Optimization of ruthenium based catalysts for the aqueous phase hydrogenation of furfural to furfuryl alcohol

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Graphical abstract
Highlights

- Ruthenium nanoparticles supported on reduced graphene oxide catalyze the hydrogenation of furfural in water under mild conditions.
- Using a catalyst with 4 wt% of Ru (ex Ru carbonyl) supported on non-doped graphenic material a yield to furfuryl alcohol near 91% was achieved.
- This type of catalysts can be reused at least three times, without further regeneration treatments, demonstrating its suitability for potential industrial application.

ABSTRACT:

The catalytic performance of a series of 4 wt.% Ru-based catalysts in the aqueous-phase hydrogenation of furfural (FAL) to furfuryl alcohol (FOL) has been studied in a batch reactor under very mild conditions of 20°C and 10 bar hydrogen. The effects induced by different commercial supports (SiO₂, TiO₂, Al₂O₃, activated carbon and high surface area graphite) and two lab synthesized graphenic materials (with and without N-doping); as well as the influence of the catalyst preparation using three metal precursors (RuCl₃, RuNO(NO₃)₃ and Ru₃(CO)₁₂) have been assessed. Materials were characterized by mean of nitrogen physisorption (BET), transmission electron microscopy (TEM), X-ray diffraction (XRD), temperature programmed desorption (TPD), and X-ray photoelectron spectroscopy (XPS). The different supports significantly modify the catalytic behavior, with the catalysts prepared using graphenic materials.
found to produce the highest conversion of FAL and the maximum of selectivity to FOL. On these latter supports, the highest FAL yield was achieved by using triruthenium dodecacarbonyl as ruthenium precursor. Ruthenium supported on reduced graphene oxide (rGO) shows 93.3% conversion with 98% selectivity towards FOL. This catalyst was found to exhibit excellent stability, and was reused at least 4 times without loss of activity or selectivity. Characterization data suggest that the catalytic differences can be attributed to the particle size of Ru nanocrystals as well as to their interaction with the surface of graphenic materials. Furthermore, the catalytic results are influenced by the type of metal precursor and the reduction temperature, these facts suggesting that the genesis of the Ru nanoparticles can also play a key role controlling the catalytic activities obtained with these catalysts in the hydrogenation of FAL into FOL.

KEYWORDS:

Furfural; furfuryl alcohol; hydrogenation; ruthenium; reduced graphene oxide; nitrogen doped reduced graphene oxide.
1. Introduction

The use of biomass as renewable feedstock for the production of chemicals and fuels is a field of growing interest for both academia and industry, with many processes to transform biomass explored including gasification, pyrolysis and hydrolysis [1]. Lignocellulosic biomass is a widely available resource which is composed mainly of cellulose, hemicellulose, and lignin, and can be derived from the non-edible portion of biomass like bagasse, corn stover, grasses, wood, etc [2]. Furfural is a promising biomass-derived platform molecule with a huge potential to produce a large number of valuable products [3]. Furfural is generally produced by the Quaker Oats process, through an acid digestion of hemicellulosic wastes and subsequent dehydration.[4] The hydrogenation of FAL can generate several kinds of value added products such as furfuryl alcohol (FOL), tetrahydrofurfuryl alcohol (THFA), 2-methylfuran (2-MF), 2-methyltetrahydrofuran (2-MTHF), 1,4-pentanediol (1,4-PeD), and 1,2-pentanediol (1,2-PeD) (Scheme 1).
FOL can be employed in diverse applications including the production of fine chemicals, resins, vitamin C, lysine, lubricants, fragrances, dispersing agents and plasticizers [5,6], and significant effort has been devoted to the preparation of FOL. The synthesis of FOL can be performed through the selective catalytic hydrogenation of furfural either in gas phase or in liquid phase, and has been produced industrially for decades using based copper chromite catalysts [7–9]. However, harsh reaction conditions and production of large amounts of toxic waste has a negative economic and environmental impact on the process, thus the development of Cr-free catalysts is desirable. The gas phase production of FOL has been reported by Kijenski et al. [10] using Pt based catalysts on oxide supports covered with transition metal oxide monolayers. 2% Pt/TiO\textsubscript{2} monolayer/SiO\textsubscript{2} system showed the higher selectivity (94%) and a 68.3% of conversion. Nagaraja et al. [11] studied the gas-phase FAL hydrogenation using Cu/MgO catalyst, and reported high conversion of furfural (98%) with high selectivity towards furfuryl alcohol (98%).
However, such vapour phase hydrogenations are uneconomic owing to the high energy requirement for FAL vaporisation.

Liquid phase hydrogenation of FAL to FOL employing noble and non-noble metals has been explored, with the most promising heterogeneous catalysts reported to be based on Raney Ni [12], Mo doped Co-B amorphous alloys catalysts [13] and noble metals such as Pt [14], Ru [15,16], and Pd [17]. However, in most of the reported processes an organic solvent such as ethanol, methanol, propanol, butanol or octane, is employed, with few studies utilizing water as a solvent. Obviously water is desirable as solvent from a green chemistry perspective, but in some cases this is acidulated by for example sulfuric acid. Nakagawa and coworkers [18] reported silica supported Pd-Ir alloy catalysts for the aqueous-phase hydrogenation of FAL which while showing >99% conversion after 4 hours these exhibit low selectivity toward FOL, favouring THFA. High conversions of FAL were also obtained by Lesiak et al. [19] using alumina supported Pd-Cu nanoparticles, but also exhibited poor selectivity towards FOL even though relatively mild conditions of 90°C, 20 bar of H₂ were employed. A series of Pd-Cu/MgO catalysts for the selective hydrogenation of FAL in water were studied by Fulajtarova et al. [20], were reported to exhibit complete conversion of FAL and >98% to FOL after 80 min of reaction, however elevated temperatures of 110°C and 6 bar of H₂ were employed.

Recently Mironenko et al. [21] studied Pd and Ru catalysts supported on carbon nanotubes (CNT) and carbon black in the hydrogenation of FAL under mild conditions (50°C, 5 bar of H₂ and using water as solvent). Pd/CNT samples were the most active, attaining 97% of selectivity at a 40% of conversion. However, the Ru samples showed very low activity irrespective of the support nature and reaction conditions. This fact was attributed to water adsorbed on the
ruthenium surface, so \( \text{H}_2\text{O} \text{-Ru} \) interactions seem to be much stronger than the \( \text{H}_2\text{O} \text{-Pd} \) one, leading to lower activities.

Chen et al. [6] reported that graphitic carbon nitride nanosheet supported Pt exhibits high FAL conversion and high selectivity to FOL during hydrogenation in water at 100°C. The authors claimed that the large surface area of the support (142 m\(^2\) g\(^{-1}\)) allows a uniform dispersion of the nanoparticles and hence, FAL adsorption ability on the nanosheets contributes to improved catalytic behaviour.

Full conversion of FAL and 100% selectivity to FOL was reported by Yang et al. [22] employing Ru nanoparticles supported on Al based metal-organic frameworks with benzene-dicarboxylic acid as linkers. FAL hydrogenation was performed in water at room temperature (20°C) at a pressure of \( \text{H}_2 \) of 5 bar. They suggested that in-situ reduction of Ru species occurs over the support surface accounting for the high activity observed. However, no recyclability test for the catalyst was reported and the metal: FAL ratio used was quite high.

In a recent publication [23], Ru-Sn alloys supported on activated carbon (AC) were presented as a promising catalyst for the aqueous-phase hydrogenation of FAL to FOL. While 90% conversion and 95% selectivity to FOL observed after 5 hours of reaction at 90°C very high metal:FAL ratios were required to achieve this high yield to FOL.

The high cost of Pt and Pd [24] and lack of more economically attractive and stable heterogeneous catalyst systems, had led to significant efforts being devoted to the development of more economically viable Ru based catalysts. Furthermore, for the development of a sustainable process, that could translate into an industrial setting, these catalysts should be able to function effectively using water as solvent [25]. To stabilize highly dispersed Ru attention should also be paid to the effect of the support materials on catalytic performance. Nevertheless,
for the aqueous phase hydrogenation of FAL into FOL, to the best of our knowledge, there are no systematic comparisons on the impact of support properties and the application of graphenic materials as supports for Ru based hydrogenation of FAL to FOL. So in the present study we aim to compare different metal oxides (Al₂O₃, SiO₂ and TiO₂) and carbonaceous materials (activated carbon, high surface area graphite and graphenic materials) as supports of Ru catalysts. The preparation and some characteristics of the Ru supported on carbonaceous materials has been reported in our previous reference [26].

In view of the above, here we report on a systematic and comparative study of supported Ru based catalysts in the hydrogenation of FAL into FOL in water at room temperature. The effect of metal precursor, support material and reduction temperature on the catalytic properties was investigated, and correlated with the results from catalyst characterization. The stability and recyclability of the optimized catalyst was determined to assess the suitability for a tentative industrial application.

2. Experimental section

2.1 Preparation of supports

Graphenic materials were prepared via thermal treatment of graphite oxide (GO). GO was synthesized from natural graphite flake (325 mesh) supplied by Alfa Aesar (purity 99.8%) following a modification of the Brodie’s method as described elsewhere.[26] The synthesized GO was dried under vacuum to constant weight in a desiccator over P₂O₅ at room temperature. Exfoliation of the obtained GO was carried out in a vertical quartz reactor under inert (N₂) and reactive atmospheres (NH₃) yielding reduced graphene oxide (rGO) and nitrogen-doped graphene oxide (NrGO) respectively.
Apart from the two lab prepared graphenic materials five commercial supports were also employed as support of Ru metallic nanoparticles. These are: SiO$_2$, TiO$_2$, Al$_2$O$_3$, activated carbon, and a high surface area graphite. The activated carbon (denoted as AC, $S_{\text{BET}} = 1190$ m$^2$ g$^{-1}$, 313 m$^2$ g$^{-1}$ external surface area) was provided by Oleicola el Tejar, Córdoba Spain, while SiO$_2$ ($S_{\text{BET}} = 465$ m$^2$ g$^{-1}$) was obtained from Fluka, TiO$_2$ ($S_{\text{BET}} = 50$ m$^2$ g$^{-1}$) and Al$_2$O$_3$ ($S_{\text{BET}} = 187$ m$^2$ g$^{-1}$) from Degussa. Finally the high surface area graphite material (HSAG400, $S_{\text{BET}} = 396$ m$^2$ g$^{-1}$) was supplied by TIMCAL.

2.2 Preparation of catalysts

Ru supported catalysts, with a ruthenium loading of 4 wt.% were prepared by wetness impregnation with Ru$_3$(CO)$_{12}$ dissolved in acetone (catalyst series denoted with “CO”) as described elsewhere [26].

Two other series of Ru catalyst were prepared using water:ethanol (1:1) solutions of RuCl$_3$ (series denoted as “Cl”) or Ru(NO)(NO$_3$)$_3$ (series labelled with “NN”) as precursor. For these two series the graphenic materials were impregnated by incipient wetness method [26].

It should be indicated that before studying in the reaction test all the prepared samples were activated by reduction under hydrogen flow (60 mL min$^{-1}$) at 300ºC (or 350ºC) for 2 h, to decompose the precursor and assure their initial metallic state. Once the reduced samples are at room temperature, a helium flow (50 mL min$^{-1}$) is passed for 5 h in order to passivate the metallic surfaces. The reduced/passivated catalysts were exposed and stored under air up to their evaluation in the reaction or characterization studies.
2.3 Material characterizations

The textural characterization and surface area (S\text{BET}) determinations were obtained from the nitrogen adsorption (-196 °C) isotherms, which were acquired using an ASAP model 2020 instrument. Transmission Electron Microscopy (TEM) micrographs of the supports and of the catalysts were taken on a JEOL JEM-2100F microscope at 200 kV. The samples were ultrasonically suspended in ethanol before deposition over a copper grid with carbon coated layers. The average metal particle sizes in the catalyst were calculated using the following formula[26]:

\[ d = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \]

where \( n_i \) is the number of particles with diameter \( d_i \).

The samples were also analysed by X-ray diffraction (XRD), using a Polycrystal X’Pert Pro PANalytical diffractometer with Ni-filtered Cu/K radiation (\( \lambda = 1.54 \) Å) operating at 45 kV and 40 mA. For each sample, Bragg’s angles between 4° and 90° were scanned at a rate of 0.04°/s. All the catalyst were analysed by X-ray photoelectron spectroscopy (XPS) using an Kratos AXIS Supra spectrophotometer, which operated with a monochromatic Al K\(_a\) source (1486.7 eV). Spectra were analysed with CasaXPS software and RSF database by fitting after Shirley background correction.

Additionally, the adsorption/desorption of the reactant, FAL, and the two main reaction products, FOL and tetrahydrofurfuryl alcohol (THFA), was studied by temperature programmed desorption (TPD) for the case of the Ru(CO)/rGO catalyst. These experiments were carried out under vacuum in a conventional volumetric apparatus connected to a RGA-200 SRS mass spectrometer[27]. Three aliquots of reduced catalyst samples were stirred at 20°C for 20 hours under 10 bar of helium with 50 mL of 0.03M solutions of FAL, FOL and THFA, respectively.
Each sample was dried overnight under vacuum in a desiccator over \( \text{P}_2\text{O}_5 \) at room temperature. The samples were evacuated for 30 min at room temperature and then heated to 500ºC at a 5ºC min\(^{-1}\) rate analysing the evolved gas by the quadrupole mass spectrometer.

### 2.4 Reactivity measurements

The hydrogenation of FAL was carried out in a 75 mL Teflon-lined steel autoclave reactor (Parr 4560), equipped with a mechanical stirrer (500 rpm). By some preliminary studies, using the same catalyst, it was determined that under this stirring velocity there is not internal mass transfer limitations. The reactor was charged with 50 mL of an aqueous solution containing 150 mg of FAL and 25 mg of the reduced catalyst in suspension. The system was flushed three times with high purity He. Subsequently the reactor was pressurised up to 10 bars with \( \text{H}_2 \). The reaction vessel was kept at 20ºC with a water bath. Aliquots of the reactor liquids were collected periodically, filtered and the reaction product mixture was analysed by gas chromatography, Varian 3350 equipment, provided with a FID detector and a Supelco SPB-5 column (30m length × 0.53mm internal diameter × 0.5µm film thickness). The samples for analysis were prepared by dilution of 350 µL of the reaction products with 650 µL of a 0.02M ethanolic solution of decane as internal standard.

Carbon mass balances in the reaction studies are higher than 95% in all the catalytic determinations. Calibration curves for the observed products were determined by injecting known concentrations of reference commercial products and decane as internal standard. Some of these experiments were repeated twice in order to check reproducibility of these measurements.
The conversion of FAL was calculated as:

\[ C(\%) = \frac{FAL_i - FAL_f}{FAL_i} \cdot 100 \]

where FAL\(_i\) represents the initial FAL concentration and FAL\(_f\) the final FAL 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 performances.

The selectivity of each product was calculated as:

\[ S_i(\%) = \frac{mol_i}{mol_t} \cdot 100 \]

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.

3. Results and discussion

3.1 Material characterisation

The particle sizes of the ruthenium nanoparticles in the reduced catalysts were determined by TEM. Fig. 1 shows representative TEM images of the catalysts and their histograms with particle size distribution. The average diameters of the Ru nanoparticles for the supported catalysts are summarized in Table 1, which shows the particle sizes for these Ru crystallites are in the range from 1.3 to 2.7 nm. From Table 1 it can be seen that the particle size of Ru nanoparticles strongly depends on the support and precursor used, as well as on the temperature of reduction used.
Figure 1. TEM images and particle size distribution of the catalyst: (a) Ru(CO)/rGO, (b) Ru(CO)/TiO$_2$, (c) Ru(CO)/SiO$_2$, (d) Ru(CO)/Al$_2$O$_3$, (e) Ru(NN)/rGO, (f) Ru(CO)/HSAG after reduction at 300ºC or 350ºC (*). For Ru(NN)/rGO, Ru(CO)/rGO and Ru(CO)/HSAG samples, two temperatures of reduction were applied (300ºC and 350ºC), with the TEM measurements for these catalysts indicating that the size of Ru nanoparticles were affected depending on the applied temperature. Lower temperatures can lead to less sintering of the Ru atoms, leading to smaller metallic particle sizes than the catalysts reduced at 350ºC. When rGO support is considered, the ruthenium particle size change slightly with the metal precursor in the order: Ru(Cl) > Ru(NN) ~ Ru(CO) [26]. Comparison of Ru catalysts supported on the different materials, prepared from the Ru$_3$(CO)$_{12}$ precursor, reveals that smaller particle sizes were obtained on rGO support, which could be
rationalized as a consequence of the lower specific surface area of HSAG (396 m² g⁻¹), SiO₂ (465 m² g⁻¹), NrGO (483 m² g⁻¹), and AC (313 m² g⁻¹ external surface area) compared to rGO (904 m² g⁻¹). Thus the higher surface area of rGO promotes the narrow and uniform distribution of the metallic precursor, leading to the particle size observed. In the case of TiO₂ and Al₂O₃ in spite of their relatively low surface areas, some chemical interactions between the Ru carbonyl precursor and the support surface can take place, directing the generation of smaller Ru nanoparticles after reduction. Furthermore, Ru(CO)/HSAG, Ru(CO)/SiO₂ and Ru(CO)/AC catalysts exhibit the highest average particle size and also the broadest range of crystal size distributions.

The XRD patterns of the catalysts prepared over different supports are not shown for the sake of brevity. No peaks related with the formation of crystalline Ru were detected. This might be attributable to the small particle size of Ru nanoparticles in these samples, as was evidenced in the dTEM values reported in Table 1. Small particles are below the XRD detection threshold because they do not have enough range ordering to constructively interfere with X-rays [28].

XPS is a powerful technique to identify the chemical states of the surface elements, and was used to analyze the interaction of Ru nanoparticles on the different graphenic supports. Due to the partial overlapping of Ru 3d₃/₂ peaks with that of C 1s, the Ru 3p signal was used to study the chemical states of Ru in the samples. A previous study of our group [26] reported that N atoms in the structure of N doped graphene could favour donation of electron density towards Ru active site in Ru(Cl)/NrGO samples, showing a shift to lower binding energies of the Ru 3p₃/₂ and Ru 3p₁/₂ peaks compared to Ru(Cl)/rGO. The Ru 3p XPS spectrum for Ru(NN)/rGO and Ru(CO)/rGO catalysts showed two peaks corresponding to Ru 3p₃/₂ and Ru 3p₁/₂ (Table 2). These peaks appeared at higher binding energies than the binding energies reported for Ru(NN)/NrGO and Ru(CO)/NrGO peaks respectively. In agreement with our previous findings
[26], the latter results confirm that N doped graphene exhibit an electronic interaction with the Ru nanoparticles thanks to a systematic electron transfer from the support to the Ru.

3.2 Catalytic results

Table 3 summarizes the results obtained for the hydrogenation of FAL to FOL in water at room temperature (20ºC) and 10 bars of H₂ over the Ru catalysts prepared from different precursors and with different support materials. Negligible conversion of products was observed in blank tests carried out without catalyst under our reaction conditions (entry 1) and with the bare rGO itself (entry 2), showing that Ru sites are indispensable for catalytic FAL conversion under our experimental conditions.

The activities obtained with catalysts prepared from Ru(NO)(NO₃)₃ and Ru₃(CO)₁₂ precursors over rGO (entries 4 and 5) were higher than the activity observed using a RuCl₃ derived catalyst (entry 3). The presence of residual chlorine on the surface of the Ru(Cl)/rGO catalyst has been reported previously [26]. The poisoning of Ru nanoparticles by anchored chlorine atoms, blocking and reducing the number of active sites, seems to be the reason of this different behaviour. Using Ru(NO)(NO₃)₃ and Ru₃(CO)₁₂ derived catalysts, FAL conversions of 72.9% and 82.7% respectively with 98% selectivity towards FOL were reached after 5 hours. On the other hand, the catalyst Ru(CO)/rGO was studied at another reaction temperature, 100 ºC and at the same pressure 10 bar. The main findings of this experiment are: an increase in the conversion values, and particularly a selectivity shift from FOL to THFA at higher reaction times. At this point it should be noticed that while at 100 ºC, the consecutive reaction of transforming of FOL into THFA takes place; at lower reaction temperatures, 20 ºC, this second hydrogenation reaction is hindered.
Several Ru catalysts prepared using Ru(CO)$_{12}$ as Ru precursor over different supports (entries 5-11) were tested under the same reaction conditions. The supports studied include rGO, NrGO, AC, HSAG, SiO$_2$, Al$_2$O$_3$, and TiO$_2$. From Table 3 it can be seen that the achieved FOL selectivities with all the Ru studied catalysts were higher than 97%. Interestingly, when rGO was replaced by other support materials lower conversions (25-63% versus 83%) were observed. For Ru(CO)/AC, Ru(CO)/HSAG, Ru(CO)/SiO$_2$ and Ru(CO)/NrGO catalysts the poor catalytic activities can be attributed to the differences in Ru average particle sizes (1.8-2.7 nm Table 1) compared with the Ru(CO)/rGO catalyst (1.4 nm). Furthermore, the outstanding catalytic performances of Ru(CO)/rGO and Ru(NN)/rGO can be also associated with the narrow mean particle size of Ru (see histograms in Fig. 1) and the high dispersion of Ru nanoparticles, aspects that we have related to the noteworthy high surface area of this support (904 m$^2$ g$^{-1}$). However, the considerable difference in terms of catalytic activity observed over Ru(CO)/Al$_2$O$_3$ and Ru(CO)/TiO$_2$ catalysts (entries 9 and 11 respectively) compared to Ru(CO)/rGO, cannot be attributed to the Ru crystallite sizes, as all these catalysts have very small Ru particle size (Table 1). The different catalytic properties induced by Al$_2$O$_3$ and TiO$_2$ supports on the Ru nanoparticles, may be related with the intrinsic acid-base properties of these support materials, with Al$_2$O$_3$ being an acidic support and TiO$_2$ being an amphoteric reducible support. However, rGO is an inert support, whose outstanding surface properties may originate from high surface area and weaker electronic interactions with the Ru nanoparticles. The inert surface of this rGO support may also favour efficient hydrogenation of FAL by Ru, when compared with oxidic supports (case of Ru(CO)/Al$_2$O$_3$ and Ru(CO)/TiO$_2$ catalysts), due to weakened adsorption of FAL/FOL over the graphenic support and more facile product desorption. In short, undoubtedly,
the support plays a key role in the performance of the studied Ru catalysts and among the examined supports, rGO is the most preferable for the hydrogenation of FAL.

Comparison of three Ru catalysts, Ru(CO)/rGO, Ru(NN)/rGO and Ru(CO)/HSAG reduced under \( \text{H}_2 \) at 350 °C (entries 4, 5 and 7) and at 300°C (entries 12-14) reveals that catalytic activity, in the aqueous-phase hydrogenation of FAL, can be optimized. This reduction temperature dependence of the catalytic results is displayed in Figure 2. Systematically smaller Ru nanoparticles obtained pre-treating the catalysts at 300°C (Table 1) are more active in the FAL hydrogenation than those reduced at 350°C. For instance, Ru(CO)/HSAG gives a conversion of 46% when is reduced at 350°C, increasing this value to 50% by the use of a lower pre-treatment temperature. The most noteworthy remark from these comparative data is that, with the catalyst Ru(CO)/rGO, FAL can be almost completely converted, and with 98% of selectivity towards FOL. The same behaviour is obtained using Ru(NN)/rGO, 97% of selectivity towards FOL, when reduced at 300°C (entry 13). Thus we have been able to optimize a supported catalyst, combining the surface properties of rGO and very small Ru nanoparticles, that permits to achieve near 100% yield FOL from FAL.
Figure 2. Conversion of FAL into FOL over Ru(CO)/rGO, Ru(NN)/rGO and Ru(CO)/HSAG reduced at 300ºC (red) and 350ºC (red). Reaction conditions: FAL, 1.56 mmol, 25 mg of catalyst, molar ratio FAL/M=157, H_2 O 50 ml, H_2 10 bars, 20ºC, 5 hours.

Based on the above catalytic results, we have examined the stability of Ru(CO)/rGO and Ru(NN)/rGO catalysts reduced at 300ºC, in particular, their reusability. Four successive rounds were conducted with the solid recovered by filtration and washed thoroughly with water. As shown in Figure 3, for Ru(NN)/rGO, the initial conversion of FAL was maintained for at least two runs, for the third and fourth runs the conversion of FAL strongly decreased during the recycling experiment. No loss in the selectivity towards FOL was observed. Therefore, a clear reduction in the intrinsic activity was observed for the Ru (NN)/rGO catalyst. For Ru(CO)/rGO no catalyst deactivation was observed after 3 rounds. For the fourth round, conversion of FAL slightly decreased. Also the selectivity to FOL kept stable during the recycle process. This
indicates that Ru(CO)/rGO catalyst was generally stable showing a minor deactivation during the recycling experiment. Consequently, in a first step Ru(CO)/rGO exhibit better stability upon reuse compared to Ru(NN)/rGO.

**Figure 3.** Stability of the A) Ru(CO)/rGO and B) Ru(NN)/rGO catalysts during the recycling uses for the hydrogenation of Furfural. Reaction conditions: FAL 1.56 mmol, 25 mg of catalyst, molar ratio FAL/Metal=157, H₂O 50 ml, H₂ 10 bars, 20°C, 5 hours.

In order to elucidate the causes of the catalyst deactivation a series of complementary experiments were carried out. So the concentration of potential leached ruthenium in the filtered aqueous solution was studied by inductively coupled plasma mass spectrometer. For the hydrogenation reaction solutions obtained from the Ru(NN)/rGO and Ru(CO)/rGO catalysts after the recycling experiments, no detectable leaching of ruthenium was identified. To preclude a loss of activity produced by a Ru sintering mechanism, the spent catalysts were studied by TEM. Based on the TEM measurements (Table 4), a slightly increase in the mean diameters of the Ru nanoparticles and no essential changes in the particle size distribution after the fourth cycles were observed. Given the mild reaction conditions, no sintering was expected to be
produced in the tested catalysts. To study a possible change in the oxidation state of the Ru nanoparticles, XPS analyses were carried out over the spent catalysts. The Ru 3p XPS spectra of the fresh samples contain two peaks which can be assigned to Ru\(^0\) species [29]. The XPS spectra for the spent samples upon recycling show an increase of oxygen content in the samples that concomitantly can be due to adsorbed reactant or products in the spent catalysts (see below TPD experiments). Also a shift in the position of the peaks corresponding to Ru 3p to higher binding energy values (Table 4) that could be partly due to oxidation of the Ru\(^0\) particles [30] to RuO\(_2\), probably occurred during the transfer and manipulation of the sample during the characterization process, was observed for the two catalysts. Hence, changes in the Ru oxidation states before and after reaction could not be assigned as contribution to the deactivation of the active sites.

Temperature programmed desorption (TPD) experiments with MS analysis of the gases evolved were carried out to exclude possible irreversible chemisorption of one of the reaction products on the surface of the Ru(CO)/rGO catalyst that can cause the deactivation phenomena. This thermal study (TPD) allows to identify the desorbed products and to discern between chemisorbed and physisorbed products in base to the strength of the adsorption and its thermal stability. These experiments, carried out over aliquots of the catalyst that have been 20 hours in contact with aqueous solutions containing FAL, FOL or THFA, are shown in Figure 4. The evolved FAL, FOL and THFA appears as desorption profiles, following in the MS univocal molecular ions (95, 98 and 71, respectively). In the FAL desorption (Figure 4a) the most abundant specie of the obtained spectra appear at m/z=95. Considering that boiling points of FAL is 162°C, and that desorption profiles of FAL appear in the range 120-155 °C we have considered this peak as due to physisorbed FAL. Also it can be appreciated a small shoulder at about 230°C, assignable to some species of chemisorbed FAL. In this experiment negligible peaks for m/z values 98 and 71
were detected, so in the absence of hydrogen FOL is not produced. FOL desorption (Figure 4b) is followed by the m/z=98 ion. Considering that boiling point of FOL is 170 ºC, the peaks located at 170-225 ºC can be associated to physisorbed species. The small peak at 270ºC should correspond to traces amounts of chemisorbed FOL. The simultaneous evolution of FAL (m/z = 95) possibly indicates the dehydrogenation of FOL during the run of the TPD experiment, as no FAL was detected in the solution after the adsorption process. Finally, THFA, who boiling point is 178 ºC, was followed by the signal m/z=71. The lack of m/z=71 during the TPD suggests that physical adsorption of THFA is not taking place. At this point we can assume that the observed physisorbed species might be located on the support surface, while the chemisorbed ones would be in interaction with the Ru nanoparticles. This spatial distribution in the catalyst could explain the reduced amount of chemisorbed species in comparison with physisorbed ones. Nevertheless, the presence of strong adsorption sites able to chemisorb FOL (Figure 4b) seems to indicate that the slight deactivation of Ru(CO)/rGO catalyst after 4 runs could be caused by obstruction of metallic sites by FOL.
Figure 4. TPD-MS of (a) FAL, (b) FOL and (c) THFA from thermally treated catalyst

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. Thus, the slight deactivation could be related to a small loss of mass during recovery of the Ru(CO)/rGO catalyst between successive runs and/or to the irreversible chemisorption of FOL over the Ru active sites. But the relevant finding is that these results prove that the highly active Ru(CO)/rGO catalyst shows excellent reusability under the employed reaction conditions, without significant loss of catalytic activity or selectivity.

A comparative evaluation between our best performant catalysts with those previously published is summarized in Table 5. It should be notice that in all reactions presented in Table 5, water was the solvent (or the reaction media). The comparison among catalysts in Table 5 is not straightforward since the reaction condition variables, such as temperature, pressure, reaction time or molar reactant-metal ratio, are not similar. However, considering that we work at lower reaction temperature and/or higher molar reactant-metal ratio, the performance of our graphene material supported Ru catalysts is clearly superior to those reported in the literature. It should be remarked that if we try to relate, in this general Table 5, the catalytic performances (conversion, selectivity) with other reaction parameters, such as weight of catalysts or concentrations of FAL, no systematic correlations can be established. Among others, all these results are obtained at different reaction temperatures, initial furfural concentrations (varying in the range of 0.3 to 5.3 FAL wt. % in water), volume of reactors, or are given at distinct times in reaction. All these together make impossible to isolate a precise effect of one of these parameters.
4. Conclusions

In this paper, we have reported a remarkable stable catalyst for the hydrogenation of FAL in water under mild conditions (20ºC and 10 bar of H₂) based on ruthenium nanoparticles supported on reduced graphene oxide. The results obtained confirm that the performance of these catalysts in the catalytic hydrogenation of FAL is strongly influenced by the support material, the reduction temperature and the used ruthenium precursor. All these parameters are responsible for the achievement of average sizes and distributions of Ru crystallites that can be tailored to improve the catalytic properties of a given composite material.

The characterization results allowed us to explain the observed differences in terms of catalytic behavior for each synthesized material. These results point out that not only smaller Ru particle sizes lead to higher catalytic activities and selectivities, but also the special surface properties of graphenic materials have a major contribution in the improvement of the catalytic features. In summary our best results, catalytic activity and selectivity, were obtained over the sample Ru(CO)/rGO (93% conversion and 98% of selectivity toward FOL) and additionally we have demonstrated that this catalyst can be reused several time in the reaction process without further reactivation or regeneration treatments.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.
ACKNOWLEDGMENT

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REFERENCES

Table 1. Characteristics of the ruthenium catalysts reduced in hydrogen for 2 h.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>$d_{\text{TEM}}^a$ (nm)</th>
<th>$d_{\text{TEM}}^b$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(Cl)/rGO</td>
<td>1.5*</td>
<td>-</td>
</tr>
<tr>
<td>Ru(NN)/rGO</td>
<td>1.4*</td>
<td>1.3</td>
</tr>
<tr>
<td>Ru(NN)/NrGO</td>
<td>1.7*</td>
<td>-</td>
</tr>
<tr>
<td>Ru(CO)/rGO</td>
<td>1.4*</td>
<td>1.3</td>
</tr>
<tr>
<td>Ru(CO)/NrGO</td>
<td>1.8*</td>
<td>-</td>
</tr>
<tr>
<td>Ru(CO)/AC</td>
<td>2.4*</td>
<td>-</td>
</tr>
<tr>
<td>Ru(CO)/HSAG</td>
<td>2.3*</td>
<td>1.8</td>
</tr>
<tr>
<td>Ru(CO)/Al$_2$O$_3$</td>
<td>1.2</td>
<td>-</td>
</tr>
<tr>
<td>Ru(CO)/SiO$_2$</td>
<td>2.7</td>
<td>-</td>
</tr>
<tr>
<td>Ru(CO)/TiO$_2$</td>
<td>1.3</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ Sample reduced at 350°C $^b$Sample reduced at 300°C $^c$From reference [26]

Table 2. XPS data of Ru catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BE Ru 3p$_{3/2}$ (eV)</th>
<th>FWHM</th>
<th>Ru/C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(NN)/rGO</td>
<td>462.3</td>
<td>3.7</td>
<td>0.005</td>
</tr>
<tr>
<td>Ru(NN)/NrGO</td>
<td>462.0</td>
<td>3.6</td>
<td>0.004</td>
</tr>
<tr>
<td>Ru(CO)/rGO</td>
<td>462.7</td>
<td>3.9</td>
<td>0.004</td>
</tr>
<tr>
<td>Ru(CO)/NrGO</td>
<td>462.5</td>
<td>3.5</td>
<td>0.005</td>
</tr>
</tbody>
</table>
Table 3. Catalytic performance of ruthenium catalysts in the hydrogenation of FAL

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Sel FOL (%)</th>
<th>Sel THFA (%)</th>
<th>TOF (s(^{-1}) x10(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Blank</td>
<td>3.2</td>
<td>100</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>rGO</td>
<td>3.0</td>
<td>100</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>Ru(Cl)/rGO</td>
<td>49</td>
<td>98</td>
<td>2</td>
<td>4.97</td>
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<tr>
<td>4</td>
<td>Ru(NN)/rGO</td>
<td>73</td>
<td>98</td>
<td>2</td>
<td>7.89</td>
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<tr>
<td>5</td>
<td>Ru(CO)/rGO</td>
<td>83</td>
<td>98</td>
<td>2</td>
<td>8.59</td>
</tr>
<tr>
<td>6</td>
<td>Ru(CO)/NrGO</td>
<td>63</td>
<td>97</td>
<td>3</td>
<td>6.86</td>
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<tr>
<td>7</td>
<td>Ru(CO)/HSAG</td>
<td>46</td>
<td>99</td>
<td>1</td>
<td>7.82</td>
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<tr>
<td>8</td>
<td>Ru(CO)/AC</td>
<td>55</td>
<td>99</td>
<td>1</td>
<td>5.97</td>
</tr>
<tr>
<td>9</td>
<td>Ru(CO)/Al(_2)O(_3)</td>
<td>28</td>
<td>100</td>
<td>0</td>
<td>1.97</td>
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<tr>
<td>10</td>
<td>Ru(CO)/SiO(_2)</td>
<td>30</td>
<td>100</td>
<td>0</td>
<td>5.15</td>
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<tr>
<td>11</td>
<td>Ru(CO)/TiO(_2)</td>
<td>25</td>
<td>100</td>
<td>0</td>
<td>2.63</td>
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<tr>
<td>12</td>
<td>Ru(NN)/rGO(^a)</td>
<td>93</td>
<td>97</td>
<td>3</td>
<td>8.97</td>
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<tr>
<td>13</td>
<td>Ru(CO)/rGO(^a)</td>
<td>93</td>
<td>98</td>
<td>2</td>
<td>9.63</td>
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<tr>
<td>14</td>
<td>Ru(CO)/HSAG(^a)</td>
<td>50</td>
<td>98</td>
<td>2</td>
<td>6.57</td>
</tr>
</tbody>
</table>

Reaction conditions: FAL, 1.56 mmol, 25 mg of catalyst, molar ratio FAL/Metal=157, H\(_2\)O 50 ml, H\(_2\) 10 bars, 20°C, 5 hours. Reduction temperature 350°C. \(^a\) Reduction temperature 300°C. \(^b\) TOF Calculated based on the moles of FAL converted per mole surface metallic ruthenium at the 240 min reaction time.
Table 4. XPS and TEM characterization of the fresh and spent Ru(NN)/rGO and Ru(CO)/rGO catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>dTEM (nm)</th>
<th>O (%)</th>
<th>BE Ru 3p3/2 (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ru(NN)/rGO fresh</td>
<td>1.3</td>
<td>6.2</td>
<td>462.3</td>
</tr>
<tr>
<td>Ru(NN)/rGO spent</td>
<td>1.5</td>
<td>11.8</td>
<td>463.1</td>
</tr>
<tr>
<td>Ru(CO)/rGO fresh</td>
<td>1.3</td>
<td>6.1</td>
<td>462.7</td>
</tr>
<tr>
<td>Ru(CO)/rGO spent</td>
<td>1.4</td>
<td>10.9</td>
<td>463.1</td>
</tr>
</tbody>
</table>

Table 5. Comparative data of the FAL hydrogenation over different metal supported catalyst using water as solvent media

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>FAL:M ratioa</th>
<th>T (°C)</th>
<th>H₂ pressure (bar)</th>
<th>Time (h)</th>
<th>Conversion (%)</th>
<th>FOL selectivity (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>2%Pd-1%Ir/SiO₂</td>
<td>480</td>
<td>20</td>
<td>80</td>
<td>6</td>
<td>100</td>
<td>&lt;1%</td>
<td>18</td>
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<tr>
<td>5%Pd-1.5%Cu/Al₂O₃</td>
<td>11</td>
<td>90</td>
<td>20</td>
<td>2</td>
<td>100</td>
<td>41</td>
<td>19</td>
</tr>
<tr>
<td>5%Cu/Al₂O₃</td>
<td>6</td>
<td>90</td>
<td>20</td>
<td>2</td>
<td>81</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>1.5%Pd/CNT</td>
<td>856</td>
<td>50</td>
<td>5</td>
<td>-</td>
<td>95</td>
<td>52</td>
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<td>5</td>
<td>-</td>
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<td>88</td>
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<tr>
<td>5%Pd-5%Cu/MgO</td>
<td>133</td>
<td>130</td>
<td>8</td>
<td>0.9</td>
<td>100</td>
<td>99</td>
<td>20</td>
</tr>
<tr>
<td>3%Ru/Al-MIL-53s</td>
<td>40</td>
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<td>5</td>
<td>2</td>
<td>100</td>
<td>&gt;99.9</td>
<td>22</td>
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<tr>
<td>5%Pd/C₃N₄</td>
<td>376</td>
<td>100</td>
<td>10</td>
<td>5</td>
<td>&gt;99</td>
<td>&gt;99</td>
<td>6</td>
</tr>
<tr>
<td>3%Ru-2.5%Sn/AC</td>
<td>73</td>
<td>90</td>
<td>12.5</td>
<td>5.5</td>
<td>90</td>
<td>95</td>
<td>23</td>
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<tr>
<td>Ru(CO)/rGO</td>
<td>157</td>
<td>20</td>
<td>10</td>
<td>5</td>
<td>93</td>
<td>98</td>
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<td>Ru(NN)/rGO</td>
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<td>20</td>
<td>10</td>
<td>5</td>
<td>93</td>
<td>97</td>
<td>This work</td>
</tr>
</tbody>
</table>

aFAL: Metal ratio