

## Catalytic Hydrogenation of Levulinic Acid Using Ruthenium Dioxide Supported on Zeolites

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Levulinic acid (LA) is a substance, which can be obtained from cellulosic biomass via acid hydrolysis. 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. In this work, the reaction of LA hydrogenation to GVL was carried out using series of Ru-containing catalytic systems based on zeolites (HZSM-5, HBeta, HY, HMordenite). It was shown that synthesized catalyst based on zeolite HZSM-5, containing RuO<sub>2</sub> as an active phase, can provide high yields of GVL (up to 98 %) for less than 1 h upon relatively mild reaction conditions (100 °C, 1 MPa). Moreover, it was shown that the observed catalytic activity and stability depends on the concentration of RuO<sub>2</sub> on the catalyst surface as well as on distribution of catalytically active phase.

### 1. Introduction

In recent years, the search for new eco-friendly ways of production of fuels and energy is of high importance. Fast industrial development accompanied by the growth of the world population has led to excessive consumption of fossil fuels. As an alternative, plant biomass has been investigated as renewable source of energy and carbon (Mamun et al., 2017). As a result of processing of lignocellulosic biomass, a number of valuable chemical compounds can be obtained (Protsenko et al., 2016): furfural, 5-hydroxymethylfurfural (Garcia-Sancho et al., 2017), valeric acid, levulinic acid (LA) and other carboxylic acids and their esters (Yan et al., 2015). While being produced via acid hydrolysis of lignocellulosic biomass, LA can be converted into platform chemicals, one of which is GVL (Filiz et al., 2017). GVL is a non-toxic compound, "green" solvent and fuel additive synthesized by selective catalytic hydrogenation of LA and used as a feedstock for the production of valeric acid and its esters, 5-nonanone and 2-methyltetrahydrofuran (Alonso et al., 2013). Thus LA and GVL are important platform chemicals having high economic impact (Derle and Parikh, 2014).

At present, the effective transformation of renewable bio-materials into fuel additives using heterogeneous catalytic systems is widely studied. The development of new, efficient and environmentally friendly heterogeneous catalysts is a complex task in an industrial scale. In the context of the use of heterogeneous catalysts, there are several publications on the use of mixed oxides in biomass processing. For example, it has been shown that the use of mixed cerium and niobium oxides containing high percentage of niobium increases the number of Brønsted acid centers (BAC), thereby increasing the rate of fructose dehydration in 5-hydroxymethylfurfural (Guo et al., 2017). Mixed zirconium/tungsten oxides were used in the xylose dehydration process. It was shown that the introduction of aluminum into the catalyst composition leads to an increase in the conversion rate and yields of target products (Zhang et al., 2017). Aluminosilicates (or zeolites) are a promising type of solid catalysts and supports for heterogeneous catalysis due to their thermal and chemical stability, the ability to control acidity and structure (Dulie et al., 2020).

Zeolites represent a large group of aluminosilicate minerals, which are structurally composed of [SiO<sub>4</sub>]<sup>4-</sup>

tetrahedra arranged in such a way that large pores are formed in the crystals. Aluminum ions isomorphically replace silicon ions in the zeolite framework providing the existence of Lewis acid centers (LAC) and BAC. At present, more than one hundred varieties of synthetic zeolites are known (Brazovskaya and Golubeva, 2020). Zeolites are used as part of heterogeneous acidic composite catalysts in many industrial processes, such as catalytic cracking, hydrocracking, selective molding, hydroisomerization, dewaxing, alkylation, conversion of methanol to gasoline, reduction of NO<sub>x</sub>, etc. (Corma, 2003). As supports, zeolites are widely used in hydrogenation reaction (Mishra et al., 2013), since they are able to provide high catalytic activity with respect to various compounds under relatively mild conditions.

Currently, there are many heterogeneous catalytic systems for the transformation of LA into GVL: mono- and bimetallic systems based on non-noble (Ni (Hengst et al, 2015), Cu (Yanase et al., 2020), Zr (Demolis et al., 2014)) and noble (Ru (Piskun et al., 2018), Pd (Muñoz-Olasagasti, 2019), Ir (Wang et al., 2020)) metals, among which Ru is one of the most widely used one. Among the supports used for the synthesis of LA hydrogenation catalysts, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, and zeolites (HBeta, ZSM-5, and HY) are widely used (Muñoz-Olasagasti et al., 2019).

According to research, zeolite-based catalysts contribute to achieving high GVL yields (more than 90 %), due to the presence of BAC and LAC, hydrothermal stability, and porous structure. For example, Zhang et al. investigated the 5 % Ni/HZSM-5 catalyst in the LA hydrogenation reaction (Zhang et al., 2018). The maximum yield of GVL (100 %) using this catalyst was obtained at 210 °C and 3 MPa of hydrogen in 3 hours of reaction in an aqueous medium. Simakova et al. studied ruthenium (4 wt. %) catalytic systems based on aluminosilicates with different silica modules: HZSM-5 (SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> = 250); HBeta (30); HY (5); HUSY (30), preliminarily reduced in the H<sub>2</sub> flow (Simakova et al., 2019). The reaction was carried out in a medium of 1,4-dioxane at 165 °C and a hydrogen pressure of 1.6 MPa for 3.5 h, with the highest activity shown by 4 % Ru/HBeta. Gundekari et al. synthesized the catalyst based on hydrated ruthenium oxide (HRO) deposited on HBeta zeolite, which allowed achieving 100 % LA conversion in 7 min of the reaction in an aqueous medium at 100 °C and 5 MPa of H<sub>2</sub> (Gundekari and Srinivasan, 2019).

Earlier, it was shown (Nikoshvili et al., 2017) that the use of catalysts based on hyper-cross-linked polystyrene impregnated with RuO<sub>2</sub> allowed the development of active and selectivity catalysts of LA hydrogenation (more than 99 % yield of GVL was achieved for 2 h of the reaction at 90 °C and 2 MPa of hydrogen partial pressure in aqueous medium). It is noteworthy that ruthenium (IV) oxide has unique redox properties due to the presence of coordinative unsaturated of metal centers on the surface. This work is addressed to the study of RuO<sub>2</sub> immobilized on different zeolites in order to explore the support effect.

## 2. Experimental

### 2.1 Materials

ZSM-5 (silicate modulus (SM) equal to 40) in Na form was purchased from CJSC “Nizhegorodskie sorbenty” (Nizhny Novgorod, Russia). Zeolites Mordenite (SM = 20), Y (SM = 30) and Beta (SM = 25), all in Na form, were purchased from Alfa Aesar GmbH (Germany). Ruthenium hydroxychloride (Ru(OH)Cl<sub>3</sub>, Ru content 45.05%) was purchased from Aurat Ltd. (Moscow, Russia). LA (≥ 98 %) was purchased from Merck KGaA, Germany. GVL (ReagentPlus®, 99 %). Tetrahydrofuran (THF, ≥ 99.9%) and methanol (MeOH, ≥ 99.9%) were purchased from Sigma-Aldrich and were used as received. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 35-40%) and sodium hydroxide (NaOH, ≥ 99.5%) were 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

Before the catalyst synthesis, all the zeolites were transferred in Hform. In a typical experiment, 25 g of zeolite (ZSM-5, Mordenite, Y or Beta) were treated for 24 h with aqueous solution of NH<sub>4</sub>Cl (concentration 1 mol/L). Then zeolite was centrifuged and washed till neutral pH. After that obtained HZSM-5 was dried for 3 h at 105 °C with following calcination at 500 °C for 15 h. Resulting HZSM-5, HMordenite, HY or HBeta were used as catalytic support for RuO<sub>2</sub>.

Synthesis of zeolite-based catalysts was carried out by the incipient wetness impregnation method. In a typical experiment, 3 g of HZSM-5 were impregnated with aliquot of complex solvent (consisting of THF, MeOH and water in a ratio of 10 : 1 : 1) with dissolved therein calculated amount of Ru(OH)Cl<sub>3</sub> for 10 min. The Ru-containing zeolite was dried at 70 °C for 30 min, dried catalyst was treated with 10-20 mL of NaOH aqueous solution (concentration of 0.1 mol/L) at 80 °C and continuous stirring with the addition of 50 mL of H<sub>2</sub>O<sub>2</sub>, which allowed formation of a mixture of RuO<sub>2</sub>, Ru(OH)<sub>3</sub> and Ru<sup>0</sup> as a result of transformation of the initial precursor (Ru(OH)Cl<sub>3</sub>). Resulting catalyst was washed with distilled water until neutral pH and dried again at 70°C.

In this way, the following catalysts were synthesized (Ru content was confirmed by the XFA): Ru/HZSM-5

(4.2 wt. % of Ru); Ru/HBeta (3.8 wt. % of Ru); Ru/HY (4.0 wt. % of Ru); Ru/HMordenite (4.9 wt. % of Ru).

### 2.3 Procedure of levulinic acid hydrogenation

The hydrogenation reaction of LA to GVL (Figure 1) was carried out in Parr Series 5000 Multiple Reactor System at a stirring rate of 1000 rpm using cross-type stir bar, which allowed effective mixing in the reactor vessel. Reaction temperature was 100 °C. Partial hydrogen pressure was 1 MPa. Water was used as a solvent (total volume of liquid phase was 50 mL). In the case of Ru/HZSM-5, LA-to-catalyst ratio was 50 g/g. For other three samples the catalyst loading was varied in order to provide equal molar ratio of LA-to-Ru as it was in the case of Ru/HZSM-5.

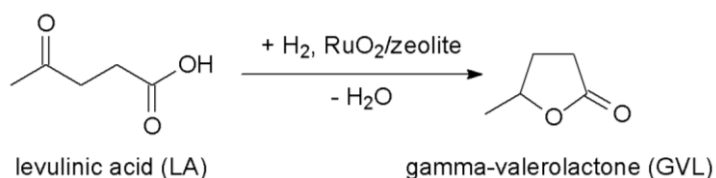


Figure 1: Simplified scheme of LA hydrogenation to GVL

Samples of the reaction mixture were analyzed via gas chromatography (Kristallux 4000M) equipped with flame ionization detector and capillary column ZB-WAX (60 m × 0.53 mm i.d., 1 μm film thickness). Temperatures of detector and injector were 250 °C and 300 °C, respectively. Column temperature was programmed as follows: 150 °C (13 min) then heating up to 230 °C (30°C/min) and then 230 °C for 7 min. Helium (30 mL/min) was used as a carrier gas. The concentrations of the reaction mixture components were calculated using absolute calibration method using chemically pure components of reaction mixture.

### 2.4 Catalyst characterization

Synthesized Ru/HZSM-5, Ru/HMordenite, Ru/HY, Ru/HBeta were characterized by liquid nitrogen physisorption, X-ray fluorescence analysis (XFA), X-ray photoelectron spectroscopy (XPS), scanning transmission electron microscopy (STEM).

Liquid nitrogen physisorption was carried out using Beckman Coulter SA 3100. Prior to the analysis, samples were degassed in Becman Coulter SA-PREP at 150°C under nitrogen for 1 h.

XFA was performed using Zeiss Jena VRA-30 spectrometer (Mo anode, LiF crystal analyzer and SZ detector). Analyses were based on the Co Kα line and a series of standards prepared by mixing 1 g of zeolite with 10-20 mg of standard compounds. The time of data acquisition was constant at 10 s.

XPS data were obtained using Mg Kα (hν = 1253.6 eV) radiation with ES-2403 spectrometer (Institute for Analytic Instrumentation of Russian Academy of Sciences, St. Petersburg, Russia) equipped with energy analyzer PHOIBOS 100-MCD5 and X-Ray source XR-50. 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.

STEM characterization was carried out using FEI Tecnai Osiris instrument operating at an accelerating voltage of 200 kV, equipped with high-angle annular dark field (HAADF) detector. Samples were prepared by embedding the catalyst in epoxy resin with following microtoming (ca. 50 nm thick) at ambient temperature. For the image processing Digital Micrograph software and TIA were used. Holey carbon/Cu grid was used as a sample support.

## 3. Results and discussion

According to the XPS data, all the zeolite-based samples contained on the surface ruthenium mainly in the form of RuO<sub>2</sub> (binding energy (BE) of Ru 3d<sub>5/2</sub> was 281.3 eV) and Ru(OH)<sub>3</sub> (BE of Ru 3d<sub>5/2</sub> was 282.1 eV). The content of RuO<sub>2</sub> (in at. %) among all the forms of ruthenium decreased in the range: Ru/HZSM-5 > Ru/HMordenite > Ru/HY > Ru/HBeta. This range is in good agreement with catalytic activity observed during the first run in LA hydrogenation (see Table 1).

Liquid nitrogen physisorption revealed that after ruthenium deposition the porosity of all the zeolites decreased to some extent. The strongest decrease of specific surface area (SSA), according to Brunauer-Emmett-Teller model, was observed for Ru/HMordenite (from 487 m<sup>2</sup>/g to 52 m<sup>2</sup>/g), indicating strong blockage of zeolite pores with ruthenium species. For Ru/HZSM-5 and Ru/HY, the SSA of initial zeolites decreased by about 100-

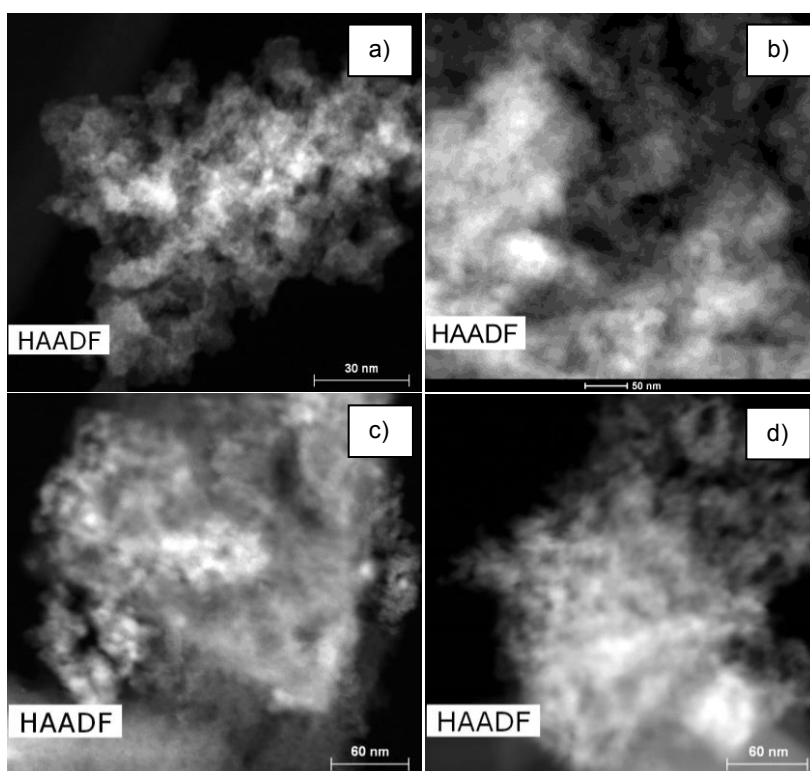
130 m<sup>2</sup>/g. In the case of Ru/HBeta the SSA changed slightly (only by 41 m<sup>2</sup>/g), which indicates the most uniform Ru distribution after the impregnation (Figure 2b).

*Table 1. Influence zeolite type on the LA conversion (temperature 100 °C, partial hydrogen pressure 1 MPa, stirring rate 1000 rpm)*

Sample designation	Conversion of LA, %	$R_o$ , mmol(LA)/h
Ru/HZSM-5	99.8	245.7
Ru/HBeta	46.1	33.0
Ru/HY	53.9	78.0
Ru/HMordenite	71.8	108.0

\*Calculated for the reaction time 2 h

Figures 2 show the HAADF STEM images for all the samples. As it can be seen, the distribution of Ru is different, and Ru/HY (Figure 2c) as well as Ru/HMordenite (Figure 2d) seems to have the worst distribution of catalytically active phase, while in the case of Ru/HZSM-5 the distribution of RuO<sub>2</sub> is satisfactory (Figure 2a).



*Figure 2: HAADF STEM images of Ru/HZSM-5 (a), Ru/HBeta (b), Ru/HY (c) and Ru/HMordenite (d)*

Catalytic systems Ru/HZSM-5, Ru/HBeta, Ru/HY and Ru/HMordenite were tested in the reaction of LA hydrogenation (Table 1). The highest conversion of LA (99.8 %) was found for Ru/HZSM-5 and can be attributed to the highest percentage of RuO<sub>2</sub> on its surface. Ru/HBeta allowed achieving only 46.1 % of LA conversion for 2 h of the reaction in spite of the most uniform distribution of catalytically active phase (Figure 2b). In the case of Ru/HY and Ru/HMordenite, the LA conversion was 53.9 % and 71.8 %, respectively. Simakova et al. have shown that complete LA conversion and 98 % selectivity can be reached in 3.5 h in 1,4-dioxane medium at 165 °C and 1.6 MPa of H<sub>2</sub> using 4 %-Ru/HBeta at LA-to-catalyst weight ratio about 27 g/g. Catalysts synthesized in this work are more active, that is likely due to the fact that RuO<sub>2</sub> instead of metallic ruthenium was the active phase. Recently, HRO/HBeta was shown to be extremely active in LA hydrogenation (Gundekari and Srinivasan, 2019). Higher activity of HRO/HBeta in comparison with the synthesized Ru/HZSM-5 can be explained by the difference in the procedure of catalyst synthesis, which resulted in different morphology.

Stability of synthesized catalytic systems was studied in three consecutive runs. After catalytic experiments zeolite-based samples were separated from reaction mixture by simple vacuum filtration using membrane filter

(Nylon, 0.22  $\mu\text{m}$  pore size, 50 mm diameter) and thoroughly washed with water and dried at 70  $^{\circ}\text{C}$ . It is noteworthy that for the repeated use, several (at least 3) catalyst samples were collected from previous runs and averaged catalyst sample was taken for further run. In this way all the reaction conditions remained unchanged including the LA-to-catalyst weight ratio.

In the case of Ru/HZSM-5 (Figure 3a) and Ru/HMordenite (Figure 3d), gradual decrease of catalytic activity was observed in three consecutive runs, which was mainly due to the loss of catalytically active phase ( $\text{RuO}_2$ ). The decrease of activity is likely due to predominant location of ruthenium (IV) oxide on the surface of these zeolites, which makes it mechanically unstable and susceptible to attrition.

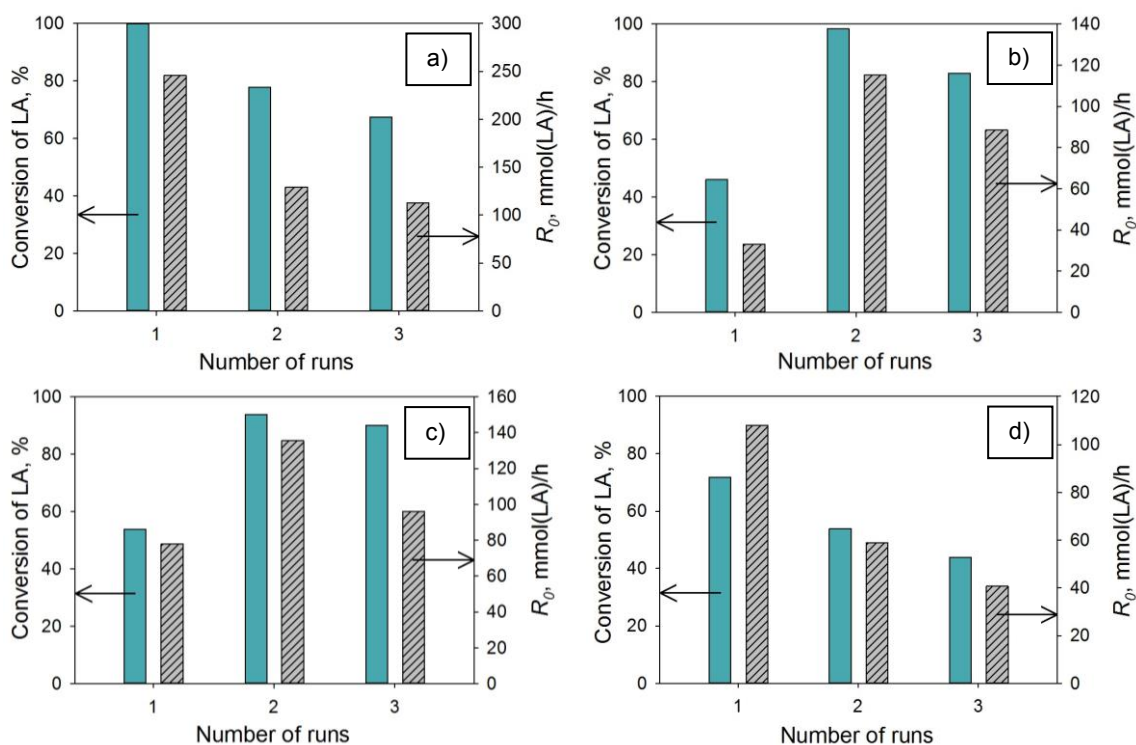


Figure 3: Influence of repeated uses on the conversion of LA and the initial reaction rate ( $R_0$ ) of the catalyst samples Ru/HZSM-5 (a), Ru/HBeta (b), Ru/HY (c) and Ru/HMordenite (d)

In contrast, two other samples (Ru/HBeta (Figure 3b) and Ru/HY (Figure 3c)) the nearly double increase of LA conversion was found in the second and third runs. This fact is likely associated with an increase in the percentage of  $\text{RuO}_2$  after the first run.

#### 4. Conclusions

In this work, ruthenium-containing catalytic systems based on zeolites of different types (HZSM-5, HBeta, HY and HMordenite) were studied in the reaction of LA hydrogenation to GVL at a temperature of 100  $^{\circ}\text{C}$  and partial hydrogen pressure of 1 MPa in aqueous medium. It was shown that the use of Ru/HZSM-5 allows achieving 98 % of LA conversion at 100 % selectivity with respect to GVL in 60 minutes of the reaction, which makes it a promising catalyst for the selective LA hydrogenation. However, this catalyst underwent gradual decrease of activity at three consecutive runs, likely due to the loss of catalytically active phase ( $\text{RuO}_2$ ). Ru/HMordenite was also shown to have tendency to the decrease of activity, while two other Ru-containing zeolite-based catalysts (Ru/HBeta and Ru/HY), in contrast, were most active in the second run, after which catalytic properties were stabilized.

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