Selective Hydrogenation of Levulinic Acid to Gamma-Valerolactone Using Polymer-Based Ru-Containing Catalysts

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This work is devoted to the investigation of the possibility of use of ruthenium-containing catalysts on the basis of polymeric matrix of hypercrosslinked polystyrene (HPS) in hydrogenation of levulinic acid to gamma-valerolactone, which is a semi-product for obtaining of liquid fuel components. Catalyst 5 %-Ru/MN100 was shown to allow carrying out the hydrogenation of levulinic acid in aqueous medium with high yields of gamma-valerolactone (higher than 99 %) and it can compete with traditional catalyst 5 %-Ru/C. It is noteworthy that synthesized HPS-based catalyst has high activity, and thus the necessity of addition in reaction mixture of acidic co-catalysts is absent.

1. Introduction

At present the process of biofuel production on the basis of levulinic acid (LA) causes high interest of many scientists engaged in these developments. LA is one of the substances, which can be obtained from cellulosic biomass via acid hydrolysis (Sivasubramaniam and Amin, 2015). LA can serve as a precursor in the synthesis of gamma-valerolactone (GVL) (Carvalheiro et al., 2008). Furthermore, LA can be transformed to 2-methyltetrahydrofurane (2-MTHF), which is a fuel additive. It is noteworthy that 2-MTHF is permissible to mix up to 70 % with gasoline without causing harm to the internal combustion engines, and thus similar mileage is reached. Although there is a possibility of direct LA transformation to 2-MTHF, improved yields can be achieved by indirect pathways, which proceed through the production of GVL as an intermediate (Huber and Corma, 2007). Thus GVL is one of the most widespread lactones, which can be obtained by hydrogenation of LA (De Souza et al., 2014) (see Figure 1).
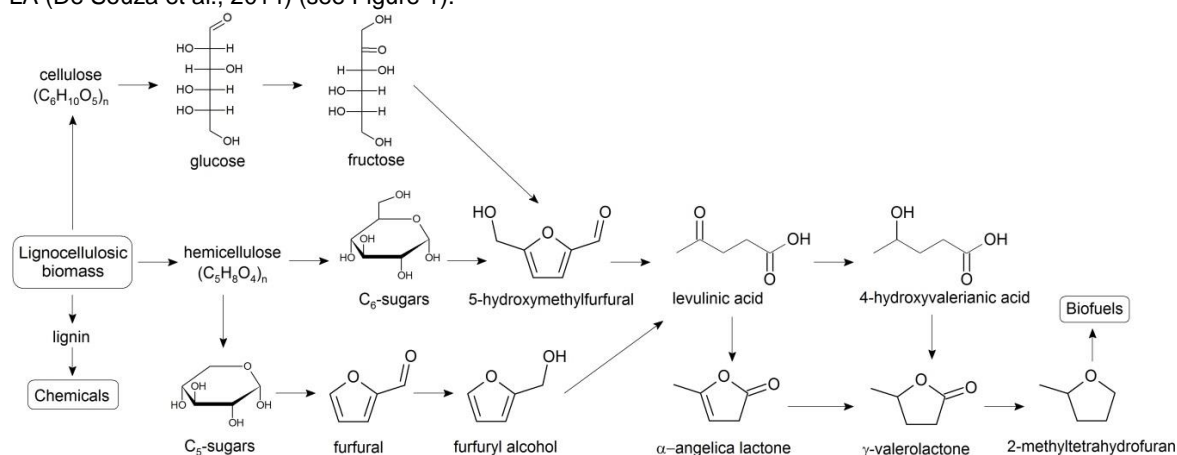

Figure 1: Scheme of LA transformation to GVL and 2-MTHF

LA hydrogenation to GVL is a catalytic process. During hydrogenation of LA, homogeneous and heterogeneous catalysts are used (Mehdi et al., 2008), and formation of various products besides GVL is possible. The major by-products are 1,4-butanediol, LA esters and gamma-hydroxyvaleric acid (an intermediate in the hydrogenation process of LA to GVL). The latter was found in case of alcohols as solvents. Heterogeneous catalysts of LA hydrogenation are usually less active in comparison with homogeneous ones, and require high temperature and pressure. However, the choice of heterogeneous systems is preferable in industry due to the complexity of separation of homogeneous catalysts from the reaction mixture (Wright and Palkovits, 2012).

As a result of numerous studies the series of heterogeneous catalysts was defined, those intended for implementation of LA transformation to GVL in a wide range of reaction conditions. These are catalysts based on noble metals, such as Ru (Al-Shaal et al., 2012), Pd (Yan et al., 2015), Pt (Upare et al., 2011) and Ni (Hengst et al., 2015), supported on organic (activated carbon) and inorganic (oxides of titanium, aluminium, silicon, etc.) supports. The catalysts based on Co (Zhang et al., 2013), Cu, Fe (Yan and Chen, 2014), Cr (Yan and Chen, 2013) are also used, but they require more tough reaction conditions and GVL yields are significantly lower in comparison with the catalysts containing noble metals.

5 %-Ru/C (Galletti et al., 2012), 10 %-Pd/C and Raney Ni (Yan et al., 2009) are the most widespread heterogeneous catalysts of GVL synthesis from LA. Currently, the conventional catalyst of LA hydrogenation is 5 %-Ru/C (Selva et al., 2013), the use of which allows achieving high yields of GVL. To ensure high degree of LA conversion, such solvents as alcohols (methanol, ethanol, butanol), 1,4-dioxane and water are used (Al-Shaal et al., 2012).

It is noteworthy that particle size and degree of dispersion of the catalytically active phase play significant role in increasing of the GVL yield. Additionally, productivity of Ru catalyst is determined by such factors as pore size, degree of crystallinty, mechanical strength, presence of modifiers, etc. (Kluson and Cerveny, 1995).

Ortiz-Cervantes, C. et al. (Ortiz-Cervantes and Garcia, 2013) have been studied the catalytic properties of Ru particles, synthesized by *in situ* decomposition of $Ru_3(CO)_{12}$ with the use of triethylamine as a stabilizer in the hydrogenation reaction of LA under the following conditions: temperature 130 °C, hydrogen pressure 0.5 – 2.5 MPa; moreover, formic acid was used as a source of hydrogen. Tetrahydrofuran (THF), methanol, isopropanol and water were used as solvents. It should be noted that the average diameter of Ru particles was 1-3 nm, depending on the used solvent and the concentration of the stabilizer. It was shown that an LA ester was the main product while using alcohols as solvents. The high yield of GVL (99 wt.% was obtained at a relatively low H_2 pressure (2.5 MPa) in the case of water acting as a solvent (reaction time 24 h).

Thus it can be concluded that in order to achieve high degrees of LA conversion, the use of nanoscale ruthenium particles having high surface area and allowing competing with the traditional industrial catalysts such as Ru/C is important. However, for successful use of Ru nanoparticles in LA hydrogenation the latter should be stabilized.

Successful solution of the problem of providing control over the size of catalytically active metal particles and their monodispersity is possible via the use of stabilizing agents, the most promising among which are polymers due to the variety of their properties (presence of functional groups, molecular weight, crosslinking degree, hydrophilicity or hydrophobicity, etc.), varying of which can effectively influences the processes of particle formation.

In this work we propose to use hypercrosslinked polystyrene (HPS) as a support for the synthesis of effective catalysts of LA hydrogenation to GVL.

2. Experimental

2.1 Materials

Hypercrosslinked polystyrene (HPS) was purchased from Purolite Int. (U.K.), as Macronet MN100 and MN270. Ruthenium hydroxychloride ($Ru(OH)Cl_3$) was purchased from Aurat Ltd. (Moscow, Russia). Levulinic acid (≥ 98 %) was purchased from Merck KGaA, Germany. Gamma-valerolactone (ReagentPlus®, 99 %) was purchased from Sigma-Aldrich. Ruthenium on activated carbon, 5 % Ru, unreduced, ca. 50 % moisture (designated as 5 %-Ru/C) were obtained from Acros Organics, Belgium. Reagent-grade THF, methanol, acetone, hydrogen peroxide were purchased from Sigma-Aldrich and were used as received. Sodium hydroxide (NaOH) was obtained from Reakhim (Moscow, Russia). Reagent grade hydrogen of 99.999 % purity was received from AGA. Distilled water was purified with an Elsi-Aqua (Elsico, Moscow, Russia) water purification system.

2.2 Catalyst synthesis

HPS-based Ru-containing catalysts were synthesized via conventional wet-impregnation method according to the procedure described elsewhere (Sapunov et al., 2013) upon variation of the HPS type (MN100 bearing amino groups or MN270 without functional groups) and metal loading. In a typical experiment, 3 g of pretreated (washed with distilled water and then with acetone to remove chloride and iron ions), dried and crushed (< 63 μm) granules of HPS were impregnated with 7 mL of the solvent mixture consisting of 5 mL THF, 1 mL methyl alcohol and 1 mL water, with dissolved therein calculated amount of ruthenium hydroxotrichloride

(Ru(OH)Cl$_3$) for 10 min. The Ru-containing polymer was dried at 70 °C for 1 h, with impregnated Ru(OH)Cl$_3$ refluxed in 21 mL of NaOH aqueous solution (concentration 0.1 mol/L), then added with continuous stirring 2 mL of hydrogen peroxide. The catalyst was washed with distilled water until pH 6.4 – 7.0, and lack of response to chloride ions, and dried again at 70 °C and kept in air. In this way, Ru-containing systems with calculated ruthenium loading of 3 wt.% (3 %-Ru/MN270 and 3 %-Ru/MN100) and 5 wt.% (5 %-Ru/MN270 and 5 %-Ru/MN100) were synthesized. All the catalyst samples were reduced in hydrogen flow (flow rate 100 mL/min, temperature 300 °C, duration 2 h).

2.3 Catalyst testing

The hydrogenation reaction was carried out in Parr Series 5000 Multiple Reactor System (autoclave type reactor) at a stirring speed of 1500 rpm, at variation of such process parameters as temperature (80 – 150 °C), hydrogen pressure (1 – 4 MPa) and LA-to-catalyst ratio (50 – 200 g/g). As solvent water was used (volume of liquid phase was 50 mL). Samples of reaction mixture were analyzed via HPLC method using absolute calibration method.

3. Results and Discussions

To find optimal reaction conditions of LA hydrogenation over Ru-containing catalysts, testing of commercial sample 5 %-Ru/C was carried out. It is noteworthy that before the testing, 5 %-Ru/C catalyst was reduced in hydrogen flow at 300 °C for 2 h (designated as 5 %-Ru/C-H$_2$).

Study of the temperature effect for 5 %-Ru/C-H$_2$ was carried out under following conditions: total hydrogen pressure 3 MPa, LA-to-catalyst ratio 100 g/g. The temperature was varied in the range from 80 up to 150 °C. It was found that temperature decrease from 150 °C to 120 °C results in corresponding decrease of LA hydrogenation rate (see Figure 2). However, with further decrease in temperature from 120 °C to 100 °C the reaction rate even increases and reaches values observed at 130 °C. This is probably due to the fact that with increasing temperature decreases the solubility of hydrogen. Among all the solvents usually used in catalytic processes, water has the lowest solubility of hydrogen. Thus, it can be assumed that at variation of reaction temperature, change in the rate constant of LA hydrogenation, overlaps with the change in hydrogen partial pressure and its concentration of in liquid phase, and at 100 °C the reaction proceeds fast enough at optimal concentration of dissolved hydrogen.
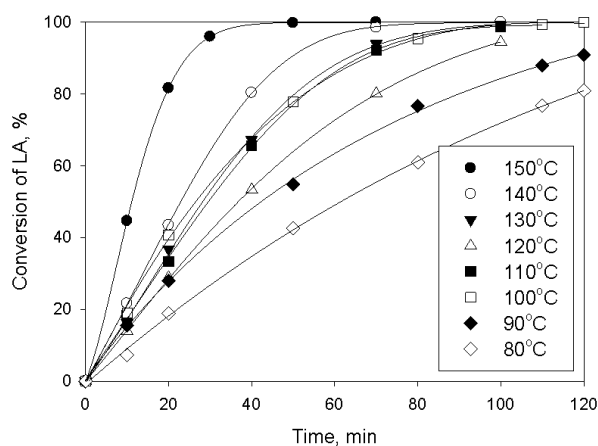

Figure 2: Kinetic curves of LA conversion at variation of reaction temperature for 5%-Ru/C-H$_2$ catalyst

To confirm this assumption, for the catalyst 5%-Ru/C-H$_2$ the effect of the reaction temperature at constant hydrogen partial pressure was investigated under following conditions: hydrogen partial pressure 3 MPa, LA-to-catalyst ratio 100 g/g. The temperature was varied in the range from 100 °C up to 140 °C (see Figure 3).

Based on the presented data, it can be concluded that the decrease of temperature from 140 °C to 100 °C corresponding decrease of reaction rate is observed. Thus, the variation of temperature at constant hydrogen partial pressure allows evaluating properly the effect of temperature on the rate of LA hydrogenation, so all the following experiments were carried out at constant hydrogen partial pressure and 100 °C was chosen as the optimal temperature.

Thus the investigation of the effect of hydrogen partial pressure was carried out using a 5%-Ru/C-H$_2$ at following conditions: temperature 100 °C, LA-to-catalyst ratio 100 g/g (see Figure 4).

Based on the presented dependences (Figure 4) it can be concluded that at the hydrogen partial pressure of 1 MPa the reaction rate sharply decreases that is accompanied by the change of the form of kinetic curve. It

should be also noted that from the point of view of catalytic processes, which are carried out in industrial scale, it is important to provide the high yields of desired product under the mildest conditions. It was found that at the hydrogen partial pressure of 2 MPa, 98 % yield of GVL is achieved for 120 min of reaction duration, so all the further experiments were performed at 100 °C and 2 MPa of hydrogen partial pressure.
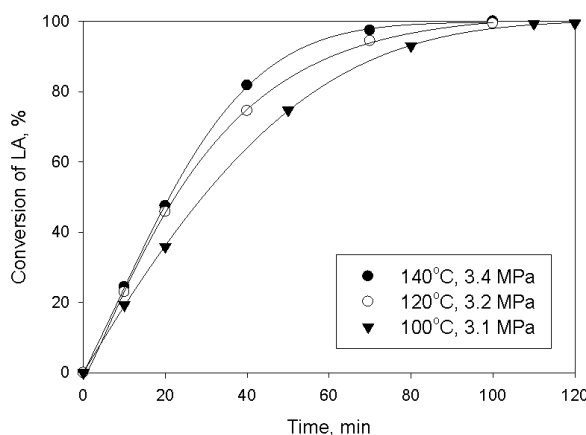

Figure 3: Kinetic curves of LA conversion at variation of reaction temperature at constant hydrogen partial pressure for 5%-Ru/C-H$_2$ catalyst (total hydrogen pressure in the system is shown)
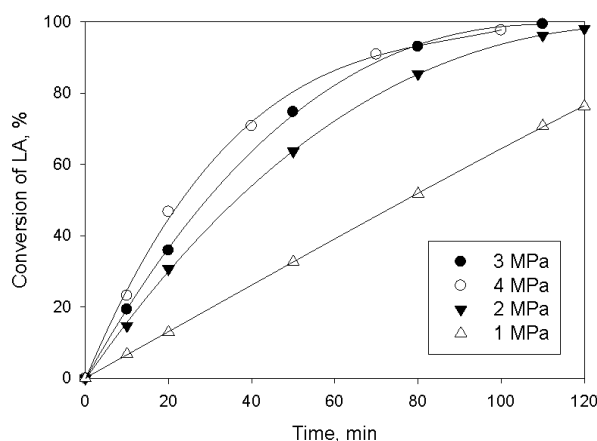

Figure 4: Kinetic curves of LA conversion at variation of hydrogen partial pressure for 5%-Ru/C-H$_2$ catalyst

While studying the kinetic peculiarities of heterogeneous catalytic processes, the elimination of both external and internal diffusion limitations is an important question. Internal diffusion limitations are usually overcome by crushing of catalyst granules, that is why HPS was crushed to the sizes below 63 µm (Manaenkov et al., 2014). To ensure the absence of external diffusion limitations all the experiments were done at vigorous stirring (1500 rpm). Besides, we investigated the effect of LA-to-catalyst ratio under following conditions: temperature 100 °C, the H2 partial pressure of 2 MPa (see Table 1).

Obviously, that with the decrease of LA-to-catalyst ratio the observed reaction rate increases. However, the specific rate of LA hydrogenation, considering the Ru content and calculated at 50 % of LA conversion, remains almost constant (see Table 1), which is an indirect proof of the absence of both internal and external diffusion limitations.

Table 1: Effect of LA-to-catalyst ratio on LA hydrogenation for 5%-Ru/C-H$_2$ catalyst

LA-to-catalyst ratio, g/g	Time to achieve conversion, min	Conversion of LA, %	Specific hydrogenation rate, $R_{50\%}$, molLA/(molRu·min)
200	250	97.6	23.4
100	120	98.1	24.5
50	50	97.9	21.6

Thus, for the commercial catalyst 5%-Ru/C-H$_2$ the following conditions of LA hydrogenation to GVL were chosen, allowing achieving LA conversion of 98 % for 120 min at 100 % selectivity on GVL: temperature 100 °C, hydrogen partial pressure 2 MPa, LA-to-catalyst ratio 100 g/g.

Besides, the activity of 5%-Ru/C-H$_2$ was compared with activity of initial (unreduced) 5%-Ru/C catalyst (see Figure 5).
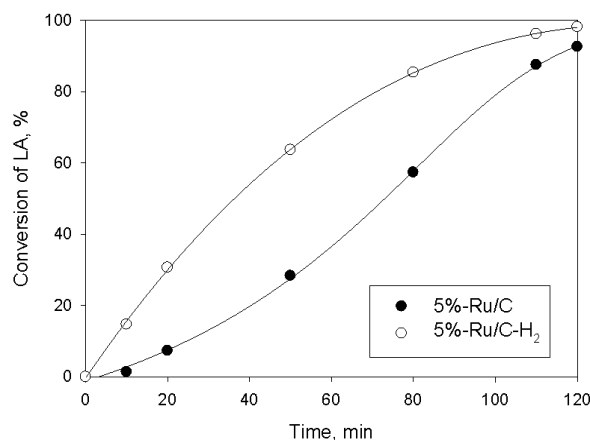

Figure 5: Comparison of kinetic curves of LA conversion for 5 %-Ru/C and reduced 5%-Ru/C-H$_2$

It was found that preliminarily reduction of 5 %-Ru/C catalyst in hydrogen flow allows significantly increasing the degree of LA conversion from 92.5 % to 98.1 % during 120 min of reaction. It is noteworthy that long induction period (up to 100 min) is present in the case of unreduced 5 %-Ru/C, which is likely due to the process of Ru reduction *in situ* and formation of catalytically active sites.

Testing of synthesized Ru/HPS samples was carried out in LA hydrogenation at the following chosen conditions: temperature 100 °C, hydrogen partial pressure 2 MPa, LA-to-catalyst ratio 100 g/g. It was found that activity of the catalyst based on non-functionalized HPS (3 %-Ru/MN270) is approximately two times lower than activity of the catalyst based on HPS containing amino groups (3 %-Ru/MN100) (see Figure 6).

Activity of the synthesized HPS-based catalysts was estimated in comparison with the activity of 5 %-Ru/C-H$_2$, because all the Ru/HPS catalysts were also reduced in hydrogen flow before the reaction. It was found that the increase of Ru loading in the case of Ru/MN270 from 3 % up to 5 wt.% allows increasing the reaction rate in 1.5 times.
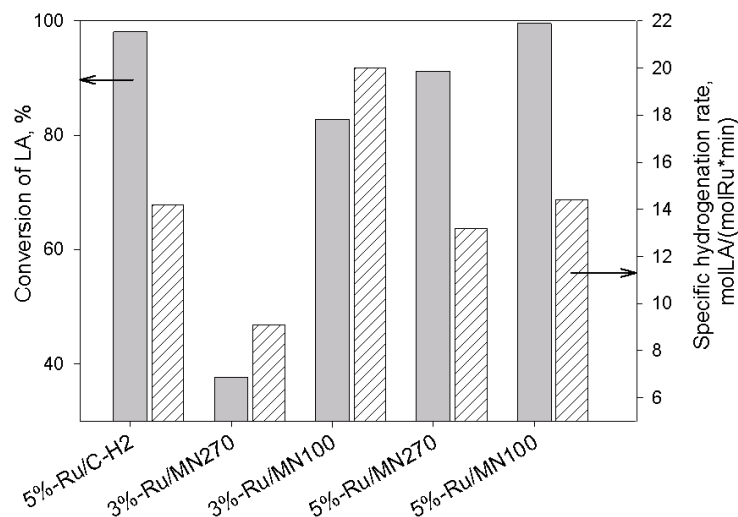

Figure 6: Data testing of the synthesized catalysts on the basis of HPS in comparison to selected commercial catalyst (5 %-Ru/C-H$_2$)

However, the LA conversion (91.2 %) does not exceed the value obtained for the commercial sample 5 %-Ru/C-H$_2$ (98.1 %). The replacement of non-functionalized MN270 to MN100 containing amino groups leads (as well as in the case of the samples containing 3 wt.%t of Ru) to noticeable increase of LA conversion up to 99.6 % (for the sample 5 %-Ru/MN100).

4. Conclusions

Thus, we can conclude that 5 %-Ru/MN100 can compete with the commercial catalyst 5 %-Ru/C-H$_2$, and Ru-containing catalysts based on HPS of MN100 type can be considered as promising for possible use in the hydrogenation of LA for GVL production.

Acknowledgments

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