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Hydrogenation of levulinic acid using Ru-containing catalysts based on hypercrosslinked polystyrene

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Abstract: This work is devoted to the investigation of the possibility of the use of Ru-containing catalysts on the basis of polymeric matrix of hypercrosslinked polystyrene (HPS) in the hydrogenation of levulinic acid (LA) to gamma-valerolactone (GVL). HPS-based Ru-containing catalysts were synthesized at variation of HPS type (MN100 bearing amino groups or MN270 without functional groups) and metal content. Catalyst 5%-Ru/MN100 was shown to compete with commercial 5%-Ru/C and to allow carrying out the hydrogenation of LA in aqueous medium with high yields of GVL (more than 99%).

Keywords: gamma-valerolactone; hydrogenation; hypercrosslinked polystyrene; levulinic acid; ruthenium nanoparticles.

1 Introduction

At present, the search for new sources of energy is of high importance due to the limited sources of fossil fuels. 2-Methyltetrahydrofuran (2-MTHF) is one of the key biomass-derived compounds which can be used as a fuel additive [1]. 2-MTHF can be synthesized via direct processing of levulinic acid (LA), which is in turn can be obtained from cellulose-containing biomass including wastes such as corn stalks, flax shive, wood wastes, etc. However, synthesis of 2-MTHF from gamma-valerolactone (GVL) as an intermediate is preferable [2, 3].

The scheme of LA transformation to GVL and 2-MTHF is presented in Figure 1.

LA transformation to GVL takes place via catalytic hydrogenation. LA hydrogenation reaction is usually carried out by using various heterogeneous catalysts based on noble metals such as Ru, Pd and Pt [5]. Commercial Ru/C is the most promising catalyst for hydrogenation of LA [6].

New heterogeneous catalytic systems based on polymer-stabilized Ru nanoparticles (NPs) can serve as alternatives to Ru/C. It noteworthy that the size and dispersity of Ru NPs are two of the key factors influencing the behavior of Ru-containing catalysts of LA hydrogenation [6, 7]. The use of polymers [e.g. hypercrosslinked polystyrene (HPS)] as supports allows high dispersion of metal NPs to be achieved and ensures the stability of their catalytic properties (prevention of aggregation and leaching).

At present, HPS-based catalysts are successfully used in various hydrogenation reactions and they exhibit good activity and selectivity [8, 9]. Therefore, in this work we propose to use HPS-stabilized Ru-containing NPs as a catalyst of selective hydrogenation of LA.

2 Materials and methods

2.1 Materials

HPS was purchased from Purolite Int. (Llantrisant, Wales, UK) as Macronet MN100 (bearing amino groups) and MN270 (non-functionalized). Ruthenium hydroxychloride [Ru(OH)Cl₃] was purchased from Aurat Ltd. (Moscow, Russia). LA (≥98%) was purchased from Merck KGaA (Darmstadt, Germany).

GVL (ReagentPlus, 99%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). Ruthenium on activated carbon, 5% Ru, unreduced, ca. 50% moisture (designated as 5%-Ru/C) was obtained from Acros Organics (Geel, Belgium). Reagent-grade tetrahydrofuran, methanol (MeOH), acetone and hydrogen peroxide (H₂O₂) were purchased from Sigma-Aldrich (St. Louis, MO, USA) 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 (Tver, Russia). Distilled water was purified with an Elsi-Aqua (Elsico, Moscow, Russia) water purification system.

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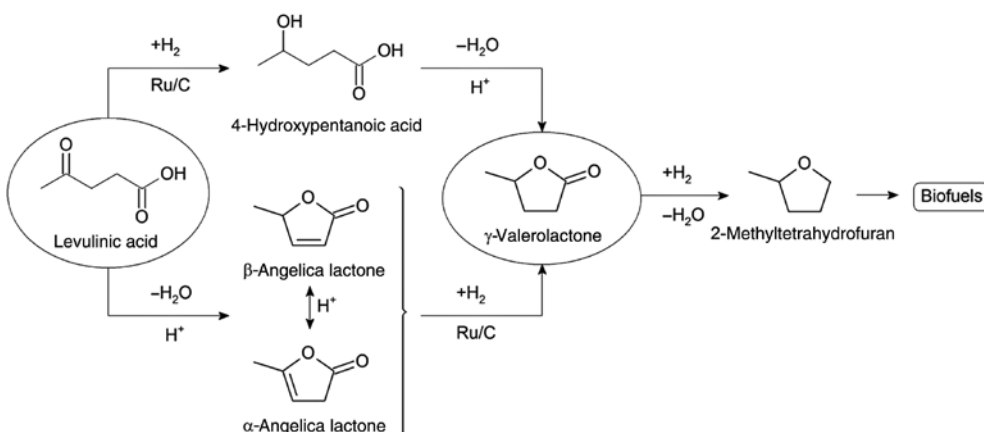


Figure 1: Levulinic acid (LA) transformation to gamma-valerolactone (GVL) and 2-methyltetrahydrofuran (2-MTHF) [4].

2.2 Catalyst synthesis

HPS-based Ru-containing catalysts were synthesized via a conventional wet-impregnation method according to the procedure described elsewhere [8, 9] upon variation of the HPS type (MN100 or MN270) and metal content. 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 complex solvent (consisting of 5 ml of tetrahydrofuran, 1 ml of MeOH and 1 ml of water) with the dissolved therein calculated amount of $\text{Ru}(\text{OH})\text{Cl}_3$ for 10 min.

The Ru-containing polymer was dried at 70°C for 1 h; the dried catalyst was boiled with 21 ml of NaOH aqueous solution (concentration of 0.1 mol/l) at continuous stirring and then 2 ml of hydrogen peroxide was added. The resulting catalyst was washed with distilled water until neutral pH and dried again at 70°C. In this way, Ru-containing systems with calculated ruthenium content 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 Catalytic testing

The hydrogenation reaction was carried out in a Parr Series 5000 Multiple Reactor System (PARR Instrument, Moline, IL, USA) (autoclave type reactor) at a stirring rate 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). Water was used as a solvent (total volume of liquid phase was 50 ml). Samples of reaction mixture were analyzed via HPLC (Ultimate 3000, DIONEX, Sunnyvale, CA, USA) using the absolute calibration method. A Reprogel-H column (500 \times 10 mm, number of theoretical plates 160,000) was used. HPLC was carried out under the following conditions: eluent flow (9 mmol/l solution of H_2SO_4) 0.5 ml/min; column temperature 25°C; eluent pressure 10 MPa; and time of analysis 120 min (for 1 sample). Qualitative identification of substances and their assignment to the corresponding peaks in the chromatogram was carried out using the individual pure substances standards.

Repeated reaction runs with the same catalyst batch delivered concentration values that were reproducible within $\pm 1\%$.

Conversion of LA was defined as $X_{\text{LA}} (\%) = (C_{\text{LA},0} - C_{\text{LA}}) \times C_{\text{LA},0}^{-1} \times 100$, and selectivity with respect to GVL was given as $S_{\text{GVL}} (\%) = C_{\text{GVL}} \times (C_{\text{LA},0} - C_{\text{LA}})^{-1} \times 100$.

Catalytic activity was characterized by the rate of LA conversion, which was calculated in the range of LA conversion corresponding to the linear dependence on observed kinetic curves, and designated as R , $[\text{mol}_{\text{LA}} \cdot \text{mol}_{\text{Ru}}^{-1} \cdot \text{min}^{-1}]$. $R = (N_{\text{LA},X2} - N_{\text{LA},X1}) \times N_{\text{Ru}}^{-1} \times (\tau_2 - \tau_1)^{-1}$, where $N_{\text{LA},X2}$ and $N_{\text{LA},X1}$ are the numbers of moles of LA converted by the reaction time τ_2 and τ_1 , respectively; N_{Ru} is the total number of moles of Ru participating in the reaction.

3 Results and discussion

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).

Table 1 shows the results of testing of 5%-Ru/C- H_2 catalyst under variation of temperature, hydrogen pressure and LA-to-catalyst ratio.

During the study of the temperature effect for 5%-Ru/C- H_2 , it was found that the temperature decrease from 150°C to 120°C results in a corresponding decrease of LA hydrogenation rate (Table 1, entries 5–8). However, further decrease in temperature from 120°C to 100°C causes an unexpected increase of reaction rate (Table 1, entries 2–4), which reaches values, observed at 130°C (Table 1, entry 6). This is likely due to the fact that higher temperature can result in the decrease of hydrogen solubility. It is noteworthy that among the solvents usually used in catalytic processes, water has the lowest hydrogen solubility. 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

Table 1: Results of catalytic testing of 5%-Ru/C-H₂ at variation of reaction conditions.

Entry	Temperature (°C)	Total H ₂ pressure (MPa)	LA-to-catalyst ratio (g/g)	X _{LA} (%; after 100 min of reaction)	R (min ⁻¹)
1	80	3.0	100	72	16
2	90	3.0	100	84	26
3	100	3.0	100	99	35
4	110	3.0	100	99	30
5	120	3.0	100	99	24
6	130	3.0	100	99	31
7	140	3.0	100	~100	38
8	150	3.0	100	~100 ^b	78
9	100	3.1	100	98	33
10	120	3.2	100	99	40
11	140	3.4	100	~100	42
12	100	1.1	100	64	12
13	100	2.1	100	94	28
14	100	3.1	100	98	33
15	100	4.1	100	98	43
16	100	2.1	50	~100 ^c	23
17	100	2.1	100	94	28
18	100	2.1	200	62	28

^aSelectivity in all the experiments was >99%; ^b70 min of reaction time; ^c60 min of reaction time.

LA, Levulinic acid.

concentration in liquid phase, and at 100°C the reaction proceeds fast enough at optimal concentration of dissolved hydrogen.

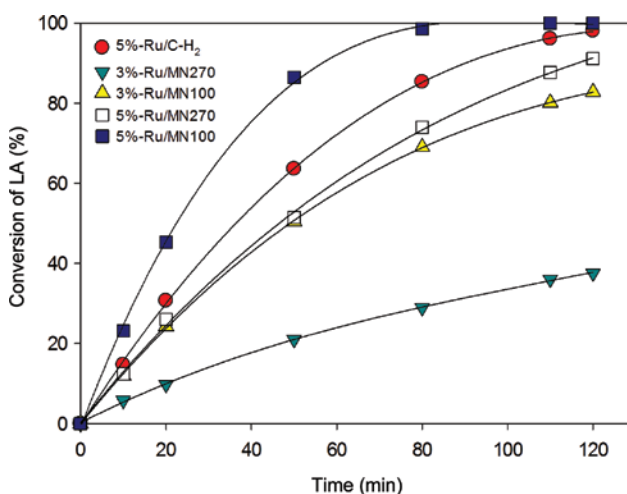
To confirm this assumption, the effect of the reaction temperature at constant hydrogen partial pressure was investigated (Table 1, entries 9–11). It was found that the decrease of temperature from 140°C to 100°C causes a corresponding decrease of reaction rate.

The investigation of the effect of H₂ partial pressure was carried out (Table 1, entries 12–15). Based on the presented data, it can be concluded that at the hydrogen partial pressure of 1 MPa, the reaction rate sharply decreases. It should be also noted that from the point of view of catalytic processes, which are carried out in an 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, while at 3 MPa, the yield is 99%. As the difference in GVL percentage accumulated by 120 min of reaction is negligible, all the further experiments were performed at 100°C and 2 MPa of H₂ partial pressure.

While studying the kinetic peculiarities of heterogeneous catalytic processes, the elimination of both external and internal diffusion limitations is important.

Internal diffusion limitations are usually overcome by crushing of catalyst granules (HPS was crushed to sizes below 63 µm, see also Ref. [8, 9]). To ensure the absence of external diffusion limitations, all of the experiments were done at vigorous stirring (1500 rpm). In addition, we investigated the effect of LA-to-catalyst ratio (Table 1, entries 16–18). With the decrease of LA-to-catalyst ratio the observed reaction rate increases (see the increase of LA conversion from 62% up to 100%). However, the specific reaction rate *R* remains almost constant, which is an indirect proof of the absence of both internal and external diffusion limitations.

Testing of synthesized Ru/HPS samples was also carried out. It was found that activity of the catalyst based on non-functionalized HPS (3%-Ru/MN270) is 2.5 times lower than activity of the catalyst based on HPS containing amino groups (3%-Ru/MN100) (see Figure 2 and Table 2).

**Figure 2:** Comparison of kinetic curves of levulinic acid (LA) hydrogenation over 5%-Ru/C-H₂ and Ru/hypercrosslinked polystyrene (HPS) catalysts (temperature 100°C, H₂ partial pressure 2 MPa, LA-to-catalyst ratio 100 g/g).**Table 2:** Results of catalytic testing of Ru/hypercrosslinked polystyrene (HPS) catalysts at chosen reaction conditions (temperature 100°C, H₂ partial pressure 2 MPa, levulinic acid [LA]-to-catalyst ratio 100 g/g).

Entry	Catalyst	X _{LA} (%; after 100 min of reaction)	R (min ⁻¹)
1	3%-Ru/MN270	34	14
2	3%-Ru/MN100	77	35
3	5%-Ru/MN270	83	23
4	5%-Ru/MN100	~100	38

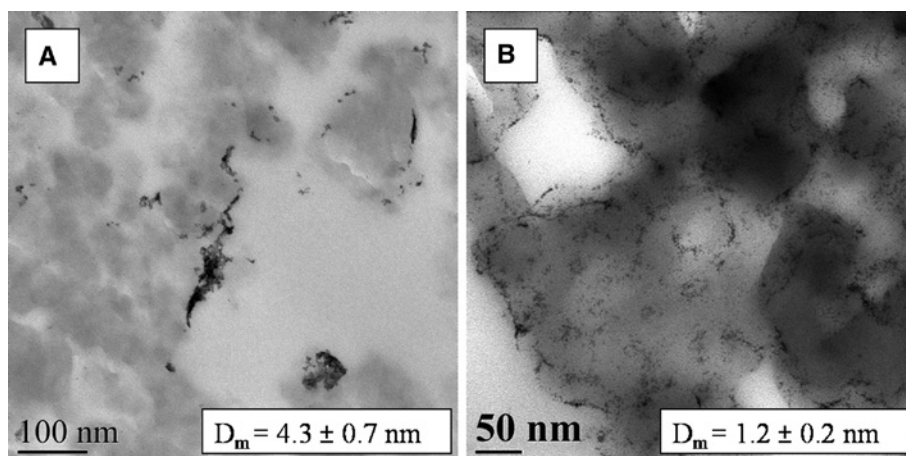


Figure 3: Transmission electron microscopy (TEM) images of (A) 3%-Ru/MN270 and (B) 3%-Ru/MN100.

To explain the observed difference in behavior of 3%-Ru/HPS catalysts, transmission electron microscopy (TEM) study was carried out using a JEOL JEM1010 instrument (JEOL Ltd., Tokyo, Japan) at 80 kV acceleration voltage. It was found that the mean diameter of Ru-containing NPs for 3%-Ru/MN270 is 4.3 ± 0.7 nm (Figure 3A) which is almost four times higher in comparison with that of 3%-Ru/MN100 (Figure 3B), for which NPs have a mean diameter of 1.2 ± 0.2 nm. This difference is likely due to the relatively higher hydrophilicity of MN100, which allows more uniform distribution of $\text{Ru}(\text{OH})\text{Cl}_3$ inside the HPS matrix. It should be noted that in both the samples Ru-containing NPs form aggregates and are located closer to the external surface of the polymer, forming “tracks”. Thus, the use of MN100 instead of MN270 allows a strongly increasing catalytic activity, and TEM data are in accordance with the data of catalytic testing (Figure 2).

It is noteworthy that the increase of Ru content in the case of Ru/MN270 from 3 wt.% up to 5 wt.% allows increase in the reaction rate of more than 1.5 times. However, the LA conversion (91%) achieved for 120 min does not exceed the value obtained for 5%-Ru/C- H_2 (98%). The replacement of MN270 to MN100 (for the samples with Ru content of 5 wt.%) also results in noticeable increase of LA conversion >99% (see Figure 2). Furthermore, it was found that the activity of 5%-Ru/MN100 is 1.4 times higher (38 min^{-1} for 120 min of reaction time) than the activity of 5%-Ru/C- H_2 .

By the method of X-ray photoelectron spectroscopy (XPS), the effect of preliminary reduction in hydrogen flow on the composition of the surface of 5%-Ru/C- H_2 and 5%-Ru/MN100 was investigated. XPS analysis was carried out using Mg K α ($h\nu = 1253.6 \text{ eV}$) radiation with an ES-2403 spectrometer (Institute for Analytic Instrumentation of RAS, St. Petersburg, Russia) equipped with an energy analyzer PHOIBOS 100-5MCD (SPECS,

Berlin, Germany) and X-Ray source XR-50 (SPECS, Berlin, Germany). All of the data were acquired at X-ray power of 250 W. Survey spectra were recorded at an energy step of 0.5 eV with an analyzer pass energy 40 eV, and high resolution spectra were recorded at an energy step of 0.05 eV with an analyzer pass energy 7 eV. Samples were allowed to outgas for 180 min before analysis and were stable during the examination. The data analysis was performed by CasaXPS.

The XPS data revealed that the surface of reduced samples of both 5%-Ru/C- H_2 and 5%-Ru/MN100 contains ruthenium in the form of RuO_2 with different degrees of hydration. However, preliminary treatment of 5%-Ru/C in H_2 flow allowed obtaining also Ru(0) (12.5at.%), while in the case of 5%-Ru/MN100, no metallic ruthenium was found after the reduction (see Table 3).

Figure 4 shows high resolution spectra of Ru 3d and C 1s sublevels and their model decomposition for 5%-Ru/C- H_2 (Figure 4A) and 5%-Ru/MN100 (Figure 4B).

However, despite the fact that 5%-Ru/C- H_2 contains Ru(0), showing higher activity in hydrogenation of LA to GVL than RuO_2 [11], the observed activity of 5%-Ru/C- H_2 is lower in comparison with that of 5%-Ru/MN100.

Thus, it can be concluded that the size of the Ru-containing NPs plays the key role, influencing the behavior

Table 3: Qualitative and quantitative composition (at.%) of the surface of 5%-Ru/C- H_2 and 5%-Ru/MN100 (the values of binding energy of Ru 3d $_{5/2}$ [10] are shown in parentheses).

Sample compound	5%-Ru/C- H_2	5%-Ru/MN100
Ru(0)	12.5 (280.1)	–
RuO_2	62.6 (280.8)	50.5 (281.1)
$\text{RuO}_2 \cdot n\text{H}_2\text{O}$	24.9 (282.6)	49.5 (282.3)

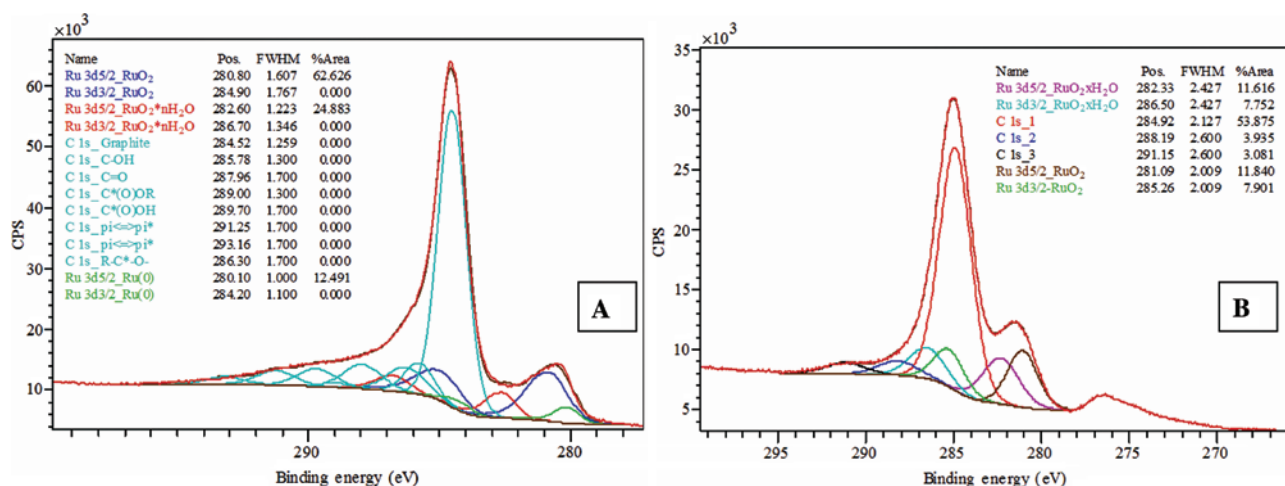


Figure 4: High resolution spectra of Ru 3d and C 1s sublevels for (A) 5%-Ru/C-H₂ and (B) 5%-Ru/MN100.

of ruthenium-containing catalysts of LA hydrogenation rather than the content of metallic ruthenium.

4 Conclusions

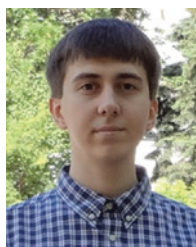
The use of HPS as a support for development of the catalysts of LA hydrogenation to GVL is prospective. HPS of MN100 type (bearing amino groups) in contrast to non-functionalized MN270 allows formation of tiny Ru-containing NPs (about 1–2 nm in diameter), during the pre-treatment of Ru-containing catalyst based on MN100 in hydrogen flow, which reveal high activity in LA hydrogenation. The 5%-Ru/MN100 is shown to compete with commercial 5%-Ru/C catalyst reduced in hydrogen flow, despite the fact that 5%-Ru/C-H₂ contains Ru(0), showing higher activity in hydrogenation of LA to GVL than RuO₂.

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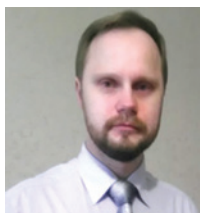


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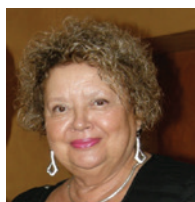
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