

Eötvös Loránd University
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Value-increasing heterogeneous catalytic conversion of levulinic acid and its derivatives

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Ph.D. Thesis

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Introduction and objectives

Nowadays, fossil carbonaceous materials (coal, oil, natural gas) are the primary sources of energy and carbon in the production of energy and chemicals, respectively. The conversion of the chemical energy of fossil-derived organic materials into other forms of energy like heat, mechanical or electrical, is accompanied by adverse effects on the environment. The only way to slow down the decay of our environment is to replace the use of fossil fuels with inexhaustible and renewable energy sources, such as, hydro, wind, solar and geothermal. It is also important that the chemical industry should use renewable carbon resources, like biomass and carbon dioxide as raw material as much as possible. It is a directive of the European Union that by the year 2030, 32 % of the consumed energy should be renewable. The renewable energy content of transport fuels should be increased to 14%.

Lignocellulose-based biomass is the largest available resource of renewable organic material. Its non-food or feed fraction is sufficient to meet the carbon needs of chemical industry. The major components of lignocellulose are carbohydrate polymers (cellulose and hemicellulose). Applying chemical/biochemical processes they can be converted first into monomer sugars and then into alcohols, furfural derivatives and carboxylic acids. All these compounds can serve as platform raw materials for the chemical industry. Establishing the scientific and technological founds of the chemical utilization of lignocellulose is a timely and important task of research and development.

Levulinic acid (LA, 4-oxopentanoic acid) is a low molecular weight organic acid, containing keto and carboxyl groups, is a promising platform molecule. The production of LA is economically feasible by acid catalyzed hydrolysis of plant biomass. Nowadays it is produced commercially using the so called "Biofine" process. Due to its reactive functional groups, LA is relatively easy to be further converted. Its oxygen content can be reduced by catalytic hydrodeoxygenation (HDO). Catalytic dehydration, hydrogenation, and hydrogenolysis are key reactions. Through consecutive catalytic hydrogenation and dehydration steps, LA can be further transformed into more valuable chemicals even on industrial scale. Through γ -valerolactone (GVL) intermediate chemicals can be prepared, such as pentane-1,4-diol (1,4-PD), which can be used as a polymer component, and 2-methyltetrahydrofuran (2-MTHF), pentanoic acid esters, alcohols and alkanes, which can be used as fuel surrogates and solvent. By appropriate choice of catalyst and reaction parameters, catalytic hydroconversion of levulinic acid can be stopped at GVL formation. GVL is a renewable, environmentally friendly

solvent that can be used as a food and fuel additive and as raw material in the production of fragrances and cosmetics.

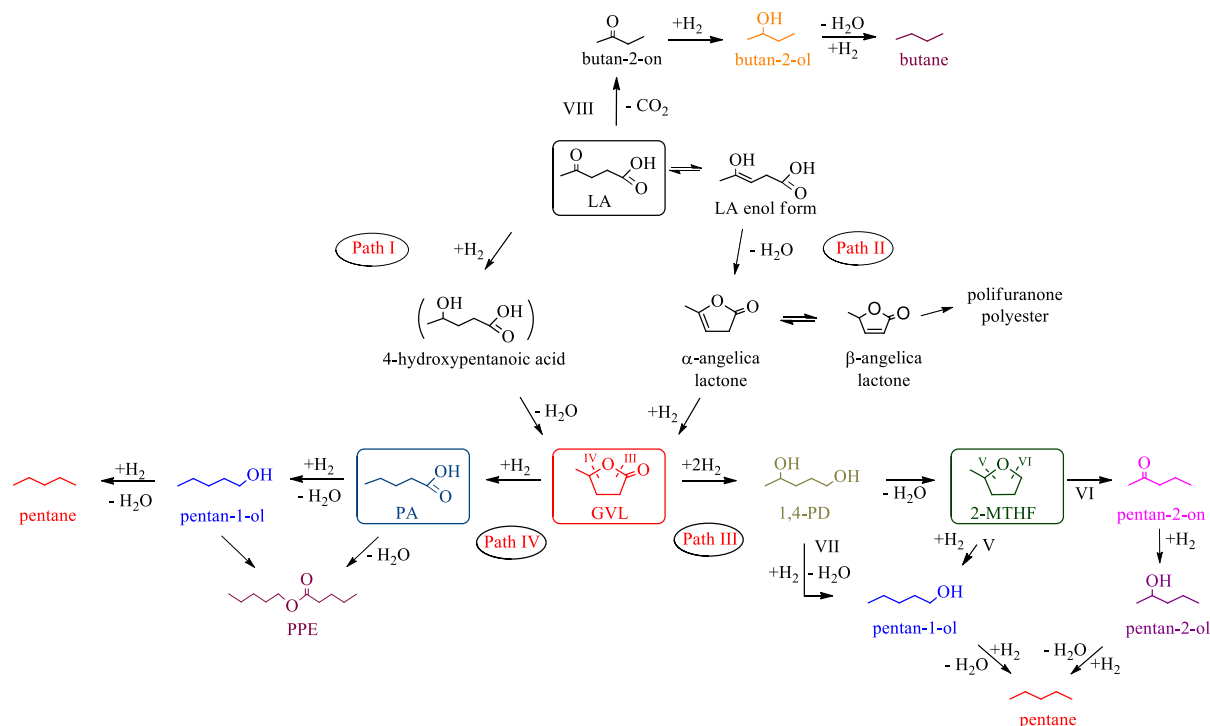
The hydroconversion of LA was investigated on oxide-supported heterogeneous catalysts, containing transitional metals in gas and liquid phase reactions. Hydrogen gas was used as a reducing agent. Hydrogen is a preferred reactant because it can also be produced using renewable solar energy and can be easily separated from the liquid products of the reaction. My aim was to explore the reaction network of LA hydroconversion, to find relationships between the acidity of bifunctional catalysts, the nature of the supported metal, and the catalytic behavior, and ultimately, to further understand the catalytic mechanism.

Methods

The heterogeneous catalytic hydroconversions were carried out in a fixed bed flow-through reactor. The reaction temperature was 200–300 °C, the pressure 1-30 bar and the space velocity was chosen in the range of 0.1-1 ($\text{g}_{\text{catalyst}}/\text{g}_{\text{reactant}}$) hours. The H_2 /reactant molar ratio was 12. By impregnation I prepared Co- and Ni-catalysts using aqueous solutions of Co and Ni salts. SiO_2 , $\gamma\text{-Al}_2\text{O}_3$ and H-Beta zeolite were used as support. The impregnated support was calcined and then reduced *in situ* in the reactor prior to the catalytic measurements. The reduction process was investigated by temperature-programmed reduction (H_2 -TPR) experiments. The specific surface area of the catalysts was calculated from nitrogen adsorption isotherms using the BET method. The metal content of the catalysts was determined by atomic absorption spectroscopy (AAS). The crystalline metal oxide and metal phases formed on the supports were identified by X-ray powder diffractometry (XRD). The average particle size was calculated from the powder diffractogram using the Scherrer equation and the dispersion. The hydrogen adsorption method was used to determine the metal dispersion. Hydrogen adsorption capacity was measured by temperature-programmed H_2 desorption (H_2 -TPD). The acidity of the catalysts was characterized by the infrared spectra of adsorbed pyridine (FT-IR).

Research results

The substantiated reaction network of LA and GVL transformations presented here serves the better understanding of the research results summarized in the theses.



Theses

1. I have shown that the reduced catalysts contain Lewis acid centers in addition to metal (Co_n^0 , Ni_n^0) centers. Lewis acid centers are formed by the interaction of the unreduced cobalt and nickel oxide species with the silica support. These centers catalyze dehydration reactions.

(Described in publications No. 1. and 3.)

2. I have confirmed that over catalyst with dehydration (acid) and hydrogenation (metal) functions γ -valerolactone (GVL) is formed from LA via the intermediate angelica lactone. The possibility of GVL formation via 4-hydroxypentanoic acid intermediate that could have formed by hydrogenation of the carbonyl group of levulinic acid, was excluded.

(Described in publications No. 1. and 3.)

3. I was the first to detect surface carboxylate anions formed in LA chemisorption on Co/SiO_2 catalyst. The IR bands of adsorbed LA at 1576 and 1442 cm^{-1} were assigned to the

asymmetric ($\nu_{\text{as}}(\text{COO}^-)$) and symmetric ($\nu_{\text{s}}(\text{COO}^-)$) vibrations of the carboxylate group. The adsorption sites must be cobalt/cobalt oxide formations, interacting with the support, because carboxylate anions were not obtained from the interaction of LA and SiO_2 support.

(Described in publication No. 1.)

4. I have shown that on the Lewis acid/Lewis base (Co-cation/oxide anion) centers of the cobalt oxide the heterolytic dissociation of LA takes place and a surface levulinate anion and proton are formed. It is probable that the enol form of levulinate, 4-hydroxy-3-pentenoate, is the activated species leading to GVL formation. From 4-hydroxy-3-pentenoate α -angelica lactone is formed by dehydration and intramolecular ring closure. Hydrogenation of the carbon-carbon double bond of the angelica lactone on metal Co_n^0 centers gives GVL.

(Described in publication No. 1.)

5. I have shown that by appropriate choice of reaction conditions on Co/SiO_2 and $\text{Co/Al}_2\text{O}_3$ catalysts, the hydroconversion of LA can be stopped at the formation of GVL. Not only the hydrogenation of the angelica lactone but also the hydrogenolysis of the formed GVL ester bond ($\text{O}-(\text{C}=\text{O})$) takes place at the metal centers of the freshly reduced catalyst. Pentane-1,4-diol (1,4-PD) is formed which, upon dehydration followed by ring closure is converted to 2-methyltetrahydrofuran (2-MTHF). The surface carboxylate structures formed in the catalytic reaction reduce the hydrogenation activity of the catalyst and inhibit the further conversion of GVL.

(Described in publication No. 1.)

6. I proved that the initial rate of GVL formation increases with the concentration of metallic cobalt on SiO_2 and Al_2O_3 supported cobalt catalysts. This suggests that the rate-determining step in GVL formation is the hydrogenation of angelica-lactone.

(Described in publication No. 1.)

7. I have shown that by increasing the reaction temperature, the reaction of LA HDO over the Co/SiO_2 catalyst shifts from GVL formation to 2-MTHF formation. By increasing the temperature, the carboxylate coverage of the active cobalt centers is reduced, thereby the hydrogenation and the GVL ester bond hydrogenolysis activity of the catalyst increases.

(Described in publication No. 1.)

8. I have shown that GVL is the final product on Co/Al₂O₃ catalyst in the hydroconversion of LA over a relatively wide temperature range (200-300 ° C). The opening of the GVL ring is inhibited because of the low hydrogenation activity of the catalyst due to the strong interaction between the cobalt oxide and the Lewis acidic γ -Al₂O₃ support.

9. I proved that the formation of GVL is the primary reaction on the highly dispersed Ni/SiO₂ catalyst from LA. Furthermore, I have shown that by changing the space time and the pressure, the GVL ring opening can be controlled. At high space time and atmospheric pressure GVL is converted to pentanoic acid (PA). Pentanoic acid is formed on the catalyst without Brönsted acid sites by hydrogenolysis reaction. At higher pressures (10-30 bar), with higher hydrogen coverage of active metal centers, the ester bond (O-(C=O)) of GVL is cleaved to form pentane-1,4-diol (1,4 PD) by uptake of two hydrogen molecules. 1,4-PD is dehydrated on the Lewis acid sites and 2-MTHF becomes the major product.

(Described in publication No. 3.)

10. I have confirmed that on the strong Brönsted acidic Co/H-Beta zeolite catalyst from LA or GVL pentanoic acid is formed via the pentenoic acid intermediate through protonation/rearrangement/deprotonation/hydrogenation mechanism. At higher temperatures, further reduction of pentanoic acid produces pentan-1-ol, and then pentane is formed through pent-1-ene intermediate. The reaction between pentanoic acid and pentan-1-ol produces pentanoic acid pentyl ester (PPE). It has been shown that SiO₂ and Al₂O₃ supported catalysts with lower Co-dispersion are not active in GVL conversion to pentanoic acid.

11. I verified that the pentan-2-ol product on the Co/SiO₂ catalyst is mainly obtained by hydrogenation of the pentan-2-one intermediate formed by cleavage of the 2-MTHF C-O bond. Pentan-1-ol is formed primarily by hydrogenation following dehydration of 1,4-PD. The primary product of GVL conversion is 2-MTHF, while pentan-1-ol is formed in the secondary reaction.

(Described in publication No. 2.)

12. I proved that during the first step of GVL hydroconversion the carbonyl group of GVL is hydrogenated and 2-hydroxy-5-methyltetrahydrofuran intermediate is formed. Subsequently, the C-O bond next to the hydroxyl group in the furan ring is cleaved and the intermediate is converted to pentane-1,4-diol by the addition of a second hydrogen molecule.

Hydrogenolysis of the C-O bond next to the furan ring methyl group was excluded because of the formation of a less stable geminal diol. On the Lewis acid centers 1,4-PD is converted to 2-MTHF by dehydration. It is probable that GVL molecules interacting with the OH groups on the silica support are the activated species.

(Described in publication No. 2.)

Conclusions

I have studied the heterogeneous catalytic hydroconversion of levulinic acid and its derivatives. Understanding the reaction mechanism can help to scale up the process. The Co and Ni catalysts I have prepared can be used for the continuous production of high value-added compounds.

Publications related to the thesis

1. **Novodárszki Gy.**, Solt E. H., Valyon J., Lónyi F., Hancsók J., Deka D., Tuba R., Mihályi R. M., *Selective hydroconversion of levulinic acid to γ -valerolactone or 2-methyltetrahydrofuran over silica-supported cobalt catalysts*, **Catal. Sci. Technol.** 9 (2019) 2291-2304. DOI:10.1039/C9CY00168A. *IF*₂₀₁₉: 5,726
2. **Novodárszki Gy.**, Solt E. H., Lendvay Gy., Mihályi R. M., Vikár A., Lónyi F., Hancsók J., Valyon J., *Hydroconversion mechanism of biomass-derived γ -valerolactone*, **Catalysis Today** 336 (2019) 50-62. DOI:10.1016/j.cattod.2019.02.020. *IF*₂₀₁₉: 4,888
3. **Novodárszki Gy.**, Valyon J., Illés Á., Dóbé S., Deka D., Hancsók J., Mihályi R. M., *Heterogeneous hydroconversion of levulinic acid over silica-supported Ni catalyst*, **Reaction Kinetics, Mechanisms and Catalysis** 126 (2019) 795-810. DOI:10.1007/s11144-018-1507-9. *IF*₂₀₁₉: 1,428

Presentations and posters related to the thesis

1. 14th Pannonian International Symposium on Catalysis, High Tatras, Slovak Republic, 3-7 September 2018
Heterogeneous catalytic hydroconversion of gamma-valerolactone
Novodárszki Gy., Mihályi R.M., Hancsók J., Deka D., Valyon J.

2. Változatok Négy Intézetre Doktori Konferencia, Budapest, Magyarország, 2016. November 24.
Levulinsav hidrokonzverziója hordozós átmenetifém katalizátorokon
Novodárszki Gy., Mihályi R.M., Valyon J.
3. XXII. Nemzetközi Vegyészkonferencia, Temesvár, Románia, 2016. November 3-6.
Biomasszából nyerhető platformvegyületek heterogén katalitikus átalakítása
Novodárszki Gy., Mihályi R.M., Onyestyák Gy., Valyon J.
4. 13th Pannonian Symposium on Catalysis, Siófok, Magyarország, 19-23 September 2016
Heterogeneous catalytic hydrogenolysis of γ -valerolactone
Novodárszki Gy., Mihályi R.M., Illés Á., Dóbbé S. Valyon J.
5. 2nd Training School, University of Leipzig, Leipzig, Germany, 29-30 August 2016
Heterogeneous hydroconversion of biomass derived platform molecules
Novodárszki Gy., Mihályi R.M., Onyestyák Gy., Valyon J.
6. Summer School on „Green Chemistry”, La Rochelle, France, 5-7 May 2015
Heterogeneous hydroconversion of levulinic acid over silica-supported Co catalyst
Novodárszki Gy., Mihályi R.M., Valyon J.
7. XXI. Nemzetközi Vegyészkonferencia, Csíksomlyó, Románia, 2015. Szeptember 23-27.
Biomasszából nyerhető oxigén és nitrogén tartalmú szerves vegyületek heterogén katalitikus átalakítása
Novodárszki Gy., Mihályi R.M., Valyon J.
8. XX. Nemzetközi Vegyészkonferencia, Kolozsvár, Románia, 2014. November 6-9.
A γ -valerolakton előállítás és átalakítása hasznos anyagokká
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9. 12th Pannonian Symposium on Catalysis, Trest, Czech Republic, 16-20 September 2014
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Other publications

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2. **Novodárszki Gy.**, Valyon J., Illés Á., Dóbe S., Mihályi R.M., *Synthesis and characterization of Al-magadiite and its catalytic behavior in 1,4-pentanediol dehydration*, **Reaction Kinetics, Mechanisms and Catalysis** 121 (2017) 275-292. *IF*₂₀₁₇: 1,515
3. Barthos R., **Novodárszki Gy.**, Valyon J., *Heterogeneous catalytic Wacker oxidation of ethylene over oxide-supported Pd/VO_x catalysts: the support effect*, **Reaction Kinetics, Mechanisms and Catalysis** 121 (2017) 17-29. *IF*₂₀₁₇: 1,515
4. Barthos R., Hegyessy A., **Novodárszki Gy.**, Pászti Z., Valyon J., *Structure and activity of Pd/V₂O₅/TiO₂ catalysts in Wacker oxidation of ethylene*, **Applied Catalysis A: General**, 531 (2017) 96-105. *IF*₂₀₁₇: 4,521
5. **Novodárszki Gy.**, Onyestyák Gy., Barthos R., Wellisch Á.F., Thakur A.J., Deka D., Valyon J., *Guerbet alkylation of acetone by ethanol and reduction of product alkylate to alkane over tandem nickel/Mg,Al-hydroxalite and nickel molybdate/γ-alumina catalyst systems*, **Reaction Kinetics, Mechanisms and Catalysis** 121 (2017) 69-81. *IF*₂₀₁₇: 1,515
6. Onyestyák Gy., **Novodárszki Gy.**, Wellisch F.Á., Kalló D., Thakur A.J., Deka D., *Co and Ni catalysts loaded on typical well-ordered micro- and mesoporous supports for acetic acid reduction*, **Reaction Kinetics, Mechanisms and Catalysis** 121 (2017) 109-119. *IF*₂₀₁₇: 1,515
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9. Illés Á., Farkas M., Zügner G.L., **Novodárszki Gy.**, Mihályi R.M., Dóbe S., *Direct and relative rate coefficients for the gas-phase reaction of OH radicals with 2-methyltetrahydrofuran at room temperature*, **Reaction Kinetics, Mechanisms and Catalysis** 119 (2016) 5-18. *IF*₂₀₁₇: 1,264
10. **Novodárszki Gy.**, Onyestyák Gy., Wellisch F.A., Pilbáth A., *Catalytic alkylation of acetone with ethanol over Pd/carbon catalysts in flow-through system via borrowing hydrogen route*, **Acta Chimica Slovenica** 63 (2016) 251-257. *IF*₂₀₁₆: 0,983
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12. Valyon J., Lónyi F., **Novodárszki Gy.**, Someus E., *Valorization of pyro-oil obtained from animal by-products*, **Proceedings of the 10th Conference on Sustainable Development of Energy, Water and Environment Systems**, Zágráb, Horvátország (2015) 1-10.
13. Illés Á., Fakras M., Gombos E., Zügner G.L., **Novodárszki Gy.**, Dóbé S., *Kinetics of the reaction of OH radicals with the biofuel molecule 2-methyltetrahydrofuran*, **Proceedings of the European Combustion Meeting** (2015) 1-10.
14. **Novodárszki Gy.**, Rétfalvi N., Dibó G., Mizsey P., Cséfalvay E., Mika L.T., *Production of platform molecules from sweet sorghum*; **RSC Advances** 4 (2014) 2081-2088.
IF₂₀₁₄: 3,840
15. Tukacs J.M., Király D., Strádi A., **Novodárszki Gy.**, Eke Zs., Dibó G., Kégl T., Mika L.T., *Efficient catalytic hydrogenation of levulinic acid: A key step in biomass conversion*; **Green Chemistry** 14 (2012) 2057-2065. *IF₂₀₁₇: 6,828*

Other presentations and posters

1. XXIII. Nemzetközi Vegyészkonferencia, Temesvár, Románia, 2017. Október 25-28.
Al-Magadiit előállítás, jellemzése és katalitikus aktivitásának vizsgálata a biomassza eredetű 1,4-pentándiol dehidratálásában
Novodárszki Gy., Valyon J., Deka D., Mihályi R.M.
2. 7th FEZA Conference "The Zeolites: Materials with Engineered Properties", Sofia, Bulgaria, 3-7 July 2017
Synthesis and Characterization of Al-Magadiite and its Catalytic Behavior in Dehydration of Biomass-derived 1,4-Pentenediol
Novodárszki Gy., Valyon J., Deka D., Mihályi R.M.