Solvent-free Hydrodeoxygenation of γ -Nonalactone on Noble Metal Catalysts Supported on Zirconia

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Abstract

The possibility to valorize levulinic acid (LA) dimers to lignocellulose-based biofuels via hydrodeoxygenation (HDO) was assessed using γ -nonalactone (GNL) as a model compound. Catalytic HDO experiments were performed in a batch reactor at 280 °C and at an average pressure of 57.5 bar H₂. Noble metal (Ru, Rh, Pd, and Pt) catalysts supported on ZrO₂. All the catalysts were active in removing oxygen from the reactant. However, the most selective catalyst for hydrocarbons (24%) was ruthenium. Unlike the other tested catalysts, Ru also provided branched hydrocarbons. In view of Ru's comparatively high selectivity to hydrocarbons, it was tested at various reaction temperatures (220–280 °C) for 300 min. The experiments at lower temperatures resulted in less hydrocarbons and more intermediate products, such as alcohols. In total, nearly 70 products were identified, and some of the reactions that likely occurred in the HDO experiments were discussed. The production of hydrocarbons from GNL highlights the potential of LA dimers as a route to lignocellulose-based biofuels.

Keywords Levulinic acid dimer · γ -Nonalactone · Hydrodeoxygenation · Noble metal · Hydrocarbon · Fuel

1 Introduction

Concerns regarding climate change and the insufficiency of fossil-based materials have directed the attention of research towards bio-based alternatives [1]. One of these alternatives is lignocellulose, which is considered as an abundant resource for replacing fossil-based fuels [2]. The raw materials derived from lignocellulose, which contain many

functional groups, can be transformed into various chemical intermediates and final products [3]. Levulinic acid (LA), in addition to furfural, is one of the most important platform chemicals [4–6], which can be produced from lignocellulosic sugars: hexoses or pentoses [5].

LA, a γ -keto-carboxylic acid (C₅H₈O₃), is highly reactive and has several applications as a specialty chemical in agriculture, chemical industry, and in the food industry [7]. γ -Valerolactone (GVL) is an important chemical produced from LA via homogeneous (e.g. RuCl₂(PPh₃)₃) or heterogeneous (e.g. Ru/C) catalysis [8]. Recently, the catalytic conversion of GVL to fuels has been studied [8]. So far, the target has been to produce bio-based oxygenates to be blended with gasoline. For example, the production of 2-methyltetrahydrofuran (MTHF), which can be blended with gasoline, has been reported by Bozell et al. [9]. Hydrocarbons are usually considered undesired products in the hydrodeoxygenation (HDO) of GVL, because the carbon chain is too short for transportation fuels. In fact, heavier hydrocarbons are necessary for bio-based jet fuel or diesel [10]. Converting GVL to pentenoic acid offers at least two possible routes to heavier hydrocarbons [8].

Bond et al. [11] studied the ring-opening of GVL to pentenoic acid, which in turn was decarboxylated to butenes.

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Butenes were further oligomerized to higher alkanes [12]. Another route to alkanes proceeded via pentenoic acid hydrogenation to pentanoic acid [13, 14], which was ketonized to 5-nonanone and finally deoxygenated to alkanes [15]. Moreover, the aldol condensation of various lignocellulose-derived carbonyl compounds to form larger molecules (up to C_{15}) has been studied recently [3]. These compounds can be subsequently converted into diesel fuel components [16]. For the LA platform, aldol condensation into LA dimers was first described by Blessing et al. [17]. This route was further explored recently by Kåldström et al. [18]. The aldol condensation of LA was performed in hydrogenating conditions in the presence of a strong cation exchange resin containing palladium. The products were mostly C_{10} , branched dimers containing carboxyl, carbonyl, and lactone moieties [18]. These dimers might be a suitable feedstock for HDO in order to obtain hydrocarbons.

γ -Nonalactone (GNL) is a C_9 compound having two oxygen atoms. It can be considered as a model compound for LA dimers, representing the lactone moieties present in them. Because the preservation of the dimers' carbon chains is desired, the study of a compound with a long sidechain is relevant. In biofuel production, HDO is used to increase the energy density of the feed by removing oxygen as water [19]. To our knowledge, GNL has not been studied in HDO, although it is analogous to GVL.

Conventional HDO is performed with sulfided catalysts, such as NiMo and CoMo on Al_2O_3 , which require sulfur replenishing. However, sulfur from this process contaminates the product, requiring additional processing for sulfur removal [19]. Another option is to utilize bifunctional noble metal catalysts, which are known for their ability to activate and eliminate the carbonyl, as experienced by fatty acids and their esters [20]. They have also been found to be active in the HDO of lignin-derived guaiacol [21]. By using a less acidic support than conventional γ - Al_2O_3 , such as ZrO_2 , excess coking could be prevented [20].

In this work, the HDO of GNL was studied as a model compound for LA dimers using noble metal catalysts supported on ZrO_2 . The goal was to obtain components suitable for transportation fuels and to minimize the yield of oxygenates. A possible reaction network is discussed, including a diester compound that has not been reported previously in the context of lactone HDO.

2 Experimental Section

2.1 Materials

Reagents purchased from Sigma-Aldrich were utilized without further purification including GNL (98%), 2-butanol (99%), 2-propanol ($\geq 99.5\%$), 3-octanone ($\geq 98\%$), octanoic

acid ($\geq 99\%$), 3-octanol (99%), octane (analytical standard), nonanoic acid (98%), methyl nonanoate ($\geq 97\%$), 4-nonanone (sold 'AS IS' without purity identification), 1-nonanol (98%), nonane (analytical standard), hexanoic acid ($\geq 99\%$), hexane ($\geq 95\%$), heptanoic acid (96%), heptane (anhydrous, 99%) and *n*-methyl-*n*-trimethylsilylfluoroacetamide (98.5%). 4-Nonanol [Assay (GC, area%): $\geq 96.5\%$ (a/a)] and 2-heptanone ($\geq 98\%$) were purchased from Merck KGaA and acetonitrile (99.9%) and formic acid (99%) from VWR Chemicals, and these chemicals were also utilized without further purification. The chemicals used in the Karl-Fisher titration were: Merck's Apura® two component titrant containing MeOH and iodine, Merck's Apura® solvent for volumetric Karl-Fisher titration containing MeOH and imidazole, and Merck's Apura® water standard (1% H_2O).

All gases were purchased from Oy AGA Ab including hydrogen utilized in the HDO experiments (purity 5.0) and gases required for the various analytical techniques: hydrogen (purity 5.0), helium (purity 4.6), argon (purity 5.0), synthetic air (purity 5.0), oxygen (purity 5.0) and nitrogen (purity 5.0). Two calibration gas mixtures from Oy AGA Ab were utilized. The first contained 40 mol% nitrogen, 5 mol% methane, 10 mol% ethane, 5 mol% ethene, 10 mol% propane, 5 mol% propene, 5 mol% acetylene, 10 mol% butane and 10 mol% isobutene. The second contained 15 vol% carbon monoxide, 15 vol% carbon dioxide, 15 vol% hydrogen, 40 vol% nitrogen and 15 vol% methane.

Monoclinic ZrO_2 from Saint-Gobain NorPro was used as a catalyst support. Metal precursors were purchased from Sigma-Aldrich [Rh(III) nitrate solution (10 wt% Rh in > 5 wt% HNO_3)], Alfa Aesar [Pt(IV) nitrate solution (15 wt% Pt) and Pd(II) nitrate solution (12–16 wt% Pd)] and Acros Organics [Ru(III) chloride hydrate (35–40 wt% Ru)].

2.2 Catalyst Preparation

The ZrO_2 support was ground, sieved to 0.25–0.42 mm, and calcined in synthetic air at 600 °C for 10 h. The metal catalysts (nominally 3 wt%) were prepared by incipient wetness impregnation using appropriate amounts of aqueous solutions of metal precursors. For this purpose, the pore volume of the support was estimated by its water uptake capacity, which was approximately 40 wt%. During the impregnation, the precursor solution was added drop by drop and mixed with a spatula. Several batches were prepared with a typical size of 3 g. After impregnation, the catalysts were dried at room temperature for 5 h and in an oven at 100 °C overnight. The prepared catalysts were thermally treated (300 °C) under synthetic air flow of 100 mL/min for 3 h (heating rate 30 °C/h). The catalysts' particle size was assumed to be the same as for the support after impregnation. In the case of the Ru catalyst, the chloride from the precursor could not

be fully removed during heat treatment and reduction (see Sect. 4).

2.3 Catalyst Characterization

2.3.1 X-ray Fluorescence

The metal loadings of the prepared catalysts were analyzed by X-ray fluorescence (XRF). Each sample was ground and pressed into a tablet using Boreox® binder and an aluminum cup. The measurements were performed with a Rigaku ZSX Primus wavelength dispersive spectrometer.

2.3.2 X-ray Diffraction

X-Ray diffraction (XRD) analysis to detect the crystallographic phases present on the support oxide and the metal catalyst was executed with a PANalytical X'Pert PRO MPD Alpha-1 diffractometer with Cu K α 1 radiation (45 kV and 40 mA) for the fresh catalysts. The X-ray scanning range was 4.5°–120° (2 θ) with a step of 0.0131°. The samples were ground for the analysis.

2.3.3 Physisorption

Isothermal (–196 °C) nitrogen physisorption measurements in liquid nitrogen were performed using a Thermo Scientific's Surfer equipment. Specific surface areas were calculated from adsorption isotherms according to the Brunauer–Emmett–Teller theory (BET) [22]. The total pore volume and average pore diameter were calculated based on the Barrett–Joyner–Halenda method (BJH) [23]. Prior to the N₂ adsorption, each catalyst sample (about 300 mg) was weighed in a quartz tube and evacuated in elevated temperature (200 °C, 3 h) in order to remove any adsorbed components and moisture. For the spent catalyst, the evacuation was performed at lower temperature (120 °C, 5 h) to avoid the burning of the possible carbonaceous material formed in the experiment.

2.3.4 Chemisorption

Active metal dispersion and average metal particle size were calculated from the chemisorption of hydrogen or carbon monoxide using a Thermo Scientific's Surfer equipment. Each sample (about 300 mg of fresh, calcined catalyst or spent, washed catalyst after experiment) was weighed in a U-shaped quartz tube and supported with quartz glass wool. Prior to the measurements, the samples were reduced in hydrogen flow at 290 °C for 3 h. Afterwards, degassing down to pressure 10^{–5} Torr was performed under the same temperature for 2 h. Adsorption measurements were performed at 35 °C except with Ru catalyst (75 °C) as suggested

by Shen et al. [24] CO was chosen as probe molecule for Pt to avoid hydrogen spillover and for Pd to avoid bulk hydride formation [25], and it was also used for Rh. For Ru, H₂ was selected as suggested by Shen et al. [24] Two chemisorption isotherms were measured: the first of the total adsorption and the second of the reversible adsorption. Degassing the sample down to pressure 10^{–5} Torr was performed isothermally between the two measurements to remove all reversibly adsorbed gas. The irreversibly adsorbed monolayer volume was obtained from the linear regression of the subtracted isotherm to zero pressure from which the dispersion and particle size were calculated [25]. The metal particles were assumed to be spherical, and the adsorption stoichiometry was assumed to be two for H₂. For CO, the adsorption stoichiometry is more controversial, but an approximation of CO and metal stoichiometry of 1:1 has been widely used for noble metals in previous studies as listed in the Handbook of Heterogeneous Catalysis [25], and was also adopted in this work.

2.3.5 Scanning Transmission Electron Microscopy

Scanning transmission electron microscopy (STEM) images were taken from the fresh and spent catalysts to estimate the average size of the metal nanoparticles deposited on the support before and after the experiment. A JEOL JEM-2200FS high resolution microscope was used at 200 kV acceleration voltage and with magnifications from 3 × 10⁶ to 8 × 10⁶. Energy-dispersive X-ray spectroscopy (EDS) was applied alongside with STEM to detect the chemical elements present in the sample. STEM images were used to measure particle diameters. The numbers of measured particles were 84 for ruthenium, 59 for rhodium, 49 for palladium, and 198 for platinum. In the case of the spent catalysts, 328 particles were measured for Ru, 355 for Rh, 380 for Pd, and 646 for Pt. Statistical inferences were applied to estimate the sampling error, as described in Online Resource.

2.3.6 Thermogravimetric Analysis

The amount of solids deposited on the catalysts during HDO reactions was determined by thermogravimetric analysis (TGA) for the spent catalysts. Tests were performed in a TA Instruments' TGA Q500 equipment. Around 20 mg of spent, unwashed catalyst was dried in pure nitrogen ramping from room temperature up to 250 °C at 10 °C/min (GNL boiling point 243 °C). The ramp was followed by a 5 min hold at 250 °C. Afterwards, the same procedure was repeated up to 900 °C on the dried sample with pure oxygen.

2.4 HDO Experiments

HDO experiments were performed in a three phase system, solvent-free, and with the catalyst forming a slurry with the liquid. A 100 mL batch reactor by Parr was used. Before each experiment, 0.6 g of catalyst was placed in the reactor and dried in nitrogen at 180 °C. After 1 h, the vessel was flushed with N₂ and cooled to 30 °C. Then, the catalyst was reduced in 20 bar H₂ at 290 °C for 1 h (the degree of catalyst reduction was not checked before experiment) while stirring at 200 rpm; afterwards, the reactor was cooled to room temperature and vented to atmospheric pressure. For HDO, the reactor was heated to reaction temperature prior to adding 23 mL (22.0–22.2 g) of GNL and pressurizing the reactor to 60 bar H₂. During HDO, the reactor was stirred at 700 rpm. H₂ was replenished periodically, every time the pressure had decreased to 55 bar, in order to maintain an average pressure of 57.5 bar. After the experiment, the reactor was cooled to room temperature with the aid of a water bath. Then, a gas sample was taken and the reactor was vented and opened for the recovery of the liquid and the spent catalyst. Finally, the product mixture was analyzed. The mass balances typically closed with a loss of 5 to 10%. Calculated carbon balances for each experiment are reported in the Online Resource Table S5.

The products were characterized by various chromatographic techniques, elemental analysis, and Karl-Fischer titration. The basis of calculation for GNL and H₂ conversion, product selectivities, and yields are presented in the Online Resource.

2.5 Product Analytics

2.5.1 Organic Phase

The components in the organic products were identified using an Agilent gas chromatograph (GC) equipped with a Zebtron ZB-wax Plus column (60 m × 0.25 mm × 0.25 μm) and a mass spectrometer (GC–MS, 7890–5975). The injection of 1 μL sample was done at 250 °C with 0.6 mL/min flow and 80:1 split ratio. The temperature program started with a 2 min hold at 60 °C, followed by heating at 7 °C/min until 160 °C with a 3 min hold, and finally, at 5 °C/min to 200 °C with a 6 min hold. The electron impact ionization MS detector was operated at 70 eV, with a quadrupole scan range of 30–500 amu. The NIST MS library was used to aid spectral interpretation.

The products were quantified by GC (HP 6890 Series) with flame ionization detector (FID). The GC column and method were identical to the ones used for GC–MS. Because of an overlapping product peak (octanoic acid) with the GNL peak, a second GC with a Sigma-Aldrich Supelco® SLB-IL111 hyper-polar fused silica capillary

column (30 m × 0.25 mm × 0.2 μm) was used for GNL conversion calculations. Using the same GC method, the hyper-polar column provided a clean GNL peak, but, unlike the ZB-wax column, it did not separate the hydrocarbons. For calibration of GNL and most products, the internal standard was 2-propanol. Not all the product compounds were commercially available, and the response factors for those components were estimated according to the effective carbon number method originally proposed by Scanlon and Willis [26]. The quantification of octanoic acid was achieved by operating the GC–MS system in the selected ion monitoring (SIM) mode. Ions 6.10 and 73.10, found only in the octanoic acid spectrum, were used to extract an independent peak, which was calibrated as for the rest of the components.

In the GNL experiments, water was formed as a HDO product. In all experiments, the organic phase contained dissolved or colloidal water. The water in the organic phase was analyzed using a SI Analytics' volumetric Karl-Fisher titrator (TitroLine 7500 KF). Prior to measurements, a water standard was used to calibrate the concentration of the titrant.

The elemental compositions of the organic phases were analyzed using a Perkin Elmer 2400 Series II elemental analyzer. Elemental compositions were used to build a van Krevelen diagram [27].

During the experiments, heavy condensation products could be formed that were nonvolatile and thus not detected with GC–MS. Heavier compounds were qualitatively identified with liquid chromatography (LC) using an Agilent 1260 HPLC-system coupled to an Agilent 6530 QTOF mass spectrometer. Moreover, some compounds that were abundant according to GC, and could not be identified with sufficient certainty using only the NIST MS library, were also searched using LC. The samples were diluted to 30/70 wt% MilliQ water/acetonitrile (ACN) solution, and the final concentration of each sample was approximately 100 ppm. The injection volume was 20 μL, and the eluent was 20/80 wt% MilliQ water/ACN solution + 0.1 wt% formic acid with a flow rate of 0.25 mL/min. A Kinetex Biphenyl column (2.6 μm × 100 mm × 2.1 mm) or a Luna Omega PS-C18 column (100 × 2.1 mm, 3 μm) with positive mode of electrospray ionization (+ESI) were utilized in the mass range of 50–1000 amu for the total ion current. For searching individual compounds, the extract ion chromatograms for selected molecular masses were recorded. Finally, the mass spectrum of a compound was obtained using an Agilent MassHunter software with a Find by Formula (FBF) algorithm that searched the expected molecular formulas with a maximum of 5 ppm difference to the calculated value.

The silylation of the organic samples was also attempted to reveal possible nonvolatile compounds. The silylation was performed by mixing ca. 20 mg of sample with 1 mL

of *n*-methyl-*n*-trimethylsilylfluoroacetamide (MSTFA). The mixtures were left to room temperature overnight prior to analysis in a Thermo Scientific Trace 1300 ISQ having an Agilent J&W HP-5 column (60 m × 0.25 mm × 0.25 μm) with He as a carrier gas (1 mL/min). The heating program started at 80 °C with a 1 min hold and continued to 300 °C (15 °C/min) with a 1 min hold. The inlet temperature was 280 °C and the injection volume 1 μL. The split ratios of 1:100 and 1:20 were attempted with a solvent delay.

2.5.2 Gas Phase

The product gas mixtures were analyzed after each experiment by an Agilent 6890 Series GC with a FID and a thermal conductivity detector (TCD). CO, CO₂, H₂ and N₂ were analyzed with the TCD connected to two columns: a HP-PLOT/Q (30 m × 0.53 mm × 40 μm) and a HP Molesieve (30 m × 0.53 mm × 25 μm). Produced hydrocarbons were analyzed with the FID utilizing a HP-AL/KCL column (50 m × 0.32 mm × 8 μm). The GC was calibrated with an Oy AGA Ab calibration gas mixture which enabled quantitative analysis. The heating program started from 40 °C with a 9.5 min hold, and the inlet temperature was 200 °C. The heating rate was 10 °C/min until the final temperature of 200 °C without any extra holds. The chromatographic analysis provided the molar composition of the gas phase. The amounts of the gases were calculated with this molar composition and the absolute pressure in the reactor at the time of the sampling (room temperature), assuming ideal gas.

2.5.3 Aqueous Phase

The produced water phase (if any) was separated using a separating funnel, and the total water was calculated as the sum of the separate aqueous phase and the water in the organic phase. The composition of the aqueous phase was qualitatively analyzed with an Agilent GC–MS equipment described earlier. In this case, the quadrupole scan range was 18–500 amu.

3 Results

3.1 Characterization of Fresh Catalysts

The nominal metal loading of the impregnated catalysts was 3 wt% in all cases. The values measured by XRF fell short by 0.5 to 0.3 percentage points (Table 1), except for palladium, for which the measured metal loading was 3.0 wt%.

Physisorption and chemisorption results are presented in Table 1. The physisorption isotherms for fresh and spent catalysts are presented in Online Resource (Figure S1). The BET surface areas of the impregnated Rh, Pd, and Pt catalysts were similar compared to the pure ZrO₂ support, but the surface area of the Ru catalyst was higher than for the support. The BJH pore volumes decreased during impregnation with Rh, Pt and Pd and increased with Ru. The average BJH pore diameters were between 10 and 13 nm. The pore

Table 1 Textural properties of fresh and spent (280 °C, 30–40% conversion) noble metal catalysts supported on zirconia

Catalyst	Physisorption			Chemisorption			STEM	
	S _{BET} (m ² /g)	Pore volume (cm ³ /g)	Average pore diameter (nm)	Irreversible adsorption capacity (μmol _{gas} /g _{cat})	Dispersion (%)	Average particle size (nm)	Average particle size (nm) ^c	Relative standard error of particle size (%) ^d
ZrO ₂	64	0.27	11					
2.7 wt% Ru/ZrO ₂	80	0.32	10	15 ^a	11 ^a	8.0	1.5	6.1
2.5 wt% Rh/ZrO ₂	58	0.23	11	209 ^b	87 ^b	1.2	2.0	5.1
3.0 wt% Pd/ZrO ₂	64	0.26	11	60 ^b	21 ^b	5.3	2.9	8.7
2.7 wt% Pt/ZrO ₂	65	0.22	13	52 ^b	37 ^b	2.7	1.9	3.2
Ru/ZrO ₂ spent	70	0.25	8	25 ^a	19 ^a	4.8	1.8	6.0
Rh/ZrO ₂ spent	54	0.22	9	35 ^b	15 ^b	7.4	4.8	4.0
Pd/ZrO ₂ spent	60	0.25	10	20 ^b	7.0 ^b	16	5.4	3.3
Pt/ZrO ₂ spent	71	0.28	10	31 ^b	23 ^b	4.5	3.8	2.7

^aH₂ chemisorption, 75 °C

^bCO chemisorption, 35 °C

^cPopulation means statistically inferred from STEM images

^dBased on a normal distribution with 95% confidence level

size distributions of the fresh and spent catalysts are presented in the Online Resource (Figure S2).

Based on chemisorption, significantly different active metal dispersions (11%–87%) were calculated for the catalysts. The Rh catalyst displayed the highest dispersion, whilst the Ru catalyst displayed the lowest. Particle sizes were determined based on both chemisorption and STEM images. A selection of the latter is presented in Online Resource (Figure S3). Because no metal particle peaks were discerned in the XRD diffractograms, it appeared that the metal particles were small and well dispersed (XRD's detection limit is ~ 3 nm) [28].

3.2 Activity of Catalysts

The HDO reactions were studied with the four noble metal catalysts at 280 °C and 57.5 bar H_2 . For each catalyst, a series of experiments was performed with increasing reaction times from 15 to 300 min. The GNL conversions as a function of reaction time are illustrated in Fig. 1. Additionally, plain ZrO_2 support was tested in a 300 min experiment, providing 13.8% GNL conversion. At comparable GNL conversion levels (30–40%), the H_2 conversion was $\sim 80\%$ with Ru and $\sim 20\%$ with the other three metals. The initial turnover frequencies (see Online Resource), based on surface metal atoms from chemisorption, were 1 s^{-1} for Ru, 0.2 s^{-1} for Rh, 0.7 s^{-1} for Pd, and 0.5 s^{-1} for Pt.

In addition to the catalytic experiments, 300 min blank, non-catalyzed experiments were performed at the same conditions as the other experiments. A blank performed before the catalyzed experiments resulted in $<2\%$ conversion and

Fig. 1 GNL conversion as a function of reaction time. Reaction conditions: 0.6 g catalyst, $\sim 3\%$ metal loading, 23 mL GNL (pure), 280 °C, 57.5 bar H_2 . Note that the Ru catalyst contained chloride species

Fig. 2 van Krevelen diagram. Molar H/C and O/C of the organic liquid product mixtures obtained with ZrO_2 -supported catalysts compared to the reactant (GNL) and to standard fuels [29]. In the case of 280 °C reactions, the reported products were obtained at 30–40% GNL conversion. The values exclude unconverted GNL and water. Reaction temperature in legend. Note that the Ru catalyst contained chloride species

blanks performed afterwards resulted in 4–6% conversion. Negligible amounts of products were detected.

The van Krevelen diagram of the organic liquid products with similar conversion levels at 280 °C (Fig. 2) provides an insight into the catalysts' HDO activity. When catalysts converted 30–40% of the feedstock, all of them eliminated some oxygen. However, the products still contained more oxygen than the amount allowed by fuel specifications [29]. On the other hand, the uptake of hydrogen was high with Ru, Rh, and Pt. The H/C ratio of the product obtained with the Pd catalyst was lower than the H/C ratios of the products obtained with the other catalysts.

3.3 Selectivity of Catalysts

The product distributions obtained with each metal at 280 °C with similar conversions, 30–40%, are presented in Fig. 3. The distributions include all the attained products in the gas, organic, and aqueous phases and the solids deposited on the catalyst during the experiment (from TGA). Because nearly 70 products were detected (Online Resource Table S1), they were categorized by functional groups. The total water in both liquid phases is reported. The aqueous phase was accounted as 100% water, although it contained traces of organic products (see below).

The Ru catalyst gave a significantly different product distribution compared to the other catalysts, especially Pd and Pt (Fig. 3). Ru had the highest selectivity to liquid hydrocarbons (close to 24%), and it was the only metal producing branched hydrocarbons, although in minor amounts (0.7% selectivity). Gaseous hydrocarbons, mainly methane, were also produced. Moreover, Ru was the only catalyst producing lactones with sidechains containing less than five carbons.

Fig. 3 Grouped product selectivities obtained with the noble metal catalysts. GNL conversion (X) is marked on top of the bars. Reaction conditions: 0.6 g catalyst, ~3% metal loading, 23 mL GNL (pure), 280 °C, 57.5 bar H_2 . The results were obtained after 300 min, 30 min, 120 min and 300 min for Ru, Rh, Pd and Pt catalysts, respectively. Note that the Ru catalyst contained chloride species

Ru produced less acids and esters than the other metals, but more ketones with nearly 20% selectivity.

The Rh catalyst (Fig. 3), compared to Ru, had a higher selectivity to acids (43%) and alcohols (8%). However, the amounts of produced ketones and hydrocarbons were lower than with Ru. Despite all characterization efforts, approximately 30% of the expected product mass with the Rh catalyst remained unaccounted, which hinders the full assessment of the catalyst's performance.

With Pd, almost 80% of the products (Fig. 3) were acids. Pd also produced esters (15%) and <3% of liquid hydrocarbons. The product distribution of Pt was similar to Pd; however, it provided less acids (28%), and more esters (29%). With Pt, the selectivity to 2-pentyl tetrahydrofuran (PTHF) was high compared to other metals (8%), and it provided the second highest selectivity towards liquid hydrocarbons (9%). With both Pd and Pt, almost no ketones were produced. About 20% of the Pt products remained unaccounted.

Within each liquid product category, the products varied from each other by their carbon count (C_4 – C_9). The share of n -octane, the most abundant hydrocarbon, in the total liquid hydrocarbons was 64% with Ru, 79% with Rh, 96% with Pd, and 81% with Pt. Hydrocarbons in the range of C_4 – C_7 were obtained with Ru and Rh, whilst Pt produced also n -nonane (16% of liquid hydrocarbons). The selectivity among the alcohols was almost exclusive to 3-octanol with Ru and Rh, to nonanols with Pd, and roughly equal to octanols and nonanols with Pt. Furthermore, nonanols varied according to the position of the hydroxyl group, i.e. carbons 1 or 4, which correspond to the carboxyl and gamma carbons of the parent lactone, respectively. Especially with Pt and Pd, also 1,4-nonanediol was obtained (Online Resource Figures S7, S11, S12 and Table S3). The four metals provided nonanoic acid as the most abundant acid and methane as the most abundant gas. In all cases except Rh, the most abundant esters were nonyl nonanoates (Online Resource Figure S9, S10 and Table S2), whereas Rh provided chiefly nonanoates of lower alcohols. The only detected aldehyde was nonanal, but the amount was low in all cases. Finally, Ru and Rh provided 3-octanone as the main ketone whilst Pt

promoted 4-nonanone almost exclusively and Pd provided both ketones in similar amounts.

LC–MS analysis of the samples with 30–40% GNL conversions revealed the existence of a diester compound, 4-nonanoyloxynonyl nonanoate ($C_{27}H_{52}O_4$). The identification of the compound was accurate (–0.46 ppm difference from the target mass). The diester formed with Pt and Pd catalysts, but not with Ru. The Rh catalyst produced possibly only a trace of the diester; the corresponding chromatographic peak was minuscule. To our knowledge, the equivalent diester in GVL HDO has not been reported in the literature. The mass spectrum of the diester and the LC–MS chromatograms are presented in the Online Resource (Figures S13, S14 and Table S4).

The development of the products throughout the reaction is depicted in Fig. 4 as product molar yields as a function of GNL conversion. The least abundant product groups are not shown. With all the metals, the acids (primarily nonanoic acid) built up as the reactions progressed. In the cases of Rh and Pd, the acids vastly outweighed all other products. Although the acid yield levels varied widely from catalyst to catalyst, they were the only product group that followed a similar pattern as a function of conversion with all four catalysts. In general, most of the products accumulated with increasing conversion in the presence of all catalysts, whilst the alcohols decayed in all cases. Exceptionally, PTHF decayed with Rh (not shown), but accumulated with Pd and Pt. With Ru, PTHF (not shown) decayed from the second to the third data point and increased afterwards.

What is stated above about the variations within the product groups at 280 °C applies throughout the conversion levels with some exceptions. At the lowest conversion with Ru, carbon monoxide, not methane, comprised the gas phase almost entirely. The proportions of these gases interchanged afterwards. The proportions of the gas contents also shifted with Pd and Pt, which evolved a greater share of C_2 to C_4 hydrocarbons at the two lower conversions, but more methane afterwards. On the other hand, Ru provided a greater amount and variety of lower esters and lower acids with increasing conversion. Finally, lower alcohols, rather than

Fig. 4 Molar yields of grouped products as a function of GNL conversion on **a** Ru/ZrO₂, **b** Rh/ZrO₂, **c** Pd/ZrO₂, **d** Pt/ZrO₂. Note the different scales in the figures. Note that the Ru catalyst contained chloride species

octanols and nonanols, were obtained at the lowest conversion with Ru and at the two lowest conversions with Pd, and Pt.

After most of the experiments at 280 °C, all the produced water was in the organic phase. Only Ru provided a separate aqueous phase at 39% conversion and Rh at 91% conversion. In the first case, the water presented a pH of 2 and ≥ 3000 mg/L chlorides (from the catalyst precursor, see Sect. 4). Traces of GNL, γ -heptalactone, and acetic, propionic, butanoic, and pentanoic acids were found in the formed water phase. The aqueous phase obtained with Rh had a pH of 5 and it contained traces of GNL and C₂ to C₇ acids.

3.4 Temperature Effect on the Performance of Ru Catalyst

Because of Ru's high selectivity towards the desired hydrocarbons at 280 °C, the Ru catalyst was studied further. The effect of reaction temperature on the performance of the Ru catalyst was examined at 220 and 250 °C for 300 min. Higher temperatures were thought to be less beneficial for LA dimers due to thermal reactions. Thus, the GNL experiments were conducted below 300 °C.

The lowest GNL conversion of 25% was achieved at the lowest tested temperature (220 °C). At 250 °C, the conversion increased to 37% and at 280 °C, to 39%. The H₂

conversion (Online Resource) was 40% at 220 °C, 60% at 250 °C, and 80% at 280 °C. Compared to the O/C ratio of GNL, some deoxygenation was observed with Ru at all the tested temperatures (Fig. 2). The O/C ratio decreased slightly with increasing temperature. On the other hand, the hydrogen content of the reaction products was considerably higher than GNL's. The H/C ratio was very similar at 220 and 250 °C, but slightly lower at 280 °C.

The product distributions obtained with the Ru catalyst at different reaction temperatures are presented in Fig. 5. By increasing the reaction temperature, the selectivity to alcohols and PTHF decreased. By contrast, more gaseous and liquid hydrocarbons, ketones, acids, and lactones with shorter (<C₅) side chains formed at higher temperatures. The amount of esters were low in all the tested temperatures and low compared to the other metals at 280 °C (Fig. 3). The lower the reaction temperature, the higher the share of products which remained unknown despite all the efforts in product analysis.

The product chain lengths hardly varied at the tested temperatures. The most abundant hydrocarbon in all cases was octane, the second was heptane, and the third, nonane. More branched hydrocarbons formed at higher temperatures, but still in low amounts. Ketones were mainly 3-octanone and 4-nonanone at all temperatures, and aldehydes were not produced at all. The main alcohols were 3-octanol, 4-nonanol,

Fig. 5 Grouped product selectivities obtained with Ru/ZrO₂ catalyst. GNL conversion (X) is marked on top of the bars. Reaction conditions: 0.6 g catalyst, ~3% metal loading, 23 mL GNL (pure), 57.5 bar H₂, 300 min. Reaction temperature in °C is in parenthesis next to labels. Note that the Ru catalyst contained chloride species

and ethanol. The selectivity to 1,4-nonanediol was inversely proportional to reaction temperature. The main acid was nonanoic acid and nonyl nonanoate was the most abundant among the identified esters. An independent aqueous phase with a pH of 4 formed at 250 °C. The aqueous phase contained traces of GNL and lower lactones, nonanoic acid, alcohols and ketones. The aqueous phase that formed at 280 °C is reported in the previous section.

3.5 Characterization of Spent Catalysts

Spent catalysts (washed with ethanol and dried at 100 °C) were characterized with physisorption, chemisorption, and STEM, after use in experiments (280 °C, 57.5 bar H₂) with 30–40% conversion. The metal contents in the spent catalysts were not measured, and for calculations based on chemisorption measurements, the metal loadings of the fresh catalysts were used. STEM images were taken from the spent samples after chemisorption (Figure S3). The BET surface areas decreased during reaction by about 10% on average, except for Pt. The metal dispersions decreased by 40–80% and the pore volumes, by 4–40%, except for Ru, for which both metal dispersion and pore volume increased by 72% and 27%, respectively. From the STEM images, the metal particle sizes increased by 20–140%. The used, unwashed catalysts were analyzed by TGA in order to estimate the amount of carbonaceous solids deposited during the experiments. After drying in inert gas up to 250 °C, about 2% ± 0.2% of the used catalysts' mass was combustible below 900 °C. Only in the case of the experiment with Ru at 220 °C, the combustible mass was 3.9% of the used catalyst. A typical TGA thermogram is presented in Figure S4.

4 Discussion

4.1 Characterization of Fresh Catalysts

Excepting Ru, the fresh catalysts had a good dispersion compared to values reported in the literature [20, 21, 30]. For Ru

and Pd, the metal particle sizes obtained by chemisorption were larger than the sizes observed by STEM. By resorting to a third technique, XRD, the metal particles appeared to be small and well dispersed, as no metal peaks were detected. The disagreement of STEM with chemisorption might have resulted from the deposited particles not being thoroughly in the metallic form. In the case of Ru, the catalyst likely remained partially chlorinated after calcination and reduction, as evidenced by the chlorides detected in the aqueous phases of some HDO products (chlorides were washable from the reactor and they were inactive in the organic phase, as shown by the blank experiments). The RuCl₃ precursor was the only source of chlorides in the overall workflow. Chlorides might have occluded chemisorption sites [31, 32]; therefore, the chemisorption results may represent the initially available catalytic active sites, whereas the STEM results may provide more accurate measurements of the particle sizes.

Fig. 6 Conversion of GNL on ZrO₂-supported catalysts at short reaction times (15 min) as a function of the amount of surface metal atoms from chemisorption (square) and average metal particle size measured by STEM (diamond). Reaction conditions: 0.6 g catalyst, ~3% metal loading, 23 mL GNL (pure), 280 °C, 57.5 bar H₂

4.2 Activity and Selectivity

There was no obvious dependence of activity on the catalysts' particle sizes (Fig. 6). However, when plotted against the amount of surface metal atoms (from chemisorption), a correlation with conversion emerges. Hence, it appears that the differences in activity between the catalysts result from the different amounts of surface atoms, due to the different atomic masses of the elements. Ru, having the lowest atomic mass, was expected to present the greatest amount of surface atoms. However, its actual position in the graph likely resulted from the initial occupation of active sites by residual Cl species, which occluded chemisorption sites [31, 33]. Nevertheless, taking the initial TOFs as a gauge of the activity per surface active site, it appears that Ru's sites were the most active (1 s^{-1}) and Rh's sites were the least active (0.2 s^{-1}).

Although an exponential dependence of conversion on temperature was expected, similar conversions were attained at 250 and 280 °C with Ru (Fig. 5). Apart from the experimental error, this similarity might result from a highly competitive adsorption of the various reaction products against GNL. On the other hand, internal mass transfer limitations could cause the similarity. External mass transfer limitations were estimated to be negligible by the Carberry criterion (see Online Resource). H_2 conversions had a more pronounced dependence on reaction temperature, possibly because H_2 and oxygenate reactants were activated on different site types [34, 35].

The H/C ratios found by elemental analysis of several HDO product mixtures, i.e. 1.9–2.3 (Fig. 2), roughly agreed with the values calculated as weighted averages of the identified products, i.e. 2.0–2.2 (Figs. 3, 5). The variations likely arise from an imperfect product characterization. Hydrogen uptake can occur both by HDO and by cracking. Thus, the H/C of GNL (1.78) can increase up to 2.22 by full deoxygenation to nonane and to higher values by further cracking. With the Ru experiments at different temperatures, the H/C obtained at 280 °C was slightly lower than at 220 and 250 °C. This agrees with the calculated ratios: 2.2 for the lower temperatures and 2.1 for 280 °C. The low temperature products were rich in alcohols and hydrocarbons with $\text{H/C} > 2.2$, whilst the 280 °C had a high contents of nonanoic acid and ketones with $\text{H/C} = 2$.

Most of the hydrogen was spent in methanation of CO on the Ru catalyst; a high amount of H_2 was consumed, which was reflected in the amount of CH_4 . The composition of the gas phase with Ru shifted from mainly CO at lower conversion to mainly CH_4 at higher conversion. According to Chen et al. [30], partially oxidized Ru (oxidation caused by surface hydroxyls on ZrO_2) allows for strong, thermally stable CO adsorption. This in turn might facilitate methanation.

Thus, the amount of CH_4 obtained with Ru/ ZrO_2 was much higher than with the other catalysts possibly due to a decarbonylation and methanation mechanism, as Ru metal favors decarbonylation [30, 36, 37]. The presence of residual Cl species has not been identified to interact with adsorbed CO species or affect their reactivity [31, 33]. The amount of methane also increased with temperature, which is explained by Arrhenius's law, as the thermodynamics were not limiting the methanation reactions at our reaction conditions (calculated via HSC Chemistry 6 software, using reactions described by Gao et al. [38]). Similarly, short-chained liquid products, formed by cracking of the GNL side-chain and of C_8 and C_9 products, increased with temperature.

Pd produced mainly nonanoic acid and esters. Pd was capable of opening the lactone ring, but its HDO activity was low. The inactivity of Pd in the hydrogenation of carboxylic acids has been reported in the literature [39]. Alcohols were formed on Pd and were directly consumed in esterification; thus, the yield of hydrocarbons was low (see Sect. 4.4).

Nearly 50% of the products with Pt were acids and esters, which agrees with previous literature [13, 40, 41]. Two GNL molecules are needed to form nonyl nonanoate, which leads to the removal of oxygen as water. Oxygen is also rejected in PTHF formation. Hence, the low O/C ratio of the Pt product with respect to GNL in the van Krevelen diagram (Fig. 2) is explained, in spite of the predominant content of oxygenates in this product (Fig. 3).

4.3 Characterization of Spent Catalysts

The metal dispersion changed during the experiments. The increase in Ru dispersion might be explained by the reduction of ruthenium chloride producing metallic sites and HCl during the experiment. With the other metals, the dispersion decreased. This was caused by particle agglomeration during the reaction, which was evidenced by the particle sizes measured from the STEM images (Table 1); the particles were larger on the spent catalysts than on the fresh ones. On the other hand, carbonaceous solids deposited on the catalysts perhaps partially covered the metals. This notion was supported by the fact that chemisorption provided greater particle size values than STEM for the spent catalysts. Chemisorption particle sizes were exaggerated because less chemisorption sites were available due to coverage with solid deposits. Less chemisorption sites translated into a lower calculated metal dispersion. Furthermore, in TGA of used catalysts (Online Resource Figure S4), the greater mass loss ($\sim 1.5\%$), from 200 to 300 °C, corresponds to coke oxidation on the metal [42], whereas the lesser mass loss ($\sim 0.5\%$), starting at 500 °C, corresponds to coke oxidation on the support. Hence, about $\frac{3}{4}$ of the quantified solid deposits were perhaps located on the metal.

Fig. 7 Summary of the GNL HDO products on noble metals supported on ZrO_2

4.4 HDO Products

The summary of the products obtained from GNL HDO with noble metals is illustrated in Fig. 7. Secondary alcohols can form directly from GNL by decarbonylation or deoxygenation of a ring-opening surface intermediate [36]. The decarbonylation route is energetically favored on Ru [36, 37]. This might explain the low yields of nonanoic acid provided by Ru as compared to the other metals. From the yield profiles (Fig. 4), it is evident that the alcohols acted as intermediates, producing hydrocarbons. The production of liquid hydrocarbons and water on Ru at 280 °C was higher than at lower temperatures. Furthermore, the amount of alcohols was lower at higher temperatures (Fig. 3). Hence, the higher temperature could promote the HDO of alcohols through Arrhenius's law, as the thermodynamic equilibrium was not restricting in the used conditions (calculated via HSC Chemistry 6 software using 3-octanol as a model compound). However, the formation of alcohols is a consequence of several reactions (e.g. ring-opening and HDO), and there might also be changes in the rates of these reactions as well as competitive adsorption to result into lower amount of alcohols at higher temperature. The amount of PTHF was inversely proportional to temperature. Analogously, the MTHF conversion in HDO on Ru/C has been reported to increase exponentially with respect to temperature, as expected from kinetics [43]. Furthermore, in the GVL literature with Ru/C, the temperature is kept low (190 °C) when high yields of 2-butanol [36] and MTHF [44] are desired.

The lactone ring can open without oxygen removal resulting in 1,4-nonanediol. The low concentrations of 1,4-nonanediol suggested that it was also an intermediate,

as reported elsewhere [36, 37, 44]. PTHF formed from 1,4-nonanediol [36, 37, 44] and reacted further on Ru/ ZrO_2 and Rh/ ZrO_2 , as attested by its low concentration and the decrease in the latter part of its yield profile on these two metals. A HDO study of MTHF reports its conversion to 2-pentanone and 1-pentanol as primary products [45]. With Ru, the amount of PTHF was high at lower temperatures and low at 280 °C (Fig. 3), whereas the amount of ketones was low at the lower temperatures and high at 280 °C. These shifts support the notion that ketones possibly formed from PTHF. Formation of secondary alcohols from 1,4-pentanediol [44] has also been observed on Ru/C. 1,4-Nonanediol reacted also with two nonanoic acid molecules to form the diester, 4-nonanoyloxynonyl nonanoate. The diester was observed only with Pt and Pd, which produced more reactants for this reaction.

In the case of Rh and Pd, relatively high shares of the products remained unaccounted (Fig. 3). In the case of Pd, it can be partly explained with the diester, which was not added to the selectivity calculations. No other nonvolatile compounds were detected either by LC–MS or GC with silylated samples.

Nonanoic acid formed and accumulated, especially on Rh and Pd. The analogous conversion of GVL to valeric acid has been studied on bifunctional catalysts [13, 40, 41]. With Al_2O_3 -containing support, the acid forms in two steps. Firstly, the lactone ring opens on the catalyst's acid sites and secondly, the resulting alkenoic acid is hydrogenated on the catalyst's metal sites. The second step is thermodynamically favorable and irreversible [46]. No alkenoic acids were observed in the present work, suggesting that the ring-opening mechanism might have been different on less

acidic ZrO_2 or that the hydrogenation of the alkenoic acid proceeded very rapidly at 57.5 bar H_2 . Although nonanoic acid esterified, mainly on Pt/ZrO_2 , its net production never declined, indicating a high rate of formation. Nonanoic acid might also be converted to *n*-octane. The decarbonylation of propanoic acid to ethane on Ru/ZrO_2 has been shown to proceed through an acyl surface intermediate, which in turn forms by hydrogenation-dehydration of a surface carboxylate [30]. Carboxylic acids are especially undesirable in fuel due to their corrosiveness [47].

Ketones formed abundantly and accumulated in the product mixtures (Fig. 4), especially over Ru/ZrO_2 . Although ketones can be hydrogenated to their corresponding alcohol, a kinetic HDO study in the literature showed that the rate of ketone formation is three orders of magnitude greater than the rate of its consumption [45]. Studies made with noble metals [48, 49] indicated that Pd and Pt were active in converting ketone to their corresponding hydrocarbon, but Rh and Ru were not active in hydrogenating the ketone group. Ketones are inadequate for fuel blends due to their ability to degrade plastics and rubber, and due to their possible instability [47].

5 Conclusions

The HDO of GNL was studied in order to assess the potential of LA dimers as intermediates to lignocellulose-based biofuels. Hydrocarbons (C_8 – C_9) were produced from GNL in HDO catalyzed by noble metals on ZrO_2 at 280 °C. The highest selectivity to hydrocarbons was achieved with Ru (nearly 24%). Rh performed similarly to Ru, but it provided higher conversion, it was less selective to hydrocarbons, and more selective to acids. Pd was mostly selective to acids, while Pt provided high yields of esters. The activity of the catalysts in terms of GNL conversion correlated with the amount of surface metal atoms. Thus, the observed differences in activity among the catalysts are likely attributable to different amounts of active sites.

Ru was tested at lower reaction temperatures (220 and 250 °C). The lower temperatures resulted in more reaction intermediates, such as alcohols and PTHF, but less ketones and hydrocarbons.

The HDO of GNL with noble metal catalysts below 300 °C proceeded through numerous oxygenated intermediates. Ru and Rh provided the largest yields of liquid hydrocarbons at the highest conversions attained, but also methanation was observed. These results can inform future research on HDO of LA dimers with noble metal catalysts for the production of biofuel components.

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Compliance with Ethical Standards

Conflict of interest All authors declared that they have no conflict of interests.

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References

1. Chen M, Smith PM (2017) The U.S. cellulosic biofuels industry: expert views on commercialization drivers and barriers. *Biomass Bioenerg* 102:52–61. <https://doi.org/10.1016/j.biombioe.2017.05.002>
2. Nanda S, Dalai AK, Kozinski JA (2014) Butanol and ethanol production from lignocellulosic feedstock: biomass pretreatment and bioconversion. *Energy Sci Eng* 2:138–148. <https://doi.org/10.1002/ese3.41>
3. Chheda JN, Huber GW, Dumesic JA (2007) Liquid-phase catalytic processing of biomass-derived oxygenated hydrocarbons to fuels and chemicals. *Angew Chem* 46:7164–7183. <https://doi.org/10.1002/anie.200604274>
4. Werpy T, Petersen G (2004) Top value added chemicals from biomass volume I—results of screening for potential candidates from sugars and synthesis gas. USA. <https://doi.org/10.2172/15008859>, <https://www.osti.gov/servlets/purl/15008859>. Accessed 14 Feb 2019
5. Climent MJ, Corma A, Iborra S (2014) Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels. *Green Chem* 16:516. <https://doi.org/10.1039/c3gc41492b>
6. Yan K, Wu G, Lafleur T, Jarvis C (2014) Production, properties and catalytic hydrogenation of furfural to fuel additives and value-added chemicals. *Renew Sustain Energy Rev* 38:663–676. <https://doi.org/10.1016/j.rser.2014.07.003>
7. Yan K, Jarvis C, Gu J, Yan Y (2015) Production and catalytic transformation of levulinic acid: a platform for speciality chemicals and fuels. *Renew Sustain Energy Rev* 51:986–997. <https://doi.org/10.1016/j.rser.2015.07.021>
8. Yan K, Yang Y, Chai J, Lu Y (2015) Catalytic reactions of gamma-valerolactone: a platform to fuels and value-added chemicals. *Appl Catal B Environ* 179:292–304. <https://doi.org/10.1016/j.apcatb.2015.04.030>
9. Bozell JJ, Moens L, Elliott DC et al (2000) Production of levulinic acid and use as a platform chemical for derived products. *Resour*

- Conserv Recycl 28:227–239. [https://doi.org/10.1016/S0921-3449\(99\)00047-6](https://doi.org/10.1016/S0921-3449(99)00047-6)
10. Bond JQ, Upadhye AA, Olcay H et al (2014) Production of renewable jet fuel range alkanes and commodity chemicals from integrated catalytic processing of biomass. *Energy Environ Sci* 7:1500–1523. <https://doi.org/10.1039/C3EE43846E>
 11. Bond JQ, Wang D, Alonso DM, Dumesic JA (2011) Interconversion between γ -valerolactone and pentenoic acid combined with decarboxylation to form butene over silica/alumina. *J Catal* 281:290–299. <https://doi.org/10.1016/j.jcat.2011.05.011>
 12. Bond JQ, Alonso DM, Wang D et al (2010) Integrated catalytic conversion of γ -Valerolactone to liquid alkanes for transportation fuels. *Science* 327:1110–1114. <https://doi.org/10.1126/science.1184362>
 13. van den Brink PJ, von Hebel KL, Lange J-P, Petrus L (2006) A process for the hydrogenation of a lactone or of a carboxylic acid or an ester having a gamma-carbonyl group. WO 2006/067171 A1. <https://worldwide.espacenet.com/publicationDetails/originalDocument?FT=D&date=20060629&DB=&local e=&CC=WO&NR=2006067171A1&KC=A1&ND=3#>. Accessed 28 Sept 2018
 14. Pham HN, Pagan-Torres YJ, Serrano-Ruiz JC et al (2011) Improved hydrothermal stability of niobia-supported Pd catalysts. *Appl Catal A Gen* 397:153–162. <https://doi.org/10.1016/j.apcata.2011.02.026>
 15. Serrano-Ruiz JC, Braden DJ, West RM, Dumesic JA (2010) Conversion of cellulose to hydrocarbon fuels by progressive removal of oxygen. *Appl Catal B Environ* 100:184–189. <https://doi.org/10.1016/j.apcatb.2010.07.029>
 16. Huber GW, Chheda JN, Barrett CJ, Dumesic JA (2005) Production of liquid alkanes by aqueous-phase processing of biomass-derived carbohydrates. *Science* 308:1446–1450. <https://doi.org/10.1126/science.1111166>
 17. Blessing RW, Petrus L (2006) A process for the dimerization of levulinic acid, dimers obtainable by such process and esters of such dimers. WO 2006/056591 A1. <https://worldwide.espacenet.com/publicationDetails/originalDocument?FT=D&date=20060601&DB=&local e=&CC=WO&NR=2006056591A1&KC=A1&ND=3#>. Accessed 28 Sept 2018
 18. Källdström M, Lindblad M, Lamminpää K et al (2017) Carbon chain length increase reactions of platform molecules derived from C5 and C6 sugars. *Ind Eng Chem Res* 56:13356–13366. <https://doi.org/10.1021/acs.iecr.7b01904>
 19. Mohammad M, Kandaramath Hari T, Yaakob Z et al (2013) Overview on the production of paraffin based-biofuels via catalytic hydrodeoxygenation. *Renew Sustain Energy Rev* 22:121–132. <https://doi.org/10.1016/j.rser.2013.01.026>
 20. Bie Y, Gutierrez A, Viljava TR et al (2013) Hydrodeoxygenation of methyl heptanoate over noble metal catalysts: catalyst screening and reaction network. *Ind Eng Chem Res* 52:11544–11551. <https://doi.org/10.1021/ie4012485>
 21. Gutierrez A, Kaila RK, Honkela ML et al (2009) Hydrodeoxygenation of guaiacol on noble metal catalysts. *Catal Today* 147:239–246. <https://doi.org/10.1016/j.cattod.2008.10.037>
 22. Brunauer S, Emmett PH, Teller E (1938) Adsorption of gases in multimolecular layers. *J Am Chem Soc* 60:309–319. <https://doi.org/10.1021/ja01269a023>
 23. Barrett EP, Joyner LG, Halenda PP (1951) The determination of pore volume and area distributions in porous substances. I. Computations from nitrogen isotherms. *J Am Chem Soc* 73:373–380. <https://doi.org/10.1021/ja01145a126>
 24. Shen X, Garces L, Ding Y et al (2008) Behavior of H₂ chemisorption on Ru/TiO₂ surface and its application in evaluation of Ru particle sizes compared with TEM and XRD analyses. *Appl Catal A Gen* 335:187–195. <https://doi.org/10.1016/j.apcata.2007.11.017>
 25. Bergeret G, Gallezot P (2008) Particle size and dispersion measurements. In: Ertl G, Knözinger H, Schuth F, Weitkamp J (eds) *Handbook of heterogeneous catalysis*, 2nd edn. WILEY-VCH, Weinheim, pp 738–746
 26. Scanlon JT (1985) Calculation of flame ionization detector relative response factors using the effective carbon number concept. *J Chromatogr Sci* 23:333–340
 27. van Krevelen DW (1950) Graphical-statistical method for the study of structure and reaction processes of coal. *Fuel* 29:269–283
 28. Behrens M, Schlögl R (2012) X-Ray diffraction and small angle X-ray scattering. In: Che M, Védrine JC (eds) *Characterization of solid materials and heterogeneous catalysts: from structure to surface reactivity*, 1st edn. Wiley-VCH, Weinheim, pp 611–652
 29. Leitner W, Klankermayer J, Pischinger S et al (2017) Advanced bio-fuels and beyond: chemistry solutions for propulsion and production. *Angew Chem* 56:5412–5452. <https://doi.org/10.1002/anie.201607257>
 30. Chen L, Zhu Y, Zheng H et al (2012) Aqueous-phase hydrodeoxygenation of propanoic acid over the Ru/ZrO₂ and Ru-Mo/ZrO₂ catalysts. *Appl Catal A Gen* 411–412:95–104. <https://doi.org/10.1016/j.apcata.2011.10.026>
 31. Nawdali M, Bianchi D (2002) The impact of the Ru precursor on the adsorption of CO on Ru/Al₂O₃: amount and reactivity of the adsorbed species. *Appl Catal A Gen* 231:45–54. [https://doi.org/10.1016/S0926-860X\(01\)00922-X](https://doi.org/10.1016/S0926-860X(01)00922-X)
 32. Narita T, Miura H, Ohira M et al (1987) The effect of reduction temperature on the chemisorptive properties of Ru/Al₂O₃: effect of chlorine. *Appl Catal* 32:185–190. [https://doi.org/10.1016/S0166-9834\(00\)80624-7](https://doi.org/10.1016/S0166-9834(00)80624-7)
 33. Mieth JA, Schwartz JA (1989) The effect of catalyst preparation on the performance of alumina-supported ruthenium catalysts. 2. The impact of residual chloride. *J Catal* 118:218–226. [https://doi.org/10.1016/0021-9517\(89\)90312-6](https://doi.org/10.1016/0021-9517(89)90312-6)
 34. Foraita S, Fulton JL, Chase ZA et al (2015) Impact of the oxygen defects and the hydrogen concentration on the surface of tetragonal and monoclinic ZrO₂ on the reduction rates of stearic acid on Ni/ZrO₂. *Chemistry* 21:2423–2434. <https://doi.org/10.1002/chem.201405312>
 35. Bie Y, Lehtonen J, Kanervo J (2016) Hydrodeoxygenation (HDO) of methyl palmitate over bifunctional Rh/ZrO₂ catalyst: insights into reaction mechanism via kinetic modeling. *Appl Catal A Gen* 526:183–190. <https://doi.org/10.1016/j.apcata.2016.08.030>
 36. Rozenblit A, Avoian AJ, Tan Q et al (2016) Reaction mechanism of aqueous-phase conversion of γ -valerolactone (GVL) over a Ru/C catalyst. *J Energy Chem* 25:1008–1014. <https://doi.org/10.1016/j.jechem.2016.11.010>
 37. Bababrik RM, Wang B, Resasco DE (2017) Reaction mechanism for the conversion of γ -Valerolactone (GVL) over a Ru catalyst: a first-principles study. *Ind Eng Chem Res* 56:3217–3222. <https://doi.org/10.1021/acs.iecr.7b00196>
 38. Gao J, Wang Y, Ping Y et al (2012) A thermodynamic analysis of methanation reactions of carbon oxides for the production of synthetic natural gas. *RSC Adv* 2:2358. <https://doi.org/10.1039/c2ra00632d>
 39. Takeda Y, Nakagawa Y, Tomishige K (2012) Selective hydrogenation of higher saturated carboxylic acids to alcohols using a ReOx–Pd/SiO₂ catalyst. *Catal Sci Technol* 2:2221. <https://doi.org/10.1039/c2cy20302b>
 40. Ayoub PM, Lange J-P (2008) Process for converting levulinic acid into pentanoic acid. WO 2008/142127 A1. <https://worldwide.espacenet.com/publicationDetails/originalDocument?FT=D&date=20081127&DB=&local e=&CC=WO&NR=2008142127A1&KC=A1&ND=4#>. Accessed 28 Sept 2018
 41. Lange JP, Price R, Ayoub PM et al (2010) Valeric biofuels: a platform of cellulosic transportation fuels. *Angew Chem* 49:4479–4483. <https://doi.org/10.1002/anie.201000655>

42. Srihiranpullop S, Praserttham P (2004) A new approach of coke characterization on metal and support for Pt/Al₂O₃ by combination of Al₂O₃ and Pt/SiO₂. *Catal Today* 93–95:723–727. <https://doi.org/10.1016/j.cattod.2004.06.067>
43. Iino A, Cho A, Takagaki A et al (2014) Kinetic studies of hydrodeoxygenation of 2-methyltetrahydrofuran on a Ni₂P/SiO₂ catalyst at medium pressure. *J Catal* 311:17–27. <https://doi.org/10.1016/j.jcat.2013.11.002>
44. Al-Shaal MG, Dzierbinski A, Palkovits R (2014) Solvent-free γ -valerolactone hydrogenation to 2-methyltetrahydrofuran catalysed by Ru/C: a reaction network analysis. *Green Chem* 16:1358–1364. <https://doi.org/10.1039/C3GC41803K>
45. Cho A, Kim H, Iino A et al (2014) Kinetic and FTIR studies of 2-methyltetrahydrofuran hydrodeoxygenation on Ni₂P/SiO₂. *J Catal*. <https://doi.org/10.1016/j.jcat.2014.07.021>
46. Bond JQ, Martin Alonso D, West RM, Dumesic JA (2010) γ -Valerolactone ring-opening and decarboxylation over SiO₂/Al₂O₃ in the presence of water. *Langmuir*. <https://doi.org/10.1021/la101424a>
47. Jenkins RW, Moore CM, Semelsberger TA et al (2016) The effect of functional groups in bio-derived fuel candidates. *ChemSusChem* 9:922–931. <https://doi.org/10.1002/cssc.201600159>
48. Faba L, Díaz E, Ordóñez S (2014) Hydrodeoxygenation of acetone-furfural condensation adducts over alumina-supported noble metal catalysts. *Appl Catal B Environ* 160–161:436–444. <https://doi.org/10.1016/j.apcatb.2014.05.053>
49. Jenkins RW, Moore CM, Semelsberger TA, Sutton AD (2017) Heterogeneous ketone hydrodeoxygenation for the production of fuels and feedstocks from biomass. *ChemCatChem* 9:2807–2815. <https://doi.org/10.1002/cctc.201601678>

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