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γ-Valerolactone can be synthesized by reduction of levulinic acid and its esters in the presence of secondary alcohols as hydrogen donors and Ru/C as catalyst. The reaction rate increases when using microwave heating. Quantitative formation of γ-valerolactone was observed within 25 minutes at 160°C under microwave heating based on levulinic acid and *i*-propanol. The reaction appears to proceed *via* a dehydrogenation-hydrogenation sequence.

Keyword: Microwave, hydrogenation, γ-valerolactone, levulinic acid, alkyl levulinates, ruthenium.

1. Introduction

Potentially obtained from lignocellulosic biomass, γ-valerolactone (γ-VL) is a very promising versatile intermediate for production of fuel additives and chemicals [1, 2]. Due to very high interest towards γ-VL, its efficient production is currently a topic of intensive research. Investigations are mainly focused on reduction of levulinic acid (LA) and its esters (LAE) by molecular hydrogen in the presence of metal catalysts [1, 3]. Application of supported metal catalysts is especially advantageous owing to simplicity of product recovery and catalyst recycling. Previous investigations evidence outstanding activity of Ru/C as catalyst for the hydrogenation [1, 4]. Although reduction of LA into γ-VL over Ru/C with H_2 as reductant is highly efficient and nearly quantitative, further development can facilitate the process economics. Application of a liquid reductant derived from biomass potentially

enhances the sustainability of a γ-VL production process and enables milder operation conditions. Formic acid was shown to be an efficient reductant for transformation of LA into γ-VL in the presence of noble metals [5-8]. Alternatively, a reduction of levulinates with an alcohol as hydrogen donor was reported catalysed by (i) complexes of Ru [9]; (ii) metal oxides and hydroxides with the best activity for ZrO_2 [10] and $Zr(OH)_4$ [11]; (iii) solid Lewis acids such as Zr-beta [12, 13] or Hf-beta [13] zeolites; (iv) solid metal-based catalysts, e.g. Raney Ni [14] or Pd/C [15]. Interestingly, all of the previously reported solid catalysts were active for transformation of LAE into γ-VL, but the rate of LA transformation into γ-VL under the same reaction conditions was significantly lower [10]. For instance, strong adsorption of LA onto basic sites of ZrO_2 appeared to be the reason for catalyst deactivation by LA [10]. In the presence of a Zr-beta zeolite, quick esterification of LA with the alcohol used as hydrogen donor takes place followed by a slow reduction of the alkyl levulinate into γ-VL [12]. Although some approaches towards synthesis of LAE from lignocellulose were proposed [2], LA remains a cheaper and therefore more attractive substrate. Though the catalytic activity of Pd/C for direct reduction of LA with alcohols was reported very recently, the reaction required KOH as co-catalyst, causing challenges in product purification [15]. Herein, we demonstrate the efficient reduction of levulinic acid and its esters in the presence of secondary alcohols as hydrogen donors and Ru/C without any co-catalyst, applying conventional and microwave heating.

2. Results and discussion

In this communication we report high efficiency of Ru/C for synthesis of γ-VL based on LA and secondary alcohols, namely *i*-propanol (^{i}PrOH) and 2-butanol (2-BuOH). The experimental part can be found in electronic supplementary information (ESI). As stated above, Ru/C is very active for reduction of LA and its derivatives with molecular hydrogen [1, 16, 17]; moreover, Yang *et al.* highlighted Ru/C as a promising catalyst for synthesis of γ-

VL based on ethyl levulinate and ^{i}PrOH [14]. We started this work from testing a Ru/C catalyst for reduction of LA with ^{i}PrOH using heating in a conventional autoclave. The reaction was successfully complete within only 2 or 3 h at 160 or 140°C, respectively (Fig. 1). In contrast to the previously reported data for basic [10] or Lewis acid [12, 13] catalysts, we found only slight traces of *i*-propyl levulinate and *pseudo-i*-propyl-levulinate in the reaction mixture. At moderate (10-20%) conversions of LA, yields of the esters reached ca. 2-4%. However, at high and full conversions of LA, the selectivity towards γ-VL was >99% and the total yield of the by-products did not exceed 0.4%. According to the literature data, the efficiency of numerous processes can be significantly improved by using microwave-assisted heating, including the production of γ-VL [15]. Indeed, the hydrogenation of LA with ^{i}PrOH over Ru/C under microwave heating was even more rapid than when using a conventionally heated autoclave (Fig. 1). It is reasonable to argue that the difference in reaction kinetics originates from improved heat transfer for MW-induced heating compared to conventional heating. For the reaction using conventional heating, an autoclave was placed into a pre-heated aluminium jacket. During the reactions, temperature was maintained by means of a thermocouple placed into a heating jacket (Fig. 1SI). In a control experiment, we found out that *ca.* 25 minutes were required to reach heat equilibrium inside of the autoclave. On the contrary, the set temperature was reached in only *ca.* 2.5 minutes when using MW-assisted heating (Fig. 2SI). Since some time is required for heating-up the reaction mixture, especially in the conventional method, the initial reaction rates were somewhat low. This is reflected by an induction period for the conversion of LA (Fig. 1). Additionally, exposed to air Ru/C catalysts contain $Ru^{\delta+}$ oxidized species which undergo *in-situ* reduction, as shown below. Therefore, the presence of the induction period can be also explained by the reduction of the catalyst generating Ru^0 active centres.

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Almost full yield of γ-VL was observed at 140°C after 60 min using microwave heating. Increasing the temperature to 160°C results in a full yield toward γ-VL within 25 min. Noteworthy, product distributions were the same for the experiments using autoclave- and microwave heating. Inspired by these promising results, we continued the investigations using microwave heating.
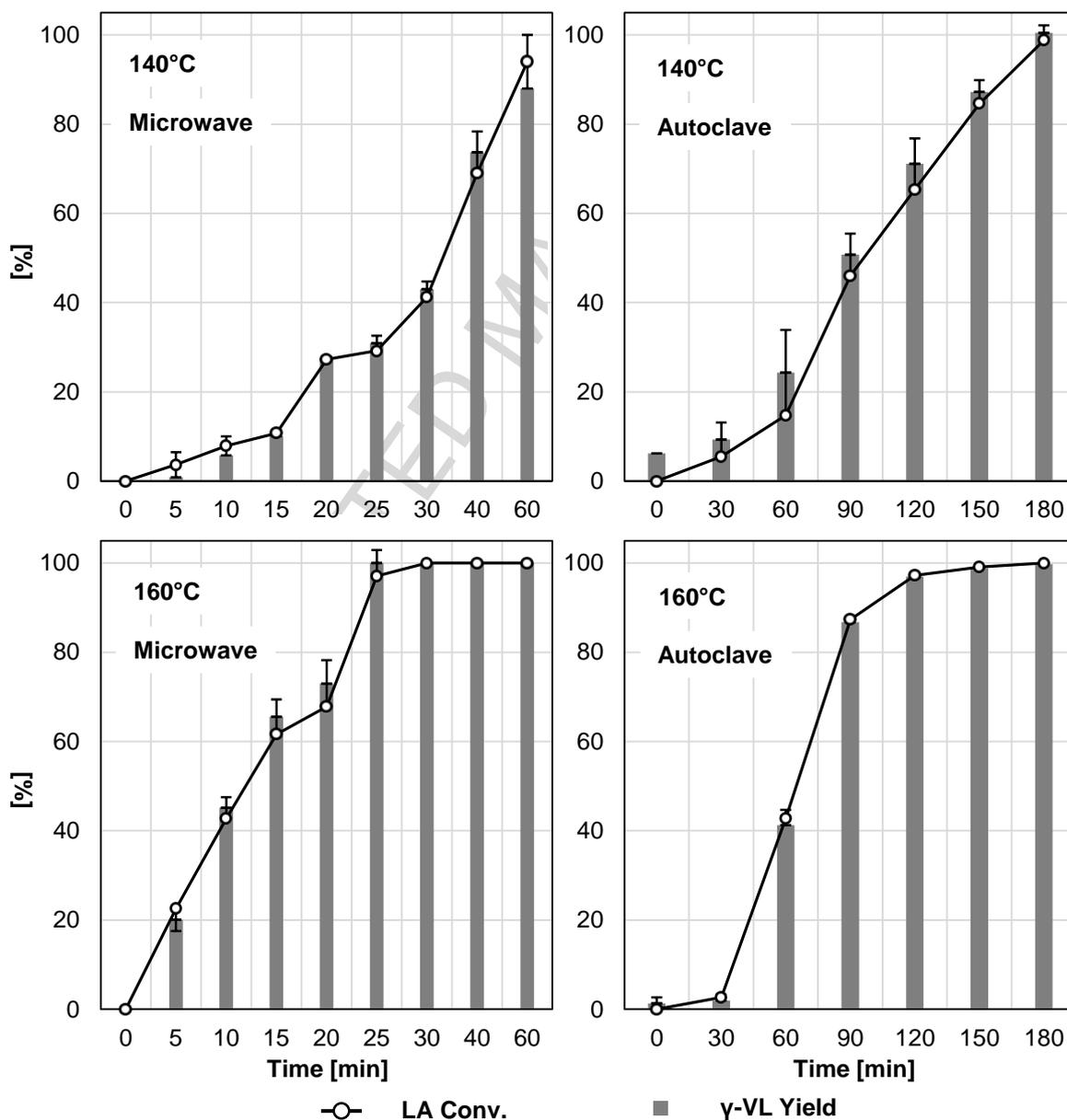
Fig. 1. Time dependence of γ-VL yield (LA (0.5 g); Ru/C (25 mg); 10 mL of ^{i}PrOH. For autoclave reactions, 10 bar N_2 were applied with 350 rpm stirring speed. 300W microwave power was used).

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Screening of catalysts showed that ruthenium exhibits the highest activity among carbon-supported metal catalysts. Poor conversions (maximum 5%) and yields (maximum 2%) were achieved by using Pt/C, Pd/C, Rh/C, Cu/C, and Ni/C. In contrast, Ru/C allowed 43% conversion of LA and 41% yield of γ-VL (after 30 min at 140°C). Unlike the observation stated by Amarasekara *et al.* [15], microwave-assisted hydrogenation of LA was possible over Ru/C and highly efficient even without the addition of alkaline additives.

The activity of Ru/C outperformed that of ruthenium catalysts loaded on other supports (Table 1, entries 1-5). Systematic studies are required for revealing the dependency of catalytic activity on catalyst properties such as metal dispersion, acidity of a support, etc. Nevertheless, even unsupported $RuCl_3 \cdot xH_2O$ was active for synthesis of γ-VL, though less efficient compared to supported catalysts (Table 1, entry 6). It is known that microwave-assisted heating of Ru^{3+} salts in the presence of a reductant such as *i*PrOH results in rapid synthesis of Ru^0 nanoparticles [18]. Produced *in-situ*, Ru^0 species are presumably active sites for synthesis of γ-VL over $RuCl_3 \cdot xH_2O$.

Application of LAE as substrates gave the following order of decreasing reactivity: LA > ML > EL > BL (Table 1, entries 1 and 7-9). The bulky alkyl chains clearly result in inhibition of the reaction. Interestingly, previously reported studies revealed no dependency of reactivity of LAE on the length of alkyl substituents when performing hydrogenation with H_2 over Ru/C [16] or conducting the reduction with alcohols over basic catalysts [10, 11]. While no intermediate was detected in the hydrogenation of LA itself, esters of γ-hydroxyvaleric acid were observed during the conversion of LAE to γ-VL. This indicates that LA and LAE are hydrogenated first to give γ-hydroxyvaleric acid and its esters prior to lactonization.

Other alcohols were tested as hydrogen donors in LA hydrogenation. Besides *i*PrOH, 2-BuOH was an active reductant in the preparation of γ-VL (Table 1 entries 1 and 10). The

lower activity of 2-BuOH in comparison to ^{i}PrOH coupled with the formation of 2-butyl levulinate could be due to steric hindrance. This was confirmed by utilizing higher alcohols like 2- and 3-octanol, which did not allow any conversion of LA. In the presence of primary alcohols such as methanol and ethanol, only esterification reactions were observed with 17% and 8.1% yield, respectively.

Table 1. Microwave-assisted hydrogenation of LA and LAE over different catalysts (substrate (4.3 mmol); catalyst (25 mg); 10 mL of ^{i}PrOH; 140°C using 300 W; 30 min).

Entry	Catalyst	Substrate	Hydrogen donor	Substrate conversion, %	γ-VL yield, %	Yield of other products, %	Acetone: γ-VL mol:mol
1	5% Ru/C	LA	^{i}PrOH	43	41	0.8[a]	2.6
2	5% Ru/CNT	LA	^{i}PrOH	16	12	3.4[a]	8.1
3	5% Ru/TiO$_2$	LA	^{i}PrOH	14	11	1.2[a]	1.2
4	5% Ru/SiO$_2$	LA	^{i}PrOH	5	2	1.4[a]	2.3
5	5% Ru/Al$_2$O$_3$	LA	^{i}PrOH	3	0	1.8[a]	-
6	RuCl$_3$·xH$_2$O	LA	^{i}PrOH	10	1	7.9[a]	5.0
7	5% Ru/C	ML	^{i}PrOH	39	34	5.4[b]	3.7
8	5% Ru/C	EL	^{i}PrOH	17	6	11.2[b]	8.9
9	5% Ru/C	BL	^{i}PrOH	13	2.4	10.3[b]	23.9
10	5% Ru/C	LA	2-BuOH	33	28	0	

[a]Total yield of *i*-propyl levulinate and *pseudo-i*-propyl levulinate; [b]Yield of a γ-hydroxyvaleric acid ester.

Focussing on the reaction mechanism, a dehydrogenation-hydrogenation path catalysed by Ru/C is suggested (Scheme 1). Analysing the gas phase of the reaction mixture showed *in-situ* formation of molecular hydrogen during the reaction. The yield of acetone always exceeded the yield of γ-VL, confirming that both reactions mostly take place independent of each other (Table 1).
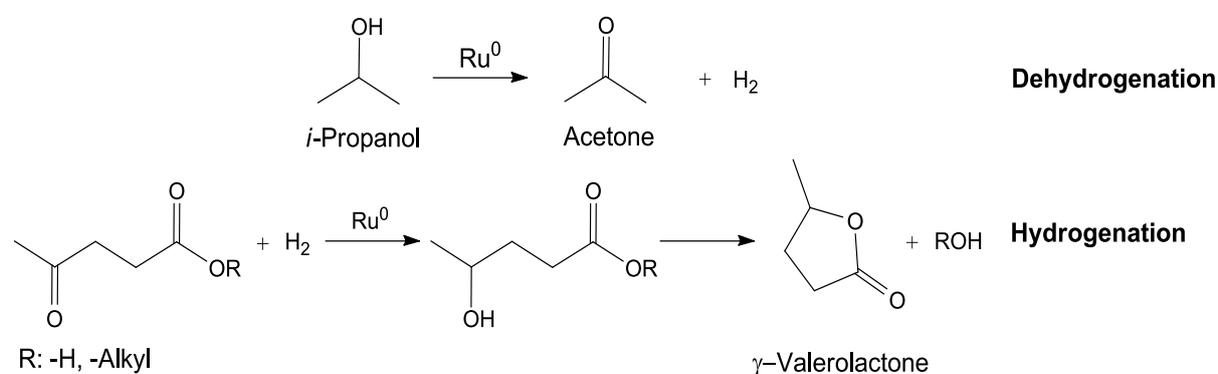
Scheme 1. Proposed dehydrogenation-hydrogenation mechanism of the synthesis of γ-VL based on LA or LAE and ^{i}PrOH.

Finally, the dependency of the oxidation state of Ru on the catalytic activity was investigated. First, Ru/C was reduced with ^{i}PrOH under microwave irradiation at 140°C for 2 min and dried at 80°C for 1 h. This sample is referred to as Ru/C-red. In order to induce the formation of surface ruthenium oxide, Ru/C was kept in air overnight at 80 or 120°C. Thus produced catalysts are referred to as Ru/C-80 and Ru/C-120. Investigation of the catalysts by means of TPR revealed the presence of a characteristic peak at ca. 100-110°C, corresponding to reduction of ruthenium oxide [19, 20]. The TPR curves of the catalysts also exhibited high-temperature peaks that were previously attested to formation of hydrocarbons due to reduction of the carbon support by H_2 in the presence of Ru species [19, 21]. Though the peak corresponding to reduction of ruthenium oxide and the high-temperature peaks partly overlap (Fig. 2), we estimated the hydrogen uptake based on the peak height (ESI Figure 3SI). Fig. 3 shows the LA conversion plotted against the hydrogen uptake of the catalyst. Remarkably, the hydrogen uptake, which correlates with the amount of surface ruthenium oxide, decreases as follows: Ru/C-120 > Ru/C-80 > Ru/C > Ru/C-red. Importantly, Fig. 3 emphasises that the conversion of LA decreases with an increasing concentration of surface ruthenium oxide, suggesting Ru^0 as catalytically active sites for LA reduction to γ-VL. Lower hydrogen uptake of Ru/C-red compared to Ru/C confirms *in-situ* reduction of surface ruthenium oxide with ^{i}PrOH. This could be further supported when considering acetone to γ -VL ratios obtained for differently pre-treated Ru/C. As mentioned above, the yield of acetone always exceeds that of γ-VL (Table 1). Remarkably, pre-oxidation of Ru/C results in further increase of acetone-to- γ-VL molar ratio: from 2 for Ru/C-red to 6 for Ru/C-120 (Table 1SI). Consequently, surface of Ru/C catalysts first undergoes reduction of ruthenium oxide to give surface Ru^0 species and acetone. Thereafter conversion of LA (Scheme 1) takes place on Ru^0 active centres to give γ-VL and acetone.
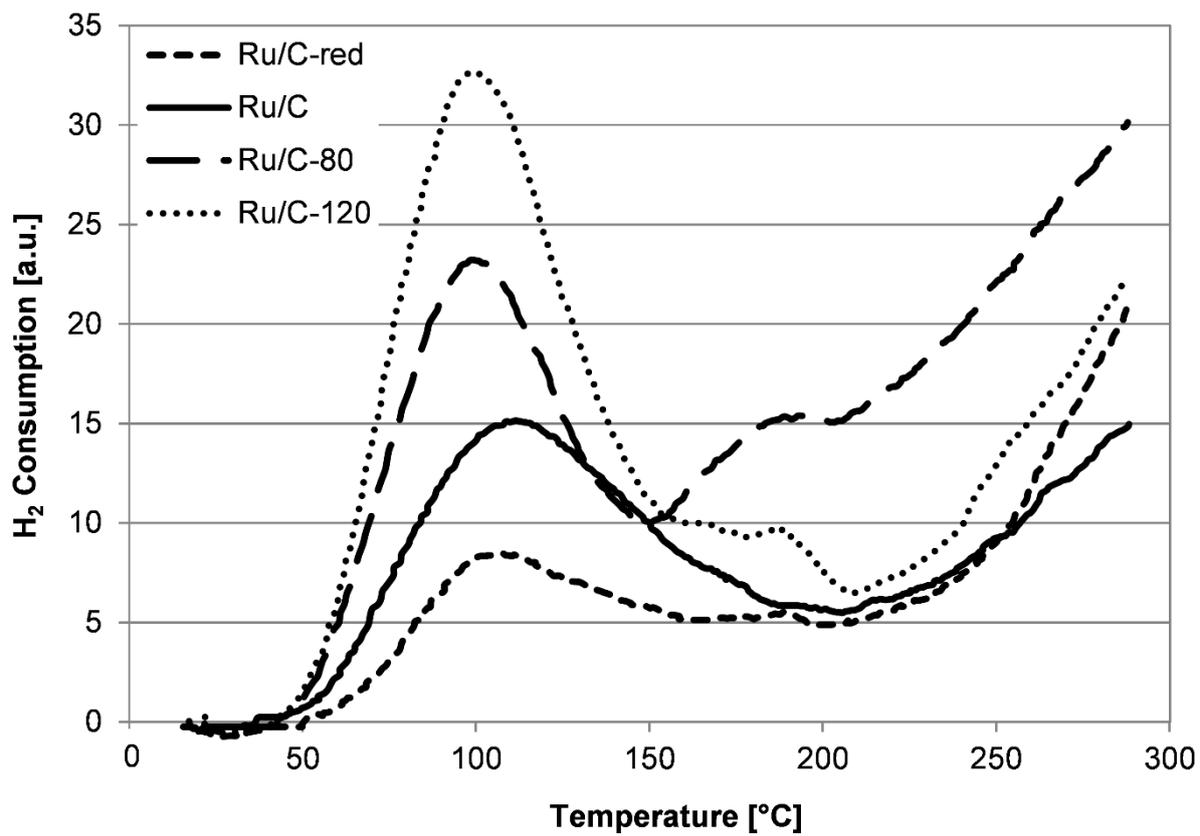
Fig. 2. TPR profiles of differently pre-treated commercial Ru/C catalysts.
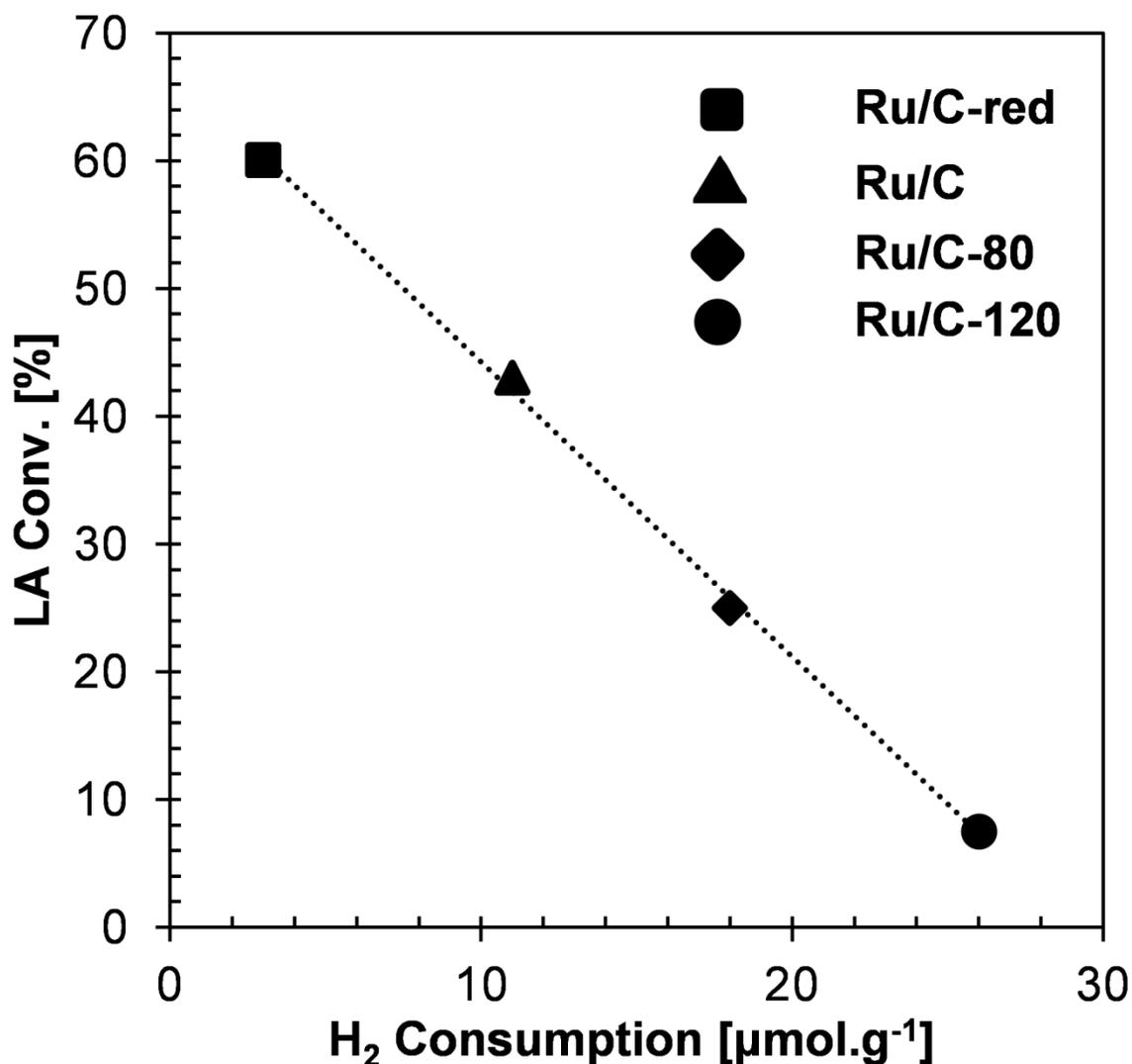
Fig.3. Dependency of LA conversion on oxidative state of Ru in the presence of differently pre-treated Ru/C (LA (0.5 g); catalyst (25 mg); 10 mL of ^{i}PrOH; 300 W, 30 min). Consumption of H_2 (calculated per gram of Ru/C) was determined by TPR.

Finally, the recyclability test was successfully conducted for Ru/C-red where a slight increase in LA conversion to γ-VL was observed in the second run to be 67% instead of 61% in the first run. We assign this observation to the reduction of the remaining unreduced Ru species during the first run. ICP-OES analysis of Ru/C revealed that ruthenium loading remains constant upon recycling.

3. Conclusion

In summary, we demonstrated that LA and LAE can be efficiently reduced with secondary alcohols into γ-VL over Ru/C. The best yields were obtained based on LA or ML as substrate and ^{i}PrOH or 2-BuOH as reductant. The reaction proceeds rapidly in conventional autoclaves and could be further accelerated under microwave heating. A two-step dehydrogenation-hydrogenation mechanism of the reaction was suggested, i.e. (i) dehydrogenation of an alcohol generates molecular hydrogen *in-situ*, (ii) hydrogenation of a substrate with H_2 into γ-VL occurs *via* γ-hydroxyvalerates. Metal Ru^0 species are active for the transformation. *In-situ* activation of the catalyst by reduction of oxidised $Ru^{\delta+}$ centres under reaction conditions was observed.

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Highlights

- Ru catalyzes reduction of levulinic acid with secondary alcohols to γ-valerolactone

- Reaction rate increases under microwave irradiation compared to conventional heating

- *i*-propanol and 2-butanol are the best reductants for levulinic acid and its esters

- The dehydrogenation-hydrogenation mechanism with Ru^0 active species was proposed.

- Ru/C exhibited stability upon recycling