



Short communication

Microwave-assisted reduction of levulinic acid with alcohols producing γ -valerolactone in the presence of a Ru/C catalyst



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ABSTRACT

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 min at 160 °C under microwave heating based on levulinic acid and *i*-propanol. The reaction appears to proceed via a dehydrogenation–hydrogenation sequence.

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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 H₂ 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 the 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 ZrO₂ [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 the 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 ZrO₂ 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 than LAE. 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 (EL) and ^{*i*}PrOH [14]. We started this work from testing a Ru/C catalyst for the 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]

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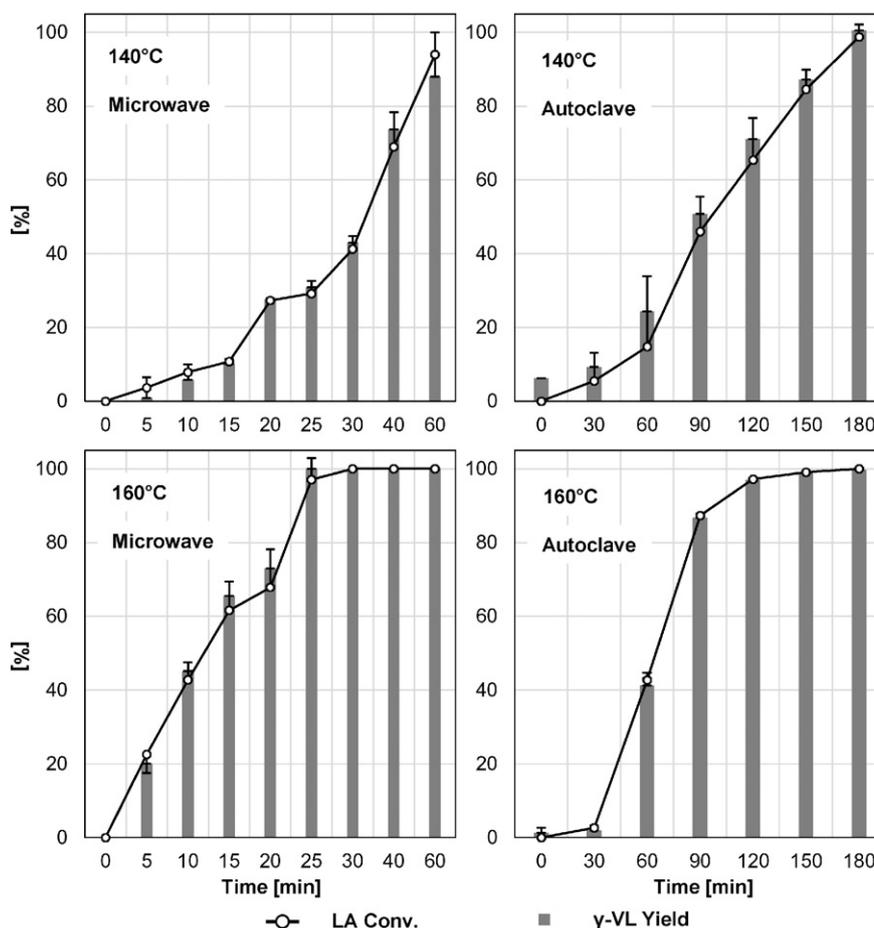


Fig. 1. Time dependence of γ -VL yield (LA (0.5 g); Ru/C (25 mg); 10 mL of i PrOH. For autoclave reactions, 10 bar N_2 was applied with 350 rpm stirring speed. 300 W microwave power was used).

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 microwave-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 min were required to reach heat equilibrium inside of the autoclave. On the contrary, the set temperature was reached in only ca. 2.5 min when using microwave-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 $Ru^{\delta+}$ oxidised 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.

Almost full yield of γ -VL was observed at 140 °C after 60 min using microwave heating. Increasing the temperature to 160 °C results

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.

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