgang K. Maser, Enrique García-Bordejé*

Instituto de Carboquímica (ICB-CSIC), Miguel Luesma Castán 4, E-50018 Zaragoza,
Spain, jegarcia@icb.csic.es

Keywords

graphene aerogel, polydopamine coating, N-doped carbon, Ru catalyst, selective oxidation.

Abstract

Reduced graphene oxide aerogels doped with nitrogen have been prepared via two different strategies, namely, direct doping of rGO nanosheets with NH_3 (GANH3) and coating the rGO nanosheets with an N-containing amorphous carbon derived from polydopamine (GADA). Both methods lead to comparable N/C ratios (3.4-4.7 %) but the relative contribution of quaternary nitrogen is 30% for GADA while only 15% for GANH3. Moreover, the N is incorporated within graphene lattice for GANH3 while it is within an amorphous carbon layer on top of graphene nanosheets for GADA. The Ru catalyst supported on the aerogels exhibited very distinct performance in the selective oxidation of benzyl alcohol depending on the support material despite having similar Ru particle size. The best performance for 5 wt% Ru on GADA can be explained by the larger reduction extent of Ru and the more hydrophobic surface. The open macroporosity of the aerogel makes it an excellent platform for using as structured catalyst in a continuous flow process.

1. Introduction

* Corresponding author: Tel.: + 34 976733977; fax.: +34 976733318 *E-mail address:* jegarcia@icb.csic.es

Liquid phase oxidation of alcohols to aldehydes with molecular oxygen has been widely studied due to its interest for fine chemical synthesis[1, 2] and, more recently, for the transformation of biomass platform molecules into value added chemicals.[3, 4] Usually Pt, Pd and Au metals have been investigated for this reaction[4] while Ru is a cheaper metal and it has been investigated in a more limited extent.[5] Regarding the support material, N-doped carbon has emerged as an outstanding support for metal nanoparticles in the aerobic oxidation of alcohols.[6] Nitrogen is believed to act as a ligand of the metal similar as occurring in homogeneous catalysis. Accordingly, a strong interaction between the metal and nitrogen on carbon takes place as found both theoretically and experimentally.[7, 8] As a consequence of to this strong interaction, there is electronic charge transfer between metal and support[9, 10] and sintering of nanoparticles is prevented,[8, 11] enhancing activity and stability of the catalyst under reaction conditions.

Besides the effect on the metal, the enhanced oxidation of benzyl alcohol using nitrogen doped supports has been attributed to the increased basicity and π -binding ability of the support while acidic supports promote side reactions.[12] N-doped graphene can be prepared from GO using different ways such as gas phase annealing of GO under NH_3 gas[13-15] or solvothermal treatment of a mixture of GO and a nitrogen-containing molecule (NH_3 or hydrazine).[16, 17] Other researchers use a nitrogen containing polymer such as polyaniline to prepare a N-doped graphene upon pyrolysis.[18] Polydopamine (PDA) is prepared by polymerization of dopamine, which has catechol and amine functionality that mimics the natural glues of living organisms such as mussels.[19] Polydopamine has the ability to form chemically adherent films on virtually any surface such as metal oxides[20, 21], carbon nanotubes[22] or even superhydrophobic perfluoroalkane surfaces.[23] PDA was also reported to carry out the simultaneous functionalization and reduction of graphene oxide.[24-27] When reduced graphene oxide aerogels are formed from GO in the presence of dopamine, it is reported that nanographene is doped with nitrogen and PDA forms crosslinking points between nanographene sheets.[25, 26]

Herein, we have used two different approaches for doping graphene aerogels with nitrogen. In one case, we have carried out the rGO aerogel formation adding NH_3 which reacts with the oxygenated surface groups of GO to produce N-doped graphene upon thermal treatment. In the other case, we developed a new synthetic approach via coating GO nanosheets with polydopamine (PDA) and subsequent post-thermal treatment. In

both strategies, we fabricate nitrogen doped graphene with relatively high nitrogen content and very accessible because all the nitrogen is on the external surface of the open macroporous structure of the aerogel. The main difference is that for NH_3 treated aerogel the nitrogen is directly bonded to the rGO carbon lattice while for PDA-coated aerogel nitrogen is bonded to an amorphous carbon layer on top of the rGO nanosheets. The catalyst prepared after supporting Ru nanoparticles were tested in the selective oxidation of benzyl alcohol to benzaldehyde. Ru catalyst on the N-doped rGO aerogels prepared by the PDA approach exhibited significantly higher catalytic activity than those prepared by the NH_3 approach, the undoped ones and a commercial Ru on alumina catalyst with the same metal loading.

2. Experimental

Graphene Oxide (water dispersion) was supplied by Graphenea®. Trizma® Base, Ethylenediaminetetraacetic acid ferric sodium salt, Hexadecane, Dopamine hydrochloride and 5% Ruthenium on alumina catalysts were supplied by Sigma-Aldrich®. Benzyl Alcohol for analysis, Benzaldehyde, Amonio Hidroxido, Nickel(II) Nitrate 6-hydrate and cyclohexane were supplied by Panreac® and Ruthenium(III) nitrosylnitrate was supplied by Alfa Aesar®.

Scheme 1 illustrates the process of catalyst preparation, of which the first step is the formation of aerogels. For the formation of the aerogel with polydopamine, a mixture consisting of 5 ml of GO solution (4 mg ml^{-1})+ 4.9 ml of H_2O + 7mg de Trizma and different amounts of dopamine (1.5 mg, 3 mg, 7 mg, 13 mg, 16 mg and 20 mg) was introduced in an autoclave and kept at 180°C overnight. The aerogel without dopamine was prepared according to the protocol used previously[28]. In brief, 200 μl of NH_3 was added to 10 ml of a 2 mg/ml GO solution until giving a basic pH (11.3). This aerogel is denoted as GANH3. The precipitated hydrogel is dried by freeze-drying to prevent the collapse of the pores, eventually leading to a graphene aerogel. The aerogel is subsequently heat-treated in N_2 flow at 800°C during 1 hour. The aerogels with dopamine are denoted as GA followed by the amount of dopamine. The aerogels previously to heat-treatment are denoted with_0 at the end of the name. When it is not state otherwise, the aerogels have been heat treated at 800°C .

Scheme 1. Illustration of the two pathways used for the preparation of N-doped graphene aerogels using the two different pathways: 1) coating with polydopamine and pyrolysis; 2) Adding NH₃ in the initial GO dispersion.

The Ru catalysts were prepared by dry impregnation. To this end, the aerogel is chopped to slices and introduced in a solution of Ruthenium(III) nitrosyl nitrate in ethanol with a concentration of 0.9972 mg/ml. The volume of solution was calculated to contain a 5 wt% of Ru respect to the weight of graphene aerogel. Subsequently, the aerogel is freeze-dried to remove the ethanol. The dried aerogel is subsequently heated at a rate of 1°C/min to 300 °C in N₂ and held during 1 h. Subsequently, the same heating process is carried out in H₂ to reduce the Ruthenium. When cooled down the catalyst is passivated with 1% O₂ overnight.

Raman characterisation was performed on a Horiba Jobin Yvon, LabRAM HR UV-VIS NIR. Raman spectra were recorded with an Ar-ion laser beam at an exciting radiation wavelength of 532 nm. The intensity of each peak was measured after subtraction of the baseline. The I_D/I_G ratios have been averaged for 10 measurements in different points of the samples.

XPS spectra were recorded with an ESCAPlus Omnicrom system equipped with a Al K α radiation source to excite the sample. All measurements were performed under UHV, better than 10⁻¹⁰ Torr. Internal referencing of spectrometer energies was made using the dominating C 1s peak of the support at 284.6 eV. The fitting was carried out using CasaXPS software after baseline Shirley method and fixing equal widths of the peaks and maximum width of 2 eV.

SEM analysis was carried out with a microscope SEM EDX Hitachi S-3400 N with variable pressure up to 270 Pa and with an analyzer EDX Röntec XFlash de Si(Li). The images were obtained both from the secondary and backscattered signal.

Surface areas were determined by N₂ adsorption at 77 K (BET) using a Micromeritics ASAP 2020 apparatus, after outgassing for 4 h at 423 K. In addition, it was also determined by CO₂ adsorption (Dubinin–Radushkevich) at 273 K in the same apparatus, after outgassing under the same conditions. The static contact angle was measured with a Attension optical tensiometer of Biolin Scientific using around 7 µL droplet of distilled water. To probe only the hydrophobicity of the graphene surface and decouple from porosity and texture effects the aerogels were pressed to form a non-porous thin film.

A transmission electron microscopy (TEM) investigation was performed with JEOL-2000 FXII electron microscope equipped with a field emission gun. Coupled there is a system for energy analysis of dispersed X-rays INCA 200 X-Sight de Oxford Instruments with resolution of 136 eV a 5.9 KeV, which allows the determination of the chemical composition in the focalized micro-region. TEM specimens were prepared by ultrasonic dispersion in ethanol of powder retrieved from the monoliths. A drop of the suspension was applied to a holey carbon support grid. The particle size distribution was determined using the ImageJ software and the average particle size was determined by statistical analysis according to the equation 1

$$d_{TEM} = \frac{\sum_i n_i d_i^3}{\sum_i n_i d_i^2} \quad \text{Eq. 1}$$

Where n_i is the number of particles of a certain average diameter (d_i).

X-ray diffraction (XRD) patterns were recorded using a Bruker D8 Advance diffractometer in configuration theta-theta using nickel-filtered CuK α radiation (wave length=1.54 Å), a graphite monochromatic source and scintillation detector. 2 θ angles from 3 to 80 ° were scanned with a length step of 0.05 and an accumulation time of 3 s. The reaction tests were carried out in a 300 ml Teflon-lined autoclave (Büchi, picoclave). 6 mg of the catalyst was introduced in the autoclave. The reaction mixture consisted of 80 µL of benzyl alcohol in 40 ml of cyclohexane as solvent and 200µL of hexadecane was added as internal standard. The standard reaction conditions were set at 80 °C and 10 Bar during 6 hours. The products were analysed by gas chromatography (GC Agilent 7820 autosampler). The TOF values were calculated as the mmol of benzyl alcohol converted divided per time and divided per mmol of Ru on the catalyst surface.

Where the moles of Ru on the catalyst surface were calculated multiplying the total mmol of Ru by the dispersion (D_{TEM}). The dispersion was calculated from the mean diameter determined by TEM (d_{TEM}) according to equation 2[29], where d_{at} is the atomic **diameter** of ruthenium, *i.e.* 0.268 nm.

$$D_{TEM} = \frac{1.23 \sqrt{d_{at} \cdot 3.32}}{d_{TEM}} \quad \text{Eq. 2}$$

3. Results and discussion

The reduced graphene oxides aerogels (rGO) denoted as GA and GANH3 were prepared as described in previous work.[28] In brief, both samples were prepared by hydrothermal treatment of GO dispersions in the absence and presence of NH_3 , respectively, followed by thermal treatment at 800 °C. GA contained negligible amount of nitrogen but GANH3 contained a 4.7 at% nitrogen. Here, we explored also another different approach to prepare aerogels doped with nitrogen based on the in-situ polymerization of dopamine (DA) simultaneously to rGO aerogel formation. In the resulting rGO aerogel, the nanosheets became coated by a polydopamine (PDA) layer. Further evidence of graphene surface modification with PDA is found by temperature programmed oxidation (TPO) in thermobalance (Figure S1). The weight loss below 450 °C can be ascribed to PDA since the graphene aerogel without PDA (GA) exhibited negligible weight loss in this temperature range. Moreover, it agrees with results in the literature in which PDA decomposition starts at around 200 °C.[30] In addition, the weight loss is correlated to the amount of dopamine added in the initial dispersion, indicating that the higher the initial concentration of dopamine, the higher the amount PDA attached to the aerogel. Furthermore, the thermal stability of the aerogel increases as the PDA content increases. This suggests that PDA binds to the more reactive sites of graphene surface making it more resistant to combustion. After pyrolysis in N_2 at 800 °C part of the nitrogen in PDA is retained in the carbonized material. This is confirmed because the nitrogen content determined by XPS increases as the loading of PDA increases (Figure S2 supporting material). For further study, we selected the aerogel prepared with 7 mg of dopamine which after pyrolysis contained a 3.4 at% of nitrogen determined by XPS. This aerogel is denoted as GADA. The Fitting of the XPS N 1s

peak for GA, GANH3 and GADA is shown in Figure 1a. GA has negligible N content while the aerogel prepared adding NH_3 (GANH3) contains a 4.7 at% N/C ratio. The aerogel GADA contains a 3.4 at% N/C ratio. The relative contribution of each nitrogen type is different for both aerogels. The relative contribution of quaternary nitrogen is significantly larger for GADA (30% of total nitrogen) than for GANH3 (15% of total nitrogen). The Raman spectra are shown in Figure 1b. Carbon materials contain usually two characteristic bands, *i.e.* G ($1578\text{--}1588\text{ cm}^{-1}$) attributed to an ideal graphitic lattice with E_{2g} symmetry and D ($1340\text{--}1347\text{ cm}^{-1}$), attributed to a disordered graphitic lattice with A_{1g} symmetry.[31, 32] The amount of defects in carbon materials is usually assessed by the I_D/I_G ratio.[31, 32] The nitrogen doped graphene aerogels have larger I_D/I_G ratios than the undoped counterpart (GA) which can be ascribed to the defects in the graphite lattice arising by nitrogen incorporation. Among N-doped aerogels, GADA has larger I_D/I_G ratio than GANH3 despite having slightly lower nitrogen content. The explanation can be found in the way of incorporation of nitrogen. Nitrogen is directly bound to carbon within the graphene lattice for GANH3, while for GADA, nitrogen is incorporate within an amorphous carbon layer coating rGO nanosheets. The amorphous carbon coating must be derived from polydopamine pyrolysis.

The structure of graphene aerogel was investigated by SEM (Figure 1 c,d,e). GA and GANH3 exhibit similar structure exposing many twisted graphene edges. The main difference between GA and GANH3 structure is that the opening are smaller for GA. In contrast, GADA image (Figure 1e) exposes less edges of rGO nanosheets and the graphene nanosheets are apparently larger, possibly because they are welded by PDA-derived carbon. The PDA coating may act as a crosslinker between the rGO nanosheets resulting less edges and apparently larger rGO nanosheets. This is another evidence of the coating with a PDA-derived amorphous carbon layer.

Figure 1. Characterization of graphene aerogel (GA), graphene aerogel doped via NH₃ (GANH3) and graphene aerogel doped via PDA coating (GADA): (a) XPS N 1s peak fitting; (b) Raman spectra; (c,d,e) representative SEM images of cross-sections of rGO aerogels GA (c) GANH3 (d) and GADA (e).

The hierarchically porous structure of the samples was confirmed by N₂ physisorption measurements. The isotherms exhibited type-IV adsorption-desorption isotherms with a hysteresis loop (Figure S3 of supplementary material). The isotherms show little uptake at low relative pressures ($P/P_0 < 0.1$), indicating the existence of low micropore volume. The significant H1-type hysteresis loops at high relative pressures ($0.4 < P/P_0 < 0.95$) indicates the abundance of mesopores. The upward trend at high relative pressures ($P/P_0 > 0.95$) may originate from the presence of macropores as those observed by SEM.[28,

33] In fact, most of the pore volume corresponds to macropores,[28] accounting for 99% of total pore volume. The micro and mesopore parameters were determined by N₂ and CO₂ physisorption and compiled in Table 1. The surface area determined by CO₂ adsorption is higher than that determined by N₂ physisorption indicating the presence of narrow micropores (<0.7 nm), also called “ultramicropores”, in which the diffusion of N₂ at 77 K is kinetically restricted.[34] In contrast, CO₂ adsorption technique is more suitable for the analysis of ultramicropores because the diffusion of CO₂ is not kinetically restricted due to the higher temperature of CO₂ adsorption–desorption isotherms (273 K). S_{CO2} is significantly higher for GADA which can be due to ultramicropores present in the amorphous carbon coating. In contrast, the surface area determined by N₂ physisorption is larger for sample without dopamine addition. The ultramicropores corresponds to the slit pores between the stacked graphene sheets. The ultramicropores does not play a role on the reaction because most of the pore volume corresponds to macropores and the Ru catalyst deposited afterwards have sizes around 1 nm and therefore they does not fit inside this kind of pores.

The surface hydrophilic-hydrophobic character of the aerogels was assessed by contact angle measurements (Figure S4 supporting material). GA exhibits a contact angle of 73° demonstrating that the material is relatively hydrophobic. Although the hydrophilicity increases when coating with PDA, after pyrolysis GADA becomes more hydrophobic than GNH3, exhibiting contact angles of 113 ° and 88 °, respectively.

Benzyl alcohol adsorption experiments were performed (Table 1). GADA exhibited three-fold higher adsorption capacity than the other aerogels. Since the stokes diameter of benzyl alcohol is 0.95 nm[35] the adsorption of benzyl alcohol in the ultramicropores is very unlikely to occur. Thus, the higher adsorption attained with GADA should be attributed to its higher hydrophobicity that favours π - π stacking of rGO with the aromatic ring of benzyl alcohol.

In summary, the two pathways used to synthesize the N-doped graphene aerogels are illustrated in Scheme 1. In pathway 1, when dopamine is added in the initial GO dispersion under basic conditions and introduced in the autoclave, an oxidative polymerization occurs, yielding polydopamine (PDA). The PDA interacts with the GO nanosheets, occurring a simultaneous reduction and auto-assembling of rGO nanosheets to form an hydrogel. Subsequently, the hydrogel is freeze-dried and pyrolysed at 800 °C to form an aerogel formed by rGO nanosheets coated by an N-doped amorphous carbon layer (GADA). In pathway 2, NH₃ reacts directly with carbon of GO or oxygenated

surface groups to form amino and amide groups, which upon pyrolysis are transformed into pyridinic, pyrrolic or quaternary nitrogen.

Table 1. Textural parameters by N₂ adsorption and CO₂ adsorption and adsorption of Benzyl alcohol

	S _{N2}	V _{N2}	S _{CO2} [*]	V _{CO2} [*]	Contact angle	Benzyl alcohol adsorption
	m ² g ⁻¹	cm ³ g ⁻¹	m ² g ⁻¹	cm ³ g ⁻¹	°	mmol/g
5%Ru/GA	171	0.42	265	0.04	79	3.7
5%Ru/GANH3	140	0.35	244	0.09	88	4.4
5%Ru/GADA	112	0.16	1740	1.12	113	11.9
5%Ru/Al ₂ O ₃	174	0.18	528	0.11	3	1.5

* Determined from CO₂ isotherm using the Dubinin-Astakhov equation

Ru catalyst was impregnated on the pyrolysed aerogels using a loading of 5 wt% Ru (± 0.1). After calcination and reduction, the catalysts were tested in benzyl alcohol oxidation at 80 °C and 10 Bar. Figure 2 compares the performance for the different catalysts and their reuse for three times. The blank test with the aerogel supports provided negligible conversion. Comparing the different catalysts, the support impacts the benzyl alcohol reaction rate significantly. The catalyst supported on GADA provided more than two fold higher productivity than GA and GANH3 supported counterparts. A commercial 5% Ru on Al₂O₃ catalyst was tested supplying about one order of magnitude lower rate than 5%Ru/GADA. The selectivity to benzaldehyde is very high for all catalysts, ranging between 85 and 100 %. The main by-product detected was toluene derived from the cleavage of hydroxyl group. In the reuse of the catalysts, the conversion decreases very slightly in the first run and it remained stable for subsequent run. Seeking for some reasons about enhanced performance of catalyst supported on PDA-carbon coated aerogel, the catalysts were characterised by *ex-situ* X-ray photoelectron spectroscopy (XPS) and high-angle angular dark field STEM (HAAD-STEM).

Figure 2. Reaction rate and selectivity to benzaldehyde in benzyl alcohol selective oxidation for two blank supports and the catalysts prepared herein. Values attained at 80 °C and 10 Bar of O₂ pressure after 6 hours of reaction.

XPS provides information about the oxidation state of ruthenium. We analyzed the region 3p_{3/2} (458–468 eV) because the binding energy of Ru 3d overlaps with the 1s region of carbon (284.6 eV). The Ru 3p_{3/2} peak was fitted to three contributions corresponding to Ru⁰, RuO₂, and hydrated RuO₂ or oxyhydroxide at 461.2–461.6 eV, 463.1–463.4 eV, and 465.2–465.9 eV, respectively (Figure 3a).[36, 37] The highest relative contribution of the peak corresponding to reduced Ru⁰ (Table 2) pertains to catalyst 5% Ru/GADA in agreement with the best catalytic performance. In addition, the Ru⁰ relative contribution is significantly larger for catalyst supported on graphene aerogels compared to alumina-supported catalyst, which can be one of the reasons to explain the one-order of magnitude higher conversion afforded for the former ones.

The Ru particle size was characterized by high-angle annular dark-field scanning transmission microscopy (HAADF-STEM). The particle size distribution is log-normal

with most of the particles of very small size and a few of larger size (inset in Figures 3b-e). The mean particle size determined by statistical analysis is very similar for all the graphene aerogel supported catalysts, exhibiting Ru average particle size around 1 nm (Table 2). Slightly smaller average Ru particle size is found for alumina-supported catalyst. No aggregation of nanoparticles takes place upon reaction and the size of subnanometric particles remains stable during reaction (Table 2), probably because the Ru nanoparticles are embedded and well anchored within graphene nanosheets.

According to TEM images, alumina supported catalyst (Figure 3e) exhibited apparently higher density of nanoparticles than graphene aerogel supported catalyst. The higher nanoparticle density is misleading because TEM gives a 2D projection of 3D materials. For graphene materials, the distribution of particles observed in TEM images (2D) is a real representation of the material because graphene is a 2D material and all particles are on the surface. Nevertheless, for alumina-supported catalyst (3D particles), TEM 2D images displays superimposed metal nanoparticles that are located at different planes, *i.e.* also inside the pores. Thus, the higher accessibility of metal nanoparticles on graphene compared to alumina could be put forward as another reason of the better performance of graphene-supported catalyst compare to alumina supported one.

Figure 3. Characterization of the used catalysts by XPS (a) and HAADF-STEM (b-d). Fitting of XPS N 1s peak (a). Representative HAADF-STEM images and particle size distribution of the catalysts: 5% Ru/GA (b), 5% Ru/GANH₃ (c), 5% Ru/GADA (d), 5% Ru/Al₂O₃ (e)

Table 2. Results of HAADF-STEM image analysis and XPS fitting

	STEM average particle diameter ^a		Dispersion	% Ru ⁰
	nm			
	before reaction	after reaction	%	
5%Ru/GA	1.05±0.7	1.05±0.7	87	41
5%Ru/GANH3	1.07±0.7	1.08±0.7	86	45
5%Ru/GADA	1.31±0.6	1.34±0.6	73	50
5%Ru/Al₂O₃	0.85±0.41	0.850±0.41	99	29

^aAverage particle diameter calculated by statistical analysis of STEM images

The benzyl alcohol reaction is known to proceed via an oxidative dehydrogenation mechanism whereby the hydroxyl group adsorb producing a metal alkoxide intermediate and subsequently it dehydrogenate on the metal surface producing and carbonyl group and a metal hydride. Finally, adsorbed hydrogen atoms are oxidized to regenerate the catalyst.[1, 4] The higher hydrophobicity of the support GADA favor the adsorption of benzyl alcohol through the aromatic ring to the rGO (Table 1). Subsequently the alcohol groups interact with the Ru metal, whereby the H-C bond is cleaved forming the alkoxy intermediate. The higher reduction degree of 5%Ru/GADA favors the abstraction of H- from the alcohol leading to the higher activity. **The quaternary nitrogen, which are predominant for GADA support, may also play a role as active sites as found in other oxidation reactions.[38]**

In addition, compared to traditional porous supports such as alumina, GADA aerogel has the advantage of improved accessibility to the metal nanoparticles for the diffusion of reactants and products. The lack of micropores on graphene aerogels (2D) ensures a faster diffusion of reactant and products for the graphene monolayer material. Moreover, the 3D structure of the rGO aerogel enables its use as structured reactor in a continuous flow chemical process.

Conclusions

N-doped reduced graphene oxide aerogels have been synthesized using two different approaches. In the first approach, NH₃ was added during aerogel synthesis (GANH3)

and in the second method, polydopamine was coated on the graphene nanosheets of aerogel(GADA). In both approaches the aerogels were pyrolysed in N₂ at 800 °C to further carbonize the aerogel and leave only the most stable nitrogen species anchored to carbon. The amount of nitrogen did not varied significantly for the two methods (3.4-4.7 % N/C). The main difference is that GADA contained a significant percentage of quaternary nitrogen (30%) while quaternary nitrogen only accounted for 15% of total nitrogen for GANH3. **The larger amount of quaternary nitrogen for GADA can be one of the reasons of the enhanced performance of the Ru catalyst on this support.** In addition, the nitrogen was incorporated within different carbon material type for each case. Nitrogen was within rGO lattice for GANH3 while it was incorporated within an amorphous carbon coating on top of rGO for GADA, rendering a more hydrophobic surface in the later case. Ru was dispersed on all rGO graphene supports with 1 nm average size. Catalyst prepared on GADA provided higher activity and selectivity in benzyl alcohol conversion than Ru on the other graphene and alumina supports. This is correlated with a higher reduction degree of Ru nanoparticles, higher adsorption capacity of benzyl alcohol and higher hydrophobicity of the support. The higher reduction degree of Ru metal catalyst is expected to favor the step of dehydrogenation of the alcohol to produce the carbonyl group.

Acknowledgements

Financial support from Spanish Ministry MINECO (project ENE2016-79282-C5-1-R), Gobierno de Aragón (Grupo Reconocido DGA T03_17R), and associated EU Regional Development Funds are gratefully acknowledged.

Reference List

- [1] M. Besson, P. Gallezot, Selective oxidation of alcohols and aldehydes on metal catalysts, *Catalysis Today*, 57 (2000) 127-141.
- [2] T. Mallat, A. Baiker, Oxidation of Alcohols with Molecular Oxygen on Solid Catalysts, *Chemical Reviews*, 104 (2004) 3037-3058.
- [3] J.J. Bozell, G.R. Petersen, Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited, *Green Chemistry*, 12 (2010) 539-554.

- [4] S.E. Davis, M.S. Ide, R.J. Davis, Selective oxidation of alcohols and aldehydes over supported metal nanoparticles, *Green Chemistry*, 15 (2013) 17-45.
- [5] X. Yang, X. Wang, J. Qiu, Aerobic oxidation of alcohols over carbon nanotube-supported Ru catalysts assembled at the interfaces of emulsion droplets, *Applied Catalysis A: General*, 382 (2010) 131-137.
- [6] P. Zhang, Y. Gong, H. Li, Z. Chen, Y. Wang, Solvent-free aerobic oxidation of hydrocarbons and alcohols with Pd@N-doped carbon from glucose, *Nature Communications*, 4 (2013) 1593.
- [7] R. Arrigo, M.E. Schuster, Z. Xie, Y. Yi, G. Wowsnick, L.L. Sun, K.E. Hermann, M. Friedrich, P. Kast, M. Hävecker, A. Knop-Gericke, R. Schlögl, Nature of the N-Pd Interaction in Nitrogen-Doped Carbon Nanotube Catalysts, *ACS Catalysis*, 5 (2015) 2740-2753.
- [8] S. Pylypenko, A. Borisevich, K.L. More, A.R. Corpuz, T. Holme, A.A. Dameron, T.S. Olson, H.N. Dinh, T. Gennett, R. O'Hayre, Nitrogen: unraveling the secret to stable carbon-supported Pt-alloy electrocatalysts, *Energy & Environmental Science*, 6 (2013) 2957-2964.
- [9] L. Roldán, Y. Marco, E. García-Bordejé, Function of the Support and Metal Loading on Catalytic Carbon Dioxide Reduction Using Ruthenium Nanoparticles Supported on Carbon Nanofibers, *ChemCatChem*, 7 (2015) 1347-1356.
- [10] P. Chen, L.M. Chew, A. Kostka, M. Muhler, W. Xia, The structural and electronic promoting effect of nitrogen-doped carbon nanotubes on supported Pd nanoparticles for selective olefin hydrogenation, *Catalysis Science & Technology*, 3 (2013) 1964-1971.
- [11] G. Vilé, D. Albani, M. Nachtegaal, Z. Chen, D. Dontsova, M. Antonietti, N. López, J. Pérez-Ramírez, A Stable Single-Site Palladium Catalyst for Hydrogenations, *Angewandte Chemie International Edition*, 54 (2015) 11265-11269.
- [12] B. Wang, M. Lin, T.P. Ang, J. Chang, Y. Yang, A. Borgna, Liquid phase aerobic oxidation of benzyl alcohol over Pd and Rh catalysts on N-doped mesoporous carbon: Effect of the surface acido-basicity, *Catalysis Communications*, 25 (2012) 96-101.
- [13] T. Horikawa, N. Sakao, T. Sekida, J.i. Hayashi, D.D. Do, M. Katoh, Preparation of nitrogen-doped porous carbon by ammonia gas treatment and the effects of N-doping on water adsorption, *Carbon*, 50 (2012) 1833-1842.
- [14] S. Sandoval, N. Kumar, A. Sundaresan, C.N.R. Rao, A. Fuertes, G. Tobias, Enhanced Thermal Oxidation Stability of Reduced Graphene Oxide by Nitrogen Doping, *Chemistry – A European Journal*, 20 (2014) 11999-12003.
- [15] D. Geng, Y. Chen, Y. Chen, Y. Li, R. Li, X. Sun, S. Ye, S. Knights, High oxygen-reduction activity and durability of nitrogen-doped graphene, *Energy & Environmental Science*, 4 (2011) 760-764.
- [16] F.M. Hassan, V. Chabot, J. Li, B.K. Kim, L. Ricardez-Sandoval, A. Yu, Pyrrolic-structure enriched nitrogen doped graphene for highly efficient next generation supercapacitors, *Journal of Materials Chemistry A*, 1 (2013) 2904-2912.
- [17] Y. Zhang, K. Fugane, T. Mori, L. Niu, J. Ye, Wet chemical synthesis of nitrogen-doped graphene towards oxygen reduction electrocatalysts without high-temperature pyrolysis, *Journal of Materials Chemistry*, 22 (2012) 6575-6580.
- [18] Z. Lin, G.H. Waller, Y. Liu, M. Liu, C.-p. Wong, Simple preparation of nanoporous few-layer nitrogen-doped graphene for use as an efficient electrocatalyst for oxygen reduction and oxygen evolution reactions, *Carbon*, 53 (2013) 130-136.
- [19] H. Lee, S.M. Dellatore, W.M. Miller, P.B. Messersmith, Mussel-Inspired Surface Chemistry for Multifunctional Coatings, *Science*, 318 (2007) 426-430.
- [20] J. Cao, C.J. Jafta, J. Gong, Q. Ran, X. Lin, R. Félix, R.G. Wilks, M. Bär, J. Yuan, M. Ballauff, Y. Lu, Synthesis of Dispersible Mesoporous Nitrogen-Doped Hollow

Carbon Nanoplates with Uniform Hexagonal Morphologies for Supercapacitors, *ACS Applied Materials & Interfaces*, 8 (2016) 29628-29636.

[21] M. Zhang, X. He, L. Chen, Y. Zhang, Preparation of IDA-Cu functionalized core-satellite Fe₃O₄/polydopamine/Au magnetic nanocomposites and their application for depletion of abundant protein in bovine blood, *Journal of Materials Chemistry*, 20 (2010) 10696-10704.

[22] H. Hu, B. Yu, Q. Ye, Y. Gu, F. Zhou, Modification of carbon nanotubes with a nanothin polydopamine layer and polydimethylamino-ethyl methacrylate brushes, *Carbon*, 48 (2010) 2347-2353.

[23] S.M. Kang, J. Rho, I.S. Choi, P.B. Messersmith, H. Lee, Norepinephrine: Material-Independent, Multifunctional Surface Modification Reagent, *Journal of the American Chemical Society*, 131 (2009) 13224-13225.

[24] Y. Wang, H. Yuan, P. Ma, H. Bai, M. Chen, W. Dong, Y. Xie, Y.S. Deshmukh, Superior Performance of Artificial Nacre Based on Graphene Oxide Nanosheets, *ACS Applied Materials & Interfaces*, 9 (2017) 4215-4222.

[25] L. Li, B. Li, J. Zhang, Dopamine-mediated fabrication of ultralight graphene aerogels with low volume shrinkage, *Journal of Materials Chemistry A*, 4 (2016) 512-518.

[26] B. Xie, X. Ren, X. Yan, Z. Dai, W. Hou, N. Du, H. Li, R. Zhang, Fabrication of pore-rich nitrogen-doped graphene aerogel, *RSC Advances*, 6 (2016) 23012-23015.

[27] K.S. Min, P. Sungjin, K. Daewon, P.S. Young, R.R. S., L. Haeshin, Simultaneous Reduction and Surface Functionalization of Graphene Oxide by Mussel-Inspired Chemistry, *Advanced Functional Materials*, 21 (2011) 108-112.

[28] E. Garcia-Bordeje, S. Victor-Roman, O. Sanahuja-Parejo, A.M. Benito, W.K. Maser, Control of the microstructure and surface chemistry of graphene aerogels via pH and time manipulation by a hydrothermal method, *Nanoscale*, 10 (2018) 3526-3539.

[29] A. Borodziński, M. Bonarowska, Relation between Crystallite Size and Dispersion on Supported Metal Catalysts, *Langmuir*, 13 (1997) 5613-5620.

[30] N. Orishchin, C.C. Crane, M. Brownell, T. Wang, S. Jenkins, M. Zou, A. Nair, J. Chen, Rapid Deposition of Uniform Polydopamine Coatings on Nanoparticle Surfaces with Controllable Thickness, *Langmuir*, (2017).

[31] R. Saito, M. Hofmann, G. Dresselhaus, A. Jorio, M.S. Dresselhaus, Raman spectroscopy of graphene and carbon nanotubes, *Advances in Physics*, 60 (2011) 413-550.

[32] F. Tuinstra, J.L. Koenig, Raman Spectrum of Graphite, *The Journal of Chemical Physics*, 53 (1970) 1126-1130.

[33] X. Yang, X. Zhuang, Y. Huang, J. Jiang, H. Tian, D. Wu, F. Zhang, Y. Mai, X. Feng, Nitrogen-enriched hierarchically porous carbon materials fabricated by graphene aerogel templated Schiff-base chemistry for high performance electrochemical capacitors, *Polymer Chemistry*, 6 (2015) 1088-1095.

[34] D. Lozano-Castelló, D. Cazorla-Amorós, A. Linares-Solano, Usefulness of CO₂ adsorption at 273 K for the characterization of porous carbons, *Carbon*, 42 (2004) 1233-1242.

[35] B. Van der Bruggen, J. Schaep, D. Wilms, C. Vandecasteele, Influence of molecular size, polarity and charge on the retention of organic molecules by nanofiltration, *Journal of Membrane Science*, 156 (1999) 29-41.

[36] R. Chetty, W. Xia, S. Kundu, M. Bron, T. Reinecke, W. Schuhmann, M. Muhler, Effect of Reduction Temperature on the Preparation and Characterization of Pt-Ru Nanoparticles on Multiwalled Carbon Nanotubes, *Langmuir*, 25 (2009) 3853-3860.

- [37] R.K. Raman, A.K. Shukla, A. Gayen, M.S. Hegde, K.R. Priolkar, P.R. Sarode, S. Emura, Tailoring a Pt–Ru catalyst for enhanced methanol electro-oxidation, *Journal of Power Sources*, 157 (2006) 45-55.
- [38] B. Stöhr, H.P. Boehm, R. Schlögl, Enhancement of the catalytic activity of activated carbons in oxidation reactions by thermal treatment with ammonia or hydrogen cyanide and observation of a superoxide species as a possible intermediate, *Carbon*, 29 (1991) 707-720.