Ru nanoparticles supported on N-doped reduced graphene oxide as valuable catalyst for the selective aerobic oxidation of benzyl alcohol

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ABSTRACT:

The catalytic performance of a series of Ru-based catalysts was evaluated for the selective aerobic oxidation of benzyl alcohol to benzaldehyde under base-free mild conditions. The effect of metal precursor (RuCl_3 , $\text{RuNO}(\text{NO}_3)_3$ and $\text{Ru}_3(\text{CO})_{12}$) and support on catalyst performance was investigated by comparing undoped (rGO) and N-doped (NrGO) reduced graphene oxide with commercial activated carbon and high surface area graphite supports. The surface chemistry and structure of materials were characterized by nitrogen physisorption (BET), transmission electron microscopy (TEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). The average Ru nanoparticle sizes were in the range from 1.4 to 2.4 nm, with the smallest particle sizes obtained on rGO support owing to its highest surface area.

Catalysts prepared from $\text{RuNO}(\text{NO}_3)_3$ and $\text{Ru}_3(\text{CO})_{12}$ precursors exhibit the highest benzyl alcohol conversion to the corresponding aldehyde, with highest conversions observed when NrGO support is employed. Catalysts prepared from $\text{Ru}_3(\text{CO})_{12}$ on NrGO support exhibit the highest activity for benzaldehyde formation, which is over three times that of commercial activated carbon supported Ru catalysts.

The differences in catalytic performance are attributed to interactions between the acidic product of the reaction and the basic surface sites of the NrGO support, and modification of the surface hydrophobicity. These factors confer a significant rate enhancement in the selective oxidation of benzyl alcohol over Ru/NrGO compared to Ru/rGO. Ru/NrGO is stable under reaction conditions, however progressive deactivation is observed owing to water accumulation at the active site. Catalysts are easily reactivated via heating, with >90% of the original activity recovered on reuse.

1. Introduction

The challenge of using biomass and its derivatives as a renewable feedstock to improve the sustainability of chemicals and fuels production is attracting significant industrial and academic interest. The conversion of biomass into chemicals is generally based in several transformation processes including thermal processes (e.g. gasification, pyrolysis and hydrothermal treatment) or biochemical platforms [1]. Lignocellulosic biomass is a widely available resource mostly composed of cellulose, hemicellulose and lignin, which when derived from the non-edible portion of biomass including bagasse, corn stover, grasses, forestry or agricultural waste, is viewed as a sustainable feedstock for use in bio-refining [2].

The selective oxidation of benzyl alcohol to benzaldehyde (Scheme 1) is an important transformation for the synthesis of precursors and intermediates in the agrochemical, pharmaceutical and perfumery industries, with benzaldehyde considered as the second most important aromatic molecule used after vanillin. While benzyl alcohol can be sourced as a natural product from plants, most benzyl alcohol is produced from petroleum-derived feedstocks via the hydrolysis of benzyl chloride. Recent reports of the application of engineered *Escherichia-coli* [3] in converting renewable glucose to bio-derived benzyl alcohol offers a promising sustainable route to produce a large number of industrially important derivatives such as benzaldehyde. However, the design of selective catalysts for benzyl alcohol oxidation are necessary to overcome challenges of by-product formation [4] from e.g. decarbonylation (benzene), hydrogenolysis (toluene) or esterification (benzyl benzoate).

Scheme 1. Reaction pathway for benzyl alcohol oxidation

Traditionally benzaldehyde is industrially produced via benzyl chloride hydrolysis derived from toluene chlorination or through toluene oxidation [5]. Extensive effort has been devoted to the production of benzaldehyde from benzyl alcohol using greener oxidation routes as replacements for conventional strong stoichiometric reagents like KMnO_4 [6], chromites [7] or HNO_3 [8]. It is well known, that these reagents are considered hazardous and generate a large amount of toxic waste, having a negative economic and environmental impact. Extensive research regarding the application of photocatalytic materials in the oxidation of benzyl alcohol has also been reported [5, 9, 10] as an alternative to stoichiometric oxidants. Other oxidants, like peroxides [11, 12, 13] have been proposed, however their production is not sustainable and present handling risks [14], thus the use of molecular oxygen as oxidant is preferable. The use of heterogeneous metallic catalysts has been extensively studied, but also often includes the use of undesirable additives such as NaOH [15], TEMPO [16, 17], NaHCO_3 [18], Na_2CO_3 [19] or K_2CO_3 [20, 21].

The additive-free synthesis of benzaldehyde can be performed through the selective oxidation of benzyl alcohol either in vapour [22, 23] or liquid phase using different types of metal catalysed processes. Choudary et al. [24] reported the application of hydrotalcite supported transition metal-based catalysts for the solvent free oxidation of benzyl alcohol, wherein Cu-Cr/HT systems exhibited the highest conversion (51%) with a 70% selectivity toward benzaldehyde.

However, solvent-free oxidation processes have drawbacks from the high temperatures needed to carry out the reaction (210 °C) and extensive catalyst deactivation during recycling tests. The use of supported Au nanoparticles has also been explored for the selective solvent-free production of benzaldehyde using molecular oxygen [25], wherein Au/U₃O₈ and Au/MgO showed the best conversions of 53% and 51% respectively, however, selectivity's were limited due to benzyl benzoate formation.

The liquid phase oxidation of benzyl alcohol to benzaldehyde over Pd catalysts has received significant attention, with Keresszegi and coworkers [26] reporting Pd/Al₂O₃ catalysts produce yields >30% after 1.5 hours at 50°C using cyclohexane as solvent. The catalytic intermediates formed at the material surface were monitored in situ by liquid phase ATR-IR spectroscopy, which revealed catalyst deactivation was attributed to strongly adsorbed CO, formed by decarbonylation of benzaldehyde, and the formation of surface water which block surface active sites. Decarbonylation results from metallic Pd sites [27], which can be minimized by maintaining high metal dispersions that stabilizes the active surface palladium oxide component critical for selective alcohol oxidation (selox) [28]. The influence of support architecture is also important for improving mass transport and increasing palladium dispersion, as demonstrated using interconnected porous KIT-6 silica frameworks [29]. Luque et al. [30] developed Pd nanoparticles supported on iron doped SBA15. Conversions of benzyl alcohol higher than 80% and high selectivity towards benzaldehyde were observed in the solvent free oxidation of benzyl alcohol at 85°C after 9h. Nitrogen doped carbon nanotubes (CNT) have been employed as supports for Pd selox catalysts, with a 54% benzyl alcohol conversion and 90% selectivity [31] obtained over 8.6% Pd/N-doped CNT after 3h reaction at 120 °C. Investigations of a series of N-doped CNT supported Pd and Pd-Au nanoparticles for the selective oxidation of benzyl alcohol

[32] revealed nitrogen functionalities incorporated by oxidation and further amination lead to an improvement in the TOF compared to pristine CNT. This promotion was attributed to the increased metal dispersion resulting from surface nitrogen groups, however, poor selectivity was observed toward benzaldehyde under solvent free conditions. When water was used as solvent the activity decreased significantly, but the selectivity toward benzaldehyde was higher than for the solvent-free conditions. Hutchings and coworkers [33] demonstrated that the incorporation of Pd into Au nanoparticles create synergistic effects improving the catalytic performance in the solvent-free oxidation of benzyl alcohol under mild conditions (100°C and 10 bar of O₂). 1%(Au-Pd)/TiO₂ samples prepared by colloidal method were the more active, achieving a 92% selectivity and 29% conversion after 4 hours. Liu et al. [34] developed Pt nanoparticles supported on graphitic TiO₂ which exhibited 100% selectivity towards benzaldehyde at 77% benzyl alcohol conversion after 10 hours at 26°C, using water as a solvent. The authors claimed that anatase content was critical to improving the catalytic behaviour, however, very high catalyst:substrate ratios (0.1g for 0.2mmol) were employed to achieve this yield to benzaldehyde. Due to the high cost and scarcity of precious metals such as Pt, Au and Pd [35] and problems of poor stability of earth abundant transition metal catalysts, Ru has attracted significant attention as an alternative lower cost metal which can maintain high catalytic efficiency. Yamaguchi et al. reported full conversion of benzyl alcohol with 100% selectivity to benzaldehyde [36] using Al₂O₃ supported Ru catalysts in 1h using trifluorotoluene solvent at 83°C and atmospheric pressure of O₂. However, again the catalyst: benzyl alcohol was very high and incomplete elimination of NaOH during washing between recycling tests could mask any catalyst deactivation. The deactivation and regeneration of RuO₂/CNT has been described by Yu et al. [37], and while 75% conversion with excellent benzaldehyde selectivity (>99%) was obtained

after 1 hour, the samples showed significant deactivation in recycling tests. In a recent publication [38] RuO₂ supported on NaY zeolites were presented as an alternative catalyst in the aerobic oxidation of benzyl alcohol to benzaldehyde. Samples exhibited only 12% conversion, but the reaction was only conducted for 3 hours at 70°C in toluene and atmospheric pressure of O₂.

Despite the interest in supported Ru catalysts for selox reactions, to the best of our knowledge, there are no systematic reports on the application of graphenic supported Ru nanoparticles for the additive-free oxidation of benzyl alcohol into benzaldehyde. Here we report the effect of graphenic support materials and Ru precursors on the catalytic performance of Ru based catalysts in the selective oxidation of benzyl alcohol to yield benzaldehyde. Detailed characterization was performed to rationalize the observed differences in catalyst activity between samples, while in-depth evaluation of the recyclability of the prepared catalytic materials is reported.

2. Experimental section

2.1 Preparation of supports

Graphenic materials were prepared via thermal treatment of graphite oxide (GO), which was synthesized from natural graphite flake (325 mesh, Alfa Aesar, purity 99.8%), following a modified Brodie method, as described elsewhere [39]. Synthesized GO was dried to constant weight at room temperature under vacuum in a desiccator over P₂O₅. Exfoliation of the resulting GO was performed in a vertical quartz reactor under inert (N₂) and reactive atmospheres (NH₃) yielding reduced graphene oxide (rGO, S_{BET} = 904 m² g⁻¹) and nitrogen-doped graphene oxide (NrGO, S_{BET} = 483 m² g⁻¹) respectively.

Commercial activated carbon (denoted as AC, $S_{\text{BET}} = 1190 \text{ m}^2 \text{ g}^{-1}$, $313 \text{ m}^2 \text{ g}^{-1}$ external surface area, supplier: Oleicola el Tejar, Córdoba Spain), and high surface area graphite (HSAG400, $S_{\text{BET}} = 396 \text{ m}^2 \text{ g}^{-1}$, supplier: TIMCAL) supports were also employed to prepare Ru catalysts.

2.2 Preparation of catalysts

4wt% Ru carbon catalysts were prepared by wet impregnation of the different carbon supports with a solution of Ru precursor, followed by evaporation of the solvent (acetone: HPLC grade 99.98% purity provided by Scharlau) on a rotary evaporator at 30 °C under vacuum. $\text{Ru}_3(\text{CO})_{12}$, (Alfa Aesar >99%), was dissolved in 100 ml solvent prior to impregnation of the support (1 g) in an opaque recipient due to the sensitivity of $\text{Ru}_3(\text{CO})_{12}$ to the light. This series of catalysts was denoted with “CO”. Catalyst synthesized using RuCl_3 (series denoted as “Cl”) or $\text{Ru}(\text{NO})(\text{NO}_3)_3$ (series labelled with “NN”) precursors, was prepared by incipient wetness method, employing the minimum volume of water:ethanol (1:1) solutions. The $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ precursor was acquired Aldrich, > 40% of Ru content, while $\text{Ru}(\text{NO})(\text{NO}_3)_3$ was provided by Alfa Aesar, with Ru content >31%. Finally the samples were dried in an air furnace at 110 °C overnight.

Prior to catalyst evaluation all Ru supported on carbon catalysts were activated by reduction under hydrogen flow (60 mL min^{-1}) at 350 °C for 2 h to decompose and reduce the Ru precursor. Reduced samples were cooled to room temperature under a helium flow (50 mL min^{-1}) for 5 h to passivate the metallic surfaces. The reduced/passivated catalysts were stored in air with no additional treatments prior to their characterization or catalytic evaluation.

2.3 Material characterizations

The textural characterization and surface area (S_{BET}) measurements were obtained from nitrogen adsorption at $-196\text{ }^{\circ}\text{C}$, which were acquired using a Micromeritics ASAP model 2020 instrument. Transmission Electron Microscopy (TEM) micrographs of the supports and of the catalysts were recorded on a JEOL JEM-2100F microscope at 200 kV. Samples were ultrasonically suspended in ethanol prior to deposition over a holey carbon copper grid. The average metal particle sizes in the catalyst were calculated based on a minimum of 300 particles using equation (1) [39]:

$$d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \quad (1)$$

where n_i is the number of particles with diameter d_i .

Samples were also analysed by X-ray diffraction (XRD), using a Polycrystal X'Pert Pro PANalytical diffractometer with Ni-filtered Cu/K radiation ($\lambda = 1.54\text{ \AA}$) operating at 45 kV and 40 mA. For each sample, Bragg angles between 4° and 90° were scanned at a rate of $0.04^{\circ}/\text{s}$.

Fresh and spent catalysts were also analysed by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Supra spectrophotometer, equipped with a monochromatic Al $K\alpha$ source (1486.7 eV) and charge neutralised. Spectra were processed with CasaXPS software, version 2.3.16, and quantified after Shirley background correction and application of relevant response factors to quantification regions.

Characterisation of leached ruthenium following reactions was performed by extraction of any soluble metals from the filtered toluene solution using 3 portions of 10 ml of water, with resulting metal concentration determined by inductively coupled plasma mass spectrometer (ICP-OES Optima 3300 DV Perkin Elmer).

2.4 Reactivity measurements

Benzyl alcohol selox was carried out using a Radleys Starfish carousel batch reactor on a 10 ml scale at 90 °C under magnetic stirring at 700 rpm, with oxygen bubbled through the reaction solution (5 ml min⁻¹, 1 bar) via 0.5 mm i.d. PTFE tubing. Preliminary studies determined this stirring velocity was sufficient to eliminate internal mass transfer limitations. 25 mg of catalyst was added to a reaction mixture comprising 8.4 mmol benzyl alcohol, 0.1 ml mesitylene as an internal standard, and 10 ml HPLC grade toluene as solvent. The catalysts were used in their original grain sizes, powder (<0.125 µm) for graphenic and HSAG supported samples and grains in the range 0.35-0.5 mm for the supported on activated carbon. In the case of this later, activated carbon, an experiment was also performed with the crushed material to make sure there was no diffusion control with the granular one. Control reactions in the absence of any catalyst, or in the presence of bare supports, were conducted in parallel and all gave negligible conversions. Aliquots of 0.25 ml of the reactor liquid was collected periodically, filtered and diluted with 1.75 ml of toluene for Gas Chromatography (GC) analysis. The reaction product mixture was analysed in triplicate by on a Varian 3900GC with CP-8400 autosampler (CP-Sil5 CB column, 15 m length× 0.25 mm internal diameter × 0.25 µm film thickness). Carbon mass balances were determined from reactant and product response factors, and found to be > 95% in all the reactions.

The conversion of benzyl alcohol was calculated as per equation (2)

$$C(\%) = \frac{BAL_i - BAL_f}{BAL_i} \cdot 100 \quad (2)$$

where BAL_i represents the initial benzyl alcohol concentration and BAL_f the final benzyl alcohol concentration. At this point it should be indicated that as we have used the same Ru loading in all

the catalysts and in the exactly the same amount of sample (25 mg) in the reaction tests, the values of catalytic conversions will be operated as description of catalytic activities.

The selectivity of each product was calculated using equation (3):

$$S_i (\%) = \frac{mol_i}{mol_t} \cdot 100 \quad (3)$$

where mol_i represents the mole of the product whose selectivity is being calculated and mol_t represents the total moles of all the products quantified.

Catalyst recycle test were performed by recovering of the solids from the reaction vessel and filtration and washing thoroughly with toluene in a vacuum flask.

3. Results and discussion

3.1 Catalyst characterisation

The reduced catalysts used in this study are identical to those described in our previous work [39]. Table 1 compiles the Ru nanoparticle average diameter determined by TEM for the reduced catalysts, from which it can be seen that the particle size of Ru nanoparticles is in the range 1.4 to 2.4 nm, and is strongly dependent on the support used. When the rGO support is considered, the Ru particle size was found to be independent of the metal precursor used. When comparing the effect of different supports, and using the $Ru_3(CO)_{12}$ precursor, smaller Ru nanoparticles were obtained on the rGO support, which could be rationalized as a consequence of rGO's higher specific surface area ($904 \text{ m}^2 \text{ g}^{-1}$) relative to HSAG ($396 \text{ m}^2 \text{ g}^{-1}$), NrGO ($483 \text{ m}^2 \text{ g}^{-1}$), and AC ($313 \text{ m}^2 \text{ g}^{-1}$ external surface area). No peaks related with the formation of crystalline Ru were detected in any of the XRD patterns[39] corroborating the small Ru particle size evidenced in the d_{TEM} values reported in Table 1.

3.2 Catalyst activity in benzyl alcohol selox

Table 1 summarizes the results obtained for the family of Ru catalysts prepared from different Ru precursors and support materials in the aerobic selox of benzyl alcohol to benzaldehyde under atmospheric pressure of O₂. Control reactions carried out without catalyst (entry 1) or with the bare graphenic supports (entry 2 and 3) show negligible conversion.

Table 1. Characteristics and catalytic performance of the carbon supported 4wt% Ru in the aerobic selox of benzyl alcohol to benzaldehyde.

Entry	Catalyst	Ru (wt%) ^a	d _{TEM} ^a (nm)	Conversion (%)	Sel Benzaldehyde (%)
1	Blank	-	-	0.4	>99
2	rGO	-	-	0.3	>99
3	NrGO	-	-	0.3	>99
4	Ru(Cl)/rGO	3.9	1.5±0.3	14	>99
5	Ru(Cl)/NrGO	4.4	2.1±0.5	16	>99
6	Ru(NN)/rGO	4.0	1.4±0.3	31	>99
7	Ru(NN)/NrGO	4.0	1.7±0.4	32	>99
8	Ru(CO)/rGO	4.3	1.4±0.3	36	>99
9	Ru(CO)/NrGO	3.9	1.8±0.4	46	>99
10	Ru(CO)/AC	4.1	2.4±0.5	16	>99
11	Ru(CO)/HSAG	4.1	2.3±0.4	18	>99

Reaction conditions: benzyl alcohol, 8.4 mmol, 25 mg of catalyst, molar ratio Substrate/M=849, toluene 10 ml, atm. pressure O₂ (5 ml min⁻¹), 90°C, 24 hours. Reduction temperature 350°C. ^a From reference [39], standard deviation of the set of values used to determine the average particle size is included for each sample.

Table 1 shows that the conversion of benzyl alcohol is strongly dependent on the nature of the Ru precursor, with catalysts prepared from Ru(NN) and Ru(CO) precursors exhibiting the highest conversions and benzaldehyde selectivities >99%. For Ru(CO)/NrGO (entry 7) and Ru(NN)/NrGO (entry 6), conversions of 46% and 32% were observed respectively after 24 hours reaction. Conversions obtained from catalysts prepared using chloride precursors (entries 4 and 5) were lower than those prepared from Ru₃(CO)₁₂ and Ru(NO)(NO₃)₃, which may be attributed to residual chlorine on the Ru(Cl)/rGO catalyst surface, as previously reported by our group [39]. Surface chlorine leads to poisoning of Ru nanoparticles reducing the number of active sites.

The support also plays a key role in the performance of the studied Ru catalysts, and for each Ru precursor the use of NrGO supports was found to give the highest conversions, while very low conversions were observed for catalysts prepared using commercial AC and HSAG supports. For Ru(CO)/AC, Ru(CO)/HSAG, catalysts the poor catalytic activities can be attributed to these having the largest Ru average particle sizes (2.3-2.4 nm Table 1) compared with the Ru(CO)/NrGO catalyst (1.8 nm). The enhanced catalytic performance of Ru(CO)/NrGO for oxidation could be associated with an electron enrichment of the Ru nanoparticles, as previously suggested from XPS measurements [40], where a systematic decrease in Ru binding energies was observed in comparison with supported Ru/rGO catalysts. In addition, the presence of the nitrogen groups in the surface of NrGO, may contribute to the reaction via a cooperative action with the Ru nanoparticles. It well known that the surface of graphenic materials exposes diverse types of functional groups, such as carboxyls, carbonyls, phenolics, hydroxyls or lactones [41], which depending on their polarity will influence the mode and strength of binding of organic compounds on the supports. Since nitrogen adatoms have an additional electron density compared to carbon atoms, p electron delocalization will occur easily in NrGO, thereby changing

the electron density of the graphenic materials. This excess of electrons changes the π - π interactions between the graphenic surfaces and the adsorbent, which will possibly modify the geometry or strength of reactant adsorption on the support, near the catalytic sites. Furthermore, N groups can enhance the interactions between the NrGO surface and acidic molecules, via dipole-dipole, or hydrogen bonding, leading to formation of donor-acceptor complexes with the delocalized p electrons of NrGO. [42]. Thus, the acidity of benzyl alcohol (pka 15.4) and more notably, acidity of benzaldehyde (pka 14.9) could be an important factor, owing to the possibility of formation of donor-acceptor complexes with the delocalized p electrons of NrGO. The production of benzaldehyde requires chemisorption of both benzyl alcohol and oxygen on the Ru surface. Thus displacement of reactively formed benzaldehyde from the metallic surface by more strongly bound alcohol, with the help of the basic sites exposed on the graphenic materials, could enhance the catalytic activity of Ru(CO)/NrGO compared to Ru/rGO shown in Figure 1. Alternatively, reactively formed water can also play a key role in inhibiting alcohol adsorption, and these experimental results can be interpreted in terms of different degrees of poisoning by water. The improved hydrophobicity of NrGO versus rGO, due to the lower content of residual oxygen functionalities [39], can also help to remove the water from the catalyst surfaces, thereby maintaining the activity for benzyl alcohol oxidation.

Figure 1. Conversion of benzyl alcohol into benzaldehyde over Ru(CO)/rGO and Ru(CO)/NrGO reduced at 350°C. Reaction conditions: Benzyl alcohol, 8.4 mmol, 25 mg of catalyst, molar ratio Substrate/M=849, toluene 10 ml, O₂ 5ml min⁻¹, 90°C, 24 hours.

Based on the above catalytic results, the stability and recyclability of the Ru(CO)/NrGO catalyst was explored over three successive reactions. Figure 2 shows that while there is a decrease in benzyl alcohol conversion from the first to the second use, no further loss was observed on the third reuse, with the conversion remaining ~ 20% and the selectivity towards benzaldehyde >99%.

Figure 2. Stability of the Ru(CO)/NrGO catalysts during the recycling uses for the oxidation of benzyl alcohol. Reaction conditions: benzyl alcohol 8.4 mmol, 25 mg of catalyst, molar ratio Substrate/M=849, toluene 10 ml, O₂ 5ml min⁻¹, 90°C, 24 hours.

To understand the loss in intrinsic activity of Ru(CO)/NrGO further experiments were carried out to elucidate the origin of potential deactivation pathways. Elemental analysis performed on the reaction mixture following the first 24 hr reaction with Ru(CO)/NrGO catalysts evidenced no detectable ruthenium eliminating metal leaching as a cause of deactivation. HRTEM measurements revealed the Ru particle size distributions were unchanged, with average particle size distributions for fresh (Table 1) and spent catalysts (Figure 3) determined to be 1.8 nm and 1.4 nm respectively, suggesting that loss of activity does not result from sintering. Given the

mild reaction conditions employed it is not unexpected that minimal sintering would be observed.

Figure 3. TEM images and particle size distribution of the fresh (a) and spent (b) Ru(CO)/NrGO catalyst.

XPS was employed to investigate whether a change in the surface composition or chemical state of the Ru nanoparticles was observed post reaction. Due to the partial overlap of Ru 3d_{3/2} XP peaks with that of C 1s, the Ru 3p signal was employed to study changes in the chemical state of Ru. Figure 4 shows a comparison of the Ru 3p_{3/2} XP spectra for the fresh and spent Ru(CO)/NrGO samples, which is centred at 463,0 eV for both samples, consistent with the presence of oxidized Ru (probably a hydrated species) [43]. Taking into account that these Ru nanoparticles are less than 3 nm in size, we could assume that they have a core-shell composition, with a metallic core and a metal oxide shell. On the other hand, as the intensity of the Ru 3p_{3/2} peaks similar for the two catalysts we can exclude leaching of Ru species to the

solvent during reaction. Furthermore, as the two samples contain similar amounts of oxidized Ru species, a change in Ru oxidation state could not be assigned as main contributions to the deactivation of the active sites.

Table 2. XPS data of fresh Ru(CO)/NrGO and spent Ru(CO)/NrGO catalysts.

Catalyst	d _{TEM} (nm)	BE Ru 3p _{3/2} (eV)	FWHM	Ru/C
Ru(CO)/NrGO fresh	1.8±0.4	463.0	3.5	0.004
Ru(CO)/NrGO spent	1.4±0.3	463.0	3.7	0.004

Taken together, these results demonstrate that the sintering of Ru nanoparticles, the oxidation of Ru species, and the leaching of ruthenium could be discarded as possible explanations for the decrease in the activity of the Ru catalysts.

Figure 4. XPS spectra of 3p_{3/2} region for fresh Ru(CO)/NrGO and spent Ru(CO)/NrGO catalysts

Catalyst poisoning by strongly adsorbed by-products is another possible cause of catalyst deactivation, and earlier work by Yu et al. [37] has suggested that water formed during the oxidation of benzyl alcohol may adsorb over Ru surfaces restricting blocking the adsorption of the reactants; an effect that may be exacerbated due to the low solubility of water in weakly polar solvents such as toluene. To investigate this, used Ru(CO)/NrGO catalyst was treated at 300 °C under a helium flow to remove water and organic residuals prior to testing the recyclability. Indeed, under such treatments catalyst activity for benzyl alcohol conversion and selectivity towards benzaldehyde was maintained, with only a minimal loss (<8%) of benzyl alcohol

conversion after the third use (Figure 5). This slight decrease in conversion could be related to a small loss of catalyst mass during recovery of Ru(CO)/NrGO between successive runs. Thus, the apparent deactivation of the Ru(CO)/NrGO catalyst under reaction conditions can be attributed to the accumulation of surface water, which is readily removed by drying to reactivate the catalyst between successive reactions. The highly active Ru(CO)/NrGO catalyst thus shows excellent reusability under the reaction conditions employed for benzyl alcohol selox, without significant loss of catalytic activity or selectivity.

Figure 5. Stability of the Ru(CO)/NrGO catalysts during the recycling uses for the oxidation of benzyl alcohol after thermal reactivation treatments between runs. Reaction conditions: benzyl alcohol 8.4 mmol, 25 mg of catalyst, molar ratio Substrate/M=849, toluene 10 ml, O₂ 5ml min⁻¹, 90°C, 24 hours.

A comparison of the performance of Ru(CO)/NrGO with those previously published is summarized in Table 3. It should be notice that all the reaction tests whose experimental results are presented in Table 3, were performed without dissolved additives (e.g. soluble bases) in the reaction media. The comparison among catalysts in Table 3 is not straightforward since the reaction condition variables, such as temperature, pressure, reaction time or molar reactant-metal ratio, are not similar. However, considering molar alcohol:Ru ratio employed in this study, the performance of our N doped graphene material compares favourably with many of those reported in the literature.

Table 3. Comparative data of the Benzyl alcohol oxidation over different metal supported catalysts

Catalyst	Benzyl alcohol:Metal molar ratios	T (°C)	O ₂ flow (ml min ⁻¹)	Time (h)	Conv (%)	Sel (%)	Ref
2%Au/U ₃ O ₈ ^a	713	130	1.5 bar	5	53	95	[25]
3%Pd/MagSBA ^a	3429	90	1 bar	9	81	83	[30]
8.7% Pd/N-CNT ^a	2975	120	20	3	91	>99	[31]
1%Pt /TiO ₂ ^b	39	26	Ambient air	10	77	>99	[34]
1.4%Ru/Al ₂ O ₃ ^c	70	83	1 bar	1	>99	>99	[36]
9.3% RuO ₂ /CN ^d	14	80	6	1	75	>99	[37]
9.2% RuO ₂ /NaY ^d	108	70	20	3	12	>99	[38]
4% Ru(CO)/NrGO ^d	849	90	5	24	46	>99	This work

^aSolventless ^bSolvent water ^cSolvent trifluorotoluene ^dSolvent toluene

4. Conclusions

The different supports strongly modify the catalytic behavior of Ru nanoparticles, the NrGO materials being those that under the experimental reaction conditions used produce the highest conversion of benzyl alcohol to the desired product. Thus, the catalytic performance is significantly enhanced by presence of N in the graphenic structure. These catalytic differences could be attributed to the interaction of the substrate and products of the reaction with the surface of N doped graphenic materials due to their weak acidity and/or to their higher hydrophobicity. Moreover, metal precursor also plays an important role on the activity of the catalysts in oxidation of benzyl alcohol. The best results were obtained over the sample Ru(CO)/NrGO showing conversions close to 50% and >99% of selectivity toward benzaldehyde. It was found that the catalyst strongly deactivated during the reaction probably due to water accumulation on the active sites, however the spent catalyst can be easily regenerated upon heating.

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