

# Hydrogenation of Biomass-Derived Levulinic Acid to Gamma-Valerolactone Using Polymer-Based Metal-Containing Catalysts

Linda Zh. Nikoshvili\*, Igor I. Protsenko, Dalia A. Abusuek, Anna O. Zaykovskaya, Alexey V. Bykov, Valentina G. Matveeva, Esther M. Sulman

Tver Technical University, A.Nikitina str. 22, 170026, Tver, Russian Federation  
 lninda@science.tver.ru

Nowadays the development of effective catalytic systems of selective hydrogenation of levulinic acid (LA) to gamma-valerolactone (GVL) is of high importance. However, there is a lack of data concerning the use of polymer-based catalyst in this process. The possibility to use of Ru-containing catalysts on the basis of hypercrosslinked polystyrene (HPS) in hydrogenation of LA to GVL is discussed. Catalyst 5%-Ru/HPS is shown to be highly active and selective in hydrogenation of LA in aqueous medium (yield of GVL more than 99%) at mild reaction conditions (90 °C, 2 MPa of hydrogen partial pressure) and the absence of co-catalysts.

## 1. Introduction

Global petro-chemical market faces increasing competition and a dependency on external sources, and is under considerable cost and ecological pressure. Biomass has received considerable attention as a sustainable feedstock that can replace diminishing fossil fuels for the production of energy, especially for the transportation sector.

The first-generation biofuels are produced from sugars, starches and vegetable oils; however, the limited availability of starting materials (due to the restricted amounts of fertile soils) and competition with food from the feedstocks are limiting factors for its production (Alonso et al., 2010). The advanced biofuels of second generation are mainly produced from lignocellulosic biomass (Figure 1), one of the most inexpensive and abundant raw materials (Climent et al., 2014). 40-50 % of the lignocellulose consists of cellulose, the most valuable component since it can be converted into various platform molecules, including levulinic acid (LA) (Weingarten et al., 2012), which can be obtained from cellulosic biomass via acid hydrolysis (Sivasubramaniam and Amin, 2015). Hydrogenation of LA to gamma-valerolactone (GVL) is one of the most promising reactions in the field of biomass valorization to fine chemicals and liquid transportation fuels (Alonso et al., 2013), and GVL is one of the most widespread lactones, which can be obtained by hydrogenation of LA (De Souza et al., 2014).

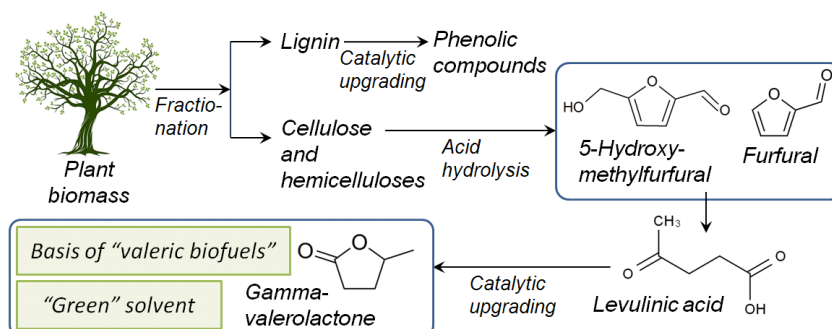


Figure 1: General scheme of biomass processing to GVL – a platform-chemical for liquid biofuels

Due to high interest towards GVL, its efficient production is currently a topic of intensive research (Piskun et al., 2016). Investigations are mainly focused on hydrogenation of LA (Al-Shaal et al., 2016) and its esters (Cai et al., 2016) by molecular hydrogen in the presence of metal catalysts. Application of supported metal catalysts is especially advantageous owing to simplicity of product recovery and catalyst recycling (Zhang et al., 2015). LA can not only serve as a precursor in the synthesis of GVL (Carvalho et al., 2008), it can be also transformed to 2-methyltetrahydrofuran, which is a fuel additive. It is noteworthy that 2-methyltetrahydrofuran is permissible to mix up to 70 % with gasoline without causing harm to the internal combustion engines, and similar mileage is reached. Although there is a possibility of direct LA transformation to 2-methyltetrahydrofuran, improved yields can be achieved by indirect pathways, which proceed through GVL as an intermediate (Huber and Corma, 2007).

One of the key issues of production of new types of fuels is the proper choice of reagents and reaction conditions. 5 %-Ru/C is one of the most widespread heterogeneous catalysts of LA hydrogenation (Selva et al., 2013). Different solvents (methanol, ethanol, butanol, 1,4-dioxane and water) can be used to achieve high conversion of LA (Al-Shaal et al., 2012). Besides the 5 %-Ru/C, which was shown to provide high yields of GVL at relatively mild reaction conditions (Protsenko et al., 2016), a number of the heterogeneous catalysts intended for the synthesis of GVL from LA has been developed as a result of numerous studies, e.g. the catalysts on the basis of noble metals such as Pd (Wright and Palkovits, 2012) and Pt (Upare et al., 2011) deposited on inorganic supports. However, it is known that the main problem of industrial biofuel production is high cost, which can be due to the necessity of the use of catalysts containing platinum, palladium and ruthenium. As regards to this issue, monometallic catalysts on the basis of Ni (Fu et al., 2016), Co (Zhang et al., 2013), Cu (Putrakumar et al., 2015), Fe (Long et al., 2015) and bimetallic ones (Ni-Cu (Obregón et al., 2014), Cu-Cr (Yan and Chen, 2013), Cu-Fe (Yan and Chen, 2014)) are perspective.

It is noteworthy that up to date there is no data on the use of polymer-based catalysts in hydrogenation of LA to GVL. Thus the methodology of this work is based on the use of hypercrosslinked polystyrene (HPS) as a support for the synthesis of heterogeneous catalysts of LA hydrogenation owing to the ability of HPS to stabilization of metal-containing nanoparticles. Earlier it was shown that Ru/HPS, especially the catalysts based on HPS of MN100 type containing amino-groups, can serve as an alternative to the commercial 5 %-Ru/C catalyst (Protsenko et al., 2016), however the bounds of high GVL yield for Ru/HPS catalysts were not studied. In the framework of this study we investigated the influence of reaction conditions on the behavior of the most promising HPS-based catalyst, i.e. 5 %-Ru/MN100. Besides, the series of catalysts containing 5 wt.% of non-noble metals (Co, Fe, Ni, Cu and Zn) was synthesized using MN100 as a support and corresponding metal acetates as precursors. However, these catalysts revealed marginal conversion of LA in aqueous medium at 200 °C and 5 MPa of hydrogen partial pressure at the absence of any co-catalysts, as it was also shown elsewhere for Cu/C (Xu et al., 2016). Thus, this work is focused on physicochemical characterisation and detailed investigation of catalytic properties of 5 %-Ru/MN100.

## 2. Experimental

### 2.1 Materials

HPS was purchased from Purolite Int. (U.K.), as Macronet MN100. Ruthenium hydroxychloride ( $\text{Ru}(\text{OH})\text{Cl}_3$ ) was purchased from Aurat Ltd. (Moscow, Russian Federation). LA ( $\geq 98\%$ ) was purchased from Merck KGaA, Germany. GVL (ReagentPlus<sup>®</sup>, 99 %) was purchased from Sigma-Aldrich. Reagent-grade THF, methanol, acetone and hydrogen peroxide were purchased from Sigma-Aldrich and were used as received. Sodium hydroxide was obtained from Reakhim (Moscow, Russian Federation). 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 catalyst was synthesized via conventional wet-impregnation method according to the procedure described elsewhere (Sapunov et al., 2013). In a typical experiment, 3 g of pre-treated (washed with distilled water and then with acetone to remove chloride and iron ions), dried and crushed ( $< 63\ \mu\text{m}$ ) granules of HPS were impregnated with 7 mL of the solvent mixture consisting of THF (5 mL), methanol (1 mL) and water (1 mL), with dissolved therein calculated amount of ruthenium hydroxychloride ( $\text{Ru}(\text{OH})\text{Cl}_3$ ) for 10 min. The Ru-containing polymer was dried at 70 °C for 1 h, refluxed in 21 mL of NaOH aqueous solution (concentration 0.1 mol/L), then 2 mL of hydrogen peroxide was added at continuous stirring. 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. In this way, 5 %-Ru/MN100 was synthesized. The catalyst was reduced in hydrogen flow at a temperature of 300 °C and  $\text{H}_2$  flow rate of 100 mL/min during 2 h (designated as 5 %-Ru/MN100-R).

### 2.3 Procedure of catalytic testing

The hydrogenation reaction (Figure 2) was carried out in Parr Series 5000 Multiple Reactor System at a stirring rate of 1500 rpm, at variation of such process parameters as temperature (70 – 120 °C) and hydrogen partial pressure (1 – 5 MPa). In each experiment, LA loading was 1 g and the catalyst loading was 0.01 g. Water was used as a solvent (volume of liquid phase was 50 mL). Samples of reaction mixture were analyzed via HPLC method using absolute calibration method.

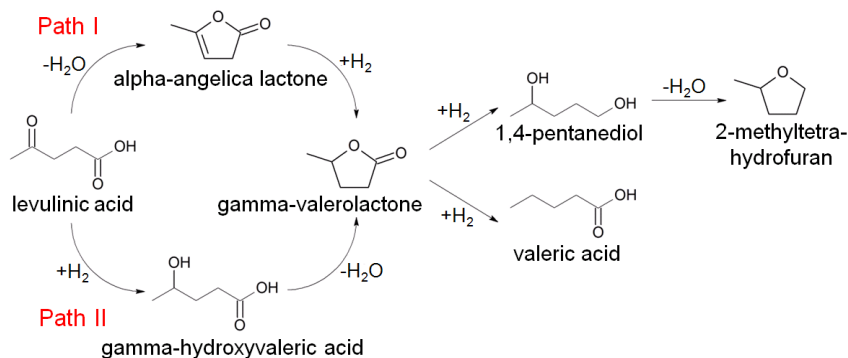


Figure 2: Scheme of catalytic hydrogenation of LA to GVL and subsequent products

### 2.4 Methods

Synthesized 5%-Ru/MN100 was characterized by liquid nitrogen physisorption, X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and scanning electron microscopy (SEM). Liquid nitrogen physisorption was carried out using Beckman Coulter SA 3100 (Coulter Corporation, USA). Prior to the analysis, samples were degassed in Becman Coulter SA-PREP at 120°C in vacuum for 1 h. Weight of each sample was above 0.1 g. XPS data were obtained using Mg K $\alpha$  ( $h\nu = 1253.6$  eV) radiation with ES-2403 spectrometer (Institute for Analytic Instrumentation of RAS, St. Petersburg, Russia) equipped with energy analyzer PHOIBOS 100-MCD5 (SPECS, Germany) and X-Ray source XR-50 (SPECS, Germany). All 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. TEM characterization was provided using a JEOL JEM1010 instrument at electron accelerating voltage of 80 kV. Samples were prepared by embedding the catalyst in epoxy resin with following microtoming at ambient temperature. Images of the resulting thin sections (ca. 50 nm thick) were collected with digital camera and analyzed with the Adobe Photoshop software package and the Scion Image Processing Toolkit. SEM/EDX analysis was carried out using a Phenom ProX instrument at electron accelerating voltage of 17 kV.

## 3. Results and Discussions

### 3.1 Catalyst characterization

The data of liquid nitrogen physisorption are presented in Table 1 and in Figure 3.

Table 1: Specific surface area (SSA) of HPS and of 5%-Ru/MN100 (freshly prepared and the reduced one)

Sample	SSA, m <sup>2</sup> /g			
	Langmuir	BET	t-plot	
			External SSA	SSA of micropores
MN100	839	724	189	603
5%-Ru/MN100	788	691	286	405
5%-Ru/MN100-R	1118	964	215	771

For all the investigated samples, the Barrett-Joyner-Halenda (BJH) pore size distribution suggested the presence of micro- (< 2 nm), meso- (2-50 nm) and macro-pores (> 50 nm) with predominant microporosity (see Figure 3 (a)). It is noteworthy that after the impregnation with Ru(OH)Cl<sub>3</sub>, the BET SSA of MN100 decreased negligibly from 724 m<sup>2</sup>/g to 691 m<sup>2</sup>/g, indicating that blockage of mainly micropores (see Table 1 and Figure 3 (b)) took place after incorporation of Ru compound. However, after the reduction of the catalyst in H<sub>2</sub> flow, noticeable increase of porosity up to 964 m<sup>2</sup>/g (BET model) was observed (mainly due to the



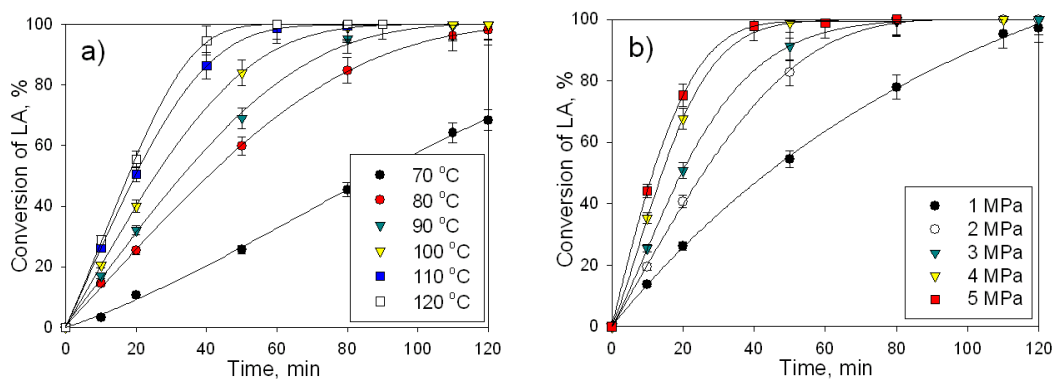


Figure 5: Influence of reaction temperature (a) and hydrogen partial pressure (b) on the rate of LA hydrogenation over 5%-Ru/MN100-R

Activity of the synthesized 5%-Ru/MN100-R was compared with the activity of commercial 5%-Ru/C, which was obtained from Acros Organics (Belgium) and reduced in hydrogen flow at the same conditions (300 °C, 2 h). It was found that at chosen optimal conditions (90 °C, 2 MPa), 5%-Ru/MN100-R has activity similar to the activity of commercial 5%-Ru/C at higher temperature and pressure (100 °C, 3 MPa), while under identical conditions the 5%-Ru/MN100-R is always more active (GVL yield is close to 100%) than 5%-Ru/C (Figure 6).

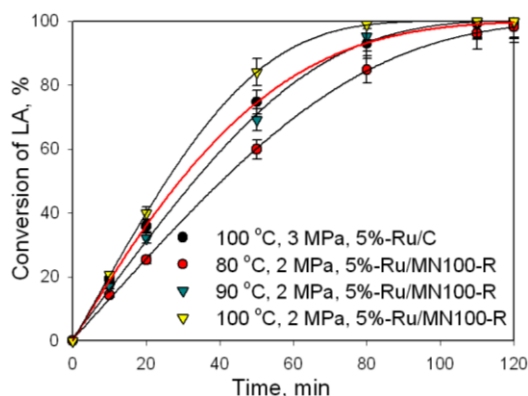


Figure 6: Comparison of commercial 5%-Ru/C and 5%-Ru/MN100-R

#### 4. Conclusions

The use of MN100 as a support for development of the catalysts of LA hydrogenation to GVL is prospective. 5 %-Ru/MN100 revealed high activity and selectivity in LA hydrogenation (yield of GVL achieved more than 99 % for 120 min of reaction duration) at mild reaction conditions (90 °C, 2 MPa of hydrogen partial pressure) in aqueous medium. 5%-Ru/MN100 can successfully compete with commercial 5 %-Ru/C catalyst reduced in hydrogen flow even despite the fact that HPS-based catalyst contains RuO<sub>2</sub> as an active phase.

#### Acknowledgments

This work was funded by the Russian Foundation for Basic Research (grant 15-08-01469). The authors thank Dr. L.M. Bronstein (Department of Chemistry, Indiana University, US) and Dr. B.D. Stein (Department of Biology, Indiana University, US) for help with TEM studies, and also Dr. A.S. Morozov and Dr. I.V. Bessonov (JSC «Advanced medical technologies», Russia) for help with SEM/EDX studies.

#### References

- Abdelrahman O.A., Heyden A., Bond J.Q., 2014, Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form  $\gamma$ -valerolactone over Ru/C., *ACS Catalysis*, 4(4), 1171-1181.
- Alonso D.M., Bond J.Q., Dumesic J.A., 2010, Catalytic conversion of biomass to biofuels, *Green Chemistry*, 12(9), 1493-1513.
- Alonso D.M., Wettstein S.G., Dumesic J.A., 2013, Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass, *Green Chemistry*, 15(3), 584-595.

- Al-Shaal M.G., Calin M., Delidovich I., Palkovits R., 2016, Microwave-assisted reduction of levulinic acid with alcohols producing  $\gamma$ -valerolactone in the presence of a Ru/C catalyst, *Catalysis Communications*, 75, 65-68.
- Al-Shaal M.G., Wright W.R.H., Palkovits R., 2012, Exploring the ruthenium catalyzed synthesis of  $\gamma$ -valerolactone in alcohols and utilization of mild solvent-free reaction conditions, *Green Chemistry*, 14(5), 1260-1263.
- Cai B., Zhou X.-C., Miao Y.-C., Luo J.-Y., Pan H., Huang Y.-B., 2017, Enhanced catalytic transfer hydrogenation of ethyl levulinate to  $\gamma$ -valerolactone over an robust Cu-Ni bimetallic catalyst, *ACS Sustainable Chemistry & Engineering*, 5(2), 1322-1331.
- Carvalho F., Duarte L.C., Girio F.M., 2008, Hemicellulose biorefineries – a review on biomass pretreatments, *Journal of Scientific and Industrial Research*, 67, 849-864.
- Climent M.J., Corma A., Iborra S., 2014, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, *Green Chemistry*, 16(2), 516-547.
- De Souza R. O. M. A., Miranda L. S. M., Rafael L., 2014, Bio(chemo)technological strategies for biomass conversion into bioethanol and key carboxylic acids, *Green Chemistry*, 16(5), 2386-2405.
- Fu J., Sheng D., Lu X., 2016, Hydrogenation of levulinic acid over nickel catalysts supported on aluminum oxide to prepare  $\gamma$ -valerolactone, *Catalysts*, 6(1), 6, doi:10.3390/catal6010006.
- Huber G.W., Corma A., 2007, Synergies between bio- and oil refineries for the production of fuels from biomass, *Angewandte Chemie International Edition*, 46, 7184-7201.
- Long X., Sun P., Li Z., Lang R., Xia C., Li F., 2015, Magnetic Co/Al<sub>2</sub>O<sub>3</sub> catalyst derived from hydrotalcite for hydrogenation of levulinic acid to  $\gamma$ -valerolactone, *Chinese Journal of Catalysis*, 36(9), 1512-1518.
- Obregón I., Corro E., Izquierdo U., Requies J., Arias P.L., 2014, Levulinic acid hydrogenolysis on Al<sub>2</sub>O<sub>3</sub>-based Ni-Cu bimetallic catalysts, *Chinese Journal of Catalysis*, 35, 656-662.
- Piskun A., de Haan J., Wilbers E., van de Bovenkamp H., Tang Z., Heeres H.J., 2016, Hydrogenation of Levulinic acid to  $\gamma$ -valerolactone in water using mm sized supported Ru catalysts in a packed bed reactor, *ACS Sustainable Chemistry & Engineering*, 4(6), 2939-2950.
- Protsenko I.I., Nikoshvili L.Zh., Matveeva V.G., Sulman E.M., Rebrov E., 2016, Selective hydrogenation of levulinic acid to gamma-valerolactone using polymer-based Ru-containing catalysts, *Chemical Engineering Transactions*, 52, 679-684.
- Putrakumar B., Nagaraju N., Kumar V.P., Chary K.V.R., 2015, Hydrogenation of levulinic acid to  $\gamma$ -valerolactone over coppercatalysts supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, *Catalysis Today*, 250, 209-217.
- Sapunov V.N., Grigoryev M.Ye., Sulman E.M., Konyaeva M.B., Matveeva V.G., 2013, D-glucose hydrogenation over Ru nanoparticles embedded in mesoporous hypercrosslinked polystyrene, *Journal of Physical Chemistry A*, 117, 4073-4083.
- Selva M., Gottardo M., Perosa A., 2013, Upgrade of biomass-derived levulinic acid via Ru/C-catalyzed hydrogenation to  $\gamma$ -valerolactone in aqueous-organic-ionic liquids multiphase systems, *ACS Sustainable Chemistry & Engineering*, 1(1), 180-189.
- Sivasubramaniam D., Amin N.A.S., 2015, Synthesis of ethyl levulinate from levulinic acid over solid super acid catalyst, *Chemical Engineering Transactions*, 45, 907-912.
- Upare P.P., Lee J.-M., Hwang D.W., Halligudi S.B., Hwang Y.K., Chang J.-S., 2011, Selective hydrogenation of levulinic acid to  $\gamma$ -valerolactone over carbon-supported noble metal catalysts, *Journal of Industrial and Engineering Chemistry*, 17(2), 287-292.
- Wagner, C.D., Riggs, W.M., Davis, L.E., Moulder, J.F., 1979, *Handbook of X-ray photoelectron spectroscopy*, Perkin-Elmer Corp.; NIST X-ray Photoelectron Spectroscopy Database, Version 3.5.
- Weingarten R., Conner Wm.C., Huber Jr. and G.W., 2012, Production of levulinic acid from cellulose by hydrothermal decomposition combined with aqueous phase dehydration with a solid acid catalyst, *Energy & Environmental Science*, 5 (6), 7559-7574.
- Wright R.H., Palkovits R., 2012, Development of heterogeneous catalysts for the conversion of levulinic acid to  $\gamma$ -valerolactone, *ChemSusChem*, 5(9), 1657-1667.
- Xu Q., Li X., Pan T., Yu C., Deng J., Guo Q., Fu Y., 2016, Supported copper catalysts for highly efficient hydrogenation of biomass-derived levulinic acid and  $\gamma$ -valerolactone, *Green Chemistry*, 18, 1287-1294.
- Yan K., Chen A., 2013, Efficient hydrogenation of biomass-derived furfural and levulinic acid on the facilely synthesized noble-metal-free Cu-Cr catalyst, *Energy*, 58, 357-363.
- Yan K., Chen A., 2014, Selective hydrogenation of furfural and levulinic acid to biofuels on the ecofriendly Cu-Fe catalyst, *Fuel*, 115, 101-108.
- Zhang J., Chen J., Guo Y., Chen L., 2015, Effective Upgrade of Levulinic Acid into  $\gamma$ -valerolactone over an Inexpensive and Magnetic Catalyst Derived from Hydrotalcite Precursor, *ACS Sustainable Chemistry & Engineering*, 3(8), 1708-1714.
- Zhang L., Lu X., Wang W., Liu Y., 2013, Hydrogenation of levulinic acid to  $\gamma$ -valerolactone over Co/Al<sub>2</sub>O<sub>3</sub> catalyst, *Gongye Cuihua*, 21(7), 68-71.