Development of catalysts for the hydrogenation of levulinic acid to gamma-valerolactone in the framework of the problem of cellulose conversion into valuable chemicals

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Abstract. Gamma-valerolactone (GVL) is a starting reagent for the production of fuels and fine chemicals. GVL can be used as a solvent, as part of an electrolyte, for the production of chemicals and fuel additives. It can be converted to liquid fuels such as valerian biofuels, liquid alkanes or valuable chemical intermediates such as 1,4-pentanediol or alkylpentenoates being biopolymer precursors. The production of GVL is based mainly on the hydrogenation of levulinic acid (LA), which can be obtained directly from cellulose by acid hydrolysis. This article describes the development of heterogeneous catalysts for the targeted conversion of LA to GVL. In order to analyze both achievements and unresolved problems in this area the emphasis was placed on the discussion of systems based on noble and non-noble metal catalysts, hydrogenation by means of hydrogen transfer.

1. Introduction
Carbohydrates, starches and fats obtained mainly from annual plants were used as first-generation biofuels. However, due to the fact that the same raw materials are used in the food industry, annual oilseeds and starchy crops are undesirable for the production of motor fuels. An alternative raw material can be lignocellulose, which forms the cell walls of woody plants. For the production of biofuels, it is possible to organize the production of a sufficient amount of lignocellulose. It is known that levulinic acid (LA) can be obtained as a result of acid hydrolysis from lignocellulose (Fig. 1).

![Figure 1](image-url). Conversion of cellulose to LA and formic acid (MA) by acid-catalyzed hydration followed by hydrogenation to GVL.
Levulinic acid (LA) is used as an additive in the production of cosmetics, plastics and textiles. Catalytic hydrogenation of levulinic acid (LA) produces gamma-valerolactone (GVL), which is the starting compound for the production of fuel and chemical compounds with added value [1-8], such as 1,4-pentanediol [9] or alkylpentenoates, which are precursors biopolymers [10]. The hydrogenation of levulinic acid (LA) to gamma valerolactone (GVL) has been extensively studied using both homogeneous and heterogeneous catalysts [11-14]. When using homogeneous catalysts, problems arise such as instability of the metal complex, complex synthesis of catalytic ligands, and difficulties in product purification [14-16]. Both metal and supported catalysts are used as heterogeneous catalysts for the hydrogenation of LA in GVL [17-20]. In this case, the reaction must be carried out under severe conditions, at high temperatures (100–270°C) and high pressure (4–15 MPa) to achieve a high yield of GVL [18, 20, 21]. In addition, in some cases, organic solvents were used that are not environmentally friendly and are not economically efficient for industry [20, 21]. In addition, metal leaching in the reaction medium and catalyst deactivation after the reaction are unsolved problems. Consequently, the catalytic conversion of LA to GVL in aqueous solutions and under mild reaction conditions is a difficult task [19]. This review is devoted to the problem of the development of heterogeneous catalysts for the hydrogenation of LA in GVL, special attention will be paid to the discussion of specific systems in order to analyze unsolved problems, and ways of their solution will be proposed.

2. Results and discussion

2.1 Reaction pathways for the hydrogenation of LA to GVL

Due to its widespread use, LA has been included by the US Department of the United States in the list of "key platform chemicals", the operation of which can lead to more efficient processing of biomass. [22]. Scheme 2 shows possible pathways of obtaining GVL from LA. The cyclization of LA in pseudo-LA, followed by reversible dehydration, leads to the formation of angelica lactone [23], which forms GVL after hydrogenation of the unsaturated C-C bond. Hydrogenation of the C = O bond and subsequent condensation of γ-hydroxyvaleric acid also leads to the formation of GVL. In addition, when treated with alcohols, LA easily undergoes esterification in liquid phase hydrogenation [24]. In gas-phase hydrogenation, the C–C bonds cleave with the formation of by-products [25, 26].

![Figure 2. Scheme of converting the LA into GVL](image)

2.1.1 GVL production using hydrogen
2.1.2 Gas-phase hydrogenation

LA hydrogenation can be carried out in two ways, as shown in Figure 3. The main advantage of a gas-phase reaction is that such systems can be suitable for a continuous process. However, such techniques are energy intensive and require a lot of energy (boiling point of LA is 245°C). Moreover, the gas-phase reactor may be incompatible with the composition of the hydrocarbon feed containing strong acid (Scheme 1). Gas-phase hydrogenation of LA to GVL was investigated on catalysts based on noble metals, such as Ru, Pd, Pt [27]. Screening of Ru/C, Pd/C and Pt/C showed that Ru/C possesses maximum activity without losing it within 10 days. The high activity and selectivity of the Ru-based catalyst was explained by the high dispersion of Ru. Gas-phase continuous processes have been reported using base metals such as Cu and Ni as catalysts [28-33]; GVL yields above 90% can be obtained on Cu [28] and Ni [31, 33]. The influence of the support on the activity and stability of catalysts based on non-noble metals, including Cu, Ni, and Co, was studied in [26]. Al2O3 performed better than SiO2 for Cu, while SiO2 showed better performance than Al2O3 for Ni and Co. 20-Cu/Al2O3 was the most selective catalyst for the formation of GVL from LA. The reaction paths for the hydrogenation of LA to GVL also depended on the catalysts. Bimetallic Cu–Co catalysts on Al2O3 were tested in [25]. 8Cu-12Co/Al2O3 showed excellent catalytic activity and stability: the GVL yield was 5.46 kg/kgkat/h with a selectivity of more than 99%. It was found that the Cu—Co/Al2O3 catalysts consist of an alloy.

![Figure 3](image-url). Hydrogenation of LA with hydrogen and formic acid

2.1.3 Liquid-phase hydrogenation

Liquid-phase hydrogenation of LA to GVL was carried out on catalysts based on both noble metals, such as Ru [34, 35], Ir, Rh [34], Re [36] and Pd [35], and base metals such as Cu [28] and Ni [34, 37, 38]. GVL yield above 97% was achieved on the catalysts Ru [34], Pd [39], or Cu [40], while Ru and Pd could operate at temperatures lower than Cu. The ester of levulinic acid (levulinate), which can be easily synthesized by esterification of LA with alcohol even at room temperature [41], is also considered an attractive raw material for GVL. Catalysts based on Ru [42, 43], Pd [44], Cu [42], and Co [45] are effective for the liquid-phase hydrogenation of levulinate to GVL, the yield of GVL was 90%.

GVL can be obtained in a very high yield using Group 8 metals 5 (wt% Ir, Rh, Pd, Ru, Pt, Re, and Ni supported on activated carbon) [34]. The Ru/C system was additionally optimized in [35]. For Ru/C, the optimum H2 pressure is 12 bar. The use of higher H2 pressures led to a noticeable decrease in the conversion of LA, presumably due to the saturation of the active sites of the catalyst with hydrogen. A similar trend was observed when studying the effect of reaction temperature. The maximum yield of GVL was observed at 130°C; at higher reaction temperatures a decrease in the yield of GVL was observed. Not only the reaction conditions, but also the nature of the support also affects the response rates. The highest GVL yield was obtained on the Ru/C catalyst, while the Ru/SiO2, Ru/Al2O3 catalysts exhibited lower activity [46]. Another parameter that can significantly affect the activity of the catalyst is the dispersion of the metal. The highest activity was exhibited by Ru nanoparticles (average crystal size 2.0 nm) [47].
Recently, the efforts of researchers have been focused on cheap catalysts based on non-noble metals, for example, Ni [33, 48-52] and Cu [53-57] for the preparation of GVL. Nickel-based catalysts, such as Ni/Al₂O₃ [48], Ni-MoOₓ/C [49], and Ni/boehmite [50], exhibit relatively high selectivity to GVL but poor stability in subsequent catalytic cycles. It was found in [50] that a gradual decrease in the reaction rate occurs due to strong leaching of Ni into solution.

2.2 Hydrogenation with formic acid

Processes that use hydrogen from steam reforming of hydrocarbon feedstocks are environmentally disadvantageous. In this regard, the synthesis of GVL using alternative hydrogen sources such as formic acid (FA) has become the focus of significant research efforts. FA is a particularly attractive source of hydrogen for the synthesis of GVL, since this compound is obtained as a result of acid-catalyzed dehydration of carbohydrates (Scheme 1). This approach allows avoiding the expensive cleaning of the LA and decreases the cost of hydrogen production. To implement this process, it is necessary to develop a catalyst being resistant to acidic solution.

Due to the ability of Ru/C to be deactivated by acids, there is a need to develop more reliable catalytic systems. In this regard, materials based on Au nanoparticles (1.2–2.5 nm) deposited on acid-resistant ZrO₂ were developed to convert FA and LA into GVL [58]. Comparison of Au/ZrO₂ with Pd-, Pt-, Ru- and Pd-containing materials and with Au/TiO₂, Au/C and Au/SiO₂ showed that when using ZrO₂ under the conditions of this study, Au was the most active metal. For the hydrogenation of LA with hydrogen and formic acid, bimetallic catalysts 4% Ag-1% Pd/AlOOH were developed, which exhibit the highest selectivity in the decomposition of formic acid, as well as the highest activity in the hydrogenation of LA (34% conversion in 5 h at 190°C) [59]. The characteristics of bimetallic Au–Ni catalysts in a one-pot combined hydrogenation reaction strongly depended on the method of their preparation; the highest GVL yield was obtained on the Au–Ni/γ-Al₂O₃ catalyst prepared by joint impregnation of both metal salts [60].

Although catalysts based on noble metals exhibit the necessary properties in this system, their high price hinders the further introduction of LA hydrogenation through the transfer of hydrogen to bioprocessing plants of a new generation. Currently, experiments using base metals are mainly focused on Cu [40; 41; 61, 56, 62, 63], Ni [56, 64–66], Fe [63, 67, 68], MnCo oxide catalysts [71] and catalysts based on Zr [69, 70], many of which require high temperature (>250°C) in the gas-phase, as well as the addition of promoters. Thus, new efforts should be invested in the development of more energy efficient processes for LA transformation.

2.3 Approaches to the development of an efficient catalyst for the synthesis of GVL

Materials containing precious (Pd [72], Ru [73, 74], Pt [53]) or base metals (Cu [75], Ni [76], Co [26, 77]) supported on various oxide (SiO₂, Al₂O₃, TiO₂, ZrO₂) and carbon supports are used as catalysts for the LA hydrogenation. However, due to the high cost of noble metals and their limited availability, special attention is paid to the development of catalysts based on non-noble metals. The key advantage of such catalysts is their low cost. However, these catalysts exhibit lower productivity, and under the conditions of the catalytic process and under the influence of the reaction medium, leaching of the active component is observed, which leads to a gradual deactivation of the catalysts. To overcome drawbacks of catalysts based on noble metals and to achieve an improvement in the performance of the process, bimetallic catalysts and highly dispersed particles of the active component stabilized in the support matrix should be used.

It has been shown that bimetallic catalysts Cu-Ni/SiO₂ [17, 78] and Cu-Co/Al₂O₃ [25] exhibit higher activity in the gas-phase and liquid-phase hydrogenation of LA. The high productivity of the Cu-Ni/SiO₂ bimetallic catalyst is explained by the inhibition of Ni carbonization and the decomposition of LA into Cu. The high stability and activity of the 8Cu-12Co/Al₂O₃ catalysts is explained by the formation of the Cu-Co alloy. In the hydrogenation of LA to GVL using FA as an internal hydrogen source, one challenge is to develop a catalyst capable of performing both reactions with high efficiency. The 4% Ag–1% Pd/AlOOH catalyst showed the highest selectivity in the
decomposition of formic acid, as well as the highest activity in the hydrogenation of levulinic acid [79]. The adsorption of CO molecules and the poisoning of the Ag-Pd alloy decrease with a strong intermetallic interaction and isolation of the Pd atoms. In [60] the high activity of Au-doped nickel catalysts in the hydrogenation of levulinic acid using formic acid as a source of hydrogen was shown for the first time. The strong interaction between Au and Ni in the alloy favors the selective and rapid decomposition of formic acid, which greatly facilitates the combined hydrogenation process. The Ni3FeNPs/C catalyst showed high selectivity in the direct hydrogenation of LA and in transfer hydrogenation [80]. Ni-Pt and Ni-Ru bimetals supported on ZrO2 and Al2O3 have been successfully used as highly active and selective catalysts for solvent free hydrogenation of LA using FA as a hydrogen source in a microwave reactor [81]. Bimetallic Ru-Ni nanoparticles on ordered mesoporous carbon [82], Cu/γ-Al2O3 doped with Ag [83] and RuSn4/C [84] showed high stability during the hydrogenation of LA in GVL. The high activity of the Ni-Nb/TiO2 catalyst is explained by the high concentration of Lewis acid sites on the catalyst surface. The catalyst is not only active and selective with respect to GVL, but also stable under optimized experimental conditions [85].

It is known that highly dispersed ruthenium is more active in the reaction of LA hydrogenation [27, 47, 86]. At present, approaches are being developed to stabilize highly dispersed forms of the active component in the support matrix. In this regard, it is promising to use mesoporous materials with an ordered pore structure that provide the reagent with access to the active component, high dispersion of the applied nanoparticles of the active component and stabilize their size. It was shown that a mesoporous structure of oxide supports TiO2-SiO2 [87], SiO2 [88] with an ordered pore structure, as well as phosphate groups on the surface of ordered mesoporous carbon [20], is required to achieve high activity.

The choice of the support is also associated with a strong metal-support interaction. For example, a new Cu/Al2O3-ZrO2 composite catalyst was developed for the catalytic hydrogenation of levulinic acid in water [89]. The high catalytic activity was attributed to the dilution of Cu with aluminum oxide, as well as the enhancement of the electronic interaction between Cu and ZrO2 as compared to the Cu/ZrO2 catalyst. It was shown by DFT that the structure of the metal-oxide interface affects the properties of a metal oxide catalyst. It was shown in [73] that ultrathin TiO2 nanoplates with deposited Ru nanoparticles had extremely high catalytic activity and the possibility of multiple uses due to the formation of the Ru–O–Ti interphase structure.

It is possible to solve the problem of the low stability of Ru-based catalysts against sintering and leaching in the hydrogenation of levulinic acid by using nanospheres in which nanoparticles are fixed inside a mesoporous shell [74]. Such a shell combines the advantages of traditional structures such as yolk and a supported catalyst, in which the active core is not only completely exposed, but is also firmly anchored to the shell due to strong metal-support interaction. Nanomaterials obtained from organometallic frameworks, in particular, a C@Al2O3 support with a honeycomb pore structure, also provide high stability and activity of Ru nanoparticles located inside the pores [90]. It is also necessary to take into account the acid-base properties of the support required for bifunctional catalysis. Copper-containing catalysts based on Zr0.8-Ce0.2O2 were developed, which were active and selective in the hydrogenation of LA using FA as a hydrogen source [79].

It should be noted that the current systems for GVL production are based solely on precious metals, and the use of base metals in general remains poorly understood. Catalysts based on non-noble metals (Ni, Co, Cu) and bimetallic catalysts are promising in the reaction of LA hydrogenation. Due to the strong magnetic properties of nickel catalysts, their easy processing, low cost and availability, Ni-systems are considered as the most promising catalysts. However, it is noted that, in comparison with catalysts based on noble metals, Ni catalysts are less resistant to leaching of the active component under reaction conditions. NiCo, NiRu and NiPd bimetallic catalysts can be used to overcome the operational and economic limitations of catalysts based on noble and base metals. In this case, an increase in catalytic activity and stability can be achieved due to the synergistic effect between metals, an increase in the dispersion of the active metal, and an increase in chemical stability, which requires a systematic approach to the synthesis of bimetallic catalytic systems. At present, the polyol method for
the synthesis of nanoparticles of bimetallic nanoparticles is very promising, since it allows one to control the size of nanoparticles and synthesize metal particles with a narrow size distribution [91]. After thermal activation under certain conditions, carbonaceous deposits are formed on the catalyst surface, which increases the resistance of the active component to leaching. Thermal activation of materials under controlled conditions will ensure the destruction of the initial phase and the formation of Ni-containing nanoparticles and clusters stabilized on the support. In this case, in comparison with low dispersed systems, an increase in the specific surface area of the active component, a strong metal-support interaction, and a decrease in metal leaching will be achieved.

Conclusions
Thus, from the analysis of literature data, it follows that the production of GVL is an object for scientific research in connection with the widespread use of GVL and the availability of LA as a raw material. A significant number of heterogeneous catalysts are proposed for this process, the most common are supported noble metals, with ruthenium being the most effective catalyst. While numerous catalysts are supported, more research is required to understand the effect of a given support on catalyst activity. It is also necessary to identify a wider range of stable systems. The question of the optimal composition of the active component, as well as the nature of the support, which provides the specified forms of stabilization of the active component, remains open. An important but unresolved task to date is the development of methods for controlling the dispersion of the active component. To control the functional properties of materials, it is necessary to develop methods for controlling the composition and dispersion of bimetallic particles by varying the methods and parameters of synthesis. It is necessary to identify the factors affecting the physicochemical properties of catalysts, their activity in the hydrogenation of LA in GVL and resistance to deactivation, and to establish the relationship "structure - catalytic properties".

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