

DOI: 10.17516/1998-2836-0211

УДК 544.472.2; 547.458.8

Hydrogenation of Levulinic Acid to γ -Valerolactone in the Presence of Ru-Containing Catalysts Based on Carbon Material “Sibunit”

Valentin V. Sychev^{a*},

Sergei V. Baryshnikov^a, Ivan P. Ivanov^a,

Mikhail N. Volochaev^b and Oxana P. Taran^{a,c}

^a*Institute of Chemistry and Chemical Technology SB RAS
FRC “Krasnoyarsk Science Center SB RAS”*

Krasnoyarsk, Russian Federation

^b*Kirensky Institute of Physics SB RAS*

Krasnoyarsk, Russian Federation

^c*Siberian Federal University*

Krasnoyarsk, Russian Federation

Received 18.01.2021, received in revised form 16.02.2021, accepted 10.03.2021

Abstract. Nanostructured 1 and 3% catalysts containing ruthenium nanoparticles supported on the initial and oxidized at different temperatures graphite-like carbon material Sibunit-4 prepared. A features of this support are mesoporous texture, hydrothermal stability and the presence of surface oxygen-containing functional groups responsible for the distribution of Ru nanoparticles and the catalyst acidic properties. The catalysts characterized using methods TEM, XPS, N₂ adsorption, pH_{pzc} and tested in the hydrogenation of levulinic acid to γ -valerolactone. It was found that the reaction rate and GVL selectivity are influenced by solvent choice, fractional composition, and acidic properties of the support. The obtained catalysts provide high activity in the reaction of direct hydrogenation of levulinic acid to γ -valerolactone (GVL yield 98 mol.%, At 160°C, 1.2 MPa H₂) and high productivity (15.9 gGVL/gCat.). Obtained catalyst can be reused several times without noticeable loss of activity.

Keywords: heterogeneous catalysis, gamma-valerolactone, levulinic acid, alkyl levulinate, hydrogenation, reduction, ruthenium, Ru/C.

Citation: Sychev V.V., Baryshnikov S.V., Ivanov I.P., Volochaev M.N., Taran O.P. Hydrogenation of levulinic acid to γ -valerolactone in the presence of Ru-containing catalysts based on carbon material “Sibunit”, J. Sib. Fed. Univ. Chem., 2021, 14(1), 5-20. DOI: 10.17516/1998-2836-0211

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* Corresponding author E-mail address: sychev.vv@icct.krasn.ru

Гидрирование леулиновой кислоты до γ -валеролактона в присутствии Ru-содержащих катализаторов на основе углеродного материала Сибунит

В. В. Сычев^а, С. В. Барышников^а,
И. П. Иванов^а, М. Н. Волочаев^б, О. П. Таран^{а, в}

^аИнститут химии и химической технологии СО РАН
ФИЦ «Красноярский научный центр СО РАН»

Российская Федерация, Красноярск

^бИнститут физики им. Л.В. Киренского СО РАН
Российская Федерация, Красноярск

^вСибирский федеральный университет
Российская Федерация, Красноярск

Аннотация. Синтезированы наноструктурированные 1 и 3 % катализаторы, содержащие наночастицы рутения, закрепленные на исходном и окисленном при разных температурах графитоподобном углеродном материале Сибунит-4. Особенность данного носителя состоит в его мезопористой текстуре, гидротермальной устойчивости и наличии на поверхности кислородсодержащих функциональных групп, ответственных за распределение наночастиц Ru и кислотные свойства катализатора. Катализаторы исследованы физико-химическими методами (ПЭМ, РФЭС, адсорбция N₂, рН_{тнз}) и испытаны в реакции гидрирования леулиновой кислоты до γ -валеролактона. Установлено, что на скорость реакции и селективность процесса по отношению к ГВЛ оказывают влияние такие факторы, как выбранный растворитель, фракционный состав и кислотные свойства носителя. Полученные катализаторы показали высокую активность в реакции прямого гидрирования леулиновой кислоты до γ -валеролактона (выход ГВЛ 98 мол.% при 160 °С, 1.2 МПа Н₂) и высокую производительность (15.9 г ГВЛ/г кат.). Данный катализатор может быть использован многократно без заметной потери активности.

Ключевые слова: гетерогенный катализ, гамма-валеролактон, леулиновая кислота, алкиллеулилаты, гидрирование, восстановление, рутений, Ru/C.

Цитирование: Сычев, В.В. Гидрирование леулиновой кислоты до γ -валеролактона в присутствии Ru-содержащих катализаторов на основе углеродного материала Сибунит / В.В. Сычев, С.В. Барышников, И.П. Иванов, М.Н. Волочаев, О.П. Таран // Журн. Сиб. федер. ун-та. Химия, 2021, 14(1). С. 5-20. DOI: 10.17516/1998-2836-0211

Introduction

The modern world economy rely heavily on the use of products (motor fuels, chemical products and synthetic polymers) derived from carbon-containing feedstock (oil and natural gas). Which causes a high demand for these raw materials, and leads to its gradual depletion. The problems of environmental pollution and global warming caused by CO₂ concentration increase in the

atmosphere (by 30% over the last 50 years) are associated with the extensive use of fossil organic resources, due to the increasing consumer demand of the growing world population. These factors stimulate research aimed to find renewable carbon-neutral organic resources, and lately a significant increase in research activity is observed related to the approaches development of plant biomass catalytic conversion [1, 2].

Lignocellulosic biomass, which is largely represented by the waste from woodworking and agricultural production, as well as highly productive herbaceous plants (miscanthus, millet, flax, hemp), is an excess, carbon-containing, and most importantly, a carbon-neutral resource, the use of which can ensure sustainable production of fuels and chemicals with high added value, and reduce the consumption of fossil raw materials [3].

Gamma-valerolactone (GVL) is one of the most valuable chemicals derived from lignocellulosic biomass. GVL is characterized by a low melting (-31°C), high boiling (207°C) and flash (96°C) points, low toxicity and low vapor pressure (0.65 kPa). GVL is highly stable, miscible with water at any ratio, does not form azeotropes. Due to these properties, GVL attracts more and more attention, and the number of publications devoted to methods of its synthesis and possible applications is steadily growing [4]. GVL can serve as a feedstock for the production of biopolymers, biofuels, and can be used both in the food and pharmaceutical industries. GVL and its derivatives can be used as additives for hydrocarbon fuels [3-7].

GVL is mainly produced by catalytic hydrogenation of levulinic acid (LA) and levulinic acid esters (LAE) produced from lignocellulosic biomass [7]. In addition, both cellulose and hemicellulose can be used as a feedstock for the production of GVL, which makes the economy of the total process more attractive [5]. Heterogeneous metal catalysts, due to their environmental friendliness, ease of use and convenience of separation, compared to homogeneous catalysts, attract the great deal of attention in the processes of direct hydrogenation (the use of molecular hydrogen) of LA and LAE to GVL. Platinum group metals such as Pt, Pd, Ru are widely used as an catalysts active component. Catalysts based on platinum and palladium provide high conversions of levulinic acid and its esters, but in terms of selectivity to GVL they are significantly inferior to catalysts based on Ru. Catalysts containing transition metals (Cu and Ni), for example, Cu/ Al_2O_3 , are quiet unstable and can quickly lose their activity as a result of the active component leaching [6].

The process of direct hydrogenation of LA and AL to GVL is carried out in the liquid phase in water or water-alcohol media, in which the use of microporous supports which prevent the transport of the substrate to catalyst active sites is excluded. The liquid phase catalysts should be developed using mesoporous, resistant to hydrothermal medium supports, such as graphite-like carbon material (CM) of the Sibunit® series [8, 9].

This work aims at aim solid catalysts development for direct hydrogenation of LA and LAE to GVL based on the mesoporous graphite-like material Sibunit bearing ruthenium nanoparticles as an active component.

Based on CM Sibunit-4, a series of supports varied by acidity and grains size was prepared and then used to obtain 1 and 3% ruthenium catalysts, characterized by different dispersion of the active component. The catalysts were investigated by TEM, N_2 adsorption, XPS, and pH_{pzc} , and tested in the process of direct hydrogenation of LA to GVL.

Experimental

In this work, the following chemicals were of reagent grade: γ -valerolactone 98% (Sigma-Aldrich), levulinic acid 98% (Sigma-Aldrich), ruthenium nitrosyl nitrate $\text{Ru}(\text{NO})(\text{NO}_3)_3$ $\text{Ru} \geq 31.9\%$ (Sigma-Aldrich), isopropanol, (Khimreaktivsnab), ethanol 96% (Khimreaktivsnab). To prepare all catalysts and solutions water purified on a Milli-Q unit (Millipore, France) was used.

Preparation of Ru/C Catalysts

Carbon samples were prepared using the commercial mesoporous carbon material Sibunit®-4 (S4) (Center of New Chemical Technologies, Federal Research Center Institute of Catalysis, SB RAS, Omsk). The carbon material was preliminarily washed in hot deionized water to remove possible metal impurities and dried in argon flow at 150°C. To obtain a desired fraction with a carbon particle size of 56-94 μm , CM was ground in a porcelain mortar and sieved. To obtain oxidized samples, sibunit was oxidized by a wet air mixture. Oxidation was carried out in a quartz cell placed in an oven. The cell filled with CM was preliminarily purged with argon (flow 200 ml/min, 0.5 h), then a mixture of 20 vol% O_2 in N_2 was fed into the cell in the presence of water vapor at a given temperature (400, 450, 500°C) (flow 200 ml/min, 2 h) [9].

Ruthenium catalysts based on the initial and oxidized S4 samples (1% Ru/C, 3% Ru/C) were obtained by incipient wetness impregnation using an aqueous solution of $\text{Ru}(\text{NO})(\text{NO}_3)_3$, followed by drying at room temperature for 2-3 h and at 60°C for 12 h. The reduction of the active component was carried out in a stream of hydrogen (flow 30 ml/min) at 300°C for 2 h (the temperature ramp 1°C/min), after cooling to room temperature in a hydrogen atmosphere the catalyst was passivated with a gas mixture of 1% O_2 in N_2 (flow 200 ml/min, 0.5 h) [9].

Characterization of the carbon supports and the supported Ru catalysts

The textural properties of the samples were determined via N_2 adsorption at 77 K using ASAP-2020 Plus analyzer (Micromeritics, United States).

High-resolution electron images for Ru/C catalysts were obtained using an HT7700 transmission electron microscope (Hitachi, Japan, 2014) with an accelerating voltage of 110 kV and a resolution of 2 Å. Particle size distribution histograms were obtained as a result of statistical (500-800 particles) processing. The mean linear particles size ($\langle d_l \rangle$) and mean surface volume particle size ($\langle d_s \rangle$) were calculated using the formulas (1) and (2):

$$\langle d_l \rangle = \sum d_i / N, \quad (1)$$

$$\langle d_s \rangle = \sum d_i^3 / \sum d_i^2 \quad (2)$$

where d_i – measured diameter of a Ru particle; N – the total number of Ru particles.

Dispersion of Ru (D_{Ru}) in prepared catalyst was calculated using formula (3):

$$D_{\text{Ru}} = 6 \cdot \frac{M_{\text{Ru}}}{a_{\text{Ru}} \cdot \rho \cdot N_0 \cdot \langle d_s \rangle} \quad (3)$$

where M_{Ru} is the atomic weight of ruthenium (0,101 kg/mol), ρ is the density of ruthenium (12410 kg/m³), a_{Ru} is the average effective area occupied by a Ru atom on the surface ($6,13 \cdot 10^{-20}$ m²), N_0 is the Avogadro number, d_s – the mean volume-surface particle size [9].

Photoelectron spectra were recorded using SPECS spectrometer with a PHOIBOS MCD9 hemispherical energy analyzer under excitation with monochromatic Al K α radiation, the electron collection angle is 90°. Element concentrations were determined from survey spectra. When the spectra were analyzed using the CasaXPS package, the nonlinear Shirley background was subtracted and the Gaussian-Lorentzian shape of the peaks was used.

The catalysts acidity was investigated by the point of zero charge (PZC) by the Seurensen de Bruijn method [10]. At first 10 ml of distilled water was introduced into a potentiometric cell, then with continuous stirring with a magnetic stirrer, at regular intervals (5-10 minutes) the CM test sample was sequentially added in small portions (0.01 g each) until the unchanged values of the potential of the glass electrode were reached [10].

Catalytic testing of obtained catalysts

The catalytic hydrogenation of levulinic acid was carried out in a 100 ml Autoclave Engineers (USA) autoclave made of Hastelloy C276 material at 160°C, 1.2 MPa H₂, with constant stirring (800 rpm) by a mechanical propeller-type stirrer with a magnetic drive. At first, an autoclave was charged with 2.5 g of levulinic acid, 0.125 mg of catalyst, and purged three times with argon with stirring. Then, hydrogen was supplied, raising the pressure in the reactor to 1.2 MPa, and then the reactor was heated to 160°C. During the experiments, samples were taken to determine the concentrations of levulinic acid and γ -valerolactone in the course of the process.

The concentrations of the substrate and the target product were determined using HPLC Milichrom A-02 (EkoNova, Russia) equipped with a UV detector (registration at $\lambda = 210$ nm) and a chromatographic column "Diaspher-250-PA", 5 μ m, 2 \times 75 mm (EkoNova, Russia), eluent – (85% 0.075M LiClO₄, 15% ACN), H₂O.

The conversion of levulinic acid, the yield and selectivity to GVL were calculated according to equations (4) – (6):

$$\chi_{LA} = \frac{C_{LA,0} - C_{LA}}{C_{LA,0}} \cdot 100\%, \quad (4)$$

$$Y_{GVL} = \frac{C_{GVL}}{C_{LA,0}} \cdot 100\%, \quad (5)$$

$$S_{GVL} = \frac{Y_{GVL}}{\chi_{LA}} \cdot 100\%, \quad (6)$$

χ_{LA} – LA conversion (mol.%); $C_{LA,0}$ – initial concentration of LA (mol/l); C_{LA} – current LA concentration (mol/l), Y_{GVL} – GVL yield (mol.%), S_{GVL} – GVL selectivity.

In order to study the effect of the Ru dispersion on the catalytic performance of obtained catalysts catalyst activity TOF (Turnover frequency) was calculated using obtained experimental data:

$$TOF = \frac{v(GVL)}{v(Ru) \times t(\text{reaction})}, \quad (7)$$

where: v (GVL) is the amount of moles of gamma-valerolactone formed, v (Ru) is the amount of moles of ruthenium in the catalyst, t (reaction) is the reaction time equal to 0.25 h and the values of the catalyst productivity in relation to GVL (P_{GVL}), reflecting the ratio of the mass of GVL formed during the reaction (gGVL) to the mass of the loaded catalyst (gCat.) [11]:

$$P_{GVL} = \frac{g_{GVL}}{g_{Cat.}} \quad (8)$$

Results and discussion

Ruthenium was chosen to be the active metal due to the highest activity in the reactions of direct hydrogenation of aliphatic carbonyl compounds [12] and the maximum selectivity to GVL among other platinum group metals [5]. Catalysts based on the mesoporous graphite-like support Sibunit-4 (S4) with a Ru particle size around 1 nm, containing 3% ruthenium, showed good catalytic performance in a number of oxidative [9] and reduction processes [8] in water and water-alcohol media. In these studies, the support was preliminarily oxidized with wet air at a temperature of 400 or 450°C to form acid groups on the surface of the support [9, 13]. This treatment also leads to a stronger binding of Ru to the support, a decrease in the size of metal nanoparticles, and as result to the increase of the Ru dispersio. In addition, the presence of acid sites on the catalyst surface can change the route of the catalytic process for the hydrogenation of LA in GVL in accordance with the scheme of this process proposed by a number of works [12, 14] (Fig. 1).

In this work, to reveal the effect of the support acidity, the active component dispersion, and the particle size of the S4 support, a series of two supports with a particle size of 54-96 μm was prepared (initial (S), oxidized at 450°C (S450) samples) and two granular supports with a particle size of 1.0-1.6 mm (initial (Sg) and oxidized at 500°C (S500g)) (Table 1). On the obtained supports, catalysts containing 3 wt.% Ru were prepared, which are hereinafter referred to as: 3RS, 3RS450, 3RSg, 3RS500g, respectively. To assess the possibility of the active component amount reduction, which is a metal of the platinum group, a catalyst was prepared with a ruthenium content of 1 wt.% (1RS450).

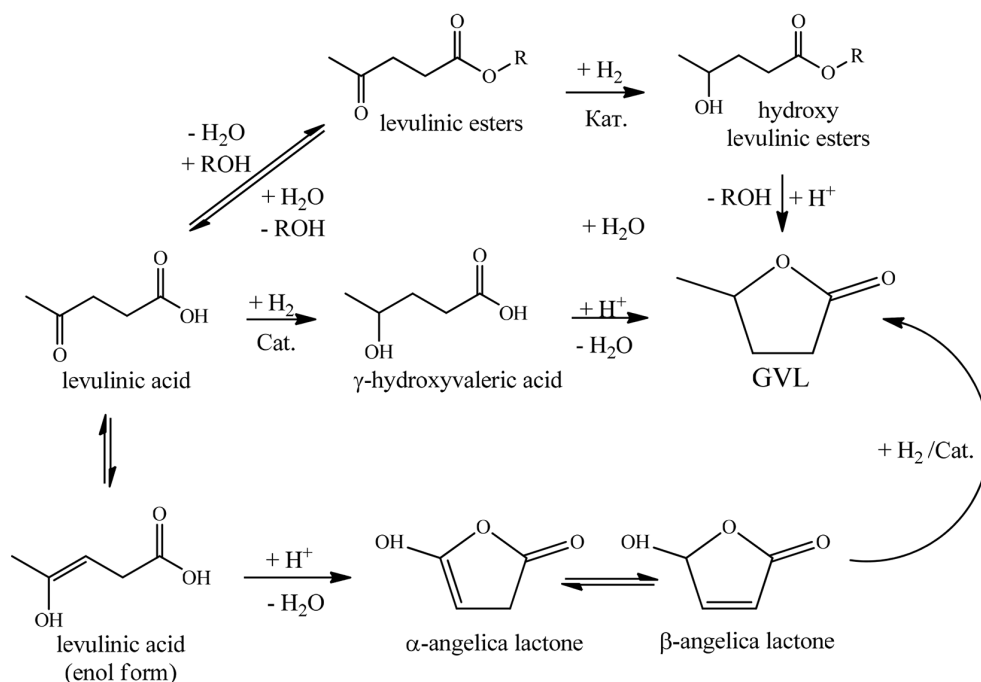


Fig. 1. Reaction pathways of LA to GVL direct hydrogenation

Table 1. Textural characteristics of carbon supports and Ru/C catalysts

№	Support/Catalyst	Code	Ru particle size, nm*				D_{Ru}^*	pH_{pzc}^{**}	Textural characteristics***		
			d_{min}	d_{max}	$\langle d_l \rangle$	$\langle d_s \rangle$			S_{BET} , m ² /g	V_{pore} , cm ³ /g	$\langle d_{pore} \rangle$, nm
1	Sib-4****	S	-	-	-	-	-	7.59	375	0.55	5.87
2	3%Ru/Sib-4****	3RS	0.60	2.73	1.22±0.01	1.48	0.88	8.01	321	0.43	5.45
3	Sib-4-ox-450****	S450	-	-	-	-	-	5.33	380	0.53	5.66
4	1%Ru/Sib-4-ox-450****	1RS450	0.52	1.79	1.06±0.03	1.27	1.03	6.06	368	0.52	4.80
5	3%Ru/Sib-4-ox-450****	3RS450	0.52	2.37	1.13±0.01	1.39	0.94	6.89	341	0.50	5.88
6	Sib-4-granules****	Sg	-	-	-	-	-	7.66	364	0.51	5.66
7	3%Ru/Sib-4-granules****	3RSg	0.76	3.46	1.42±0.02	1.71	0.77	8.05	273	0.32	4.77
8	Sib-4-ox-500-granules****	S500g	-	-	-	-	-	3.34	287	0.37	5.14
9	3%Sib-4-ox-500-granules****	3RS500g	0.69	3.14	1.30±0.01	1.53	0.85	6.44	233	0.28	4.80

* Ru particles sizes obtained by TEM statistical analysis. d_{min} , d_{max} – minimum and maximum diameter of the particles; $\langle d_l \rangle = \Sigma d_i / N$ – the mean linear particle size; $\langle d_s \rangle = \Sigma d_i^3 / \Sigma d_i^2$ – the mean volume_surface particle size. D_{Ru} – Dispersion of Ru.

** pH_{pzc} – pH of the point of zero charge.

*** Textural characteristics obtained via N₂ adsorption data analysis. S_{BET} – specific surface area (m²/g), V_{pore} – total pore volume (cm³/g), $\langle d_{pore} \rangle$ – average pore diameter (nm).

**** Fractional composition: powder – 56-94 μm; grains – 1.0 – 1.6 mm.

Characterization of the Carbon Supports and the Supported Ru Catalysts

Textural characteristics and morphology of carbon supports and ruthenium catalysts

Analysis of the textural characteristics obtained via N₂ adsorption (Table 1) of carbon supports showed that oxidative treatment leads to a decrease in the volume (V_{pore}) (0.55 and 0.53 cm³/g – samples S, S450, respectively; 0.51 and 0.37 cm³/g – samples Sg, S500g, respectively), as well as the average pore size ($\langle d_{pore} \rangle$) (5.87 and 5.66 – samples S, S450, respectively; 5.66 and 5.14 nm – samples Sg, S500g, respectively), which is more noticeable for the support oxidized at 500°C. This apparently results from loosening of the graphite-like structure of CM Sibunit-4 during oxidation, and more significant loosening at a higher oxidation temperature. The specific surface area (S_{BET}) for the support oxidized at 450°C is slightly higher (380 m²/g) than for the initial one (375 m²/g), and for the support oxidized at 500°C it is significantly lower (287 m²/g). than the original (364 m²/g). As shown in [13], such a decrease in the surface area may be due to the partial destruction of Sibunit globules during its excessive oxidation.

The Ru deposition leads to a decrease in S_{BET} (375 – 321 m²/g, 364 – 273 m²/g – unoxidized samples 3S – 3RS, 3Sg – 3RSg, respectively; 380 – 341 m²/g, 287 – 233 m²/g – oxidized samples S450 – 3RS450, S500g – 3RS500g, respectively), V_{pore} (0.55 – 0.43 cm³/g, 0.51 – 0.32 cm³/g – unoxidized samples 3S – 3RS, 3Sg – 3RS, respectively; 0.53 – 0.50 cm³/g, 0.37 – 0.28 cm³/g – oxidized samples S450 – 3RS450, S500g – 3RS500g, respectively), apparently as a result of partial blocking of some

support pores with particles of the active component (Table 1). This effect is enhanced with an increase in the amount of the active component from 1 to 3 wt.%. For the average pore diameter, the correlation with the amount of deposited metal is not so obvious. For the support S450 and catalysts IRS450, 3RS450 d_{pore} changes in the row: 5.66; 4.80; 5.88.

The morphology of the catalysts was investigated in more detail by transmission electron microscopy (TEM) (Fig. 2). Statistical processing of the obtained high-resolution images made it possible to obtain the distribution of ruthenium particles by size, as well as to calculate the particle diameters and dispersion of ruthenium for each of the catalysts (Table 1).

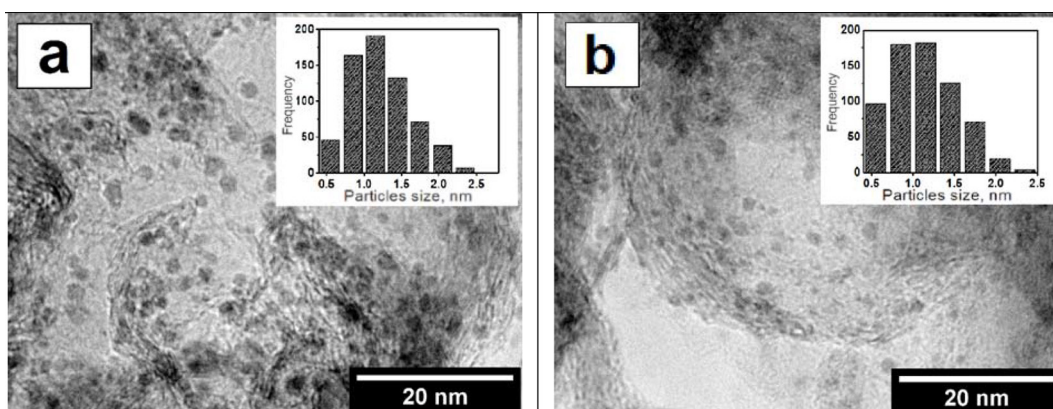


Fig. 2. TEM images of catalysts (a – 3% Ru/Sib-4, b – 3% Ru/Sib-4-ox-450)

All oxidized samples are characterized by a smaller size of ruthenium particles, the distribution of ruthenium particles on granular supports is less uniform, the average particle diameter decreases in the following order: 1.42; 1.30; 1.22; 1.13; 1.06 for catalysts 3RSg; 3RS500g; 3RS; 3RS400; 3RS450; IRS450, respectively, which indicates a more uniform distribution of ruthenium precursor when applied to oxidized samples, presumably as a result of interaction between the support surface and negatively charged oxygen-containing functional groups, the number of which increases with an increase in the oxidative treatment temperature of the support (Table 1). Dispersion increases with decreasing particle size with a more uniform distribution of ruthenium in the series: 0.77; 0.85; 0.88; 0.94; 1.03 for catalysts 3RSg; 3RS500g; 3RS; 3RS400; 3RS450; IRS450, respectively (Table 1). It should be noted that for the IRS450 catalyst, taking into account the error in determining the average particle diameter ruthenium dispersion is higher than 1, which indicates that all ruthenium atoms are on the surface and are available for reagents (Table 1).

Chemical composition of the catalysts surface

The study of the acidic properties of the supports, carried out by determination of the pH of the point of zero charge, showed a decrease in the pH_{pzc} values as the temperature of the oxidative treatment of CM increased (7.59 – 5.33 – samples 3S, 3S450; 7.66 – 3, 34 samples 3Sg, 3S500g), which may indicate an increase in the concentration of surface acid groups [9]. The deposition of ruthenium leads to a slight increase in pH_{pzc} values (7.59 – 8.01; 7.66 – 8.05; 3.44 – 6.44 – the deposition of 3 wt.%

Ru on 3S, 3Sg, 3S500g supports; for the S450 support and catalysts 1RS450 and 3RS450, pH_{pzc} changes in row: 5.33; 6.06; 6.89) due to the blocking of surface acid groups by ruthenium particles (Table 1).

The surface chemical composition was studied in more detail by the XPS method in catalysts 3RS, RS450, 3RS450. All samples are characterized by the most intense peaks in the range of 284-285 eV, typical of graphite. In the region of 285-287 eV, there are peaks characteristic of carbonyl, hydroxyl and ether groups, as well as fragments of carboxyl groups.

In the region of 281 eV, a Ru $3d_{5/2}$ peak is observed, which relates to the oxidized form of ruthenium RuO_2 . Metallic ruthenium is characterized by a peak in the region of 280 eV, however, this shift to the region of higher binding energies can also be explained by the relaxation shift, which is observed in the presence of especially small metal particles (Fig. 3) [15]. It should be noted that an increase in the oxygen content from 8.4 to 9.2 wt.% in the 3RS and 3RS450 catalysts due to increase in the oxidative treatment temperature confirms the formation of surface oxygen-containing groups on the support surface (Table 2).

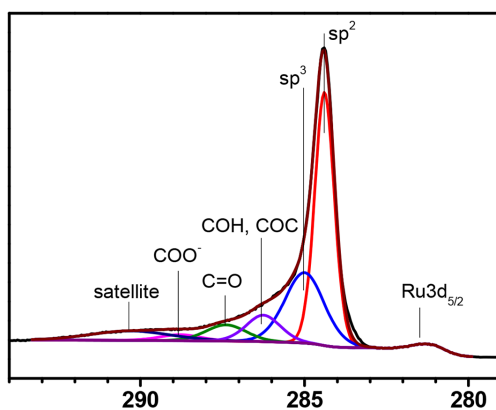


Fig. 3. C 1s XPS spectrum of prepared 3% Ru/Sib-4-ox-450 catalyst

Table 2. Elemental composition of the catalyst surface determined by the XPS method

Catalyst	C		O		Ru	
	at.%	wt.%	at.%	wt.%	at.%	wt.%
3RS	92.4	85.4	6.8	8.4	0.8	6.2
3RS450	91.9	84.9	7.5	9.2	0.6	4.7
1RS450	92	85.0	7.6	9.4	0.4	3.1

Catalytic properties

The reaction conditions play a key role in influencing both the reaction rate and the selectivity of the process. In most studies, the process of LA hydrogenation to GVL is carried out in the temperature range 130-200°C and under hydrogen pressure of 0.5-4.5 MPa [16-20]. The reaction time reaches 24-40 hours [3, 18]. Harsher reaction conditions can lead to the subsequent hydrogenation of GVL to 2-methyltetrahydrofuran and 1,4-pentanediol [5, 18, 20], taking this into account, it is recommended

to reduce the hydrogen pressure to 1.0–1.2 MPa, while maintaining a rather high process temperature 160–200°C. The obtained catalysts were tested under the same (model) reaction conditions (160°C, 1.2 MPa).

Influence of the solvent on the process

In order to study the effect of the solvent on the process of direct hydrogenation of LA to GVL, a series of experiments was carried out; a sample with 3% ruthenium content on the original, unoxidized support (No. 2, Table 1) was chosen to be the catalyst. The use of isopropanol as a solvent made it possible to obtain a GVL yield of as high as 98 mol.%, with a complete conversion of the substrate. The conversion of LA and the selectivity of the catalyst to GVL were noticeably lower in the water-ethanol mixture (82 mol.% and 64%, respectively), the use of pure ethanol as a solvent led to a significant decrease in the conversion of LA to 59 mol.%, as a result of which, the obtained yield of GVL was only 44 mol.%, while using water as a solvent, it was possible to obtain the yield of GVL up to 92 mol.% (Table 3). The high yield of GVL in isopropanol (> 98 mol.%) can be explained by a slightly higher solubility of hydrogen compared to ethanol (at 20°C, 101.325 kPa H₂, the molar fractions are $2.26 \cdot 10^4$ and $2.00 \cdot 10^4$, respectively [21]) and better hydrogen-donor properties of isopropyl alcohol in comparison with other solvents [22]. The high yield of GVL in water (92 mol.%) will be discussed in more detail in the “Study of the reaction kinetics” section.

Table 3. Influence of the solvent on the process of direct hydrogenation of LA to GVL*

№	Solvent	χ_{LA}^{**} , mol.%	S_{GVL}^{**} , %	Y_{GVL}^{**} , mol.%
1	i-PrOH	100	98	98
2***		82	92	75
3	H ₂ O	100	92	92
4	H ₂ O:C ₂ H ₅ OH	82	64	52
5	C ₂ H ₅ OH	59	75	44

*Reaction conditions: 2.5 gLA, 0.125 gCat. (3RS), 1.2 MPa H₂, 160°C, 195 min.

** Catalytic properties: χ_{LA} – LA conversion, S_{GVL} – GVL selectivity, Y_{GVL} – GVL yield.

*** Fractional composition: 1.0 – 1.6 mm (grains).

Study of reaction kinetics

Reaction kinetics show (Fig. 4) that when using water as a solvent, the maximum GVL yield (92 mol.%) was obtained in 45 minutes, while in isopropanol the maximum yield (92 mol.%) was achieved only at 105 minutes, although the maximum conversion of LA, in isopropanol, was reached faster than in water (by 15 and 75 minutes, respectively). This phenomenon can be explained by several factors: water, as a solvent, has a promoting effect on the hydrogenation process when using a ruthenium catalyst [17, 23, 24], and avoids formation of ethers (using alcohols as a solvent) as unwanted by-products the formation of which reduces the rate of formation of GVL [17-19, 25]. The promoting effect of water can be described as follows; on the one hand, coadsorbed water molecules, interacting with adsorbed acid molecules, are capable of lowering the activation energy of the hydrogenation of the carbonyl group [22]; on the other hand, water molecules adsorbed on the surface of ruthenium can

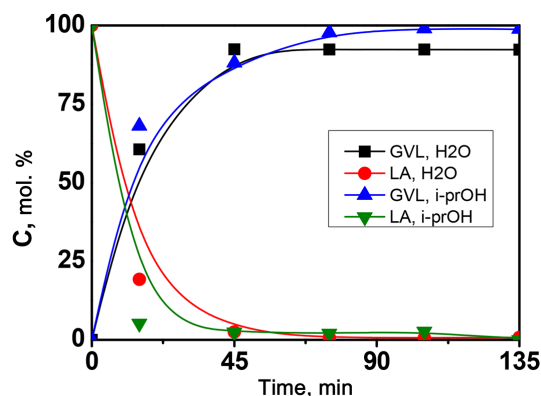


Fig. 4. Kinetics comparison of LA to GVL direct hydrogenation in water and isopropanol

polarize and undergo dissociation, which leads to the formation of surface Ru -OH groups and H⁺ ions, which are involved in the protonation of the carbonyl group [26].

The study of the influence of the fractional composition on the reaction kinetics showed an unambiguous advantage of the powder catalyst (fraction 56 – 94 μm) over granular (fraction 1-1.5 mm). There is a decrease in both the GVL yield when using a granular catalyst within reaction time (195 min) (from 92 to 89 mol.% for catalysts 3RS, 3RSg; from 83 to 78 mol.% for catalysts 3RS450, 3RS500g respectively) (Table 4), and reaction rate; for powder catalysts, the maximum yield is achieved at 45 minutes, while for granular catalysts, the kinetic curves plateau of GVL formation are not observed, which is evidently due to diffusion obstruction (Fig. 5).

The increase of the support acidity leads to the increase in the rate of GVL formation and to the decrease in the selectivity of the process, while maintaining an invariably high conversion of LA (99–100 mol.%) (Table 4, Fig. 5). The maximum selectivity of the process of direct hydrogenation of LA to GVL in an aqueous medium (92%) is achieved using catalysts 3RS and 3RSg, which have weak basic pH_{pzc} values and minimal Ru dispersion (No. 1, 2; Table 4, Fig. 6). As an intermediate product, when using Ru/C catalysts, γ-hydroxyvaleric acid (GHV)/GHV esters [25] are predominantly formed, but in some cases, for example when using dendrimer support, the main intermediate product may be

Table 4. The influence of support acidity and Ru dispersion on LA to GVL direct hydrogenation in water*

№	Catalyst	pH _{pzc} **	D _{Ru} ***	TOF***, h ⁻¹	χ _{LA} ****, mol.%	Y _{GVL} ****, mol.%	P _{GVL} ****
1	3RS	8.01	0.88	1533	100	92	15.9
2	3RSg	8.05	0.77	1188	100	89	15.3
3	3RS450	6.89	0.94	2139	100	83	14.3
4	1RS450	6.06	1.03	5503	100	79	13.6
5	3RS500g	6.44	0.85	1229	99	78	13.5

*Reaction conditions: 2.5 gLA, 0.125 gCat., 1.2 MPa H₂, H₂O 50 ml, 160°C, 195 min **pH_{pzc} – pH of the point of zero charge.

***D_{Ru} – dispersion of ruthenium.

****Catalytic properties: TOF – Turnover frequency, χ_{LA} – LA conversion, Y_{GVL} – GVL yield, P_{GVL} – GVL productivity (gGVL/gCat.).

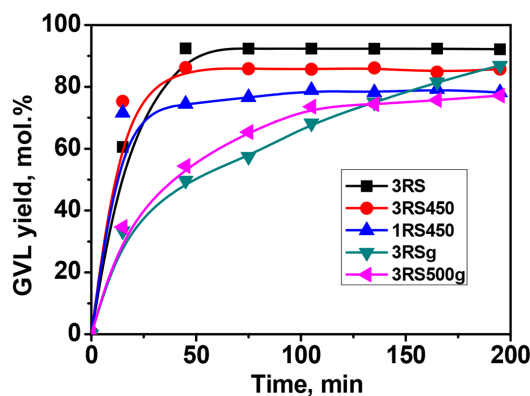


Fig. 5. Kinetic curves of GVL formation in the process of direct hydrogenation of LA for catalysts series

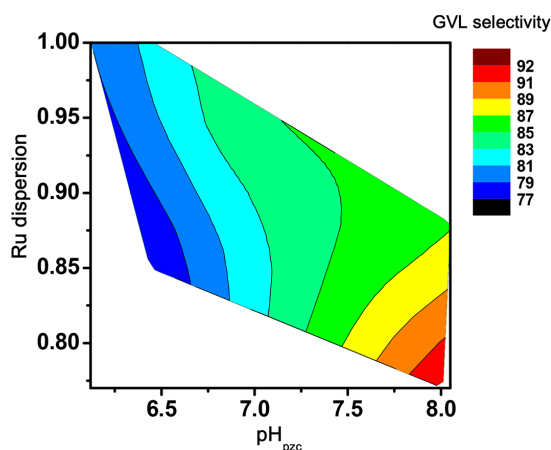


Fig. 6. The influence of catalyst pH_{pzc} and Ru dispersion on GVL selectivity

angelica lactone [24] (Fig. 1). In our case, angelica lactone was not detected in the reaction mixture. And the acceleration of the reaction as the acidity of the catalyst increases indirectly confirms the formation of GHV/GHV esters as an intermediate product [12]. An increase in the support acidity is presumably capable of accelerating the reaction both at the stage of hydrogenation of the keto group of LA and LAE and at the stage of subsequent intramolecular lactonization, when GHV/GHV esters lose a water/alcohol molecule and form a cycle (Fig. 1) [12].

Reducing the content of ruthenium in the catalyst with 3 wt.% up to 1 wt.% (samples 3RS450 and 1RS450, respectively) led to a decrease in the GVL yield from 83 to 79 mol.%, while maintaining full LA conversion. (No. 3, 4; Table 4)

Catalyst activity

For catalysts based on ruthenium, for example, Ru/C or Ru/Al₂O₃, from previous works devoted to the process of direct hydrogenation of LA to GVL, TOF values vary in the range 200 – 3322 h⁻¹ [18, 20, 24]. For the series of catalysts presented in this work, TOF values vary in the range 1229-5503 h⁻¹. The TOF values increase as the acidity of the catalysts increases; for powder catalysts 3RS and 3RS450,

TOF values are 1533 h⁻¹ and 2139 h⁻¹, respectively, for granular 3RSg and 3RS500g 1188 h⁻¹ and 1229 h⁻¹, respectively. Such an increase in TOF values is associated with an increase in the reaction rate, which is characteristic of more acidic catalysts (see the section “the study of the reaction kinetics”). Catalyst containing 1 wt.% Ru is characterized by the maximum TOF value (5503 h⁻¹), which is not surprising, since the decrease in the Ru content from 3 to 1 wt.% led to the insignificant decrease in the GVL yield by 4 mol.%, while maintaining a complete conversion of LA and reaching the maximum GVL yield (79 mol.%) within 75 minutes.

Catalyst productivity

From the point of view of industrial application of the catalyst, the amount of the formed target product (GVL productivity) is no less important parameter than the molar yield of the product [11]. For ruthenium catalysts, such as Ru/C, Ru/TiO₂, Ru/MCM-41, known from previous works devoted to the process of direct hydrogenation of LA to GVL using water as a solvent, the productivity values of GVL vary in the range 0.5-9.8 gGVL/gCat. [27, 28]. The series of catalysts presented in this work are characterized by productivity values of 13.5 – 15.9 gGVL/gCat. The highest productivity due to their maximum selectivity to GVL is demonstrated by the 3RS and 3RSg catalysts prepared using unoxidized CM Sibunit-4; the productivity values are 15.9 and 15.3 gGVL/gCat., respectively (Table 4, Fig. 7).

As the acidity of the support increases, the productivity decreases by 1.6 gGVL/gCat. for powder catalysts (3RS and 3RS450, respectively) and for 1.8 gGVL/gCat. for granular (3RSg and 3RS500g, respectively) (Table 4, Fig. 7).

Reusability tests of catalysts

For reusability tests, the catalyst providing the highest GVL yield in aqueous medium (3RS, 92 mol.%) was selected. The recycling procedure was performed according to the standard experimental procedure [16]. After synthesis, the catalyst was removed from the reaction mixture by filtration, washed with distilled water, dried and used in subsequent tests. A total of 3 cycles were performed. It was found that a 3% Ru catalyst based on CM Sibunit-4 (3RS) is stable and retains a high catalytic activity without a noticeable loss in both the LA conversion and selectivity to GVL after 3 cycles at 160°C, 1.2 MPa. H₂ and 195 min in the water (Fig. 8).

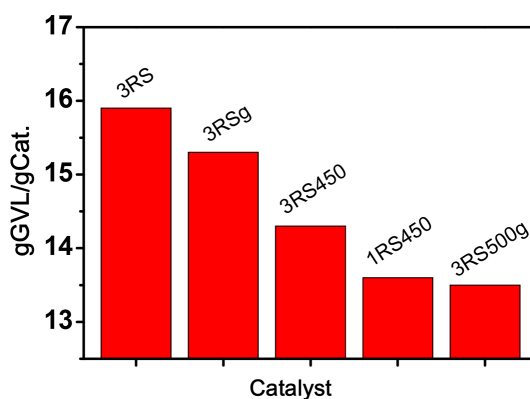


Fig. 7. Comparison of catalyst series productivity

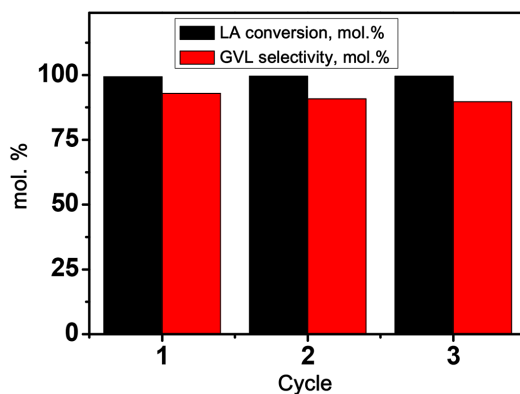


Fig. 8. Reusability tests of 3RS catalyst

Conclusion

Ruthenium catalysts based on carbon material (CM) Sibunit-4 were synthesized, characterized and tested in the reaction of direct hydrogenation of levulinic acid (LA) to γ -valerolactone (GVL). It was found, that the choice of the solvent and support acidity have a noticeable effect on the process of direct hydrogenation of LA to GVL. Water as a solvent has a promoting effect when using ruthenium catalysts. An increase in the acidity of the catalyst caused by an increase in the temperature of the oxidative treatment of the carbon support, results in the increase in the concentration of surface acid groups, which leads to the increase in the reaction rate and to the decrease in the yield of GVL, due to the decrease in the selectivity of the process, while maintaining invariably high values of LA conversion (> 99 mol.%). The maximum selectivity of the process of direct hydrogenation of LA to GVL in an aqueous medium is achieved using catalysts with weak basic pH_{pzc} values.

The activity of Ru-containing catalysts prepared using Sibunit-4 carbon material as a support is comparable to or exceeds the activity of the best Ru-containing catalysts studied in the reaction of direct hydrogenation of LA to GVL. The maximum obtained GVL yield is 98 mol.%, the TOF values of the prepared catalysts in direct hydrogenation of LA to GVL are 1229-5503 h^{-1} . The 3RS catalyst has the highest productivity among known from the literature (over 15.9 gGVL/gCat.) and can be used several times without noticeable loss of activity.

A catalyst with 3 wt.% ruthenium content, based on CM Sibunit-4 (3RS), can be proposed for the development of industrial processes for the direct hydrogenation of levulinic acid to γ -valerolactone.

Acknowledgment

This work was financially supported by the Russian Foundation for Basic Research (RFBR) (project No. 20-03-00636).

The equipment of the Krasnoyarsk Regional Center for Collective Use of the Federal Research Center of the KSC SB RAS was used.

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