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2 *Article*3 **Cascade strategy for the tunable catalytic valorization**
4 **of levulinic acid and γ -valerolactone to 2-**
5 **methyltetrahydrofuran and alcohols**6 **Domenico Licursi**¹, **Claudia Antonetti**¹, **Sara Fulignati**¹, **Michael Giannoni**¹, **Anna Maria**
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12 Received: date; Accepted: date; Published: date

13 **Abstract:** A cascade strategy for the catalytic valorization of aqueous solutions of levulinic acid as
14 well as of γ -valerolactone to 2-methyltetrahydrofuran or to monoalcohols, 2-butanol and 2-
15 pentanol, has been studied and optimized. Only commercial catalytic systems have been
16 employed, adopting sustainable reaction conditions. For the first time, the combined use of
17 ruthenium and rhenium catalysts supported on carbon, with niobium phosphate as acid co-
18 catalyst, has been claimed for the hydrogenation of γ -valerolactone and levulinic acid, addressing
19 the selectivity to 2-methyltetrahydrofuran. On the other hand, the use of zeolite HY with
20 commercial Ru/C catalyst favors the selective production of 2-butanol, starting again from γ -
21 valerolactone and levulinic acid, with selectivities up to 80 and 70 mol%, respectively. Both
22 levulinic acid and γ -valerolactone hydrogenation reactions have been optimized, investigating the
23 effect of the main reaction parameters, to properly tune the catalytic performances towards the
24 desired products. The proper choice of both the catalytic system and the reaction conditions can
25 smartly switch the process towards the selective production of 2-methyltetrahydrofuran or
26 monoalcohols. The catalytic system [Ru/C+zeolite HY] at 200 °C and 3 MPa H₂ is able to
27 completely convert both γ -valerolactone and levulinic acid, with overall yields to monoalcohols of
28 100 mol% and 88.8 mol%, respectively.

29 **Keywords:** levulinic acid; γ -valerolactone; 2-methyltetrahydrofuran; 2-butanol; 2-pentanol;
30 hydrogenation; ruthenium, rhenium, niobium phosphate

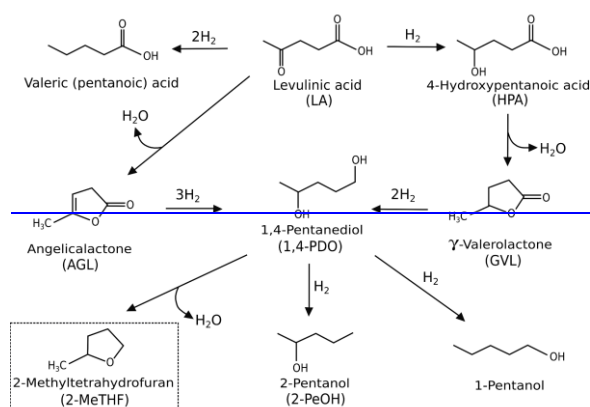
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32 **1. Introduction**

33 Nowadays, the development of clean energy sources is a principal benchmark and renewable
34 biomasses represent ideal starting materials for this purpose. In fact, as a stable and independent
35 alternative to fossil fuels, biomass has emerged as a potentially inexhaustible resource for the
36 production of energy, transportation fuels and chemicals [1,2]. Biomass resources can be
37 advantageously converted into interesting platform chemicals, such as 2-furaldehyde [3,4], 5-
38 hydroxymethyl-2-furaldehyde [5-7], levulinic acid (LA) [8,9] and γ -valerolactone (GVL) [10,11].
39 Focusing on the last two mentioned bio-chemicals, LA is a versatile bio-product, being considered
40 as one of the United States Department of Energy's (DOE's) top 12 bio-derived feedstocks. It can be
41 used as solvent, antifreeze, food flavoring agent and it can be employed for the synthesis of
42 pharmaceuticals, plasticizers, biofuels and many other high-value chemicals [9,12]. Instead, GVL is
43 one of the most important products deriving from LA hydrogenation, currently exploited for the

44 | production of both energy and carbon-based consumer products [13-175]. In this sense, it is a
45 | renewable and safe-to-store potential biofuel employed as replacement of ethanol in
46 | gasoline/ethanol blends [186, 197]. Furthermore, it can be used for the production of promising food
47 | additives [13], solvents [2048] and it is an intermediate for the synthesis of many other fine-
48 | chemicals such as [valeric biofuels/valerate](#), butene, 4-hydroxypentanol, 2-methyltetrahydrofuran
49 | and acrylic polymers [12,21-2349]. In the literature, multiple interesting pathways for the
50 | production of LA and GVL have been reported [240-262]. In this context, the possibility of
51 | upgrading these already valuable chemical intermediates into other classes of more added-value
52 | compounds, such as 2-methyltetrahydrofuran (2-MeTHF) and 2-butanol (2-BuOH), represents a
53 | smart challenging possibility. Regarding the first one, it is a versatile aprotic and hydrophobic
54 | organic solvent, which is non-toxic and non-ozone depleting in nature [273] and a promising
55 | biofuel [284], being identified as a key component for *P*-series fuels [295]. On the other hand, 2-
56 | BuOH is mainly used for the synthesis of methylethylketone, but very recently it has found other
57 | applications both as solvent and fuel additive, thanks to its high octane number [3026]. Regarding
58 | the possible synthesis of 2-MeTHF, some processes use furfural as the key intermediate, whereas
59 | some methods adopt LA. 2-MeTHF synthesis starting from furfural has been investigated more in-
60 | depth [3127-340]. Concerning the other possible route, the presence of 2-MeTHF was reported for
61 | the first time as a by-product of the LA hydrogenation with CuCr₂O₃ [354]. Afterward, many works
62 | have been published on this topic, which have partially clarified the reaction mechanism, and
63 | significantly improved the catalytic performances for the synthesis of 2-MeTHF [362-454]. Two
64 | reaction mechanisms have been proposed for 2-MeTHF synthesis from LA, the first one occurring
65 | by LA dehydration via angelicalactone (AGL) ([path A, Scheme 1](#)), whereas the second one by LA
66 | hydrogenation to 4-hydroxypentanoic acid (HPA) ([path B, Scheme 1](#)), both reported in the Scheme
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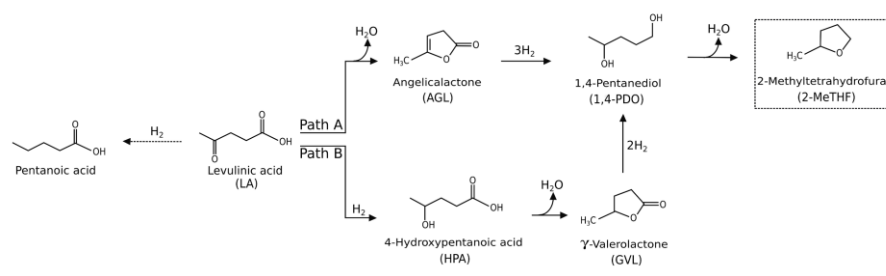


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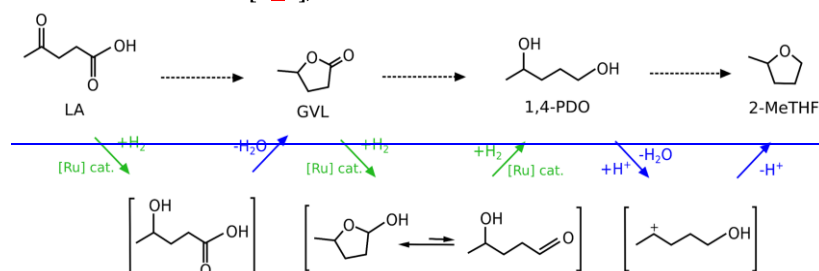


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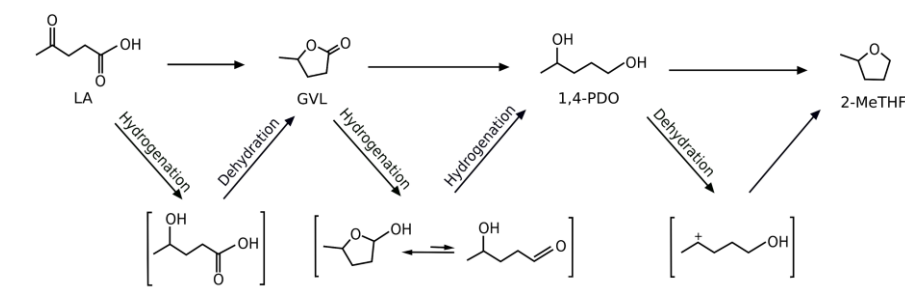
75 **Scheme 1.** Main intermediates/products deriving from Reaction pathways for LA conversion to 2-MeTHF
 76 (adapted from [32]).

77 The first pathway A was proposed by Thomas and Barile [462] and, more recently, Al-Shaal et
 78 al. [473] have demonstrated that the presence of AGL as starting material was beneficial for the one-
 79 pot conversion to 2-MeTHF, adopting a commercial Ru/C catalyst. However, the AGL path and its
 80 positive role for the 2-MeTHF production was proposed under *solvent-free* conditions [473], whilst
 81 the hydrogenation path (path B) in water medium occurs by a different mechanism, which leads to
 82 the formation of different intermediates. LA hydrogenation mechanism occurring through HPA
 83 intermediate, which has been extensively ascertained and demonstrated [484,495]. LA catalytic
 84 hydrogenation may give different reaction products, depending on the kind of the adopted catalyst
 85 and experimental conditions (path B, Scheme 1). The reaction proceeds by LA reduction to HPA,
 86 which readily dehydrates to GVL. The hydrogenation of GVL into 1,4-pentandiol (1,4-PDO) is
 87 reported to be strongly inhibited by water [4238], thus highlighting evident difficulties to perform
 88 this reaction in water already at this backward step and, even with greater difficulty, for the final
 89 1,4-PDO dehydration to 2-MeTHF [451]. Main by-products of this reaction include pentanoic acid
 90 and 1-pentanol. In greater detail, LA transformation into GVL, 1,4-PDO, and 2-MeTHF consists of
 91 consecutive series of hydrogenation/dehydration paths, both occurring via the formation of well-
 92 defined but short-lived intermediates [384], as shown in Scheme 2.



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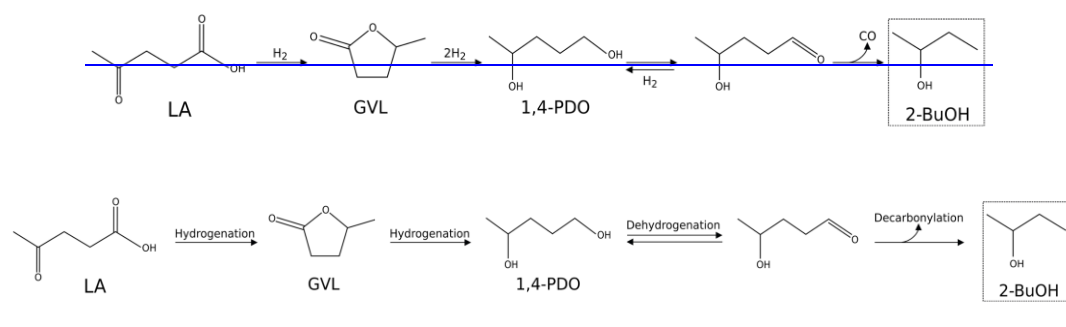


Scheme 2. LA hydrogenation and dehydration reactions to give GVL, 1,4-PDO and 2-MeTHF (adapted from [34]).

In the above scheme, the metal-catalyzed addition of H₂ to the LA keto group forms a hydroxy acid that undergoes intramolecular etherification to give GVL. Further hydrogenation of the C=O bond leads to the cyclic hemiacetal, which is in equilibrium with the open hydroxyl-aldehyde form. The remaining carbonyl group is hydrogenated to afford 1,4-PDO. Acid-catalyzed dehydration leads to cyclization of the diol by intramolecular etherification to give 2-MeTHF. A possible further reaction is the dehydration/hydrogenation of 1,4-PDO to the monoalcohols 1- or 2-pentanol. Most of these steps are reversible, which afford an additional challenge for the selectivity control. According to this mechanism, in the field of homogeneous catalysis, interesting results were reported by Mehdi et al. [373], which adopted homogeneous catalysts based on ruthenium phosphine compounds for the LA and GVL **conversionhydrogenation** to 2-MeTHF. In the case of LA, starting from Ru(acac)₃, NH₄PF₆ and PBu₃, LA was quantitatively converted to 2-MeTHF at a temperature of 200 °C, 8.2 MPa of hydrogen pressure and extended reaction times (about 46 h). Geilen et al. [384] reported that a homogeneous Ru-based molecular catalyst system bearing expensive phosphine ligands in combination with ionic and/or acid additives can selectively convert bio-derived LA into 1,4-PDO or 2-MeTHF, via formation of GVL intermediate. The authors reported the best 2-MeTHF yield of 92 mol%, employing Ru(acac)₃ as the metal precursor, triphos as the ligand, and the ionic liquid 1-butyl-2-(4-sulfobutyl)imidazolium-*p*-toluenesulfonate as an additive, working at 160 °C for 18 h, with 10 MPa H₂. Despite the promising 2-MeTHF yield, significant drawbacks for this catalytic system remain, e.g. its non-reusability, the necessity of special handling of metal complexes, the high cost for the catalyst preparation, as well as the tedious work-up procedures. Heterogeneous catalysts represent the best choice, and many interesting works have been published in this topic, such as the research of Elliot and Frye [362], which performed the hydrogenation of a 10 wt% LA aqueous solution, at a temperature range of 200–250 °C, with 10 MPa H₂. Working in water, the yields to 2-MeTHF were very scarce, adopting different hydrogenation catalysts, such as 5 % Ni/C-5 % Re/C, 50 % Ni/C, 50 % Ni/C-5 % Re/C and 50 % Ni/C-7.5 % Re/C. However, under the same reaction conditions, but using 1,4-dioxane instead of water as solvent, when a 50 % Ni/C-7.5 % Re/C catalyst was employed, the reaction rate was significantly improved, as well as the yield to 2-MeTHF which, however, reached the maximum value of 15 mol%, after 6 h of reaction. LA hydrogenation with 5 % Re/C- 5 % Pd/C improved significantly the 2-MeTHF yield, up to 90 mol%. Heterogeneous copper catalysts have been extensively used for LA conversion to 2-MeTHF [395,4036,5046]. In particular, Upare et al. [395] investigated the vapor-phase **conversionhydrogenation** of LA to 2-MeTHF in 1,4-dioxane, employing properly synthesized nanocomposite Cu/SiO₂ catalysts. The best result was claimed with an 80 % Cu/SiO₂ catalyst, obtaining in this case a maximum 2-MeTHF yield of 64 mol%, working at 265 °C for 100 h on stream, with 2.5 MPa H₂. Regarding the effect of the copper loading, the authors found that a lower one favored the selective hydrocyclization of LA to GVL, while a higher one led to further hydrogenation to 2-MeTHF and 1-pentanol, via GVL formation. The process was further improved by promoting the catalyst with Ni, e.g. Cu(72%)-Ni(8%)/SiO₂, thus achieving the best 2-MeTHF yield of 89 mol%, working at 265 °C for 300 h on steam, with 2.5 MPa H₂. Du et al. [4036] investigated the catalytic performances of a series of synthesised copper-zirconia catalysts for the

hydrogenolysis of GVL in ethanol at 200 °C with 6 MPa H₂, finding that a yield to 2-MeTHF of 6 mol% was produced when the reaction was performed at 220 °C. A further increase of the temperature up to 240 °C led to an increase in the 2-MeTHF yield up to about 13 mol%. In the attempt to improve the 2-MeTHF yield, subsequent runs were focused on the same reaction at 240 °C over a series of 30 % Cu/ZrO₂ catalysts with modified acidic properties of the catalyst surface obtained by calcination in air at different temperatures (300-700 °C), for 4 h. In the best case, a remarkable 2-MeTHF yield was improved up to 91 mol%, after 6 h of reaction. The authors proposed that the surface acidic sites in the Cu-based catalysts play a key role in the hydrogenolysis mechanism of lactones and the authors concluded that a synergistic cooperation between dispersed Cu and the acid sites of the catalyst surface was essential to facilitate the direct reduction of the carbonyl group in the GVL molecule or accelerate the subsequent dehydration of intermediate 1,4-PDO to give 2-MeTHF. Al-Shaal et al. [4238] used Ru/C as the only catalyst, under solvent-free conditions, for the one-pot LA conversion into 2-MeTHF, achieving the complete conversion at 190 °C and 10 MPa H₂, with a maximum 2-MeTHF yield of 61 mol%. Upare et al. [440] used Ru over graphene oxide for the study of LA conversion in 1,4-dioxane, producing a stable 48 mol% 2-MeTHF yield, operating at 265 °C and 2.5 MPa H₂. Mizugaki et al. [4339] used a Pt-Mo supported on acidic supports for the conversion of LA to 2-MeTHF. The most active synthesised catalyst was Pt(3.9%)-Mo(0.13%)/H-β zeolite, which allowed the maximum 2-MeTHF yield of 86 mol%, working in water at 130 °C for 24 h, with 5 MPa H₂. Obregón et al. [5147] studied the one-pot LA **conversionhydrogenation** to 2-MeTHF, with Ni/Al₂O₃, Cu/Al₂O₃ and Ni-Cu/Al₂O₃ catalysts in green solvents, such as water and biomass-derived alcohols, such as EtOH, 1-BuOH, and 2-PrOH. The best catalytic performances were achieved with bimetallic Ni-Cu/Al₂O₃ catalysts, achieving the maximum 2-MeTHF yield of 56 mol%, working in 2-PrOH, at 250 °C for 5 h, with 7 MPa H₂. Lastly, in a subsequent work, Obregón et al. [451] reported the complete LA conversion, with a maximum 2-MeTHF yield of 80 mol%, adopting a Ni-Cu/Al₂O₃ catalyst, in 2-PrOH as solvent, after 20 h at 250 °C and 4 MPa H₂.

Regarding 2-BuOH, at the moment its traditional industrial production is carried out through the acid-catalyzed hydration of 1- or 2-butene, both obtained from the C₄ fraction arising from steam cracking of oil-derived hydrocarbons [5248]. In recent years, the possibility of obtaining 2-BuOH from renewable resources has been evaluated. It is noteworthy that Shabaker et al. [5349] patented the catalytic decarboxylation of LA to methyl ethyl ketone, which was subsequently hydrogenated to 2-BuOH, employing copper faujasite as decarboxylation catalyst, and nickel or ruthenium as hydrogenation one. Al-Shaal et al. [4238] reported a total LA conversion, under solvent-free conditions, with a selectivity to 2-BuOH close to 40 mol%, adopting a 5 % Ru/C catalyst, and working at 190 °C and for 24 h, with 10 MPa H₂. Regarding the related reaction mechanism, under solvent-free conditions, 2-BuOH is predominantly formed via subsequent hydrogenation/decarbonylation reactions of the GVL [4238], as shown in Scheme 3:



Scheme 3. Reaction pathway for the 2-BuOH synthesis starting from GVL under solvent-free conditions. (adapted from [38]).

Obregón et al. [451] reported the GVL hydrogenation, achieving a maximum 2-BuOH yield of 37.3 mol%, working in 2-PrOH, at 250 °C and 4 MPa H₂. Lastly, Lv et al. [540] have recently used

nanoporous Ru for LA hydrogenation in water, reporting the combined production of both 2-BuOH and 2-Pentanol (2-PeOH), the latter derived mainly from 1,4-PDO hydrogenation, with a total [2-BuOH + 2-PeOH] yield of 78.8 mol%, working at 140 °C for 20 h, with 6 MPa H₂. Instead, when the same catalyst was employed at 100 °C and 6 MPa H₂ for 15 h, a maximum 74.6 mol% yield to 1,4-PDO was reached.

In this work, an alternative and green [approach/process](#) has been studied, which combines hydrogenation-decarboxylation of LA or of GVL to selectively give [2-BuOH + 2-PeOH] or 2-MeTHF, in the presence of commercial Ru/C and [Ru/C + Re/C] catalytic systems. The main reaction conditions, e.g. temperature, hydrogen pressure, and presence of heterogeneous acid co-catalyst (niobium phosphate or HY acid zeolite) have been investigated. This study has been carried out adopting water as the only reaction solvent and heterogeneous commercial catalytic systems, which are more economical, available, and reproducible respect to *ad hoc* prepared ones.

2. Results and Discussion

~~Starting from the~~~~Taking into account our~~ previous [encouraging](#) results [reached on](#) LA hydrogenation to GVL in the presence of Ru/C [and an acid co-catalyst](#) [554], ~~thus our~~ research ~~began started~~ from the GVL hydrogenation, which is considered to be the most demanding step, owing to the high thermodynamic stability of GVL [495]. ~~Subsequently, t~~The effect of the addition of Re/C to commercial Ru/C catalyst has been investigated, on the basis of the promising results obtained in the literature in the presence of the bimetallic Ru-Re system employed in the hydrogenation of levulinic acid and succinic acid where the introduction of Re amount improves the selectivity to 1,4-PDO [562], ~~which is~~ an intermediate towards 2-MeTHF [according our mechanism](#). Moreover, the addition of an acid co-catalyst to Ru and [Ru/C + Re/C] systems has been considered, because it is known that this acid component is able to activate [not only](#) the lactone ring opening, [but also the internal dehydration of 1,4-PDO to 2-MeTHF](#) [573, 594]. For this purpose, in the first part of this work, niobium phosphate (NBP) has been selected as co-catalyst, thanks to its well-known acidic properties, which are preserved also in an aqueous medium, even at high temperatures [7,6055]. This is an amorphous solid with strong Brønsted and medium–strong Lewis acid sites located at the surface, due to the presence of coordinatively unsaturated Nb⁺⁵ species. This acidity has been already exploited for the successful dehydration of saccharides to 5-hydroxymethyl-2-furaldehyde [7,6156,6257], and therefore its use for the 2-MeTHF synthesis [appeared is](#) really promising. The [experimental](#) results of this first group of experiments are reported in Table 1:

Table 1. Hydrogenation of GVL with Ru/C, Re/C catalysts, and NBP as acid co-catalyst. Reaction conditions: GVL: 1.68 g; Ru: 2 mg ([GVL/Ru: 847.63 mol/mol](#)); H₂O: 40 mL; PH₂: 9.0 MPa.

| Run | Catalytic system | GVL/Re mol/mol | T (°C) | t [h] | Conv. GVL (mol%) | Selectivity (mol%) | | | |
|-----|--|---|-----------|----------|------------------------|--------------------|--------|--------|---------|
| | | | | | | 2-MeTHF | 2-BuOH | 2-PeOH | 1,4-PDO |
| 1 | Ru/C 5% | / | 210 | 6 | traces | - | - | - | - |
| 2 | Ru/C 5% + NBP (1 g) | / | 200 | 3 | 31.7 | 35.2 | 42.2 | 5.7 | 12.2 |
| 3 | Ru/C 5% + NBP (1 g) | / | 200 | 6 | 40.5 | 38.9 | 34.0 | 6.5 | 14.0 |
| 4 | Ru/C 5% + NBP (1 g) | / | 180 | 6 | 3.6 | 49.2 | 27.0 | 0.1 | 5.4 |
| 5 | Ru/C 5% + NBP (1 g) | / | 210 | 6 | 71.1 | 21.0 | 66.8 | 7.7 | 0.4 |
| 6 | Re/C 10% (10 mg) | 312.33 | 210 | 6 | traces | - | - | - | - |
| 7 | Ru/C 5% + Re/C 10% (5 mg) + NBP (1 g) | 624.66 | 200 | 3 | 35.9 | 43.0 | 31.5 | 8.7 | 14.1 |

| | | | | | | | | | |
|----|--|------------------------|-----|---|------|------|------|-----|------|
| 8 | Ru/C 5% + Re/C 10% (10 mg) + NBP (1 g) | 312.33 | 200 | 3 | 36.3 | 47.2 | 23.0 | 6.1 | 18.8 |
| 9 | Ru/C 5% + Re/C 10% (20 mg) + NBP (1g) | 156.16 | 200 | 3 | 36.1 | 57.5 | 11.1 | 4.6 | 21.3 |
| 10 | Ru/C 5% + Re/C 10% (20 mg), no <u>no</u> NBP | 156.16 | 200 | 3 | 27.3 | 22.1 | 6.1 | 3.6 | 63.8 |
| 11 | Ru/C 5% + Re/C 10% (20 mg) + NBP (250 mg) | 156.16 | 200 | 3 | 30.8 | 44.6 | 7.1 | 5.1 | 30.2 |
| 12 | Ru/C 5% + Re/C 10% (20 mg) + NBP (500 mg) | 156.16 | 200 | 3 | 39.3 | 64.9 | 7.3 | 3.7 | 21.5 |

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The negligible activity ascertained in the experiment carried out in the presence of only Ru/C (run 1, Table 1) respect to that of the runs and those with [Ru/C + NBP] (runs 2-5, Table 1) confirm that the presence of the acid NBP co-catalyst is essential for GVL conversion, 2-MeTHF, and 2-BuOH being the main reaction products, together with lower amounts of 1,4-PDO and 2-PeOH, in agreement with the literature data [[4238](#)]. Thus, the acid characterbehavior of the co-catalyst favors the interaction with the carboxylic group of the lactone, enhancing in this way its ring opening and subsequent conversion [[584,6358-659](#)]. In the first run carried out in the presence of [Ru/C + NBP] (run 2, Table 1), a moderate GVL conversion and a well-balanced selectivity to both 2-MeTHF and 2-BuOH were ascertained, which could be selectively tuned to one of these products, by a further optimization of the reaction parameters, in particular reaction time and temperature. First, the effect of the reaction time was investigated, keeping constant the reaction temperature, but adopting a longer reaction time (run 3, Table 1), and it was found that this parameter has certainly a positive, albeit modest, effect on the 2-MeTHF selectivity, whilst 2-BuOH has rapidly formed already at the first stages of the reaction. On the other hand, the selectivities to 2-PeOH and 1,4-PDO progressively increase during the progress of the reaction but long reaction times are required, in agreement with other previous investigations [[373,384](#)].

The effect of temperature on 2-MeTHF and 2-BuOH formation was also investigated, adopting a reaction time of 6 h, which resulted a good compromise between the catalytic activity and the simultaneous selectivity to 2-MeTHF and 2-BuOH. For this purpose, hydrogenation runs were carried out, at lower (180 °C), and at higher (210 °C) temperature (runs 4 and 5, respectively, Table 1). As a result, GVL conversion was improved with the temperature increase, being clearly unsatisfactory for the experiment at 180 °C (run 4, Table 1). Instead, regarding the selectivity parameter, it was found that a lower reaction temperature favored the selectivity to 2-MeTHF, whereas a higher one has favored the formation of both 2-BuOH and 2-PeOH, thus supporting that the dehydration is favored by a lower temperature [[584,6358-659](#)].

Starting from the acquired results, the effect of the addition of a commercial rhenium-based catalyst (10 % Re/C) to the catalytic system composed of Ru/C and NBP was investigated. As in the case of Ru/C, also the Re/C catalyst alone (run 6, Table 1) was not active to the GVL hydrogenation, even adopting higher temperature (210 °C) and longer reaction time (6 h). Instead, its synergistic effect with [Ru/C + NBP] improves the GVL conversion and the selectivity to 2-MeTHF and 1,4-PDO, to the detriment of 2-BuOH, already with low amounts of Re/C (compare runs 7 and 2, Table 1), revealing that rhenium plays a key synergistic role in this reaction, addressing towards the diol cyclization to 2-MeTHF [[362,562](#)]. On this basis, the amount of rhenium was increased, and the corresponding catalytic performances were evaluated (runs 8 and 9, Table 1). Taking into account the achieved results, it is possible to highlight that the increase of the rhenium amount improves the selectivity to 2-MeTHF, and 1,4-PDO, in agreement with the literature data [[562](#)], whilst the selectivity to 2-BuOH drastically decreases. In our opinion, this outcome is very interesting because

256 | [# provinges](#) that it is possible to address the reaction towards the desired product, by selecting the
 257 | appropriate catalytic system. The further increase of the amount of rhenium does not allow the
 258 | corresponding improvement of the catalytic performances to 2-MeTHF, thus highlighting the
 259 | achieved optimization, under the adopted reaction conditions. Similarly, the effect of the NBP on
 260 | the catalytic performances was studied, without NBP ([run 10, Table 1](#)), and with 250, [and](#) 500 [and](#)
 261 | [1000](#) mg of it (runs [9-12](#), Table 1). From the obtained data, it is possible to note that GVL conversion
 262 | was the highest when 500 mg of NBP were employed and, under the same reaction conditions, also
 263 | the selectivity to 2-MeTHF was the highest (64.9 mol%). On the other hand, the amount of NBP
 264 | does not affect the selectivity to 2-BuOH and 2-PeOH, thus confirming that the overall catalytic
 265 | system favors the dehydration path. [For this reason, in order to obtain 2-MeTHF, the amount of 500](#)
 266 | [mg of NBP was selected for the subsequent investigation.](#)

267 | With the aim of adopting milder reaction conditions, in terms of hydrogen pressure and
 268 | temperature, an increase of the ruthenium amount from 2 up to 10 mg was studied [and the](#)
 269 | [obtained results are summarized in Table 2:](#)

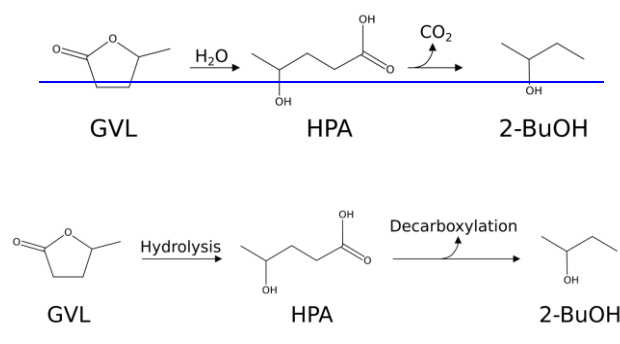
270 | **Table 2.** GVL hydrogenation reactions in the presence of different catalytic systems: effect of
 271 | hydrogen pressure, temperature, and presence of an acid co-catalyst (NBP or HY). Reaction
 272 | conditions: GVL: 2.52 g; H₂O: 40 mL; Ru: 10 mg ([GVL/Ru: 254.29 mol/mol](#)); Re: 20 mg ([GVL/Re:](#)
 273 | [234.25 mol/mol](#)), when present; NBP: 500 mg, when present; HY: 500 mg, when present; time: 3
 274 | hours.

| Run | Catalyst and co-catalyst | Reaction conditions T, P, H ₂ | Conv. GVL (mol%) | Sel. 2-MeTHF (mol%) | Sel. 2-BuOH (mol%) | Sel. 2-PeOH (mol%) | Sel. 1,4-PDO (mol%) |
|-----|-----------------------------|---|---------------------|---------------------------|--------------------------|--------------------------|---------------------------|
| 13 | 5% Ru/C NBP | 200 °C, 9.0 MPa | 98.9 | 8.5 | 75.7 | 15.8 | - |
| 14 | 5% Ru/C NBP | 200 °C, 5.0 MPa | 77.9 | 5.7 | 83.3 | 10.9 | 0.1 |
| 15 | 5% Ru/C NBP | 180 °C, 5.0 MPa | 26.6 | 9.7 | 60.6 | 4.2 | 20.7 |
| 16 | 5% Ru/C 10 % Re/C NBP | 180 °C, 5.0 MPa | 48.3 | 37.8 | 36.6 | 7.5 | 18.1 |
| 17 | 5% Ru/C HY | 180 °C 5.0 MPa | 66.3 | 21.3 | 63.3 | 13.8 | 1.6 |
| 18 | 5% Ru/C HY | 200 °C 3.0 MPa | 100 | - | 81.3 | 18.7 | - |
| 19 | 5% Ru/C 10 % Re/C HY | 200 °C 3.0 MPa | 100 | 35.7 | 47.6 | 16.7 | - |

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 276 | Adopting the catalytic system [Ru/C + NBP], the increased amount of Ru allows us to reach
 277 | almost complete GVL conversion (run 13, Table 2), and comparison between runs 13 and 14
 278 | confirms the possibility of working at milder reaction conditions, in terms of hydrogen pressure,
 279 | still achieving a satisfactory GVL conversion together with a high selectivity to 2-BuOH. On the
 280 | basis of the obtained results (run 13, Table 2 and runs 2-5, Table 1), in the presence of 10 mg of Ru,
 281 | in order to obtain 2-MeTHF, it is necessary to decrease the reaction temperature and the hydrogen
 282 | pressure. In fact, when the reaction was carried out at a lower temperature, 180 °C (run 15, Table 2),
 283 | a lower GVL conversion was achieved but, after 3 h of reaction, the selectivities to 2-MeTHF and

284 1,4-PDO were higher than those at 200 °C, thus remarking that the dehydration reaction is favored
 285 by a lower temperature, as previously stated. Again, the synergistic effect of [Ru/C + Re/C + NBP]
 286 was considered (run 16, Table 2), thus confirming that the co-presence of rhenium was beneficial for
 287 both GVL conversion and 2-MeTHF selectivity: in fact, the 2-MeTHF selectivity increases after 3 h
 288 from 9.7 mol%, in the absence of Re, up to 37.8 mol%, in its presence. In this set of hydrogenation
 289 runs, also the effect of the addition of a zeolite HY as acid co-catalyst, instead of NBP, on GVL
 290 hydrogenation was investigated, in the presence of Ru or [Ru/C + Re/C] catalytic systems. This acid
 291 catalyst is well-known for the strong Brønsted acidity, due to the bridging Si-(OH)-Al sites,
 292 generated by the presence of aluminium inside the silicate framework and the balancing proton
 293 [66]. In addition, working in aqueous medium at high temperatures, the zeolite catalytic systems, in
 294 particular those with low Si/Al ratio, are able to maintain their stability [67], despite new acid sites
 295 are formed, as the result of Si-O-Si hydrolysis, ion exchange with charge compensating aluminum
 296 cations, and/or dissociative adsorption of water on framework independent alumina [67].
 297 Preliminary runs in the presence of different amounts of HY zeolite were carried out with the [Ru/C
 298 + Re/C] catalytic system in order to compare the HY zeolite with NBP at the same total acidity level
 299 under the best reaction conditions evidenced in Table 1 (Ru: 2 mg; Re: 20 mg; GVL: 1.68 g, 200°C,
 300 9.0 MPa H₂, 3h). On the basis of these results, which have shown that HY zeolite resulted more
 301 selective towards [2-BuOH+2-PeOH] than NBP, the right amount of HY zeolite able to maximize
 302 the selectivity to [2-BuOH+2-PeOH] was investigated. Under the same employed reaction
 303 conditions (Ru: 2 mg; Re: 20 mg; GVL: 1.68 g, 200°C, 9.0 MPa H₂, 3h), a HY zeolite amount of 500
 304 mg was found to be the best one in terms of GVL conversion and selectivity to [2-BuOH + 2-PeOH].
 305 For this reason, in order to obtain [2-BuOH + 2-PeOH], this amount of HY zeolite was employed for
 306 the subsequent investigation. ~~Lastly, the~~ The hydrogenation run carried out in the presence of zeolite
 307 HY co-catalyst and Ru/C at 180 °C and 5.0 MPa H₂ (run 17, Table 2) shows that the presence of this
 308 different acid component significantly enhances GVL conversion respect to the corresponding
 309 experiment with Ru/C and NBP (run 15, Table 2), as well as the selectivity to 2-MeTHF and 2-
 310 PeOH, to the detriment of 1,4-PDO. Further balancing the temperature and H₂ pressure (200 °C, 3.0
 311 MPa) a total conversion of GVL can be reached (run 18, Table 2) with complete selectivity to [2-
 312 BuOH + 2-PeOH]. This different behavior is due to the preferential reaction pathway, which follows
 313 the decarboxylation route, which is known to occur in the presence of faujasite zeolites [53,49,68],
 314 according to the Scheme 4:

315

316
317

318

319 **Scheme 4.** Proposed reaction pathways for the formation of 2-butanol from GVL. (adapted from
 320 [38]).

321 The occurred decarboxylation was confirmed by qualitative analysis of the gaseous phase,
 322 which revealed the presence of carbon dioxide as the main reaction product. It is remarkable that
 323 the reaction conditions adopted in run 18 allowed us to reach a productivity to [2-BuOH+2-PeOH]
 324 of 840 mmol gRu⁻¹ h⁻¹.

325 On the other hand, the addition of rhenium, together with zeolite HY (run 19, Table 2), favors
 326 the 2-MeTHF formation, in agreement with the previous experiments with NBP.

From all the catalytic results, it is possible to underline that the two employed metals (Ru and Re) play a synergic role in this reaction. In this regard, Di et al. [69] studied the employment of Ru/C, Re/C and bimetallic Ru-Re/C catalysts in the hydrogenation of succinic acid and γ -butyrolactone in water at 200°C and 8.0 MPa, finding that Ru metal positively contributes to the hydrogenolysis mechanism, whereas Re metal to the hydrogenation one. A similar role of the two metals can be proposed for the present study. In particular, starting from GVL, in the presence of [Ru/C + acid co-catalyst], the Ru species can promote the conversion of GVL (assisted by the presence of the acid co-catalyst which favours the ring-opening) to 2-BuOH through the formation of the intermediate HPA, or to 1,4-PDO (through the hydrogenation), which can be converted to 2-MeTHF, in the presence of the acid co-catalyst. The conversion of GVL to 2-BuOH requires the break of C-C bond with the formation of CO₂ (decarboxylation route). This hypothesis is confirmed by our experimental results: in fact, as reported in runs 2-5 in Table 1 for NBP, the main products result 2-BuOH deriving from the decarboxylation route of GVL through the break of C-C bond of the intermediate HPA, and 2-MeTHF deriving from the internal dehydration of 1,4-PDO obtained by hydrogenation. The same behaviour is also observed in the presence of HY zeolite (run 17, Table 2). When Re/C is added to [Ru/C + acid co-catalyst], the second metal component -(Re/C) promotes the hydrogenation of GVL through its opening-ring and hampers the decarboxylation path, thus causing the increase of the amount of 1,4-PDO, precursor of 2-MeTHF, and, as a consequence, the formation of 2-MeTHF. In fact, in the case of NBP, comparing run 2 with run 9 (Table 1), the addition of Re/C causes a decrease of 2-BuOH selectivity, from 42.2 to 11.1 mol%, thus limiting the decarboxylation route, together with an increase of 2-MeTHF and 1,4-PDO selectivities, from 35.2 to 57.5 mol%, and from 12.2 to 21.3 mol%, respectively. Also for the runs (runs 18 and 19, Table 2) carried out in the presence of HY zeolite, it is possible to highlight the same trend: in fact, the addition of Re/C causes a decrease of 2-BuOH selectivity, from 81.3 to 47.6 mol%, and an increase of 2-MeTHF selectivity, from 0 to 35.7 mol%.

The most promising experiments for the production of 2-MeTHF and [2-BuOH+2-PeOH] (runs 16 and 18, Table 2, respectively) were considered as references for the evaluation of the catalyst reusability. The stability of the adopted systems, [Ru/C + Re/C + NBP] and [Ru/C + HY], under the adopted reaction conditions, was verified, showing constant catalytic performances, even after five recycling tests. In addition, the ruthenium and the rhenium catalysts have shown a good resistance to leaching, as confirmed by ICP-OES analysis, which has excluded metal releases in solution.

Taking into account that GVL can be obtained by LA, with the aim of developing a direct cascade process LA to 2-MeTHF or LA to monoalcohols, occurring through the formation of the GVL intermediate but without its isolation, the [Ru/C + NBP] catalytic system was tested also for the one-pot LA conversionhydrogenation, investigating the effect of the reaction temperature. The results are reported in Table 3.

Table 3. LA hydrogenation reactions carried out in the presence of [Ru/C, NBP] catalytic system, at different reaction temperatures. Reaction conditions: LA: 1.99 g; Ru: 2 mg (LA/Ru: 866.12 mol/mol); NBP: 1 g; H₂O: 40 mL; PH₂: 9.0 MPa; time: 3 hours.

| Run | Catalyst and co-catalyst | T (°C) | Conv. LA (mol%) | Sel. GVL (mol%) | Sel. 2-MeTHF (mol%) | Sel. 2-BuOH (mol%) | Sel. 2-PeOH (mol%) | Sel. 1,4-PDO (mol%) |
|-----|--------------------------|--------|-----------------|-----------------|---------------------|--------------------|--------------------|---------------------|
| 20 | 5% Ru/C, NBP | 200 | 99.7 | 73.4 | 8.8 | 9.9 | 0.9 | 1.3 |
| 21 | 5% Ru/C, NBP | 210 | 99.9 | 70.6 | 8.7 | 13.8 | 1.5 | 1.7 |

The chosen reaction conditions guarantee the almost complete LA conversion, and the reaction is very selective towards GVL, thus confirming the real possibility to build a cascade process. The selectivity to the reaction products is almost constant in the two experiments (200 and 210 °C),

370 therefore suggesting the adoption of the lower reaction temperature. Afterward, on the basis of the
 371 [obtained se-promising](#) results, this reaction was studied more in detail, increasing the Ru amount
 372 from 2 to 10 mg, and employing different reaction conditions, in terms of temperature and
 373 hydrogen pressure. Also in this case, the effect of the acid co-catalyst was considered. The obtained
 374 results are summarized in Table 4.

375 **Table 4.** LA hydrogenation reactions carried out in the presence of [Ru/C + NBP (or HY)] catalytic
 376 system, at different reaction temperatures and hydrogen pressure. Reaction conditions: LA: 1.99 g;
 377 Ru: 10 mg ([LA/Ru: 173.22 mol/mol](#)); Re: 20 mg ([LA/Re: 159.57 mol/mol](#)); NBP: 500 mg, HY: 500 mg,
 378 when present; H₂O: 40 mL; time: 3 hours.

| Run | Catalyst and co-catalyst | Reaction Conditions T, P H ₂ | Conv. LA (mol%) | Sel. GVL (mol%) | Sel. 2-MeTHF (mol%) | Sel. 2-BuOH (mol%) | Sel. 2-PeOH (mol%) | Sel. 1,4-PDO (mol%) |
|-----|--------------------------|---|-----------------|-----------------|---------------------|--------------------|--------------------|---------------------|
| 22 | 5% Ru/C, NBP | 180 °C, 5.0 MPa | 100 | 36.2 | 10.1 | 37.8 | 13.0 | 2.9 |
| 23 | 5% Ru/C, HY | 180 °C, 5.0 MPa | 100 | 30.8 | 3.8 | 35.0 | 28.7 | 1.7 |
| 24 | 5% Ru/C, HY | 180 °C, 3.0 MPa | 100 | 46.8 | 3.6 | 36.5 | 13.1 | - |
| 25 | 5% Ru/C, HY | 180 °C, 1.0 MPa | 100 | 81.1 | 0.6 | 13.6 | 4.7 | - |
| 26 | 5% Ru/C, HY | 200 °C, 3.0 MPa | 100 | 7.9 | 3.3 | 68.9 | 19.9 | - |
| 27 | 5% Ru/C, NBP | 200 °C, 3.0 MPa | 100 | 25.8 | 7.0 | 52.0 | 15.2 | - |
| 28 | 5% Ru/C, 10% Re/C, NBP | 180 °C, 5.0 MPa | 100 | 35.1 | 27.8 | 19.5 | 6.0 | 11.6 |

379 Working at 180 °C and 5.0 MPa of hydrogen, after 3 h of reaction, the higher amount of Ru
 380 allowed the complete LA conversion. The selectivity to 2-MeTHF has decreased from 10.1 to 3.8
 381 mol% when NBP was replaced by zeolite HY, whilst 2-BuOH remained the main reaction product
 382 (runs 22 and 23, Table 4). On the basis of these results, taking into account that 2-BuOH derives
 383 from the decarboxylation reaction, the following study with [Ru + HY] system was carried out
 384 decreasing the hydrogen pressure (compare runs 23, 24 and 25, Table 4). The decrease of hydrogen
 385 pressure below 3.0 MPa has evidenced a significant reduction of GVL successive reactions, and
 386 therefore this pressure value was kept for the subsequent [reactionhydrogenation](#) runs. When the
 387 temperature was increased from 180 to 200 °C (run 26, Table 4), an increase of selectivity to 2-BuOH
 388 and 2-PeOH was ascertained, as previously observed for the GVL [conversionhydrogenation](#) tests in
 389 the presence of an acid co-catalyst (runs 3 and 4, Table 1). Moreover, adopting these new optimized
 390 reaction conditions, the comparison between zeolite HY and NBP was investigated (runs 26 and 27,
 391 Table 4). The presence of zeolite HY provides a higher GVL conversion: the remaining GVL at the
 392 end of the reaction was higher for run 27 (in the presence of NBP), rather than for run 26, where the
 393 total yield to monoalcohols was 88.8 mol%, with a productivity of 510 mmoles gRu⁻¹ h⁻¹. [This](#)
 394 [experimental result is really promising, especially if compared with Up to now](#), the best overall [2-
 395 BuOH + 2-PeOH] yield [up to now](#) reported in the literature, amounting to 78.8 mol%, reached for
 396 LA hydrogenation in water at 140 °C and 6.0 MPa H₂ in the presence of synthesized nanoporous
 397 ruthenium [540]. [Now theOur](#) experimental finding confirms that the adopted acid zeolite HY
 398

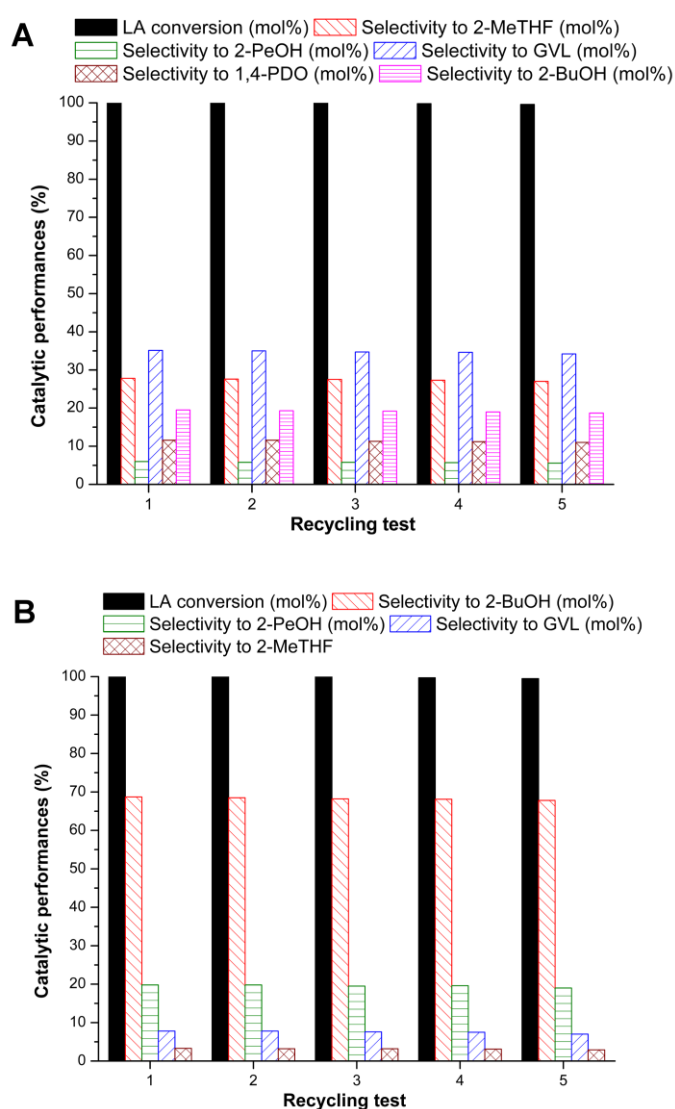
399 enhances the subsequent hydrogenation/decarboxylation reaction towards the formation of 2-
 400 BuOH and 2-PeOH. Lastly, taking into account that the formation of 2-MeTHF is boosted in the
 401 presence of NBP, the addition of Re/C, together with Ru/C and NBP acid co-catalyst was
 402 investigated (run 28, Table 4). The result allowed a further increase of the selectivity to 2-MeTHF
 403 (compare runs 23 and 28, Table 4), thus confirming the positive role of rhenium for the 2-MeTHF
 404 production, already observed in the corresponding GVL conversionhydrogenation run (compare
 405 runs 15 and 16, Table 2).

406

407

408 The reactionhydrogenation experiments with the highest [2-BuOH + 2-PeOH] and 2-MeTHF
 409 selectivities (runs 26 and 28, Table 4, respectively) were considered as reference for performing
 410 subsequent recycling tests, as reported in Figure 1:

411



412

413 **Figure 1.** Recycling tests for LA hydrogenation of: A) [Ru/C + HY] catalyst (run 26, Table 4, as direct
 414 run); B) [Ru/C + Re/C + NBP] catalyst (run 28, Table 4, as direct run).

415 The above data confirm the good performances of the adopted [Ru/C + HY] and [Ru/C + Re/C +
 416 NBP] catalysts, even after five recycling tests. Moreover, the catalyst shows no significant leaching,
 417 thus further justifying its stability and reusability.

418

419 3. Materials and Methods

420 3.1. Materials

421 5 wt% Ru/C (50% moisture) was purchased from Engelhard ([average diameter: 2.0 nm](#)), 10
422 wt% Re/C was purchased from Strem ([average diameter: 10.4 nm](#)) and both used as received.
423 Levulinic acid, γ -valerolactone, 2-methyltetrahydrofuran and 2-butanol were obtained by Sigma
424 Aldrich and used as received. Zeolite HY (CBV 500) was purchased from Zeolyst International
425 ([ratio SiO₂/Al₂O₃ mol/mol: 5.2; acidity: 1.5 mmol/g measured by NH₃-TPD](#)) [70] and it was treated at
426 510 °C for 2 h before its use. Instead, niobium phosphate ([acidity: 0.33 mmol/g measured by an
427 acid–base titration in water using 2-phenyl-ethylamine as the basic probe](#)) [24] was kindly provided
428 from CBMM (Companhia Brasileira de Metalurgia e Mineração), and treated at 255 °C for 6 h,
429 under high vacuum (5 Pa) before its use [7].

430 3.2. Hydrogenation reactions

431 Hydrogenation reactions were carried out in a stainless steel 100 mL mechanically stirred Parr
432 4560 autoclave, equipped with a P.I.D. controller 4843. In a typical procedure, the proper amount of
433 the selected catalyst/catalysts, together with the acid co-catalyst (when necessary), was introduced
434 in the reactor under an inert atmosphere. The autoclave was closed, evacuated up to 65 Pa and a
435 solution of the starting feedstock in 40 mL of water was introduced by suction. The reactor was then
436 pressurized with hydrogen and heated to the desired temperature, maintaining a stirring speed of
437 500 rpm, a value which was ascertained to assure the absence of mass transfer limitations. During
438 the reaction, the pressure value was manually held constant at the chosen value by repeated
439 hydrogen feeds. The course of the reaction was monitored by periodically sampling the liquid from
440 a sampling valve and analyzing it by gas-chromatography. Recycling experiments of the
441 commercial catalysts were carried out in a similar manner: after removing through the sample
442 valve the liquid reaction mixture, the autoclave containing the catalyst/catalysts was evacuated and
443 charged again for the subsequent catalytic cycle. All experiments were carried out in duplicate and
444 the composition of the reaction mixtures resulted reproducible to within $\pm 5\%$.

445 3.3. Analysis of the reaction products

446 Quantitative analyses were performed with an HP 5890 gas-chromatograph equipped with an
447 HP 3396 integrator, a flame ionization detector, and a PONA capillary column (50m x 0.2 mm x 0.5
448 μm) with a stationary phase 100 % dimethylpolysiloxane. The transport gas was nitrogen and the
449 flow was 1 mL min⁻¹. The adopted temperature program for G.C. separation was the following: 50
450 °C (3 min)–20 °C min⁻¹–200 °C (10 min). Qualitative analyses were carried out using the gas-
451 chromatograph Hewlett-Packard HP 6890 with an MSD HP 5973 detector, employing a G.C.
452 column Phenonex Zebron with a stationary phase of 100 % methylpolysiloxane (length of the
453 column: 30 m, inner diameter: 0.25 mm and thickness of the stationary phase: 0.25 μm). The
454 transport gas was helium and the flow was 1 mL min⁻¹. Gaseous phase was qualitatively analyzed
455 by G.C. using an Agilent HP6890 chromatograph and a Restek Shincarbon ST column (2 m x 1 mm),
456 and a thermal conductivity detector (TCD). The carrier gas was helium, with a constant flow rate of
457 15 mL min⁻¹, and an inlet temperature of 100 °C. The adopted temperature program for the analysis
458 of a gas volume of 100 μL was the following: 35 °C (5 min)–8 °C min⁻¹–200 °C (5 min).

459 Conversion parameter was calculated on the basis of the adopted starting feedstock, e.g. GVL
460 or LA, as follows:

$$461 \text{ GVL or LA conversion (mol\%)} = (\text{converted moles of GVL or LA} / \text{starting moles of GVL or LA}) * 100 \quad (1)$$

462 Instead, the selectivity to the main reaction products, e.g. 2-MeTHF, 2-BuOH, 2-PeOH, and 1,4-
463 PDO, was calculated always with respect to the starting feedstock, e.g. GVL or LA, as follows:

$$464 \text{ Selectivity to the product (mol\%)} = (\text{obtained moles of product} / \text{converted moles of GVL or LA}) * 100 \quad (2)$$

465 Lastly, catalyst productivity to give (2-BuOH + 2-PeOH) was calculated as follows:

466
$$\text{Productivity} = \text{millimoles (2-BuOH + 2-PeOH)} / (g_{\text{metal}} \times \text{time (hour)}) \quad (3)$$

467 Ruthenium and rhenium leaching was established on the reaction solution by inductively
468 coupled plasma-optical emission spectrometry (ICP-OES), employing a Spectro-Genesis instrument
469 and using a software Smart Analyzed Vision.

470

471 4. Conclusions

472 In this research, a cascade strategy for the catalytic valorization of levulinic acid and γ -
473 valerolactone to 2-methyltetrahydrofuran or to monoalcohols, 2-butanol and 2-pentanol, has been
474 studied and optimized. In the perspective of an economic, environmental and sustainable
475 development, only commercial catalytic systems have been employed, adopting water as the only
476 green medium. It is noteworthy our choice of employing only water whilst, in most of the best case
477 studies reported up to now in the literature, different organic solvents have been specially used,
478 mainly 1,4-dioxane or alcohols, as well as *solvent-free* conditions, with the aim of improving the
479 selectivity to the target products. Taking into account our greener perspective, both hydrogenation
480 reactions have been optimized, investigating the effect of temperature, hydrogen pressure, amounts
481 of rhenium, niobium phosphate or acid zeolite HY. The appropriate choice of the catalytic
482 system/reaction conditions can tune this process toward to the selective production of 2-
483 methyltetrahydrofuran or monoalcohols. For the first time, the use of ruthenium and rhenium
484 catalysts, both supported on carbon, together with niobium phosphate as acid co-catalyst, has been
485 claimed in the [conversionhydrogenation](#) of γ -valerolactone and levulinic acid to 2-
486 methyltetrahydrofuran, obtaining selectivities up to a maximum of about 65 and 28 mol%,
487 respectively. On the contrary, the use of zeolite HY, together with the commercial Ru/C catalyst,
488 favors the selective production of the monoalcohols 2-butanol and 2-pentanol. It is remarkable that
489 the catalytic system [Ru/C + zeolite HY] at 200 °C and 3 MPa H₂ is able to completely convert both
490 γ -valerolactone and levulinic acid, with overall yield to monoalcohols [2-butanol + 2-pentanol] of
491 100 mol% and 88.8 mol%, respectively. To the best of our knowledge, these yields are the best up to
492 now reported for the synthesis of monoalcohols from these renewable starting materials.

493 These promising results allow [us](#) to move towards the next challenge passing from model
494 compounds to real biomass hydrolysates as starting materials.

495

496 **Acknowledgments:** The authors are grateful to the PRIN 2015-Project HERCULES "HEterogeneous Robust
497 Catalysts to Upgrade Low valuE biomass Streams " (code 20153T4REF).

498 **Author Contributions:** All the authors together conceived and designed the experiments; Domenico Licursi,
499 Sara Fulignati and Michael Giannoni performed the experiments; all the authors analyzed the data and wrote
500 the paper.

501

502 **Conflicts of Interest:** The authors declare no conflict of interest.

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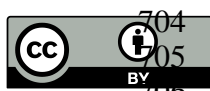
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