

Full Paper

Selective Levulinic Acid Hydrogenation in the Presence of Hybrid Dendrimer-Based Catalysts. Part I: Monometallic

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Abstract: Hybrid Ru-containing catalysts, based on poly(propylene imine) (PPI) dendrimers, immobilized in silica pores, have been synthesized. The materials obtained were characterized by TEM and XPS methods. Synthesized Ru catalysts have proved their efficiency in the selective hydrogenation of levulinic acid and its esters at 80 °C, 30 bars of H₂, and 50% volume substrate concentration in water. Quantitative yields of γ -valerolactone may be obtained for both micro- and mesoporous Ru catalysts within 2 hours with catalytic activity as high as 1610 h⁻¹. The reaction rate and selectivity on γ -valerolactone have been

Introduction

Depletion of fossil fuels makes challenge for search of alternative, renewable energy sources [1]. From the economics, ecology and sustainability points of view, a feedstock, based on biomass, appears to be attractive. Biomass raw materials like starch and lignocellulose are renewable and cheap, making it possible to produce biobased value-added chemicals such as carboxylic acids, furfurals, polyhydric alcohols and esters, and to use them as fuel additives, plasticizers and cutting oils, in the ink industry and cosmetics [1a, 2]. Among the others, levulinic (4oxovaleric) acid, obtained from acid hydrolysis of lignocellulose and similar glucose-based raw material, is considered as a potential chemical platform for production of 2-methyltetrahydrofuran (2-MTHF), 1,4-pentanediol and yvalerolactone (GVL) [1a, 3]. The last one can be used as a liquid fuel, as a food additive or as a solvent [1a, 4]; it is stable and safe to store [1a, 2, 4c, 5].

Levulinic acid can be converted into γ -valerolactone in two possible ways (Scheme 1) [3]. The first one is the direct hydrogenation of carbonyl group in 4th position to hydroxyl group, followed by cyclization, resulting in a desirable lactone. The second one suggests primary dehydration in the weakacid medium, accompanied by the ring closure, resulting in; unsaturated cyclic ester, angelica-lactone, which could be converted in γ -valerolactone through further hydrogenation.

There is a sufficient number of works and reviews, devoted to production of γ -valerolactone from levulinic acid [1a, 2]. The earliest attempts to convert levulinic acid into γ -valerolactone were undertaken as early as 1930-1950s, using PtO₂ [2, 6], Raney Ni [7] and Re black [8] as catalysts.

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found to depend on several factors, such as carrier structure, temperature, presence of water and substrate/Ru ratio.The novelty of such hybrid materials is the presence of both weak acid (SiO₂) and organic base centers (dendrimer amino groups), enhancing the dispersion of Ru nanoparticles. The presence of amino groups in the catalyst stabilize the Ru nanoparticles during the synthesis and promote adsorption levulinic acid on the surface of Ru nanoparticles during the reaction. Synthesized hybrid Ru catalysts can be reused several times without significant loss of activity.

High yields of γ -valerolactone (85-95%) were achievable here at severe conditions (temperatures up to 200 °C, pressures up to 150 bars of H₂) for a long times (up to 48 hours). Also polymerization by-products were formed [8]. Also metal-free systems, based on mixed acid oxides were developed. Thus, γ -valerolactone can be obtained from methyl levulinate in the presence of Zr-doped beta-zeolite, using 2-butanol as a hydrogen source, with the yield of 98% at 120 °C within 5 hours [11]. Analogously Al-Zr mixed oxide catalyst was applied to convert ethyl levulinate to yvalerolactone, using isopropanol both as a solvent and as a hydrogen source [5]. A GVL yield of 83% at ethyl levulinate conversion of 95.5% was achieved within 4 hours at 220 °C. The offered catalyst can be recycled for several times with the possibility of regeneration. Zirconium-based metal-organic framework UiO-66,

modified with sulfonic groups, was applied for GVL synthesis from levulinic acid and its esters, using hydrogen transfer reaction [12]. Quantitative conversions with GVL yield of 85% were achieved within 9 hours at 140 °C. High catalytic activity of UiO-66 was explained in terms of cooperative effect between Lewis-basic $Zr_6O_4(OH)_4$ clusters and Brönsted-acidic $-SO_3H$ sites arranged in a confined nanospace adjacently with each other, facilitating the successive intramolecular dealcoholization to afford GVL respectively [12].

Recently Pt/TiO₂ and Pt/ZSM-5 were proposed as effective catalysts for levulinic acid hydrogenation [4b, 4d]. GVL selectivity reached up to 95% at the temperature of 200 $^{\circ}$ C and the hydrogen pressure of 40 bars. This system, containing both acid and hydrogenating components, could be used for further conversion of γ -valerolactone to valeric acid and its esters [4d] as well as to olefins, that are the biofuel constituents [4b].

A series of metals (Ni, Re, Rh, Ir, Ru, Pd, Pt), deposited on carbon, was tested in levulinic acid hydrogenation at 150 °C and 55 bars of H₂ in 1,4-dioxane medium [9]. Among the others, Ru/C proved to be the most efficient catalyst, giving GVL yield of 72% at conversion of 80%. Pd, Rh and Ir catalysts also resulted in high selectivity on GVL (90-97%), but conversion in their presence did not exceed 50%. The cheapest Ni/C appeared to be the worst catalyst, resulting in conversion of only 2%.



Scheme 1. Possible ways of levulinic acid hydrogenation into γ -valerolactone [3].

Nonetheless, Ru-based systems proved to be the most efficient catalysts for selective levulinic acid hydrogenation into γ -valerolactone, not only among the platinum metals [2]. Herein the reaction rate and GVL yield were strongly dependent on temperature, hydrogen pressure, solvent and support nature. The most characteristic literature data on the levulinic acid hydrogenation are presented in the Table S1.

As a rule, hydrogenation of levulinic acid in the presence of heterogeneous Ru catalysts was conducted at 130-200 $^{\circ}$ C [4a, 4c, 9-10, 13-15, 18] (more rarely at 50-90 $^{\circ}$ C [3, 16-17, 19]) and 15-50 bars of hydrogen, using activated carbon [4a, 4c, 9-10, 13, 15a, 17-19], silica [14a, 15a, 19], alumina [14b, 15a, 17, 19] or titania [15-19] as carriers and water [3, 4c, 13, 15-17, 19], 1,4-dioxane [4a, 9, 14b, 15a] and alcohols as solvents [10, 15a]. Herein turnover frequencies (TOFs) reached values mostly of 100-1000 h⁻¹ (Table S1).

A nature of the carrier used as well as its acidity was proved to have the most important value in terms of catalyst activity, selectivity and stability, studied in [15a, 16-19]. Thus, under reaction carrying out in water-ethanol medium at 130 $^{\circ}$ C Ru/C appeared to be the best catalyst, giving the GVL yield of 89% after 2.5 hours, and Ru/TiO₂ was the worst, with the yield of 71% [15a]. Analogously activity of catalysts decreased in the order: Ru/C >> Ru/γ-Al₂O₃ ~ Ru/SiO₂ > Ru/TiO₂, where hydrogenation of levulinic acid was carried out under the continuous flow conditions (50 $^{\circ}$ C, 24 bars of H₂) in water [17]. Vice versa, Ru/TiO₂ appeared as the most active catalyst in [16] under batch conditions. Herein turnovers frequencies for Ru/TiO₂ reached values as high as 18543 h⁻¹ at 130 $^{\circ}$ C and 7675 h⁻¹ at 70 $^{\circ}$ C.

The influence of various acidic supports, including Nb₂O₅, TiO₂, zeolites- β and H-ZSM-5, was investigated in [18-19]. 90 ^oC, giving conversions of 1-2% within 2 hours [19], however Ru/zeolite- β and Ru/TiO₂ appeared as the best in both works [18-19].

In [3] there were prepared Ru catalysts, based on ordered mesoporous carbon (OMC), doped with H_3PO_4 and/or H_2SO_4 acids, which were examined in hydrogenation of levulinic acid at various temperatures and pressures. P-doping was found out to enhance the reaction rate, reaching the conversion of 98% after 6 hours vs. 54% for unmodified Ru/OMC (70 °C, 7 bars of H_2) (Table 1S). In contrast, S-doped catalysts were characterized by very low activities: conversions after 6 hours in their presence were 18% for Ru/OMC-S,P and 8% for Ru/OMC-S. Herein, the selectivities on γ -valerolactone for all catalysts were of 93-98%. Severization of reaction conditions (200 °C, 40 bars of H_2) allowed to enhance activity, but resulted in decrease of GVL selectivity for Ru/OMC-P due to overhydrogenation and ring-opening products formation (up to 38%) as well as in catalyst stability under reuse.

So strong influence of the support on the efficacy of levulinic acid hydrogenation may be explained in terms of the surface acidity and electronegativity [17-19] and, as a consequence, by interaction between Ru nanoparticles and support, having an effect on dispersion and stability of the formers [16]. From this point of view, grafting on surface of solid oxide the organic ligands, changing electronic properties of the former and facilitating metal nanoparticles dispersion, may become a promising way in the design of highly efficient catalysts for levulinic acid hydrogenation. As promising ligands, dendrimers may appear, that are spherically symmetrical macromolecules with the regular branched structure [20]. Heterogeneous dendrimer-based catalysts have successfully proved themselves in various processes, such as hydrogenation of phenols [21] and aromatic compounds [21b, 22], selective hydrogenation of unsaturated compounds [23].

Immobilization of dendrimer-stabilized nanoparticles on silica was also developed. PPI dendrimers, grafted on the silica-polyamine composites, were used to design very active and selective Pd catalysts for alkyne and diene hydrogenation [24]. Analogously, PAMAM dendrons, immobilized on the surface of amorphous silica or in pores of mesoporous SBA-15, were earlier applied in the selective hydrogenation of dienes and allylic alcohols [25]. However, in spite of the fact that the methods above allow to prepare recyclable and stable catalysts, the silica-dendrimer hybrids obtained are often characterized by low dendrimer content and irregular dendrimer coating of the surface: anchoring of subsequent bulky dendrons is hindered due to sterical and diffusion limitations (bulky dendrons interfere each other). As a result, metal distribution through the carrier occurs as irregular.

Recently we have developed a new approach for synthesis of dendrimer-containing both amorphous and mesoporous organosilica materials by sol-gel method, including co-hydrolysis of Si(OEt)₄ with PPI dendrimers, modified with (3-glycidoxy)propyltrimethoxysilane (Fig. 1) [26]. Impregnated with Ru nanoparticles, these catalysts have been successfully applied for effective hydrogenation of phenols to corresponding cyclohexanols [26].

In the present work we have proved the efficiency of the catalysts synthesized in the hydrogenation of levulinic acid and its esters. The novelty of such hybrid materials is the presence of both weak acid (SiO_2) and organic base centers (dendrimer amino groups), enhancing the dispersion of Ru nanoparticles through the carrier surface. It has been shown that the presence of basic amino-groups in catalyst stabilizes Ru nanoparticles during synthesis and promotes levulinic acid adsorption on the Ru surface, when hydrogenation was carried out.



Fig. 1.The structures of Ru hybrid catalysts based on PPI dendrimers, immobilized in silica pores: a) G3-dendr-SiO₂-Ru; b) G2-dendr-meso-SiO₂-Ru [26].

Results and Discussion

Hydrogenation of levulinic acid in the presence of hybrid dendrimer-based catalysts

There were two Ru catalysts, based on PPI dendrimers, immobilized in silica pores. The first one was based on dendrimer of the 2^{nd} generation and synthesized in the presence of polymeric template P123, that is poly(ethylene glycol)₂₀-*block*-poly (propylene glycol)₇₀-*block*-poly (ethylene glycol)₂₀ (Scheme S1). The second was based on the dendrimer of the 3^{rd} generation and synthesized without

polymeric template: herein dendrimer itself acted as template for pore formation (Scheme S2). Ru nanoparticles encapsulation was performed, using wetness impregnation method in two stages (Scheme S3), where the first one was the complexation of Ru³⁺ ions by dendrimer amino groups of the carrier from RuCl₃ solution in water; and the second one was the reduction of Ru³⁺ ions by sodium borohydride, resulting in Ru nanoparticles formation.

Physical and chemical properties of the catalysts, used in the current work, are presented in Tables 1 and 2 [26]. TEM photos and XPS spectra are presented in the Supporting information (Figures S1-S8)

Table 1. Physical chemical properties of the catalysts used in work [26].

Entry	Catalyst	BET surface area of initial carrier, m ² /g	BJH adsorption average pore width of initial carrier, Å	Ru, wt. %	Mean particle diameter <i>d</i> , nm
1	G3-dendr-SiO ₂ -Ru	53.9	14.1	5.4	0.97±0.09
2	G2-dendr-meso-SiO2-Ru	118.5	75.3	3.5	1.28±0.09

Table 2. Physical chemical properties of the catalysts used in work [26].

		Surface concentration by XPS, atomic %					Ru valency states at Ru 3p _{3/2} line, atomic % (eV)				
Entry	Catalyst	Ru	С	N	0	Si	Ru ⁰	Ru/RuO _x	RuO2, Ru (II) N-bound	RuO _* /Ru, Ru (III) O,N- bound	RuCl₃*xH₂O, RuO₃
1	G3-dendr-SiO ₂ -Ru	4.2	22.1	4.5	55.9	13.3	32.7 (461.3)	-	50.2 (464.0)	-	17.1 (466.6)
2	G2-dendr- <i>meso</i> -SiO ₂ -Ru	5.7	32.7	-	35.8	25.8	2.5 (460.5)	3.3 (462.2)	28.3 (463.6)	40.7 (465.0)	25.2 (466.4)

Both catalysts were examined in hydrogenation of levulinic acid. Catalyst activity (TOF = turnover frequency) was calculated as the amount of reacted substrate (v_{substr}) per mole of metal (v_{Ru}) per unit of time according to the equation:

$$\text{TOF} = \frac{V_{substr}^* \omega}{V_{R_u}^* t},$$

where ω is total yield of hydrogenation products (both $\gamma\textsc{-}$ valerolactone and 4-hydroxyvaleric acid), expressed in unit fractions.

As in [26], experimental reaction time, applied for TOF calculations, was that time, at which hydrogenation kinetic curve had a maximum slope, corresponding to 30-50% conversions in the majority of cases. If induction period took place, then only time interval with maximum slope of the curve would be taken into account for TOF calculation. Here induction period was subtracted from the reaction time, for which noticeable conversions (~ 20-50%) were observed.

It should be noted, that reaction conditions play here an important role, influencing the reaction rate and products distribution. Thus, the use of alcohols as solvents often results in side ester formation [2, 10, 16, 27]. 1,4-dioxane and THF may undergo decomposition, especially at high temperatures [2, 4a, 9, 18-19, 27]. Therefore, the water appears to be attractive not only as "green" solvent, but also as medium, excluding possible side reactions [16, 27].

Another important factor, that impacts the reaction rate and selectivity, is temperature. In many works hydrogenation of levulinic acid was carried out at 130-200 °C to obtain the maximum GVL yield [1-2, 4a, 5, 9, 13, 16, 18, 27]. At the same time, the use of high temperatures requires more sophisticated equipment or may cause side reactions, attributed to solvent decomposition [18, 27] or key product (γ valerolactone) overhydrogenation [18, 27]. Mild temperatures (50-90 °C) were applied in [3, 17, 19, 28]. Hence, the temperature of 120 °C was chosen as initial. Also we tested our catalysts at 80 °C to find out a possibility to carry out the hydrogenation of levulinic acid under milder conditions.

As regards to hydrogen pressure, the latter of 25-40 bars was used in most of the works [2-3, 9, 13, 16-19, 27-28]. In some cases overhydrogenation was observed [4a, 10, 18, 27], so it was recommended to decrease pressure to 10-12 bars to get optimal GVL yields. However, in this case reaction conditions were sufficiently more severe (160-200 $^{\circ}$ C) [18, 27], and the process was conducted for a very long time (24-40 hours) [4a, 27] that facilitated side products formation. Therefore, the hydrogen pressure of 30 bars was chosen as operational.

The results obtained are presented in Table 3. As one can see, Ru nanoparticles, stabilized by dendrimers, immobilized in pores of mesoporous silica, effectively catalyze hydrogenation of levulinic acid at 120 °C. Quantitative GVL yields may be obtained already within 2 hours at Ru loadings of 0.02-0.06% mol (Entries 1-2). No products of overhydrogenation (pentanoic acid, methyltetrahydrofuran, 1,4-pentanediol) were observed.

Table 3. High-temperature hydrogenation of levulinic acid in the presence of G2-dendr- meso-SiO₂-Ru catalyst

Entry	Substrate/Ru, mol/mol	Conv., %	TOF, h ⁻¹	Products
1	1700	100	825	γ-valerolactone 97% Angelica-lactone 3%
2	4250	100	2030	γ-valerolactone 95.5% Angelica-lactone 4.5%
3	8505	84	3322	γ-valerolactone 93% Angelica-lactone 7%
4	17010	5	42.5	γ-valerolactone 5% Angelica-lactone 95%
5	34020	1	0	Angelica-lactone 100%

Reaction conditions are: 120 $^{\circ}$ C, 2 hours, 30 bars of H₂, V(substr.) = V(H₂O).

It should be noted, that analogous results were achieved in literature at least for 4-5 hours only, as a rule, at TOF values mostly of 200-1000 h^{-1} for both conventional heterogeneous catalysts, such as Ru/C or Ru/Al₂O₃ [13, 17-18; 27], and ligand-free Ru nanoparticles [27, 29]. Herein, homogeneous Ru catalysts, stabilized by phosphine ligands, demonstrated unexpected low activity in the levulinic acid hydrogenation (only 200 h^{-1}) [28-29], whereas their immobilization on the polymeric carrier resulted in a sufficient drop of TOF values down to 80 h^{-1} [29].

Decrease in temperature from 120 to 80 °C led to corresponding retard of the reaction, and quantitative GVL yields were could to be achieved only within 6 hours (Table 4). Nonetheless, the TOF values obtained are still superior to the majority, reported in literature [2-3, 17, 19], even at higher temperatures [2, 13, 18-19, 27] (See Table 1S).

 Table 4. Medium-temperature hydrogenation of levulinic acid in the presence of G2dendr-meso-SiO2-Ru catalyst

Entry	Substrate/Ru, mol/mol	t, h	Conv., %	TOF, h ⁻¹	Products
1	1700	6	100		γ-valerolactone 97.5% Angelica-lactone 2.5%
2	1700	2	100	1610	γ-valerolactone 91% Angelica-lactone 9%
3	1700	1	79	1010	γ-valerolactone 90.5% Angelica- lactone 9.5%
4	1700	0.5	54		γ-valerolactone 87.5% Angelica-lactone 12.5%
5	4250	0.5	2	101	γ-valerolactone 59.5% Angelica-lactone 40.5%
6	8505	0.5	< 0.5	0	Angelica-lactone 100%

Reaction conditions are: 80 $^{\circ}$ C, 30 bars of H₂, V(substr.) = V(H₂O).

The results obtained can be explained in terms of high dispersion of Ru nanoparticles, provided by the moieties of PPI dendrimers in the catalyst structure. G2-PPI-meso-SiO₂-Ru catalysts appeared only less active, than Ru/TiO₂,

obtained in [16], for which TOFs as high as 18543 $h^{\text{-1}}$ at 130 ^{0}C and 7675 $h^{\text{-1}}$ at 70 ^{0}C were obtained.

As can be seen from Tables 3 and 4, along with γ -valerolactone, angelica-lactone, containing unsaturated C=C double bond, is also formed. The parts of these two products sufficiently depend on substrate to catalyst ratio. Thus, we can observe a sharp decrease in GVL yield for substrate/Ru ~ 17010 at 120 °C and for substrate/Ru ~ 4250 at 80 °C, while the part of angelica-lactone, vice versa, increasing. At very low conversions (~ 1%) angelica-lactone is the only reaction product. Hence, we can conclude, that in the presence of Ru nanoparticles, immobilized in pores of the mesoporous silica, modified with dendrimers, hydrogenation of levulinic acid proceeds through the formation of angelica-lactone as an intermediate product (dehydration and cyclization stage) preferentially, and thereafter hydrogenation takes place.

The possible reason of the preferential formation of angelica-lactone as an intermediate product and its fast

hydrogenation into y-valerolactone can be the presence of PPI dendrimers in the catalyst structure. At high excess of acid under the reaction conditions dendrimer amino groups are protonated, forming ion pairs between quaternized poly(propylene imine) dendrimers and levulinate anion nearby the surface of Ru nanoparticles (Scheme 2). Then another levulinic acid molecule is easily absorbed through hydrogen bonding and undergoes cyclization to angelica-lactone. The close proximity of Ru surface to reacting species in the catalyst structure facilitates further hydrogenation to yvalerolactone (C=C double bond is reduced much easier than C=O). Therefore the introduction of denrimer amino groups has not only effectively improved the dispersion of Ru nanoparticles, decreased the average size of Ru nanoparticles to as small as 1-2 nm, but also facilitated the adsorption of levulinic acid, the latter contributing the increase in the activity of the catalyst as well as in the case of N-doped mesoporous carbon [30].



Scheme 2. Hydrogenation of levulinic acid in the presence of dendrimer-stabilized Ru nanoparticles.

The presence of water had a significant influence on the catalyst activity and selectivity, which had been already noticed in [16]. Some interesting results were obtained during the variation of water to levulinic acid volume ratio (Table 5). The highest GVL selectivity, as well as TOF value, was obtained at the ratio of 1:1, while both the increase and the decrease in water to levulinic acid volume ratio resulted in downfall of these parameters (Table 5). Similar results were also got in [16], where levulinic acid was quantitatively converted to γ -valerolactone at weight water content of 65-70% within a period of 0.5 hour. Carrying out the reaction in neat levulinic acid resulted in decrease of conversion to 62% within 2 hours vs. 100%, while all other conditions being equal (80 °C, 30 bars of H₂, substrate/Ru ~ 1700); herein, the GVL selectivity decreased to 81.5% (vs. 87.5%, Table 5, Entry 2).

Table 5. The influence of water on levulinic acid hydrogenation

Entry	Levulinic acid to water ratio (v : v)	Conv., %	TOF, h ⁻¹	Products
1	<mark>2 : 1</mark>	52	1061	γ-valerolactone 60% Angelica-lactone 40%
2	<mark>1 : 1</mark>	54	1671	γ-valerolactone 91% Angelica-lactone 9%
3	<mark>1:2</mark>	61.5	1444	γ-valerolactone 69% Angelica-lactone 31%

Reaction conditions are: 300 μL of levulinic acid, substrate/Ru ~ 1700, 30 min, 80 ^{0}C , 30 bars of H_2.

Water, as solvent, has a promoting effect on Ru-catalyzed hydrogenation [16, 21a, 22, 31]. Water molecules, adsorbed

on ruthenium surface, are able to polarization and therefore may undergo dissociation; as a consequence, active surface Ru–OH species and free H⁺ ions in solution are formed [31ce]. The evolved H⁺ ions protonate the electron-rich carbonyl group in levulinic acid molecules as well as dendrimer amino groups, resulting in water elimination and the unsaturated cycle formation (Scheme 1). Hence water presumably acts as co-catalyst in hydrogenation of levunic acid, that is confirmed by increase in conversion, when the water is in excess (Table 5, Entry 3).

Decrease in the yield of γ -valerolactone may be attributed to acceleration in H⁺ production [31c] and, as a consequence, to accumulation of the unsaturated intermediate, angelicalactone, for which local substrate to catalyst ratio appears to be very high, reducing the reaction rate. Hence, one may assume, that namely the second, hydrogenation step, of the reaction is rate-limiting, while the first one, that is of dehydration and cyclization, resulting in the angelica-lactone formation, proceeds much more quickly.

Other factors, hindering the subsequent angelica-lactone hydrogenation, may be attributed to the local diffusion limitations, caused by dendritic ligands, as well as to rigid and relatively bulky structure of angelica-lactone, requiring larger adsorption sites in comparison with initial levulinic acid (where carbonyl group only must be adsorbed). Proceeding of the levulinic acid hydrogenation through the angelica-lactone as intermediate (not 4-hydroxyvaleric acid) even in the absence of added water can be explained in terms of water molecules, retained among polar dendrimer branches or by silica framework, or adsorbed on the surface of Ru nanoparticles [21a, 26].

Replacement of mesoporous catalyst G2-PPI-dendrmeso-SiO₂-Ru by microporous G3-PPI-dendr-SiO₂-Ru resulted in appearance of induction period (~ 1 hour), a sharp decrease of the reaction rate at the initial stage (Figure 2). It should be noted, that induction period is typical for Ru catalysts [31d-e, 32] and may be explained in terms of surface oxides, coating Ru nanoparticles (Ru surface is easy oxidized at storage [32]) and, therefore, needed for reduction [31d, 32]. However, according to XPS data, G3-PPI-dendr-SiO₂-Ru catalyst contains higher percentage of Ru⁰ on its surface in comparison with G2-PPI-dendr-*meso*-SiO₂-Ru (Table 2, Figures S5-S8), for which induction period was not observed.



Figure 2. Comparative hydrogenation of levulinic acid in the presence of dendrimer-based Ru hybrid catalysts. Reaction conditions are: 300 μ L of levulinic acid, 5 mg of catalyst (S/Ru ~ 1100-1700), 300 μ L of water, 80 °C, 30 bars of H₂.

The given phenomenon can be explained by differences in support structure between these two catalysts. First of all, in narrow micropores (~ 1.5 nm), that are in G3-PPI-dendr-SiO₂-Ru catalyst, metal nanoparticles (~ 1 nm) much stronger interact with silica walls [33], and, as a consequence, are more slowly reduced. On the other hand, bulky and hindered PPI dendrimers of the 3rd generation (1.5-2 nm in diameter), located in the narrow channels of microporous carrier, cause diffusion limitations, retarding in such way a migration to catalytic centers of both levulinic acid and water molecules. The latters are responsible for "washing out" of the adsorbed water and oxygen from Ru nanoparticles and, therefore, for catalyst activation [31].

Maximum TOF value for G3-PPI-dendr-SiO₂-Ru catalyst achieves 927 h⁻¹. Removal of water from the substrate medium abruptly stops the reaction or makes the induction period very long. Thus, a conversion was equal to zero even after 2 hours of the reaction carried out.

Nonetheless, in the presence of G3-PPI-dendr-SiO₂-Ru quantitative GVL yield can also be achieved within 6 hours at 80 $^{\circ}$ C – as for G2-PPI-dendr-*meso*-SiO₂-Ru (Figure 2). Also a high GVL selectivity (> 90%), observed for G3-PPI-dendr-SiO₂-Ru, even at low conversions of levulinic acid (10-50%), should be noted, whereas angelica-lactone still appears to be a minor reaction product.

Here one may assume, that in micropores, in the presence of small Ru nanoparticles (~ 1 nm) [26], the process of dehydration-cyclization is the rate-limiting step. Probably it may be connected with ionic and hydrogen interactions between multiple aminogroups of the dendrimer (30 for G3 vs. 14 for G2) and carboxylic group of levulinic acid, retarding the conversion of the latter. This suggestion is in accordance with that mentioned above, explaining the appearance of induction period for G3-PPI-dendr-SiO₂-Ru catalyst by diffusion limitations, caused by hindered PPI dendrimers.

After that, while the local angelica-lactone concentration nearby Ru catalytic centers is low, the following hydrogenation occurs quickly. This assumption is confirmed indirectly by hydrogenation of levulinic acid under pressure of 10 bars, when conversion decreased from 76% only to 70% within 2 hours under the other conditions being equal (S/Ru ~ 1100, 80 °C, V(substr.) = V(H₂O)).

Replacement of levulinic acid by its esters resulted in significant changes in catalyst behavior (Figure 3, Tables 7-8). First of all, competition between sterical and electronic factors, being typical of dendrimer-based Ru catalysts in hydrogenation of alkyl-substituted phenols and aromatics [21-22], was observed for both mesoporous and microporous catalysts. Thus, one can see a slight decrease in activity when passing from levulinic acid to methyl levulinate and then increase, when methyl levulinate is replaced by ethyl levulinate (Figure 3).



Figure 3. Comparative hydrogenation of levulinic acid and its esters in the presence of Ru catalysts, based on dendrimer-modified silica. Reaction conditions are: 80 $^{\circ}$ C, 30 bars of H₂, V (substr.) = V (H₂O).

Also it should be noted, that activity of G2-dendr-*meso*-SiO₂-Ru in ethyl levulinate hydrogenation appeared to be superior to that for levulinic acid (1830 h⁻¹ vs. 1608 h⁻¹). Reversed situation is observed for G3-dendr-SiO₂-Ru catalyst (667 h⁻¹ vs. 927 h⁻¹). Hence, one may suppose, that +*I*-effect had predominant influence in case of mesoporous G2-dendr-*meso*-SiO₂-Ru catalyst, while sterical influence is more important for microporous G3-dendr-SiO₂-Ru catalyst. When butyl levulinate was used as a substrate, sharp decrease in activity was observed for both catalysts (Figure 3). The latter phenomenon, appearing as downfall in activity for bulk substrates, is typical for dendrimer-based catalysts [20-26].

The predominant product in hydrogenation of levulinic esters was γ -valerolactone (Tables 6-7); its selectivity was much higher, than earlier was obtained in hydrogenation of levulinic acid (Tables 3-4), and reached up to 99.5% for both catalysts, analogously to [5, 16]. 4-hydroxyvaleric acid and its esters were observed as minor reaction products with a common part up to 7% for G2-dendr-*meso*-SiO₂-Ru catalyst (Table 6, Entries 4, 8, 12). Vice versa, their common part was extremely high (40-65%) for G3-dendr-SiO₂-Ru within short reaction times (Table 7, Entries 5, 10, 14). Also this catalyst was characterized by induction period, earlier observed in levulinic acid hydrogenation (Figure 2).

Therefore one can suggest, that hydrogenation of levulinic esters undergoes mostly through hydrolysis to levulinic acid, that is converted into γ -valerolactone according to the known pathways (Scheme 3), at least at the beginning of reaction. Herein the amino groups of PPI dendrimers are not protonated and therefore promote basic hydrolysis of levulnic esters. This way is apparently typical for catalyst G3-PPI-dendr-SiO₂-Ru, that is characterized by small pore size and high sterical hindrances due to dendrimers of the 3rd generation used.

Herein, production of H⁺ ions, required for cyclization to angelica-lactone, is retarded, and only hydrogenation of carbonyl group becomes preferential. Then, with the increased conversion and H⁺ accumulation, hydrolysis portion also increased, assumed as relation of levulinic acid to remained substrate. Thus, the portion of levulinic acid reached already 7% at a conversion of about 50% for G2dendr-*meso*-SiO₂-Ru catalyst, increasing up to 70% at quantitative conversions. For sterically hindered G3-PPIdendr-SiO₂-Ru the part of hydrolysis was much higher and reached 30-90%. Herein, exposure to hydrolysis for both catalysts decreased in the order: Et > Me >> Bu.

Nonetheless, cyclization of levulinic esters into angelicalactone with the alcohol evolved (Scheme 3) can also take place due to the cooperative effect between Lewis-acid SiO₂ and Brönsted-base amino groups of the dendrimers analogously to [12]. Herein the amount of angelica-lactone exceeds that of 4-hydroxyvaleric acid and its esters in case of G2-dendr-*meso*-SiO₂-Ru within short reaction time (Table 6, Entries 4, 8, 12).

Analogous tendency was observed for G3-PPI-dendr-SiO₂-Ru after passing the induction period (Table 7). Herein, selectivity on γ -valerolactone, higher than for G2-dendr-*meso*-SiO₂-Ru, was observed even at much lower conversions of levulinic esters.



Scheme 3. Suggested ways for levulinic esters hydrogenation.

Table 6. Hyc	rogenation of	levulinic este	rs in the presen	ce of G2-dendr-me	so-SiO2-Ru catalyst
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Entry	Substrate	Substrate/Ru, mol/mol	t, h	Conv., %	TOF, h ⁻¹	Products
1			6	100		γ-valerolactone 99.5% Angelica-lactone 0.5%
2			2	95		γ-valerolactone 95% Angelica-lactone 5%
3	Methyl levulinate	1585	1	75	1484	4-hydroxyvaleric acid 0.5% γ-valerolactone 92.5% Angelica-lactone 7%
4			0.5	52		4-hydroxyvaleric acid 2% γ-valerolactone 88% Angelica- lactone 10%
5			6	100		γ-valerolactone 100%
6			2	100		γ-valerolactone 99.5% Angelica-lactone 0.5%
7	Ethyl levulinate	1526	1	87	1830	γ-valerolactone 99% Angelica-lactone 1%
8			0.5	<mark>61.5</mark>		4-hydroxyvaleric acid 0.5% γ-valerolactone 97% Angelica- lactone 2.5%
9			6	17		γ-valerolactone 98% Angelica- lactone 2%
10			2	<mark>16.5</mark>		4-hydroxyvaleric acid 0.5% Butyl 4-hydroxyvalerate 1% γ-valerolactone 89% Angelica- lactone 9.5%
11	Butyl levulinate	1470	1	12	162	4-hydroxyvaleric acid 1.5% Butyl 4-hydroxyvalerate 2% γ-valerolactone 78.5% Angelica- lactone 18%
12			0.5	8		4-hydroxyvaleric acid 3% Butyl 4-hydroxyvalerate 3.5% γ-valerolactone 62.5% Angelica- lactone 31%

Reaction conditions are: 80 $^{\rm 0}C,$ 30 bars of H₂, V(substr.) = V(H₂O).

Table 7. Hydrogenation of levulinic esters i	n the presence of G3-dendr-	SiO ₂ -Ru catalyst
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Entry	Substrate	Substrate/Ru, mol/mol	t, h	Conv., %	TOF, h ⁻¹	Products
1			6	57		γ-valerolactone 99% Angelica-lactone 1%
2			2	34		γ-valerolactone 98.5% Angelica-lactone 1.5%
3	Methyl levulinate	1030	1.5	6	568	4-hydroxyvaleric acid 1% Methyl 4-hydroxyvalerate 2% γ-valerolactone 91% Angelica- lactone 6%
4			1	2		4-hydroxyvaleric acid 4.5% Methyl 4-hydroxyvalerate 3.5% γ-valerolactone 84% Angelica- lactone 8%
5			0.5	0.5		4-hydroxyvaleric acid 5.5% Methyl 4-hydroxyvalerate 36% γ-valerolactone 38.5% Angelica- lactone 20%
6			6	76		γ-valerolactone 100%
7			2	45		γ-valerolactone 99.5% Angelica-lactone 0.5%
8			1.5	11.5	667	4-hydroxyvaleric acid 3% γ-valerolactone 93.5% Angelica- lactone 3.5%
9	Ethyl levulinate	990	1	2.5		4-hydroxyvaleric acid 3.5% Ethyl 4-hydroxyvalerate 5.5% γ-valerolactone 84.5% Angelica- lactone 6.5%
10			0.5	0.5		4-hydroxyvaleric acid 5% Ethyl 4-hydroxyvalerate 49.5% γ-valerolactone 30.5% Angelica- lactone 15%
11			6	14		4-hydroxyvaleric acid 2.5% Butyl 4-hydroxyvalerate 3% γ-valerolactone 93.5% Angelica- lactone 1%
12			2	4.5		4-hydroxyvaleric acid 3% Butyl 4-hydroxyvalerate 3.5% γ-valerolactone 88.5% Angelica- lactone 5%
13	Butyl levulinate	950	1.5	2	46	4-hydroxyvaleric acid 4.5% Butyl 4-hydroxyvalerate 13.5% γ-valerolactone 75% Angelica- lactone 7%
14			1	1		4-hydroxyvaleric acid 9% Butyl 4-hydroxyvalerate 56% γ-valerolactone 23% Angelica- lactone 12%
15			0.5	0		-

Reaction conditions are: 80 $^{\circ}$ C, 30 bars of H₂, V(substr.) = V(H₂O).

Recycling test

Catalysts G2-PPI-dendr-*meso*-SiO₂-Ru and G3-PPI-dendr-SiO₂-Ru were tested for the possibility of recycling in the hydrogenation of levulinic acid in water medium. The recycling test was performed similarly to the standard procedure for hydrogenation in the presence of ruthenium catalysts [20a]. Because of the slow sedimentation of catalyst particles from the aqueous solution of γ -valerolactone as well as of levulinic acid (See Figures S9-S10 in the Supporting information), the reaction mixture was additionally diluted with ethanol and centrifuged. After that, the reaction solution was decanted and new portions of levulinic acid and water were added to the remaining catalyst. For both catalysts six reaction cycles were conducted totally. Results are presented in Figures 4 and 5.

As one can see form Figures 4 and 5, the use of centrifugation allow to recycle heterogeneous dendrimerbased catalysts without significant loss of activity and selectivity on γ -valorolactone. Total turnover numbers were 7507 and 9159 for catalysts G2-PPI-dendr-*meso*-SiO₂-Ru and G3-PPI-dendr-SiO₂-Ru correspondingly.

Therefore, hybrid catalysts based on Ru nanoparticles, that are immobilized in silica pores, modified with PPI dendrimers, can be successfully reused for several times.

Conclusions

Hybrid catalysts, based on Ru nanoparticles, that are immobilized in dendrimer-modified silica pores, have been prepared and successfully examined in hydrogenation of levulinic acid and its esters under mild conditions. It was found, that reaction rate and selectivity on γ -valerolactone were strongly dependent on the complex of factors, such as carrier structure, temperature, the presence of water and substrate/Ru ratio. All this made it possible to suggest the

probable mechanism of reaction, that mostly underwent through angelica-lactone, not 4-hydroxyvaleric acid.



Figure 4. Recycling of G2-PPI-dendr-*meso*-SiO₂-Ru catalyst in levulinic acid (LA) hydrogenation. Reaction conditions are: 300 μ L of levulinic acid, 300 μ L of water, substrate/Ru ~ 1700, 1 h., 30 bars of H₂, at 80 °C.



Figure 5. Recycling of G3-PPI-dendr-SiO₂-Ru catalyst in levulinic acid (LA) hydrogenation. Reaction conditions are: 300 μ L of levulinic acid, 300 μ L of water, substrate/Ru ~ 1100, 2 h., 30 bars of H₂, at 80 ^oC.

Mesoporous G2-PPI-dendr-meso-SiO₂-Ru catalyst converted levulinic acid into angelica-lactone fast enough, while the latter was hydrogenated to y-valerolactone much slower. Herein, substrate to catalyst ratio, as well as water content in the reaction medium, played a crucial role, influencing the GVL selectivity. In contrast, for G3-PPI-dendr-SiO₂-Ru, cyclization of levulinic acid into angelica-lactone was found to be the rate-limiting step, while the subsequent hydrogenation proceeded fast, and high GVL selectivities (≥ 90%) can be obtained even at low levulinic acid conversions (~ 10%). Herein preferential formation of angelica-lactone as the main intermediate product may be explained in terms of cooperation interactions between base aminogroups of dendrimers and acid sites of SiO₂ support, favouring the cyclization.

Quantitative yields of γ -valerolactone may be realized for both microporous and mesoporous catalysts within 2 hours at 120 °C and within 6 hours at 80 °C, with TOF values significantly exceeding those reported in literature.

Replacement of levulinic acid by its esters resulted in corresponding decrease in activity, typical for dendritic catalysts. γ -valerolactone was a predominant reaction product with a selectivity of 97-99.5%. Levulinic esters were found to undergo hydrolysis during the reaction. The fraction of hydrolysis products reached up to 98% (with respect to unreacted substrate) for G3-PPI-dendr-SiO₂-Ru, which was characterized by small narrow pores and high sterical hindrance.

In a whole, the presence of PPI dendrimers in catalyst structure enhanced the Ru nanoparticles dispersion and, as a consequence, favoured to high activity of the catalysts in hydrogenation of levulinic acid and its esters. Herein dendrimer amino groups additionally facilitated substrate adsorption on the Ru surface, acting as basic or acidic (when protonated) co-catalysts.

The catalysts synthesized may be reused several times without s ignificant loss of activity, however their effective recycling requires additional centrifugation procedure.

Experimental Section

Chemicals

Levulinic acid H₃CC(=O)CH₂CH₂COOH (Aldrich, 98%) was used as a main substrate. Levulinic esters (methyl, ethyl and butyl) were synthesized according to standard procedure by alkylation of levulinic acid with corresponding alcohols in acid medium [34].

For synthesis of mesoporous hybrid dendrimer-based catalysts were used: ruthenium (III) chloride RuCl₃ ("Aurat" OJSC, Purum, 47.80% of Ru content), poly(propylene imine) (PPI) dendrimers of the 2nd (DAB(NH₂)₈) and 3^{rd} generations (DAB(NH_2)_{16}) with a diaminobutane core (earlier prepared according to literature procedure [35]). (3glycidoxypropyl)trimethoxysilane (Aldrich, ≥ 98%), poly(ethylene glycol)block-poly(propylene glycol)-block-poly(ethylene glycol) with the average number molecular weight M_n of 5800 (Pluronic P 123, Aldrich) $HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2CH_2O)_{20}H \quad and \quad tetraethoxysilane$ Si(OEt)₄ (Aldrich, \geq 99%).

Synthetic procedures the dendrimer-based catalysts

The synthesis of microporous G3-dendr-SiO₂ hybrid support [26]. Into 10 mL single-neck round-bottom flask, equipped with a magnetic stirrer and a reflux condenser, 1.04 g (0.617 mmol) of DAB(NH₂)₁₆ dendrimer and 5 mL of ethanol were placed. Then, after dendrimer had been completely dissolved in ethanol, 1.5 mL (6.8 mmol) of (3-glycidoxypropyl) triethoxysilane were added dropwise at room temperature, while stirring. Therefore one epoxy group of modifier fell on 2 end amino groups of the dendrimer. Reaction was carried out at 70 $^{\circ}$ C for one hour, while stirring. Herein the reaction mixture gradually thickened and later turned into white flake-like gelatinous precipitate.

Then a preliminary homogenized mixture of 10 mL (45.121 mmol) of Si(OEt)₄ and of 2 mL of aqueous (36%) hydrochloric acid was added to the product obtained. After a short while stirring, white gelatinous residue was formed. The mixture obtained was transferred into a chemical glass beaker, after that 2 mL of aqueous (25%) ammonia and 5 mL of water were added to it. The white homogeneous gel formed was staved in drying chamber for 3 hours under a gradual temperature increase from 60 to 110 °C. A yield of the product obtained (as white powder) was 4.8 g (88%).

IR (cm⁻¹): 3446.70 (O-H_{st} and N-H_{st} NH-C(-OH), broad unresolved band); 2940 (C-H_{st}); 2927.73 (C-H_{st}, CH₂-O_{st}); 2845 (C-H_{st}, CH₂-N_{st}); 1750 (C=O_{st} in CH₂-C(=O), weak band); 1666.48 (C=O_{st} in CH₂-C(=O...H), weak band; NH_{2d}); 1539.64 (NH_{2d}); 1465.15 (CH_{2d}); 1325, 1200, 1070.46 (C-O_{st}, C-N_{st} in NH-C(-OH)); 958.68; 799.85 (O-H_d); 750 (N-H_d, CH_{2g}, weak unresolved band).

XPS (eV): 103.2 (SiO₂, Si 2p, 19.5%); 285.7 (NCH₂CH₂CH₂N, NCH₂CH₂O, C 1s, 24.3%); 399.3 (NCH₂CH₂CH₂N, NCH₂CH₂O, N 1s, 5.1%); 532.7 (SiO₂, OCH₂CH₂O, O 1s, 51.1%).

 13 C NMR (δ , ppm): 75 (-CH₂CH₂OCH₂); 66 (-(CH₂)₂CHOH); 58 (NCH₂CH₂CH₂CH₂CH₂M); 53 (NCH₂CH₂CH₂N); 46 (NCH₂CH₂CH₂NHCH₂); 38.5

The synthesis of mesoporous G2-dendr-meso-SiO₂ hybrid support [26, 36]. The first stage of synthesis was carried out analogously to the previous procedure. Into a 25 mL single-neck round-bottom flask, equipped with a magnetic stirrer and a reflux condenser, 1.445 g (1.87 mmol) of DAB(NH₂)₈ dendrimer and 5 mL of ethanol were placed. Then 1.65 mL (7.5 mmol) of (3-glycidoxypropyl)triethoxysilane were added dropwise at room temperature, while stirring. Reaction was carried out at 80 °C for 2 hours while stirring, and the flask content gradually turned into viscous red oil. This reaction mixture was kept for a night at room temperature, after that it turned into a rose-orange gel, that was further evaporated on a rotary evaporator, giving a glass-like fragile residue, weighing 3.3 g.

At the next stage, 1.46 g of Pluronic P123 were placed into a 100 mL glass beaker, containing a solution of 52.5 mL of deionized water and 0.325 mL of concentrated hydrochloric acid (Sigma-Tech, Chemical Grade). The mixture obtained was subjected to stirring at 50 °C for 3 hours, gradually growing turbid. After that a previously obtained and ground modified dendrimer was added to the resultant colloid solution of polymer, followed by stirring for 2 hours.

Then 1.6 mL of concentrated hydrochloric acid (Sigma-Tech, Chemical Grade) were added to 8.3 mL (37.2 mmol) of Si(OEt)₄, placed into a 25 mL glass beaker. This solution was added to the earlier obtained mixture of Pluronic P123 and Si(OEt)₃-modified dendrimer. Therefore, one mole of the end modified amino groups of the dendrimer fell on the 5 moles of Si(OEt)₄. A viscous milky-white mixture formed, which did not gelate for a night. This residue was staved in drying chamber for 3 hours under a gradual temperature increase from 60 to 110 $^{\circ}$ C, after that it was subjected to stirring with 50 mL of water and 75 mL of ethanol at 70 $^{\circ}$ C, to have the polymer washed out. Then 2 mL of aqueous ammonia (25%) and 5 mL of water were added, resulting in a white fluffy precipitate. After that, 2 mL of concentrated hydrochloric acid (Sigma-Tech, Chemical Grade) and 5 mL of water were added. After night the residue obtained was subjected to centrifugation, washed out with water and ethanol and dried in the air. The product was isolated as cream powder, weighing 7.72 g.

 ^{13}C NMR ($\delta,$ ppm): 86 (-OCH_2N-); 74 (-CH_2CH_2O); 44 (NCH_2CH_2CH_2D); 30 (NCH_2CH_2CH_2N); 16 (SiCH_2CH_2CH_2O).

The synthesis of catalyst G2-dendr-meso-SiO₂-Ru [21, 26, 37]. A 500 mg portion of the meso-DAB-PPI-G2-GlycdSiO₂ hybrid support, 10 mL of the distilled water and 99 mg (0.48 mmol) of RuCl₃ were placed into one-neck 50 mL round-bottom flask, equipped with a reflux condenser and a magnetic stirrer. Then another 5 mL of water were added. The reaction was carried out for 8 hours at room temperature, while stirring. After that the reaction mixture was evaporated on a rotary evaporator, giving dark-grey powder residue, weighing 441 mg (73.6%).

To reduce Ru (III) to Ru (0), 5 mL of aqueous solution of NaBH₄ (70 mg, 1.85 mmol) were added dropwise to a suspension of catalyst precursor (441 mg) in 5 mL of ethanol, while stirring. Then additional 5 mL of ethanol were passed through the dropping funnel to wash NaBH₄ residues down to the reaction mixture. Herein the violent effervescence was observed. The reaction was conducted for 8 hours at room temperature, while stirring. After that, the suspension was centrifuged, and the residue was washed with water and ethanol, to be separated from the soluble unreacted NaBH₄ and its oxidation product Na₂B₄O₇, and then dried in the air. The product was isolated as black-grey powder with the yield of 400 mg (66.8%).

ω_{Ru} (UV-Vis.): 3.5%.

XPS (eV): 103.2 (SiO₂, Si 2p, 25.8%); 280.2 (Ru^o, Ru/RuO_x and RuO₂, Ru (II) N-bound, Ru 3d_{5/2}), 281.7 (RuCl₃ or RuO₂, Ru 3d_{5/2}), 282.4 (RuO_x/Ru or RuCl₃*xH₂O, Ru 3d_{5/2}), 283.0 (RuO₃, Ru 3d_{5/2}); 284.2 (Ru^o, Ru/RuOx and RuO2, Ru (II) N-bound, Ru 3d3/2), 285.8 (RuCl3 or RuO2, Ru 3d_{3/2}), 286.7 (RuO_x/Ru or RuCl₃*xH₂O, Ru 3d_{3/2}), 287.2 (RuO₃ or Ru (III/IV) O,N-bound, Ru 3d_{3/2}); 283.7 (C-Si or C=M, C 1s, 6.9%), 285.0 (NCH₂CH₂CH₂N SiCH₂CH₂CH₂O, С 1s, 15.1%), and 286.2 (NCH₂CH₂CH₂N, -CH₂CH₂N \rightarrow Ru⁰, NCH₂CH₂O, OCH₂CH₂O, C 1s, 6.8%), 287.6 (O-C-O, $-CH_2CH_2O \rightarrow RuO_x$, C 1s, 3.0%), 288.9 (O-C-O, C 1s, 0.8%);460.5 (Ruº, Ru 3p3/2, 0.1%), 462.2 (RuO2, Ru (II) N-bound, Ru 3p3/2, 0.2%), 463.6 (RuCl₃, Ru 3p_{3/2}, 1.6%), 465.0 (RuO_x/Ru or RuCl₃*xH₂O, Ru 3p3/2, 2.3%), 466.4 (RuO3 or Ru (III/IV) O,N-bound, Ru 3p3/2, 1.4%); 530.8 (RuOx, O 1s, 19.0%), 532.6 (SiO2, O-Si-CH2, OCH2CH2O, O 1s, 16.8%)

 13 C NMR (ô, ppm): 84 (-OCH₂N-); 73 (-CH₂CH₂O); 65 (-(CH₂)₂CHOH); 51 (NCH₂CH₂CH₂CH₂N); 23.3 (NCH₂CH₂CH₂N); 8.7 (SiCH₂CH₂CH₂O).

The synthesis of catalyst G3-dendr-SiO₂-Ru [21, 26, 37]. The synthesis of hybrid DAB-PPI-G3-GlycdSiO₂-Ru was performed according to the above described procedure. 500 mg of a microporous hybrid carrier DAB-PPI-G3-

GlycdSiO₂ and 94 mg (0.45 mmol) of RuCl₃ in 15 mL of water were taken as initial substances. An intermediate product was isolated as dark-grey powder, weighing 563 mg (yield of 95%).

At the next step, 563 mg of the earlier obtained precursor and 171 mg (4.5 mmol) of NaBH₄ in the mixture of 5 mL of water and 10 mL of ethanol were taken to reduce Ru (III) to Ru (0). NaBH₄ was added here portionwise, and self-heating of the reaction mixture was observed. The product obtained was isolated as dark-grey powder with the yield of 539 mg (99%).

ω_{Ru} (UV-Vis.): 5.4%.

XPS (eV): 103.0 (SiO₂, Si 2p, 13.3%); 278.2 (Ru^o, Ru 3d_{5/2}, 1.35%), 281.1 (RuO₂ or RuCl₂ N-bound, Ru 3d_{5/2}, 2.1%), 282.7 (RuO₃ or RuCl₃ N-bound, Ru 3d_{5/2}, 0.7%)4 283.2 (Ru^o, Ru 3d_{3/2}), 285.2 (RuO₂ or RuCl₂ N-bound, Ru 3d_{3/2}), 286.9 (RuO₃/Ru or RuCl₃*H₂O, Ru 3d_{3/2}); 283.5 (C-Si or C=M or C=N, C 1s, 3.3%), 285.7 (NCH₂CH₂CH₂N, SiCH₂CH₂CH₂O, NCH₂CH₂CH₂N, -CH₂CH₂N→Ru⁰, -CH₂CH₂N⁺, C 1s, 13.0%), 287.8 (O-C O, O-C-N, OCH₂CH₂N+, CH₂CH₂O→RuO₃, C 1s, 5.0%), 289.6 (-C(OCH₂-)₃ or NCH₂CH₂CH₂N/ OCH₂CH₂O (sat), C 1s, 0.6%); 461.3 (Ru^o, Ru 3p_{3/2}), 464.0 (RuO₂ or RuCl₂ N-bound, Ru 3p_{3/2}), 466.6 (RuO₄/Ru or RuCl₃*xH₂O, Ru 3p_{3/2}); 397.8 (N=Ru_{das} or -CH₂C=N→Ru or C=N-C, N 1s, 1.6%), 400.0 (NCH₂CH₂CH₂N, NCH₂CH₂O, -CH₂N→Ru, N 1s, 1.9%), 402.8 (NR4⁺, R₃N⁺→O⁻, N 1s, 1.0%); 531.4 (RuO₃, RuO₄/Ru, O 1s, 12.6%), 532.9 (SiO₂, O-Si-CH₂, OCH₂CH₂O, O 1s, 29.3%), 534.5 (RuCl₃*xH₂O, H₂O--N/H₂O--O, O 1s, 13.9%).

Analyses and Instrumentations

Analysis by transmission electron microscopy (TEM) was conducted using a LEO912 AB OMEGA microscope with electron tube voltage of 100 kV. The count of particles and calculation of mean particle size was performed by processing the obtained microimages using the "Image J" program.

X-ray photoelectron studies (XPS) were carried out using a LAS-3000 instrument, equipped with a photo-electronic analyzer with retarding potential OPX-150. To excite photoelectrons, aluminum anode X-ray radiation was used (AIK_{α} =1486.6 eV) with a tube voltage of 12 kV and emission current of 20 mA. The calibration of photoelectron peaks was performed along the C1s line with binding energy of 284.8 eV.

The solid state ¹³C CPMAS NMR spectroscopy analysis was carried out on the Varian NMR Systems 500 MHz spectrometer at an operating frequency of 125 MHz using TanCP with a spinning speed of 10 kHz.

FTIR spectra were registered with a Nicolet IR 2000 (Thermo Scientific) emploing multiple distortion of the total internal reflection method with Multi-reflection HATR accessories, containing a ZnSe crystal 45° for different wavelengths with a resolution of 4 cm⁻¹.

Analysis by means of nitrogen low-temperature adsorption and desorption was carried out on a Gemini VII 2390 instrument (Micromeritics Instrument Corp.). Nitrogen adsorption–desorption isotherms were obtained at 77 K. The samples being analyzed were previously outgassed at 150 °C for 12 h. Surface area measurements were performed according to the BET method from nitrogen adsorption points in the range P/P₀ = 0.05–0.2. Pore size distribution was calculated using the Barrett-Joyner-Halenda model (BJH). The diameter corresponding to the maximum of the pore size distribution curve was suggested as the average pore size. Total pore volume was obtained at a relative pressure P/P₀ of 0.985.

Weight content of ruthenium in samples was determined with a help of spectrophotometry method on the instrument "Agilent UV-Vis. 8453" [38]. Ru-containing samples were treated with a mixture of 2 mL of concentrated hydrochloric acid (Sigma-Tech, Chemical Grade) and 3 mL of 30% hydrogen peroxide (Aldrich). Then the solutions obtained were diluted with distilled water up to volume of 10 mL, after that 15 mL of 0.015 M 1,10-phenantroline solution (Lachema, 98%) were added to them. To reduce Ru (III) into Ru (II), 0.2-0.6 g of hydroxylamine hydrochloride (Reachim, Purum) were added to each solution with a subsequent heating in a water bath at 100 $^{\circ}$ C for 2 hours. After that all solutions were subjected to intensity of the absorption band for complex [Ru(phen)₃]²⁺ at 449 nm ($\epsilon = 1.5 \times 10^4$ M⁻¹ cm⁻¹) [39].

Atomic emission spectroscopy with inductively coupled plasma was used to measure Ru leaching at recycling tests with a help of IRIS Interpid II XPL instrument (Thermo Electron Corp., U.S.A.) in radial and axial observation modes at wavelengths of 204.5 and 85.1 nm.

Protocol for the catalytic experiments

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The required amounts of catalyst, substrate and water were placed into a thermostated steel autoclave, equipped with a glass vial insert and a magnetic stirrer. The autoclave was sealed, pressurized with hydrogen to a pressure up to 30 atm. and connected to the thermostat. Reactions were conducted at 80 and 120 °C. After the reaction passed out for the required time, autoclave was cooled below room temperature and depressurized.

The reaction products were analyzed using gas–liquid chromatography on the instrument ChromPack CP9001, equipped with a flame ionization detector and a 30 m \times 0.2 mm column containing a grafted SE-30 phase. Chromatograms were recorded and analyzed on a computer using the program Maestro 1.4. Conversion was calculated by changes in the relative area (%) of substrate and products peaks.

The reuse of dendrimer-based Ru hybrid catalysts was conducted as follows. Catalyst (5 mg), levulinic acid (300 μ l) and water (300 μ l) were placed into the thermostated steel autoclave equipped with a glass vial insert and a magnetic stirrer. The autoclave was sealed, pressurized with hydrogen up to a pressure of 30 atm. and then connected to the thermostat. The reaction was carried out for 1 hour for G2-Ru or 2 hours for G3-Ru at 80 °C. After that, the reactor was cooled below room temperature and depressurized. The reaction mixture was diluted with acetone or ethanol (2 mL) and allowed to stand for 30 min or one day. Then the mixture was separated from the catalyst located in the vial was used for the next reaction cycle without additional loading, drying, or regeneration.

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Keywords: levulinic acid • hydrogenation • Ru nanoparticles • dendrimers • organosilica

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