Original Paper

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Mesoporous carbon and microporous zeolite supported Ru catalysts for selective levulinic acid hydrogenation into γ -valerolactone

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Abstract: Ru supported on mesoporous carbon Sibunit and microporous zeolites (HZSM-5, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 250$; H-Beta, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$; H-Y, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 5$; H-USY, $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$) synthesized by the sol-gel method (CSIR-National Chemical Laboratory, Pune India) were prepared by impregnation of the corresponding supports with $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (0.1 M) followed by reduction in H_2 . Catalyst screening in levulinic acid (LA) (15 mL, 6.9 mmol) hydrogenation into γ -valerolactone (GVL) with 1,4-dioxane (165°C, hydrogen pressure ca. 16 bar) as a solvent showed higher activity and selectivity to GVL of Ru/zeolites compared to carbon supported catalysts. Among Ru/zeolites LA conversion increased as follows $\text{Ru}/\text{HZSM-5} < \text{Ru}/\text{H-Y} < \text{Ru}/\text{H-USY} < \text{Ru}/\text{H-Beta}$ demonstrating a clear advantage of H-Beta preparation method. Optimization of the support microstructure and acidity opens a reliable way for selective catalytic LA hydrogenation to GVL. The catalysts were analyzed by TEM, XRD, H_2 -TPR and N_2 physisorption to compare their physical chemical properties.

Keywords: levulinic acid; hydrogenation; Ru; γ -valerolactone; carbon; HZSM-5; H-Beta; H-Y; H-USY.

1 Introduction

Commercially available levulinic acid (LA) through the Biofine processes [1] is considered as one of the top twelve biobased platform chemicals which can be converted into a wide range of valuable chemical compounds [2]. Although various catalysts, supports, and solvents have been investigated for hydrogenation of levulinic acid into γ -valerolactone (GVL), it is generally considered that ruthenium is the most effective noble metal catalyst for LA liquid phase hydrogenation [3,4,5,6,7,8,9,10]. Some non-noble metals demonstrating also high selectivity to GVL suffered, however, from lower conversion and metal leaching leading to deactivation [11,12,13]. GVL is gaining considerable attention as a versatile building block, and can be used as a fuel additive, solvent for biomass processing, as well as a precursor for production of hydrocarbons, polymers and other valuable chemicals, having thus a great potential to reduce the consumption of petroleum-derived fossil fuels [14]. Many heterogeneous ruthenium catalysts on various supports, such as carbon, carbon nanotubes (CNT), inorganic supports (Al_2O_3 , SiO_2 , TiO_2 , ZrO_2 , Nb_2O_5) [7], commercially available zeolites such as H-ZSM-5 ($\text{Si}/\text{Al} = 25, 38, 50, 150$ and 360), H-Beta ($\text{Si}/\text{Al} = 12.5$), and HY-zeolite ($\text{Si}/\text{Al} = 5.2$) [15] were screened in the LA hydrogenation. These reactions are generally performed at a moderate reaction temperature in the range of 25–250°C under hydrogen pressures from 1 to 150 bar. Abdelrahman et al. [4] reported an experimental study on LA hydrogenation in water in a continuous packed-bed reactor using Ru on four different supports (C, SiO_2 , Al_2O_3 and TiO_2) and found the initial intrinsic hydrogenation activity was rather independent on the support type. Carbon supported ruthenium catalysts demonstrated high activity in conversion of LA into GVL due to their large surface area, developed porous structure and a neutral chemical character. It was shown that highly dispersed 5% Ru on activated carbon exhibited a

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superior catalytic performance yielding 99% selectivity under mild reaction conditions (Ru 5 wt.%, 100°C, 2.0 MPa H_2 , $C_{LAO} = 0.8 \text{ mol} \cdot L^{-1}$) [16]. At the same time it was [7] reported that Ru/Beta-12.5 had better activity than Ru/C with almost quantitative LA conversion (94%) and 66% of GVL yield after 2 h reaction (Ru 1 wt.%, 90°C, 4.5 MPa H_2 , $C_{LAO} = 0.6\text{--}0.7 \text{ mol} \cdot L^{-1}$, $m_{cat} = 0.06 \text{ g}$, stirring at 2000 rpm). Guo and co-workers [15] found that Ru/HY-zeolite was more active and selective than Ru/Beta-12.5 under applied conditions (Ru 3 wt.%, 70°C, 1.0 MPa H_2 , $C_{LAO} = 0.1 \text{ mol} \cdot L^{-1}$, $m_{cat} = 0.0056 \text{ g}$, stirring at 600 rpm). However, a proper comparison is difficult as most studies are focused on one support only and a limited number of systematic studies with different supports is available. Subsequently no conclusions can be made about the most selective support. Moreover, no comparison of carbon and zeolites supported Ru catalysts is available apart from a recent study [7], where, however, only one zeolite (Ru/Beta-12.5) was compared with carbon. Not only the support nature but also different reaction conditions, namely type of solvent, resulted in different catalytic behavior of Ru catalysts [12, 17]. Among different solvents, such as water [18], alcohols [8, 19], dioxane [10], and supercritical CO_2 [20] were used in levulinic acid hydrogenation. Less attention has been devoted to influence of support acidity or basicity even if it was recognized that surface acidity plays an important role in the product distribution [11, 21, 22, 23, 24]. It was reported [23] that Zr-beta zeolite, rich in Lewis acid sites (Lewis/Brønsted acid ratio of 8.4) led to high activity (100% LA conversion at 118°C in 10 h) and selectivity toward GVL (96%). High GVL yields were also reported over a PtRe/C catalyst, where Re apparently influences the acidic properties of platinum [25].

The current study is aimed at performing a comparable study of Ru supported on mesoporous carbon Sibunit and microporous zeolites (HZSM-5, H-Beta, H-Y, H-USY) prepared using the same impregnation method in elective hydrogenation of levulinic acid into g-valerolactone. Catalyst activity (in terms of the initial rate and turnover frequency (TOF)) and selectivity to GVL were determined and the best catalyst for subsequent studies was selected.

2 Experimental methodology

2.1 Materials

All starting materials were reagent grade chemicals such as levulinic acid ($\geq 99\%$, Acros Organics), decane (TU

6-09-659-73), nitrogen ($\geq 99.95\%$), hydrogen ($\geq 99.95\%$), argon ($\geq 99.95\%$). For zeolites synthesis the following reagents were used: for H-ZSM-5 sodium silicate (27-28% SiO_2 ; 7.5 - 8.5% Na_2O ; LOBA), aluminium sulphate (98% LOBA), tetra propyl ammonium bromide (TPAB, 99.5 %, LOBA), sulphuric acid, for H-Beta zeolite sodium aluminate (43.8% Al_2O_3 , 39.0% Na_2O), silica sol (40% SiO_2), tetraethylammoniumhydroxide (TEAOH, aq. 30% wt/wt solution), sodium hydroxide (AR), deionized water; for H-Y zeolite sodium hydroxide (97 %, LOBA), potassium hydroxide (86% LOBA), silica sol (29.5% SiO_2 , 0.2% Na_2O , V P Chemicals, India), sodium aluminate solution $NaAlO_2$ (43.8 % Al_2O_3 , 39 % Na_2O , Otto Chemie, India).

For preparation of the carbon supported catalyst, mesoporous carbon Sibunit ($S_{BET} = 350 \text{ m}^2 \cdot g^{-1}$) was applied.

$RuCl_3$ hydrate (TU 2625-066-00196533-2002 Kraszvetmet, Krasnoyarsk) was used as a catalyst precursor.

2.2 Preparation of zeolites

Samples of zeolites were synthesized by the sol-gel method.

To prepare H-ZSM-5 zeolite, a suspension of sodium silicate was added to an aqueous solution of TPAB. The mixture was stirred at a room temperature until a clear solution was obtained and a solution of aluminum sulfate was added under constant stirring. Stirring continued until a homogenous slurry was formed followed by adjusting pH of the gel to 10-10.5 using 1 M sulfuric acid solution. Further stirring was continued for 4 h at room temperature. The final gel mixture was put in an autoclave and subjected to a step wise thermal treatment (100°C for 12 h, 120°C for 5 h, 140°C for 15 h, 170°C for 48 h) under static conditions (autogenous pressure). The solid product was separated by centrifugation, washed several times with distilled water and ethanol, dried overnight at 110°C, and calcined in air at 550°C for 10 h. To convert Na-form of ZSM-5 to the proton form, ZSM-5 was subjected for three ion-exchange steps using NH_4NO_3 (1 M) solution at 70°C for 6 h. After sufficient washing, the solid was recovered, dried and calcined at 500°C for 6 h under flowing air to convert it into the proton form.

For preparation of H-Beta zeolite, sodium aluminate and NaOH were dissolved in distilled water and added into an aqueous solution of tetraethyl ammonium hydroxide under stirring. Silica sol was added slowly under vigorous stirring to the above mixture. The slurry was stirred for 5-6 h to obtain a homogeneous gel mixture. This final gel

was then transferred into a stainless-steel autoclave. The molar composition of the gel was $6.0 (\text{TEA})_2\text{O} : 2.4 \text{Na}_2\text{O} : 30.0 \text{SiO}_2 : \text{Al}_2\text{O}_3 : 840.0 \text{H}_2\text{O}$. The final gel mixture was subjected to hydrothermal crystallization at 140°C for 98 h. After complete crystallization the autoclave was allowed cooled down at $50\text{--}60^\circ\text{C}$ and the solid product was separated by centrifugation, washed several times with distilled water and ethanol, dried overnight at 110°C , and calcined in air at 550°C for 10 h. Transformation of the sodium to proton form was done in the same way as for H-ZSM-5.

H-Y zeolite was prepared following the gel composition and the overall procedure reported elsewhere [26]. H-Ultra Stable Y zeolite was prepared by repetitive dealumination of H-Y zeolite by steaming.

2.3 Preparation of catalysts

Several catalysts, containing 4% of Ru, namely 4% Ru/Sibunit, as well as 4% Ru/HZSM-5, 4% Ru/H-Beta, 4% Ru/H-Y, 4% Ru/H-USY were prepared by incipient wetness impregnation with an aqueous solution of RuCl_3 hydrate (0.1 M). Thereafter, the samples were dried at 110°C for 17 h and reduced by molecular hydrogen from room temperature up to 350°C temperature with a ramp rate of 2 K/min . In addition, the samples were treated with hydrogen during 3 h at 350°C temperature to remove the excess of chloride.

2.4 Catalysts characterization

Metal nanoparticles as-synthesized and immobilized on carbon supports were analyzed by transmission electron microscopy (TEM) to estimate Ru NPs size, X-ray fluorescent analysis (XRF) to control Ru content, X-ray diffraction (XRD) to monitor microstructure, and low-temperature N_2 physisorption to determine the pore volume and the average pore size.

TEM photographs were taken with a Hitachi-9000 NAR apparatus. The samples for TEM were prepared by placing a drop of a colloidal PVP-Ru dispersion or the sample suspension in ethanol onto a perforated carbon coated copper grid, followed by evaporating the solvent. The mean particle diameter and the standard deviation were calculated by counting at least 250 NPs from the enlarged microphotographs.

Semi-quantitative analysis of the metal concentration was performed using wavelength dispersive X-ray fluorescence (WDXRF) spectrometry with the powder pellet method. Undiluted samples (0.5 g) were milled

and put in the 29 mm diameter die. The intensities of the metal lines in the samples were measured in vacuum conditions on an ARL Advant'X spectrometer equipped with a rhodium anode X-Ray tube. Excitation conditions were as follows: tube voltage of 50 kV; current of 40 mA; collimator with a divergence of 0.25° ; LiF200 crystal was used as a monochromator; scintillation counter was used as a detector; counting time was 12 s. The content of elements in the sample was estimated using a semi-quantitative method by means of a QuantAS program for standard-less analysis.

The chemical composition in terms of Si/Al ratio was determined by inductively coupled plasma–optical emission spectroscopy (ICP-OES, model: Perkin–Elmer Optima3000DV).

The textural properties were determined using physisorption of nitrogen at 77K in a Micromeritics Model ASAP 2400 equipment. The specific surface area was calculated using the BET method within the relative partial pressure range of 0.05–0.25.

The phase purity and crystal phase identification of zeolite samples were determined by powder X-ray diffraction (XRD). XRD patterns of zeolites were recorded on X-ray diffractometer (P Analytical PXRD system, Model X-Pert PRO-1712) using $\text{CuK}\alpha$ radiation at a scanning rate of 0.083 s^{-1} in the 2θ ranging from 5° to 50° . XRD pattern of the carbon material Sibunit was recorded with X-ray diffractometer D8 Advance (Bruker, Germany) using $\text{CuK}\alpha$ radiation and LynxEye detector by scanning in the 2θ -angle range from 15° to 60° with a step of 0.05° and acquisition time of 9 s at each point. An in-plane crystallite size $\langle L_a \rangle$ and a stacking height $\langle L_c \rangle$ was determined by width of the peaks 100 and 002, correspondingly.

Acidity of zeolites in terms of desorbed mmol of NH_3 was calculated by temperature-programmed ammonia desorption (TPAD) using a Micromeritics AutoChem 2910 (USA).

TG-DTA-MS was performed with a Netzsch STA 409 PC equipped with a mass spectrometer SRS UGA 200. The measurements were carried out using corundum crucibles. DTA sample holder and the crucible were preheated to 1000°C in an air flow. Correction curves were recorded in accordance with the TPR experimental conditions from $50\text{--}800^\circ\text{C}$ with the temperature ramp $10^\circ\text{C}\cdot\text{min}^{-1}$ under argon, and thereafter in a mixture of argon and hydrogen (15% hydrogen in argon).

2.5 Catalytic experiments

Liquid phase LA hydrogenation in an aprotic solvent 1,4-dioxane (15 mL, 6.87 mmol) was carried out in a stainless-steel autoclave (150 ml) with efficient stirring at a constant hydrogen pressure. In a typical experiment LA hydrogenation was performed with the catalyst loading of 0.03 - 0.24 g Ru catalyst at 165°C and 16 bars in the absence of mass transfer limitations as was established previously.

The impact of the internal diffusion was determined through the estimation of the Weisz-Prater criterion. The influence of external diffusion resistance was suppressed by conducting experiments at the stirring speed of 1100 rpm, which was shown to be efficient enough in elimination external mass transfer limitations. Influence of the gas/liquid mass transfer was elucidated by performing preliminary experiments with different catalysis loadings. Based on these experiments LA hydrogenation was carried out with the catalyst loading over Ru/H-Beta and Ru/H-USY with 0.03 g, over Ru/H-Y and Ru/H-ZSM-5 catalysts with 0.12 g, and over Ru/C 0.24 g. For comparable graphical analysis, in what follows, the X axis was normalized with the catalyst content.

Samples of the reaction mixture were withdrawn from the reactor at appropriate intervals and analyzed by gas chromatography (Chromos GC-1000 chromatograph) equipped with a flame ionization detector using BP20 capillary column (60 m/0.25 mm/0.25 μ m) at 323-473 K and a heating rate of 10 K $\cdot$ min⁻¹. For analysis of the liquid phase, the temperature was increased from 323 till 523 K with the temperature ramp of 10 K $\cdot$ min⁻¹. Temperature of the detector was the same as for the evaporator being 523 K, the carrier gas was hydrogen with the flow rate 20 cm³ $\cdot$ min⁻¹. Identification of the reaction components was carried out by chromatographic mass spectrometry with VG-7070 GC/MS using ZB-Wax capillary column (length 30 m/inner diameter 0.25 mm/film thickness 0.25 μ m) and Agilent 5973N EI/PCI using VF-5ms capillary column (30 m/0.25 mm/0.25 μ m).

Conversion of LA and selectivity to GVL were estimated from the peak areas based on the internal standard technique using GC keeping 100% mass balance for carbon containing reaction components. Selectivity to GVL was calculated based on the following equation: selectivity = yield of the product/total yield of all products.

TOF was calculated as a number of formed GVL moles per mole of exposed catalytic site per unit time during the first 30 min of the reaction corresponding to the linear part of the kinetic curves according to the following equation: $TOF = n_{GVL} / n_{Ru} \cdot D_{Ru} \cdot t$, where n_{GVL} is GVL molar amount after 30 min, n_{Ru} (mol) the amount of Ru in the

Table 1: Textural characteristics for Sibunit and synthesized zeolites.

Support	SSA, m ² •g ⁻¹	PV, cm ³ •g ⁻¹	d _{av} , Å
Sibunit	350	0.56	63.6
H-ZSM-5	230	0.21	-
H-Beta-NCL	456	0.22	-
H-Y-NCL	550	0.45	-
H-USY	650	0.46	-

catalyst, D_{Ru} is the dispersion of Ru particles, calculated from Ru mean diameter (d_{Ru}) assuming their spherical shape according to eq. [5], and $t=30$ min is the reaction time.

The GVL formation rate ($r_{form\ GVL}$, mol GVL $\cdot$ s⁻¹) was determined from the experimentally obtained concentration-time profiles.

3 Results and Discussion

3.1 Catalyst support characterization

The surface area, pore size and its distribution, metal dispersion, crystallinity, composition of the support, etc., are factors governing performance of the catalysts in hydrogenation reactions. Sibunit was as a support due to its high surface area, tunable pore sizes, and controllable structures providing for example better performance in sugar hydrogenation compared to CDC and CNF supported Ru catalysts [27]. Prepared Ru catalysts on mesoporous carbon Sibunit and microporous zeolites (H-ZSM-5, SiO₂/Al₂O₃ = 250; H-Beta, SiO₂/Al₂O₃ = 30; H-Y, SiO₂/Al₂O₃ = 5; H-USY, SiO₂/Al₂O₃ = 30) with the metal loading 4 wt.% were characterized by different physical chemical methods to determine a potential correlation between catalyst properties and performance in LA hydrogenation.

3.1.1 N₂ physisorption and acidity

Specific surface area and pore volume of zeolites (H-Beta, H-USY, HZSM-5, H-Y), and carbon Sibunit used as supports are shown in Table 1. According to N₂-physisorption data, Sibunit was mainly characterized by the presence of mesopores, while zeolites exhibited the microporous structure (Table 1).

Figure 1: X-ray diffraction patterns of the supports: a) Sibunit, b) H-ZSM-5, c) H-Beta, d) H-Y.

3.1.2 XRD analysis of supports

According to the XRD data (Fig. 1a) Sibunit is characterized by graphite-like structure with a higher interplanar spacing $d_{002} = 3.47 \text{ \AA}$, a stacking height $\langle L_c \rangle$ about 3.3 nm and an in-plane crystallite size $\langle L_a \rangle$ about 3.0 nm. The X-ray diffraction patterns of H-ZSM-5, H-Beta and Y-type zeolite depicted in Fig. 1 b-d, show all characteristic peaks of zeolite MFI [28], BEA [29], and FAU [30] with no contribution of other crystalline or amorphous phase/s.

3.1.3 Acidic properties of zeolites

Acidity of H-ZSM-5, H-Beta and H-USY calculated by TPA is tabulated in Table 2. Due to a higher $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar

Table 2: Acidic characteristics of synthesized zeolites.

Support	$\text{SiO}_2/\text{Al}_2\text{O}_3$	Acidity (mmol of $\text{NH}_3 \cdot \text{g}^{-1}$)
H-ZSM-5	256	0.27
H-Beta	28.5 ± 2.5	0.53
H-Y	5 ± 0.5	-
H-USY	30	0.74

ratio, acidity of H-ZSM-5 ($0.265 \text{ mmol of NH}_3 \cdot \text{g}^{-1}$) was lower than H-Beta and H-USY zeolites. Although H-Beta and H-USY have nearly the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio, H-USY displayed higher acidity ($0.74 \text{ mmol of NH}_3 \cdot \text{g}^{-1}$) than H-Beta ($0.53 \text{ mmol of NH}_3 \cdot \text{g}^{-1}$) which may be attributed to better accessibility of acidic sites in H-USY zeolite than in H-Beta.

Figure 2: H_2 -TPR profiles of Ru/C catalyst.

3.2 Catalyst characterization

3.2.1 Characterization by TG-DTA-MS

For TPR analysis a Ru/C sample prepared by impregnation of the support with the chloride precursor was studied prior to its reduction in hydrogen. The results of TG-DTA-MS are presented in Fig. 2. H_2 -TPR profile shows two main reduction peaks at about 140°C and 218°C, corresponding to reduction of Ru^{4+} to Ru^{3+} and Ru^{3+} to Ru^0 [32], respectively.

It was found that reduction of Ru/C should be conducted at *ca.* 220°C under temperature ramp comparable with TPR conditions. For Ru on zeolites the reduction temperature differs from that of Ru/C due to stronger metal support interactions. On the basis of the literature data [31, 32] the consumption peak of Ru^{3+} species interacting with a zeolite is shifted to a higher reduction temperature and complete reduction of Ru over zeolites can be reliably achieved at temperature before 300°C (not shown). Thus, 350°C was used for reduction of all Ru catalysts in this work.

3.2.2 XRF and TEM analysis of catalysts

XRF analysis indicated that Ru loading was comparable in all catalysts corresponding to *ca.* 3.9-4.0 wt.% Ru, since the same amounts of the support and the precursor were used.

According to TEM data the average particle sizes of Ru were (Fig. 3) 1.6 nm for 4% Ru/H-Y, 2.0 nm for 4% Ru/H-Beta, with both samples characterized by a single mode Ru NPs distribution, while bimodal Ru NPs distributions with the average Ru NPs diameter of *ca.* 2.1 nm for 4% Ru/H-USY, and a larger size for 4% Ru/H-ZSM-5 were determined for other zeolites (Fig. 3). TEM analysis for

Table 3: Characterization of Ru catalysts.

Catalyst	d_{Ru} , nm	Ru loading, %
Ru/Sibunit	2.1	4.0
Ru(NPs)/Sibunit	2.4	3.73
Ru/H-Beta	2.0	3.9
Ru/H-USY	2.1	4.0
Ru/HZSM-5	1.6-20	3.9
Ru/H-Y	1.6	4.0

Ru/Sibunit displayed that Ru average particle size was *ca.* 1.3 nm. The catalysts exhibit spherical nanodispersed particles uniformly distributed over the support surface except Ru/HZSM-5 where Ru NPs formed agglomerates in the form of chains of different sizes. Carbon supported Ru sample was studied by XPS showing that all catalysts exhibit metal nanoparticles as the active components with a small fraction of metal being in an oxidized state (not shown).

Data showing the Ru NPs size and the metal loading determined for reduced Ru catalysts are presented in Table 3.

3.2.3 XRD catalysts characterization

The X-ray diffraction patterns of Ru/H-ZSM-5, Ru/H-Beta and Ru/Y-type zeolite depicted in Fig. 4, shows all characteristic peaks of zeolite MFI [28], BEA [29], and FAU [30] with no contribution due to other crystalline or amorphous phase/s. The peak corresponding to Ru was not detected in Ru/H-USY and Ru/H-Y because of a very small size of Ru NPs, confirmed by TEM data (Fig. 3) whereas Ru metal phase was identified in Ru/H-ZSM-5 sample containing a significant portion of large NPs according to TEM along with small NPs (Fig. 4 c). Ru crystallite sizes in Ru/H-Beta and Ru/H-ZSM-5 determined from estimation of coherently scattering domains were found to be 16 nm. Some discrepancy with TEM data can be related to non-uniform bimodal Ru NPs size distribution in this catalyst (Table 4).

3.3 Levulinic acid hydrogenation over Ru catalysts

3.3.1 Products of LA transformation

All catalysts (4% Ru/C, 4% Ru/H-ZSM-5, 4% Ru/H-Beta, 4% Ru/H-Y, 4% Ru/H-USY) were tested in hydrogenation

Figure 3: TEM images (a-e) and histograms (a, d, e) of as-synthesized Ru catalysts: a) 4% Ru/H-Beta, b) 4% Ru/H-USY, c) 4% Ru/H-ZSM-5, d) 4% Ru/H-Y, e) 4% Ru/C; (d_n - mean diameter, SD - standard deviation; d_s - surface mean diameter).

Figure 4: X-ray diffraction patterns of the reduced Ru catalysts on zeolite supports a) Ru/H-Beta, b) Ru/H-USY, c) Ru/H-ZSM-5, d) Ru/H-Y.

Table 4: Composition of crystal phase and crystallite size in Ru/zeolites determined by XRD.

Sample	Crystal phase	Identification	Crystallite size, nm
Ru/H-Beta	$\text{Al}_2\text{O}_3 - \text{SiO}_2$	[PDF 00-057-0337]	50
	Ru	[PDF 04-001-0053]	16 (101)
Ru/H-USY	$\text{Si}_{192}\text{O}_{384}$	[PDF 00-055-0760]	61 (111)
	Ru	[PDF 01-071-3661]	n.d.*
Ru/H-ZSM-5	$\text{Al}_2\text{O}_3 * 54\text{SiO}_2$	[PDF 00-044-0003]	84 (101)
	Ru	[PDF 01-071-3661]	16 (101)
Ru/H-Y	$\text{Al}_{13}\text{Si}_{35}\text{O}_{89.5}$	[PDF 04-011-2238]	53 (111)
	Ru	[PDF 01-071-3661]	n.d.*

n.d.* - not determined because of peak overlapping

of LA in an autoclave at 165°C and 16 bar of hydrogen pressure. According to GC analysis LA hydrogenation mainly resulted in formation of the desired GVL product

both for carbon and zeolites supported Ru, whereas pentanoic acid (PA) and 2-methyltetrahydrofuran (MTHF) were observed in minor quantities. The reaction pathways proposed in the literature (Fig. 5) have been also considered for hydrogenation of LA in the current study [21]. In general, GVL can be synthesized by hydrogenation of LA to 4-hydroxypentanoic acid (4-HPA) and subsequent dehydration or by dehydration to Angelica-lactone (AL) followed by reduction (Fig 5). The yield for side products was dependent on the support not exceeding few percent.

3.3.2 Effect of hydrogen pressure over Ru/C

The effect of hydrogen pressure was studied in LA hydrogenation over Ru/C to tune catalyst activity by changing the reaction conditions. It was found that a hydrogen pressure increase from 6-16 bars gave an increase in LA hydrogenation (Fig. 6) indicating that the

Figure 5: Reaction pathway of LA transformations to GVL, 2-MTHF and pentanoic acid (PA).

reaction order in hydrogen is somewhat higher than unity which can be tentatively explained by lower catalyst deactivation at a higher hydrogen pressure. Thus, further experiments were carried out at 16 bar hydrogen pressure.

3.3.3 Effect of the support

Results on influence of different catalyst supports on LA hydrogenation and GVL formation rate are presented in Fig. 7. For Ru on the zeolitic supports the amount of pentanoic acid was noticeably higher than over carbon support but not as prominent as reported in [24] for, e.g., Ru/H-ZSM-5.

It should be noted that all Ru catalysts in the current work gave high selectivity (97-98%) for GVL at 100% conversion of LA. However, LA hydrogenation rates were different with the lowest one displayed by 4% Ru/C in comparison with more active zeolite catalysts (Table 5). Deterioration of catalytic activity of Ru/H-ZSM-5 could be seen during LA hydrogenation in an organic solvent (Fig. 7) which can be related to the smaller pore size of this catalyst. Zhang and co-workers [33] reported that deactivation of Ru/H-ZSM-5 is related to more prominent influence of carbon deposition and thus poorer accessibility for the catalyst with a smaller channel. Zhang and co-workers also stated that the types of Al species, support structure, Ru dispersion and leaching, along with carbon deposition influence activity and stability.

It can be concluded from Fig. 7 that LA conversion and GVL yield increased in the row: Ru/H-ZSM-5 < Ru/H-Y < Ru/H-USY < Ru/H-Beta.

Previously it was reported that LA hydrogenation is structure sensitive over Ru catalysts [5]. For catalysts, prepared with the RuCl_3 precursor, a volcano-type plot was found for the initial rate as function of Ru particle size, with the highest activity for Ru nanoparticles displayed with an average diameter of ca. 2 nm [5]. A similar trend was found for the catalysts prepared with other precursors. Cao et

Figure 6: Effect of hydrogen pressure on LA hydrogenation over Ru/C: $\text{P}(\text{H}_2)$ 16 bar (squares), $\text{P}(\text{H}_2)$ 6 bar (circles). Reaction conditions: 15 ml 1,4-dioxane, 6.9 mmol LA, 165°C, Ru/C 0.12 g.

al. [34] studied hydrogenation of LA using $\text{Ru}/\text{Al}_2\text{O}_3$ and Ru/C catalysts and also revealed the presence of a typical volcano-type dependence of TOF vs. mean Ru particle size where a maximum TOF was observed for the catalysts with d_{Ru} ca. 1.5 nm for both supports [34].

The impact of the Ru nanoparticle size on catalytic activity for the hydrogenation of LA in the current work was considered by comparing the initial rate of GVL formation ($r_{\text{form}}(\text{GVL})$, mol GVL $\cdot$ (mol Ru $\cdot$ s) $^{-1}$) and TOF (s^{-1}) as a function of the average Ru nanoparticle diameter determined by TEM (Table 3). TOF values are generally considered to be a better activity performance indicator as they are normalized per exposed Ru atoms (based on TEM average particle size data). For Ru/H-ZSM-5 catalyst with a bimodal NPs distribution large Ru NPs were not taken into consideration because of their low catalytic activity. Table 5 shows that the catalysts with similar Ru average NPs size (entries 1-3) showed strong discrepancies in activity. These results imply that the contribution of acidity and microstructure is very prominent when the size effect is

Table 5. Catalytic activity of Ru catalysts in LA hydrogenation. Reaction conditions: 15 ml 1,4-dioxane, 6.9 mmol LA, 165°C, $P(H_2)$ 16 bar.

Catalyst	$r_{\text{form}}(\text{GVL}),$ $\text{mol GVL} \cdot \text{s}^{-1}$	$d(\text{Ru}), \text{nm}$	$D, \%$	$\text{mol Ru} \cdot D$	$\text{TOF, mol GVL} \cdot (\text{mol Ru} \cdot \text{s})^{-1}$
1 Ru/H-Beta	0.02306	2.0	64.5	0.026	0.904
2 Ru/H-USY	0.01469	2.2	58.6	0.023	0.634
3 Ru/H-Y	0.00219	1.6	80.6	0.032	0.069
4 Ru/HZSM-5	0.00178	2.2*	58.6	0.023	0.077
5 Ru/C	0.00042	1.3	99.2	0.039	0.011

*- large Ru NPs were not considered because of their low catalytic activity

Figure 7: Comparison of catalytic activity in LA hydrogenation of Ru catalysts supported on zeolites and carbon material: a) LA conversion, b) GVL formation. Reaction conditions: 15 ml 1,4-dioxane, 6.9 mmol LA, 165°C, $P(H_2)$ 16 bar, Ru/H-Beta (diamond), Ru/H-USY (star), Ru/H-Y (circle), Ru/H-ZSM-5 (square), Ru/C (triangle), LA content (close symbols), GVL (open symbols).

eliminated by using catalysts with approximately the same size.

Ru supported on H-Beta and H-USY catalysts displayed TOF values of an order in magnitude higher than for Ru/H-Y, Ru/H-ZSM-5 and especially Ru/C. H-Beta and H-USY are characterized by similar values $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ and by the highest acidity (0.53 and 0.74 mmol of $\text{NH}_3 \cdot \text{g}^{-1}$, respectively) compared to other investigated zeolites. In particular H-ZSM-5 exhibited two-fold lower acidity (0.27 mmol of $\text{NH}_3 \cdot \text{g}^{-1}$) being also characterized by the lowest SSA $230 \text{ m}^2 \cdot \text{g}^{-1}$.

H-ZSM-5 belonging to the pentasil family is an eight-member ring zeolite, which can explain more prominent carbon deposition as the latter is related to the pore diameter and the channel framework [35]. Therefore, it is reasonable to suggest that coking blocks acidic sites located inside the channels, it more prominent in the case of Ru/H-ZSM-5. The faujasite framework of H-Y zeolite consists of sodalite cages, connected through hexagonal prisms, with the pores formed by a 12-membered ring, having a relatively large diameter of 0.74 nm. Nevertheless, activity of H-Y is on par with H-ZSM-5 displaying, however, more stable behavior. Steaming of H-Y improving mesoporosity resulted in H-USY material, which after deposition of Ru displayed much higher activity. The framework of zeolite Beta in combination with its acidity is also favorable for promoting transformation of levulinic acid into GVL apparently without deposition of carbonaceous residues.

In terms of the reaction mechanism higher acidity of a catalyst with an adequate pore structure can accelerate the second step of LA transformation into GVL, namely dehydration followed by an intramolecular esterification resulting in formation of the ring structure of GVL.

4 Conclusions

Ru catalysts with different type of microporous zeolites and mesoporous carbon Sibunit as supports were synthesized by the wet impregnation method using RuCl_3 precursor and studied in LA hydrogenation under comparable conditions to produce biofuel components from lignocellulose-derived oxygenates. Ru on microporous zeolites demonstrated higher activity than mesoporous Ru/C while similar high selectivity to GVL regardless of the support was observed. Ru supported on H-Beta and H-USY catalysts characterized by similar values $\text{SiO}_2/\text{Al}_2\text{O}_3 = 30$ and high acidity (0.53 and 0.74 mmol of $\text{NH}_3 \cdot \text{g}^{-1}$, respectively) exhibited TOF values an order of magnitude higher than for Ru/H-Y, Ru/H-ZSM-5 and Ru/C. Lower catalytic activity in the latter case can be attributed both to low acidity and non-optimal metal particle size. In the case of Ru/H-ZSM-5 smaller channels are more easily blocked by carbon deposits. Ru NPs deposited on Ru/H-USY and beta zeolites possessing higher acidity, required for the dehydration step, are more accessible for reactants allowing thus high catalyst activity.

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References

- [1] Simakova I.L., Murzin D.Yu., Transformation of bio-derived acids into fuel-like alkanes via ketonic decarboxylation and hydrodeoxygenation: design of multifunctional catalyst, kinetic and mechanistic aspects (review), *J. Energ. Chem.*, 2016, 25, 208–224.
- [2] Bozell J.J., Petersen G.R., Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited, *Green Chem.*, 2010, 12, 539–554.
- [3] Abdelrahman O.A., Heyden A., Bond J.Q., Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ -valerolactone over Ru/C, *ACS Catal.*, 2014, 4, 1171–1181.
- [4] Abdelrahman O.A., Luo H.Y., Heyden A., Román-Leshkov Y., Bond J.Q., Toward rational design of stable, supported metal catalysts for aqueous-phase processing: insights from the hydrogenation of levulinic acid, *J. Catal.*, 2015, 329, 10–21.
- [5] Piskun A.S., Ftouni J., Tang Z., Weckhuysen B.M., Bruijninx P.C.A., Heeres H.J., Hydrogenation of levulinic acid to γ -valerolactone over anatase-supported Ru catalysts: effect of catalyst synthesis protocols on activity, *Appl. Catal. A: Gen.*, 2018, 549, 197–206.
- [6] Piskun A.S., van de Bovenkamp H.H., Rasrendr C.B., Winkelman J.G.M., Heeres H.J., Kinetic modeling of levulinic acid hydrogenation to γ -valerolactone in water using a carbon supported Ru catalyst, *Appl. Catal. A: Gen.*, 2016, 525, 158–167.
- [7] Piskun A.S., Winkelman J.G.M., Tang Z., Heeres H.J., Support screening studies on the hydrogenation of levulinic acid to γ -valerolactone in water using Ru catalysts, *Catalysts*, 2016, 6(9), 131–152.
- [8] Al-Shaal M.G., Wright W.R.H., Palkovits R., Exploring the ruthenium catalysed synthesis of γ -valerolactone in alcohols and utilisation of mild solvent-free reaction conditions, *Green Chem.*, 2012, 14, 1260–1263.
- [9] Luo W., Deka U., Beale A.M., van Eck E.R.H., Bruijninx P.C.A., Weckhuysen B.M., Ruthenium-catalyzed hydrogenation of levulinic acid: influence of the support and solvent on catalyst selectivity and stability, *J. Catal.*, 2013, 301, 175–186.
- [10] Manzer L.E., Catalytic synthesis of α -methylene- γ -valerolactone: a biomass-derived acrylic monomer, *Appl. Catal. A Gen.*, 2004, 272, 249–256.
- [11] Kumar V.V., Naresh G., Sudhakar M., Tardio J., Bhargava S.K., Venugopal A., Role of Brønsted and Lewis acid sites on Ni/TiO₂ catalyst for vapour phase hydrogenation of levulinic acid: kinetic and mechanistic study, *Appl. Catal. A: Gen.*, 2015, 505, 217–223.
- [12] Dutta S., Yu I.K.M., Tsang D.C.W., Ng Y.H., Ok Y.S., Sherwood J., Clark J.H., Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-derived levulinic acid using non-noble metal catalysts: a critical review, *Chem. Eng. J.*, 2019, 372, 992–1006.
- [13] Zhang L., Mao J., Li S., Yin J., Sun X., Guo X., Song C., Zhou J., Hydrogenation of levulinic acid into gamma-valerolactone over in situ reduced CuAg bimetallic catalyst: strategy and mechanism of preventing Cu leaching, *Appl. Catal. B: Env.*, 2018, 232, 1–10.
- [14] Kuwahara Y., Magatani Y., Yamashit H., Ru nanoparticles confined in Zr-containing spherical mesoporous silica containers for hydrogenation of levulinic acid and its esters into γ -valerolactone at ambient conditions, *Catal. Tod.*, 2015, 258, 262–269.
- [15] Guo Y., Li Y., Chen J., Chen L., Hydrogenation of levulinic acid into γ -valerolactone over ruthenium catalysts supported on metal–organic frameworks in aqueous medium, *Catal. Lett.*, 2016, 146, 2041–2052.
- [16] Li C., Ni X., Di X., Liang C., Aqueous phase hydrogenation of levulinic acid to γ -valerolactone on supported Ru catalysts prepared by microwave-assisted thermolytic method, *Ranliao Huaxue Xuebao*, 2018, 46(2), 161–170.
- [17] Cen Y., Zhu S., Guo J., Chai J., Jiao W., Wang J., Fan W., Supported cobalt catalysts for the selective hydrogenation of ethyl levulinate to various chemicals, *RSC Adv.*, 2018, 8, 9152–9160.
- [18] Serrano-Ruiz J.C., Wang D., Dumesic J.A., Catalytic upgrading of levulinic acid to 5-nonanone, *Green Chem.*, 2010, 12, 574–577.
- [19] Yan Z.-P., Lin L., Liu S., Synthesis of γ -valerolactone by hydrogenation of biomass-derived levulinic acid over Ru/C catalyst, *Energy Fuels*, 2009, 23, 3853–3858.
- [20] Bourne R.A., Stevens J.G., Ke J., Poliakoff M., Maximising opportunities in supercritical chemistry: the continuous

- conversion of levulinic acid to γ -valerolactone in CO_2 , *Chem. Commun.*, 2007, 4632–4634.
- [21] Bozell J.J., Moens L., Elliott D.C., Wang Y., Neuenschwander G.G., Fitzpatrick S.W., Bilski R.J., Jarnefeld J.L., Production of levulinic acid and use as a platform chemical for derived products, *Resour. Conserv. Recyc.*, 2000, 28, 227–239.
- [22] Bui L., Luo H., Gunther W.R., Román-Leshkov Y., Domino reaction catalyzed by zeolites with Brønsted and Lewis acid sites for the production of γ -valerolactone from furfural, *Angew. Chem. Int. Edit.*, 2013, 52, 8022–8025.
- [23] Wang J., Jaenicke S., Chuah G.-K., Zirconium-Beta zeolite as a robust catalyst for the transformation of levulinic acid to γ -valerolactone via Meerwein–Ponndorf–Verley reduction, *RSC Adv.*, 2014, 4, 13481–13489.
- [24] Luo W.H., Bruijninx P.C.A., Weckhuysen B.M., Selective, one-pot catalytic conversion of levulinic acid to pentanoic acid over Ru/H-ZSM5, *J. Catal.*, 2014, 320, 33–41.
- [25] Elliott D.C., Frye J.G., US Patent 5883266, Battelle Memorial Institute, 1999.
- [26] *Verified Syntheses of Zeolitic Materials*, Second Revised Edition, Editor: Harry Robson 2001, Publisher Elsevier, Amsterdam, p. 156.
- [27] Simakova I.L., Demidova Yu.S., Glaesel J., Etzold B., Schubert T., Prosvirin I.P., Murzina E.V., Murzin D.Yu., Controlled synthesis of PVP-based carbon supported Ru nanoparticles: synthesis approaches, characterization and catalytic behavior, *Catal. Sci. Technol.*, 2016, 6, 8490–8504.
- [28] Bibby D.M., Aldridge L.P., Milestone N.B., Determination of the aluminium content of the zeolite ZSM-5 from peak positions in the X-ray powder diffraction pattern, *J. Catal.*, 1981, 72, 373–374.
- [29] Kasture M.W., Niphadkar P.S., Sharanappa N., Mirajkar S.P., Bokade V.V., Joshi P.N., Isopropylation of benzene catalyzed by H/ β zeolite catalysts with different crystallinities, *J. Catal.*, 2004, 227, 375–383.
- [30] Parise J.B., Corbin D.R., Abrams L., Cox D.E., Structure of dealuminated Linde Y-zeolite; $\text{Si}_{139.7}\text{Al}_{52.3}\text{O}_{384}$ and $\text{Si}_{173.1}\text{Al}_{18.9}\text{O}_{384}$: presence of non-framework Al species, *Acta Crystallogr.*, 1984, C40, 1493–1497.
- [31] Wei Z., Li X., Deng J., Wang J., Li H., Wang Y., Improved catalytic activity and stability for hydrogenation of levulinic acid by Ru/N-doped hierarchically porous carbon, *Mol. Catal.*, 2018, 448, 100–107.
- [32] Song W., Chen Z., Lai W., Rodríguez-Ramos I., Yi X., Weng W., Fang W., Effect of lanthanum promoter on the catalytic performance of levulinic acid hydrogenation over Ru/carbon fiber catalyst, *Appl. Catal. A: Gen.*, 2017, 540, 21–30.
- [33] Zhang B., Wu Q., Zhang C., Su X., Shi R., Lin W., Li Y., Zhao F., A robust Ru/ZSM-5 hydrogenation catalyst: insights into the resistances to ruthenium aggregation and carbon deposition, *ChemCatChem*, 2017, 9, 3646–3654.
- [34] Cao S., Monnier J.R., Williams C.T., Diao W., Regalbuto J.R., Rational nanoparticle synthesis to determine the effects of size, support, and K dopant on Ru activity for levulinic acid hydrogenation to γ -valerolactone, *J. Catal.*, 2015, 326, 69–81.
- [35] Bibby D.M., Milestone N.B., Patterson J.E., Aldridge L.P., Coke formation in zeolite ZSM-5, *J. Catal.*, 1986, 97, 493–502.

Przypisy końcowe

- 1 [] Simakova I.L., Murzin D.Yu., Transformation of bio-derived acids into fuel-like alkanes via ketonic decarboxylation and hydrodeoxygenation: design of multifunctional catalyst, kinetic and mechanistic aspects (review), *J. Energ. Chem.*, 2016, 25, 208–224.
- 2 [] Bozell J.J., Petersen G.R., Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited, *Green Chem.*, 2010, 12, 539–554.
- 3 [] Abdelrahman O.A., Heyden A., Bond J.Q., Analysis of kinetics and reaction pathways in the aqueous-phase hydrogenation of levulinic acid to form γ -valerolactone over Ru/C, *ACS Catal.*, 2014, 4, 1171–1181.
- 4 [] Abdelrahman O.A., Luo H.Y., Heyden A., Román-Leshkov Y., Bond J.Q., Toward rational design of stable, supported metal catalysts for aqueous-phase processing: insights from the hydrogenation of levulinic acid, *J. Catal.*, 2015, 329, 10–21.
- 5 [] Piskun A.S., Ftouni J., Tang Z., Weckhuysen B.M., Bruijninx P.C.A., Heeres H.J., Hydrogenation of levulinic acid to γ -valerolactone over anatase-supported Ru catalysts: effect of catalyst synthesis protocols on activity, *Appl. Catal. A: Gen.*, 2018, 549, 197–206.
- 6 [] Piskun A.S., van de Bovenkamp H.H., Rasrendr C.B., Winkelman J.G.M., Heeres H.J., Kinetic modeling of levulinic acid hydrogenation to γ -valerolactone in water using a carbon supported Ru catalyst, *Appl. Catal. A: Gen.*, 2016, 525, 158–167.
- 7 [] Piskun A.S., Winkelman J.G.M., Tang Z., Heeres H.J., Support screening studies on the hydrogenation of levulinic acid to γ -valerolactone in water using Ru catalysts, *Catalysts*, 2016, 6(9), 131–152.
- 8 [] Al-Shaal M.G., Wright W.R.H., Palkovits R., Exploring the ruthenium catalysed synthesis of γ -valerolactone in alcohols and utilisation of mild solvent-free reaction conditions, *Green Chem.*, 2012, 14, 1260–1263.
- 9 [] Luo W., Deka U., Beale A.M., van Eck E.R.H., Bruijninx P.C.A., Weckhuysen B.M., Ruthenium-catalyzed hydrogenation of levulinic acid: influence of the support and solvent on catalyst selectivity and stability, *J. Catal.*, 2013, 301, 175–186.
- 10 [] Manzer L.E., Catalytic synthesis of α -methylene- γ -valerolactone: a biomass-derived acrylic monomer, *Appl. Catal. A Gen.*, 2004, 272, 249–256.
- 11 [] Kumar V.V., Naresh G., Sudhakar M., Tardio J., Bhargava S.K., Venugopal A., Role of Brønsted and Lewis acid sites on Ni/TiO₂ catalyst for vapour phase hydrogenation of levulinic acid: kinetic and mechanistic study, *Appl. Catal. A: Gen.*, 2015, 505, 217–223.
- 12 [] Dutta S., Yu I.K.M., Tsang D.C.W., Ng Y.H., Ok Y.S., Sherwood J., Clark J.H., Green synthesis of gamma-valerolactone (GVL) through hydrogenation of biomass-derived levulinic acid using non-noble metal catalysts: a critical review, *Chem. Eng. J.*, 2019, 372, 992–1006.
- 13 [] Zhang L., Mao J., Li S., Yin J., Sun X., Guo X., Song C., Zhou J., Hydrogenation of levulinic acid into gamma-valerolactone over in situ reduced CuAg bimetallic catalyst: strategy and mechanism of preventing Cu leaching, *Appl. Catal. B: Env.*, 2018, 232, 1–10.
- 14 [] Kuwahara Y., Magatani Y., Yamashit H., Ru nanoparticles confined in Zr-containing spherical mesoporous silica containers for hydrogenation of levulinic acid and its esters into γ -valerolactone at ambient conditions, *Catal. Tod.*, 2015, 258, 262–269.
- 15 [] Guo Y., Li Y., Chen J., Chen L., Hydrogenation of levulinic acid into γ -valerolactone over ruthenium catalysts supported on metal–organic frameworks in aqueous medium, *Catal. Lett.*, 2016, 146, 2041–2052.
- 16 [] Li C., Ni X., Di X., Liang C., Aqueous phase hydrogenation of levulinic acid to γ -valerolactone on supported Ru catalysts prepared by microwave-assisted thermolytic method, *Ranliao Huaxue Xuebao*, 2018, 46(2), 161–170.