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Heterogeneous Catalytic Hydrogenation of Biobased Levulinic and Succinic Acids in Aqueous Solutions

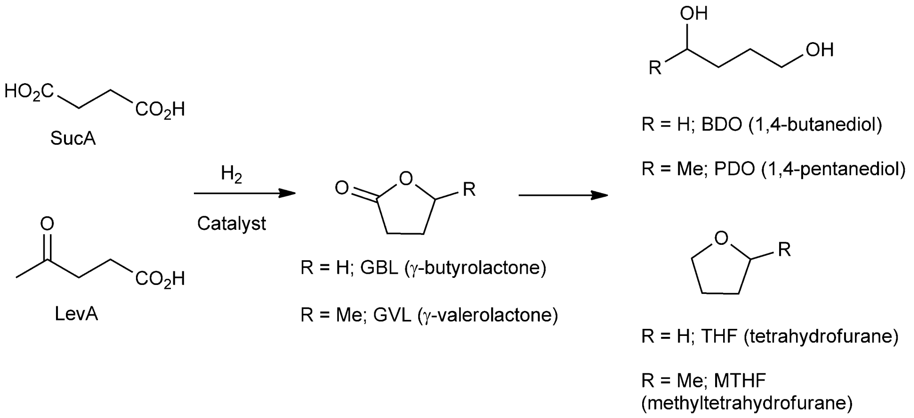
Louis Corbel-Demailly,[a, b] Bao-Khanh Ly,[a] Doan-Pham Minh,[a] Benoit Tapin,[c] Catherine Especel,[c] Florence Epron,[c] Amandine Cabiac,[b] Emmanuelle Guillon,[b] Michèle Besson,[a] and Catherine Pinel*[a]

Supported noble-metal catalysts (Ru, Pd or Pt) and the corresponding Re-promoted catalysts exhibit a high activity for the hydrogenation of biobased carboxylic acids. Levulinic acid and succinic acid are converted into the lactones or the diols depending on the nature of the catalyst and the reaction conditions. The highest selectivity to 1,4-pentanediol of 82 % is achieved at 140 °C in the presence of the 1.9 % Ru–3.6 % Re/C catalyst.

Introduction

Nowadays, a large range of acids are produced from biomass either through chemical or biochemical transformations. The production of levulinic acid (LevA) from lignocellulosic derivatives under acidic conditions has been described since the early years in the 20th century; however, large-scale applications were reported more recently that involve a continuous process based on the Biofine technology.[1] On the other hand, succinic acid (SucA) is now produced through an economically viable process from renewable sources by different companies.[2, 3]

These acids are considered to be platform molecules that can be further transformed into value-added products. The hydrogenation of these acids leads to the formation of the corresponding lactones, diols, or cyclic ethers depending on the reaction conditions and the nature of the catalysts (Scheme 1).[4–7]



Scheme 1. Catalytic hydrogenation of SucA and LevA.

To avoid the use of undesirable stoichiometric hydride reductants, the catalytic conversion of biobased carboxylic acids using molecular hydrogen under pressure has received considerable attention. The hydrogenation of SucA has been described using a large range of reaction conditions.[8–13] We recently reported efficient supported mono- or bimetallic catalysts for the selective hydrogenation of SucA in the aqueous phase.[8, 9] In the presence of Pd- or Ru-supported monometallic catalysts, γ-butyrolactone (GBL) was the main product, whereas in the presence of Pd–Re or Ru–Re catalysts 1,4-butanediol (1,4-BDO) was formed predominantly. We have shown that the Re/M ratio (M = Pd or Ru) and the nature of the support affected the reaction rate as well as the selectivity for the desired product. However, only few reports on the hydrogenation of LevA have been published. A few homogeneous and heterogeneous catalysts mainly for the formation of γ-valerolactone (GVL) have been described.[10–12] The presence of a solid-acid

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[a] *L. Corbel-Demailly, B.-K. Ly, Dr. D.-P. Minh, Dr. M. Besson, Dr. C. Pinel*
IRCELYON
Institut de recherches sur la catalyse et l'environnement de Lyon
UMR 5256 CNRS-Université Lyon1
2 Avenue Albert Einstein, 69626 Villeurbanne (France)
E-mail: catherine.pinel@ircelyon.univ-lyon1.fr

[b] *L. Corbel-Demailly, Dr. A. Cabiac, Dr. E. Guillon*
IFPEN-Lyon, BP3
69360 Solaize (France)

[c] *B. Tapin, Dr. C. Especel, Dr. F. Epron*
IC2MP
Institut de Chimie des Milieux et Matériaux de Poitiers
UMR 7285 CNRS-Université de Poitiers
4 rue Michel Brunet, 86022 Poitiers (France)

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co-catalyst increased the reaction rate of the first step of the reaction (formation of GVL, Scheme 1); an initial activation of the carbonyl group for the hydrogenation to the intermediate γ-hydroxyvaleric acid was proposed, followed by the favorable intramolecular esterification reaction to yield the lactone.[11] Ru-based complexes containing sulfonated phosphine ligands have been reported to selectively hydrogenate LevA to GVL, even in the absence of a solvent.[12] Wright and Palkovits compiled a list heterogeneous catalysts, which were developed to perform this transformation under a large range of reaction conditions.[13] More drastic conditions are needed to achieve the syntheses of 1,4-pentanediol (1,4-PDO) or methyltetrahydrofurane (MTHF). Geilen et al. reported the selective hydrogenation of LevA into 1,4-PDO (95 % yield, 18 h) at 160 °C and 100 bar in the presence of the Ru-Triphos complex [Triphos = 1,1,1-tris(diphenylphosphino-methyl)ethane, 0.1 mmol %] as homogeneous catalyst.[14] Addition of an acidic ionic liquid shifted the reaction to the selective formation of MTHF (92 %) under identical reaction conditions. The selective hydrogenolysis in ethanol at 200 °C and 60 bar of the intermediate GVL into 1,4-PDO has been reported to be efficiently performed in the presence of a Cu-ZrO_2 catalyst (30 wt %).[15]

Herein, the performances of mono- and bimetallic catalysts in the hydrogenation of LevA are reported, with a special focus on the selectivity for 1,4-PDO. The reactivity of LevA acid will be compared with the behavior of SucA.

Results and Discussion

X-Ray diffraction (XRD) patterns of the Pd and Ru monometallic catalysts showed no diffraction peak that could be attributed to the metallic phase, suggesting a small particle size (Figure 1 b). TEM analysis confirmed the presence of only small Pd or Ru particles, with the size distribution centered on 2 nm (Figure 2). On the other hand, diffraction peaks attributed to Pt crystallites were observed by means of XRD, indicating that larger particles were present on the support ($d = 5$ nm according to the Debye–Scherrer equation, Figure 1 b).[16]

The evaluation of the catalytic performances of the monometallic catalysts was carried out for both LevA and SucA hydrogenation. As an illustration, the evolution of LevA and GVL concentrations in the presence of the different monometallic catalysts is reported on Figure 3.

The Ru catalyst (2.1 % Ru/C) was the most efficient in the hydrogenation of LevA; after 10 min of reaction, complete conversion was achieved. In contrast, under the same reaction conditions, the Pd (2.7 % Pd/C) and Pt (4.1 % Pt/C) catalysts exhibited a much lower activity and the conversion after 2 h reached only 70 % and 53 % in the presence of Pd/C and Pt/C, respectively. As expected, GVL was the main product formed in the initial step of the hydrogenation reaction. In the case of the Ru catalyst, this intermediate was further transformed mainly to 1,4-PDO. However, the carbon balance reached only 80 % due to the occurrence of a large amount of cracking reactions as previously observed for the hydrogenation of SucA.[8]

Addition of Re was shown to modify the performances of the supported noble-metal catalysts in several hydrogenation reactions. Re–O interactions, evidenced through extended X-ray absorption fine structure (EXAFS) spectroscopy, were reported to be responsible for the variation in catalyst performances.[17, 18]

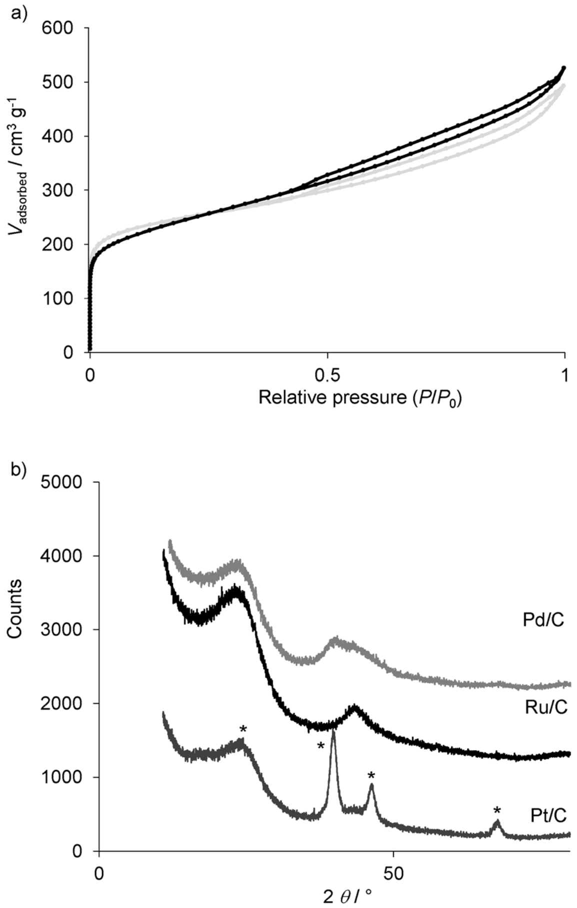


Figure 1. a) N_2 adsorption–desorption isotherms of commercial (gray) and oxidized (black) carbon; b) diffractograms of active carbon-supported monometallic catalysts. * = diffraction peaks attributed to Pt.

The bimetallic catalysts prepared from these monometallic parent catalysts were evaluated under the same reaction conditions. The conversion of LevA and the formation of GVL, in the presence of the bimetallic catalysts during 2 h, are reported in Figure 4.

Similar performances were observed for the mono- and bimetallic catalysts based on Ru, that is to say that the hydrogenation rate of LevA was very high and full conversion was achieved after 10 min. However, using the Pd- and Pt-based catalysts, the deposition of Re significantly increased the reaction rate compared to the monometallic parent catalyst and full conversion of LevA was achieved after 2 and 7 h in the presence of Pd–Re/C and Pt–Re/C, respectively. In a second step, regardless of the metallic system, GVL could be further hydrogenated to a mixture of 1,4-PDO and MTHF (Scheme 1) together with some minor byproducts, such as 2-butanol (2-BuOH) and 2-pentanol (2-PeOH), which were identified by using GC–MS (see the Supporting Information). At the beginning of the reaction, the pH value increased rapidly from 2.6 to 3.3, corre-

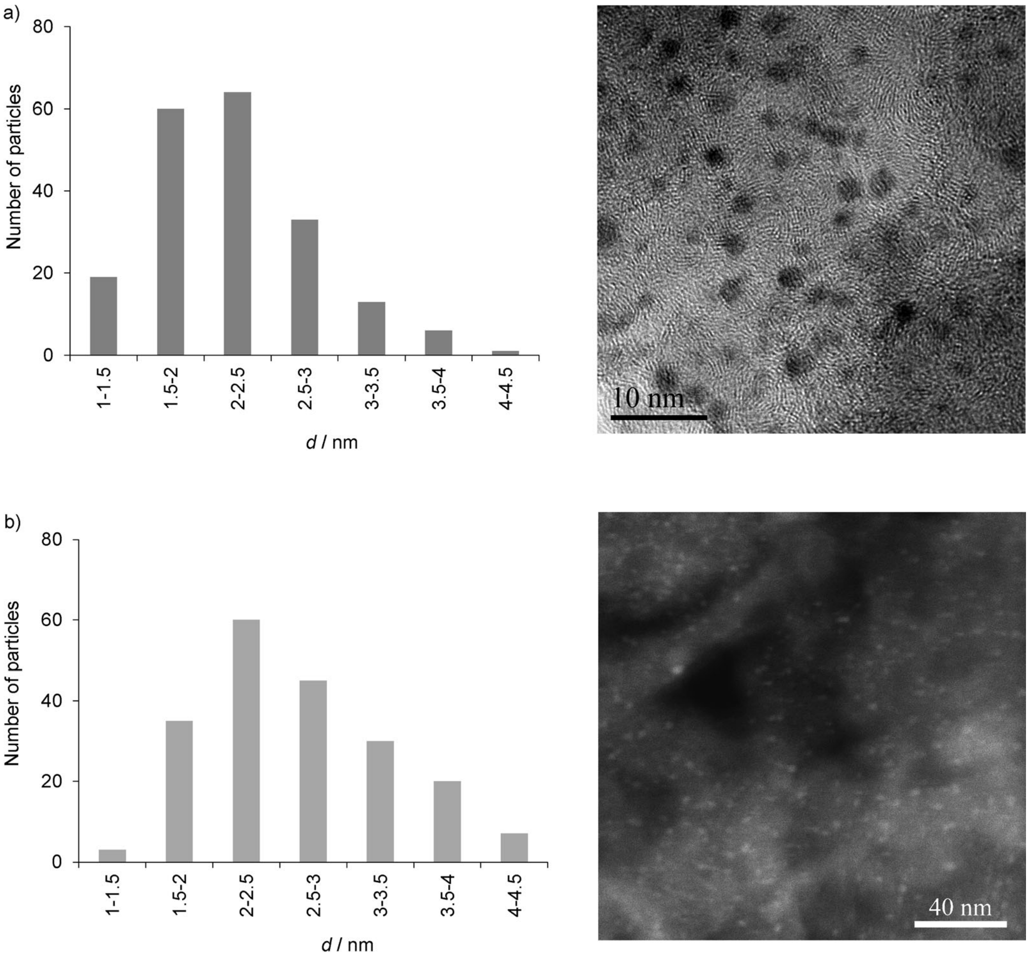


Figure 2. Particle-size distributions determined from measurements of 200 particles of a) Ru-based catalysts (2.8 % Ru–3.9 % Re/C) and b) Pd-based catalysts (2 % Pd–4 % Re/C) and the respective TEM images.

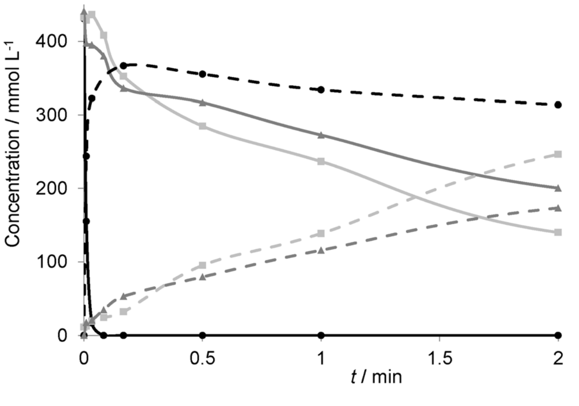


Figure 3. Hydrogenation of LevA in the presence of monometallic catalysts [2.1 % Ru/C (●); 4.1 % Pt/C (▲); 2.7 % Pd/C (■)]. Evolution of main products as a function of time: full line LevA, dotted line GVL. Reaction conditions: LevA = 430 mmol L^{-1} (150 mL), Molar ratio LevA/Ru = 2070, LevA/Pt = 2050, LevA/Pd = 1710, 160 °C, 150 bar.

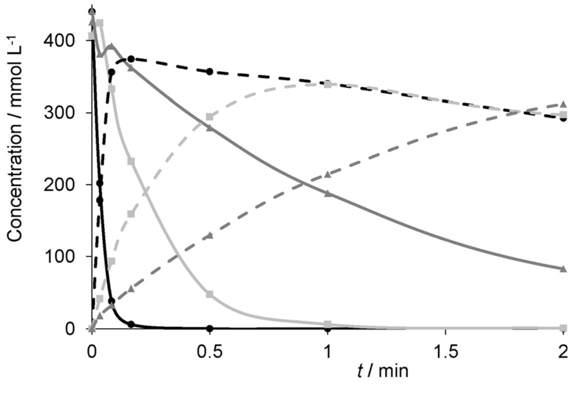


Figure 4. Hydrogenation of LevA and formation of GVL in the presence of bimetallic catalysts [RuRe (●); PtRe (▲); PdRe (■)]. Evolution of main products as a function of time: full line LevA, dotted line GVL. Reaction conditions identical to Figure 3.

sponding to the transformation of LevA into GVL, and then a further increase up to 4.7, reaching complete conversion of GVL.

In the presence of 2.8 % Ru–3.9 % Re/C the highest GVL yield (85 %) was observed after 10 min (Figure 4), whereas total conversion of GVL was achieved after 24 h, yielding mainly 1,4-PDO (55 % selectivity, Figure 5 a) together with 2-PeOH (8 %), MTHF (5 %), and 2-BuOH (3 %) in solution (Figure 5 b). We confirmed that the hydrogenation of MTHF under similar conditions yielded mainly 2-PeOH (5 % after 24 h) together with

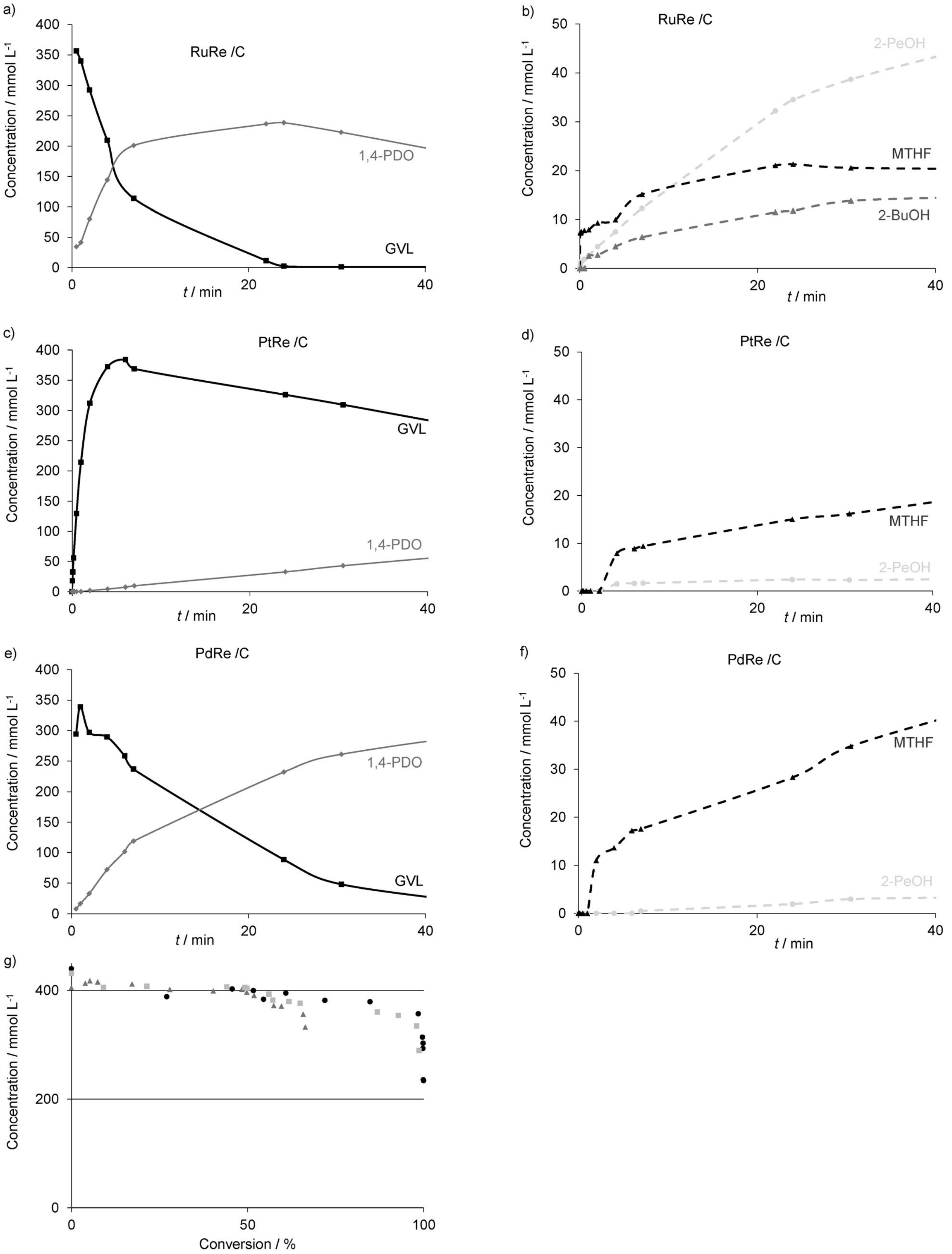


Figure 5. Hydrogenation of LevA: Evolution of the concentration of a, c, e) the main products and b, d, f) the by-products as a function of time (160 °C, 150 bar) in the presence of 2.8 % Ru–3.9 % Re/C (a, b), 3.3 % Pt–4.1 % Re/C (c, d), and 2.7 % Pd-3.9 % Re/C e), f). g) TOC concentration (expressed as C_5 equivalent molar concentration) as a function of the conversion of (LevA + GVL) [RuRe (●); PtRe (▲); PdRe (■)]. For clarity, LevA concentration was not reported.

a small amount of 2-BuOH, whereas 1-PeOH was not detected. Furthermore, a significant number of cracking reactions occurred and only 65% of the initial total carbon loading could be detected in the liquid phase at the end of the reaction [from both HPLC and total organic carbon (TOC) analysis], indicating the formation of a very large amount of gaseous products (Figure 5 g). On the other hand, in the presence of 3.3%Pt–4.1%Re/C, a very low transformation rate of GVL was observed and less than 20% GVL conversion was achieved after 24 h; low amounts of both 1,4-PDO and MTHF were formed (Figure 5 c and d). This low conversion can be partly attributed to the larger particle size of Pt compared with Ru and Pd. Using the 2.7%Pd–3.9%Re/C catalyst, significantly higher conversions were achieved compared to the monometallic catalyst: LevA completely disappeared after 1 h and subsequent hydrogenation of the GVL intermediate was observed, yielding mainly 1,4-PDO (Figure 5 e) and a minor amount of MTHF (Figure 5 f). As mentioned for Ru–Re/C, the amount of TOC in the solution decreased drastically, indicating that there was also formation of gaseous products, but to a lesser extent in comparison to the monometallic catalyst (Figure 5 g).

The efficiency of Ru–Re/C and Pd–Re/C catalysts were compared for both LevA and SucA hydrogenation, and the more active one (Ru–Re/C) was evaluated at a higher concentration (15 wt%) (Figure 6). In a previous study on SucA hydrogenation, it was observed that the selectivity to 1,4-BDO did not change for a range of SucA concentrations.[9] In the presence of Ru–Re/C and at 160 °C, full conversion of LevA was attained after 10 min, whereas SucA was only completely converted after more than 40 h (Figure 6 a and b). This result is in accordance with the different reactivities of ketone and acid functional groups towards hydrogenation (Scheme 2).[19] In both cases, the lactones (GVL or GBL) were subsequently hydrogenated into the corresponding diols (1,4-PDO and 1,4-BDO, respectively) as the main product. However, the reaction rates were different due to the fact that hydrogenation of SucA is considerably slower. In the case of LevA, hydrogenation reactions of LevA and GVL are successive reactions, whereas in the case of SucA, SucA and GBL are reduced simultaneously. The maximum GVL yield (formed from LevA) was obtained after 30 min, whereas the maximum GBL yield (formed from SucA) was only detected after 25 h. Moreover, after 2 days of reaction, a 15% mass balance loss was measured when SucA was used as the substrate, whereas a 20% loss was detected in the case of LevA. The maximum selectivity to 1,4-BDO (from SucA) was 62%, whereas 54% 1,4-PDO (from LevA) selectivity was achieved. Independent of the substrate, the selectivity to the cyclic ethers (THF or MTHF) remained low (< 10%).

Similar behaviors were achieved using the Pd–Re catalyst for the hydrogenation of a 5 wt% LevA or SucA solution (Figure 7 a and b). The hydroge-

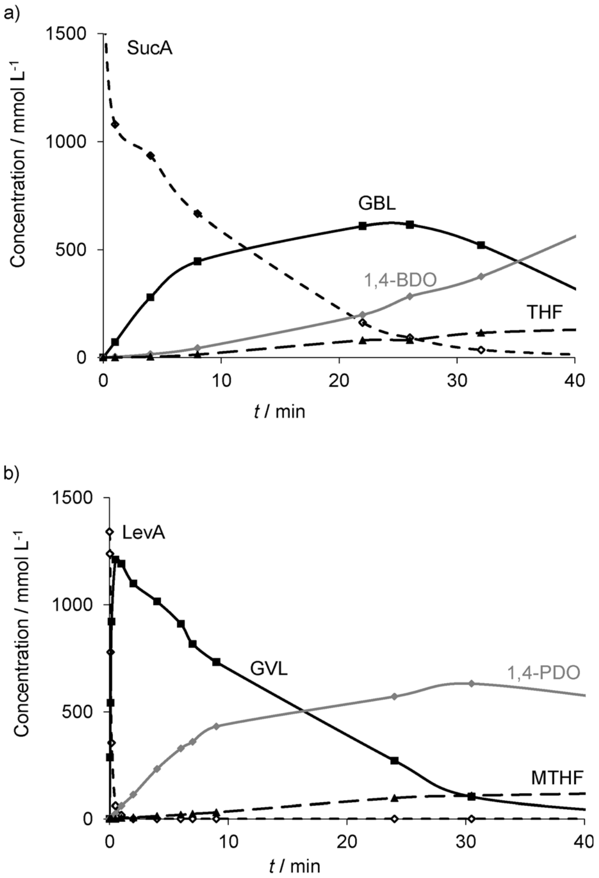
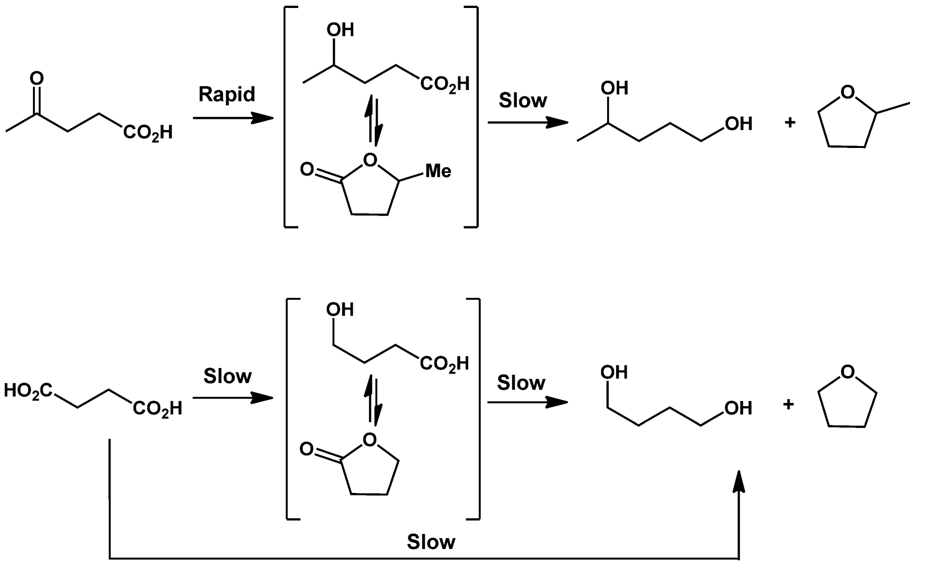


Figure 6. Evolution of the concentration of the main products as a function of time (160 °C, 150 bar, $[LevA]_0 = [SucA]_0 = 1400\ mmol\,L^{-1}$) in the presence of RuRe/C for a) SucA hydrogenation and b) LevA hydrogenation.



Scheme 2. Different reactivities of LevA and SucA during hydrogenation reaction.

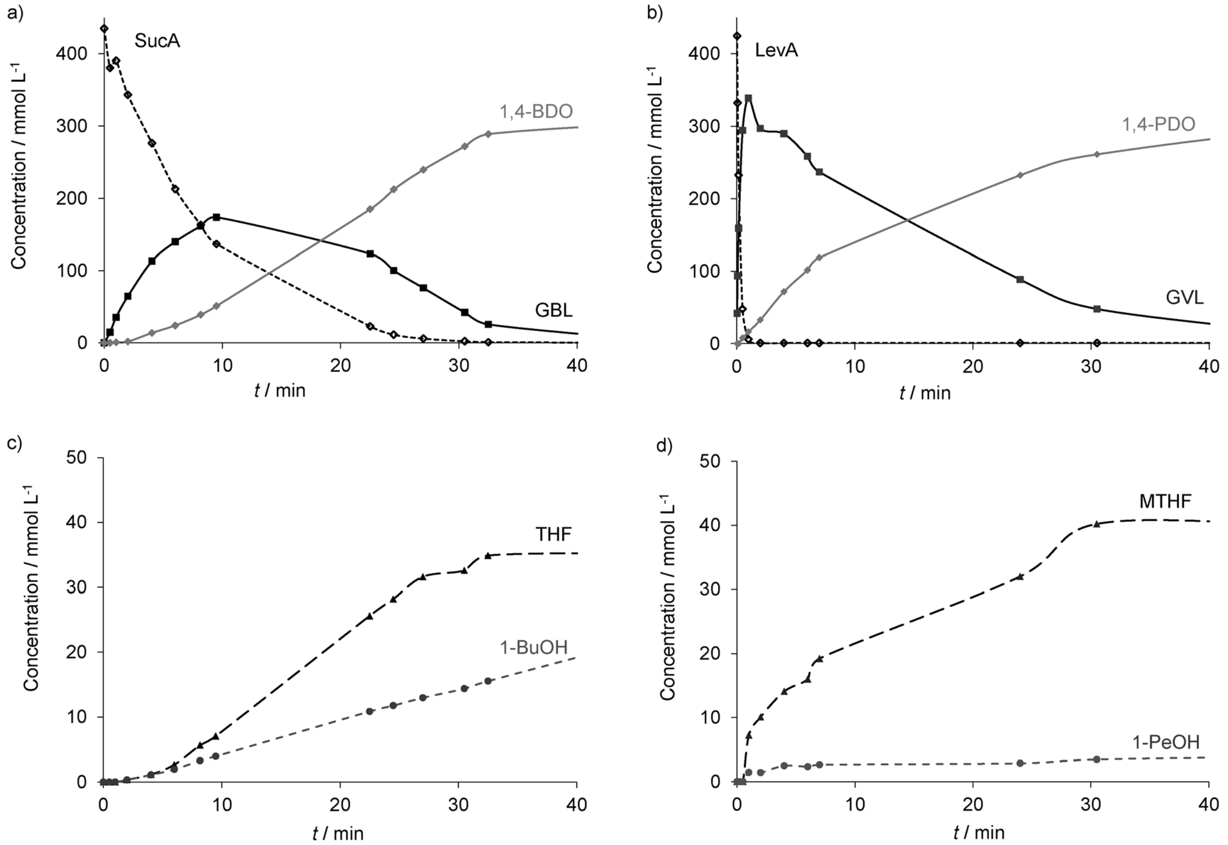


Figure 7. Evolution of the concentration of the main products as a function of time (160 °C, 150 bar, $[LevA]_0 = [SucA]_0 = 430$ mmol L^{-1}) in the presence of PdRe/C for a) SucA hydrogenation, b) LevA hydrogenation and for the by-products of c) SucA hydrogenation and d) LevA hydrogenation.

nation rate of LevA was significantly higher than that of SucA; the corresponding lactones were transformed mainly to diols, with less than 10% formation of cyclic ethers (Figure 7c and d). Using this bimetallic catalyst, 66% selectivity for 1,4-BDO and 15% carbon loss were observed during SucA hydrogenation, whereas 1,4-PDO was formed with 69% selectivity at 16% carbon loss during LevA hydrogenation. In both cases, the formation of the corresponding primary monoalcohols (1-BuOH and 1-PeOH) was observed but with a small selectivity (<5%). These results clearly show that the differences observed between LevA and SucA are only related to the first hydrogenation step and that the behavior of both lactones is similar.

To reduce the undesirable cracking products observed for LevA, we carried out the reaction at lower temperatures. The first rapid hydrogenation of LevA to GVL was not significantly affected by the temperature (in the range from 120° to 160°). However, as expected, the lower the temperature, the slower the second hydrogenation step. In the presence of Ru–Re/C, GVL was completely hydrogenated after 22 h at 160 °C (Figure 5a), whereas 48 h and 72 h were necessary to achieve complete hydrogenation at 140 and 120 °C, respectively. However, the selectivity to 1,4-PDO significantly increased from 69% to up to 80% with a decrease of the temperature (Figure 8). Simultaneously, the selectivity to ether (MTHF) and monoalcohols (1-PeOH, 2-PeOH, and 2-BuOH) decreased. This was mainly attributed to a reduced amount of degradation products that derive from cracking of the substrate or the intermediates.

Similarly, the hydrogenation of LevA in the presence of Pd–Re/C was carried out at 140 °C. The hydrogenation rate was significantly decreased, and even after 48 h 28% GVL was still present in the solution.

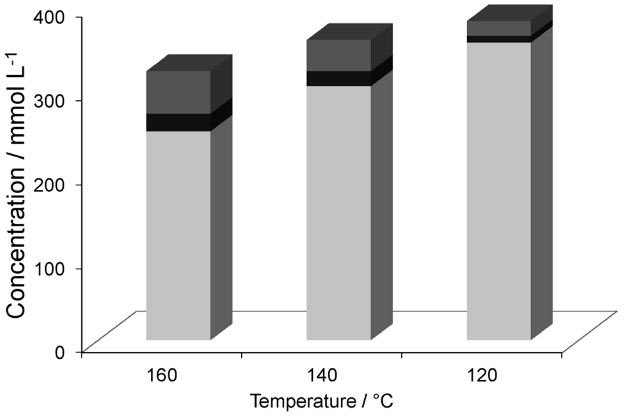


Figure 8. Influence of temperature on the product distribution at 100% GVL conversion. Reaction conditions: LevA = 430 mmol L^{-1}, 2.2% Ru–3.8% Re/C, molar ratio LevA/Ru = 2000, 150 bar. Reaction time: 160 °C = 22 h; 140 °C = 48 h; 120 °C = 72 h. Alcohols = 1-PeOH + 2-PeOH + 2-BuOH [alcohols ■); MTHF (■); PDO (■)].

The influence of pressure on LevA hydrogenation was studied by performing the reaction at 120 bar (140 °C in the presence of Ru–Re/C as catalyst, see the Supporting Information). The hydrogenation rate of GVL was only slightly reduced and full conversion was achieved after 54 h compared to 48 h at 150 bar. On the other hand, no significant influence on the selectivity was observed (71 % selectivity to 1,4-PDO).

We have previously demonstrated that in the hydrogenation of SucA the Re/M ratio strongly affected the activity of the catalysts, which was the main factor influencing the selectivity to 1,4-BDO. Different Ru–Re/C catalysts with various Re loadings (1.8 to 4.6 wt %) were prepared and evaluated for the hydrogenation of LevA at 140 °C. The properties of the Ru-based catalysts for ketone hydrogenation were significantly affected by the amount of loading of Re: the initial rate of the hydrogenation of LevA to GVL decreased as the amount of Re was increased (Figure 9 a). On the other hand, the reaction rate of the second step was much less affected by the Re/Ru ratio (Figure 9 b): the hydrogenation rate of GVL was only slightly higher in the presence of the 1.9 % Ru–1.8 % Re/C catalyst compared with 3.6 % and 4.6 % Re loadings. We observed that the selectivity to MTHF was not affected by the Re amount, whereas the selectivity to 1,4-PDO increased and the selectivity to monoalcohols decreased (Table 1). The subsequent hydrogenolysis reactions seem to have been partly suppressed because of the presence of Re. These results are in agreement with observations we reported previously for SucA hydrogenation.[8]

As mentioned above, few studies on the hydrogenation of LevA into 1,4-PDO have been published. The best catalytic results reported in literature are summarized and compared with our best result in Table 2. All reports showed that drastic conditions (pressure or temperature) are needed to obtain a good selectivity to 1,4-PDO. The Ru–Re catalytic system can efficiently and selectively hydrogenate LevA to 1,4-PDO in water.

Table 1. Influence of Re loading on the 1,4-PDO yield.

Re content [wt %]	Molar ratio Re/Ru	Yield[a] [%] 1,4-PDO	2-BuOH	2-PeOH	MTHF	Carbon balance[b] [%]
1.8	0.5	72	2	9	3	88
3.6	1	82	1	5	3	90
4.3	1.3	80	1	5	3	93

[a] Yields are for full conversion of GVL (t = 24–28 h). [b] Carbon balance determined by TOC analysis.

Table 2. Comparison of the best 1,4-PDO yield in this work with results published in the literature for LevA hydrogenation.

Catalyst	Ratio LevA/metal	P_{H_2} [bar]	T [°C]	Solvent	t [h]	$\text{Yield}_{\text{PDO}}$[a] [%]	Ref.
1.9 % Ru–3.6 % Re/C	2290	150	140	water	28	82	this work
Ru-Triphos[b]	4000	100	160	neat	18	95	[14]
Cu/ZrO2	10[c]	60	200	ethanol	6	95	[15]

[a] Yields are for full GVL conversion. [b] Homogeneous catalyst. [c] Molar ratio is for GVL/Cu.

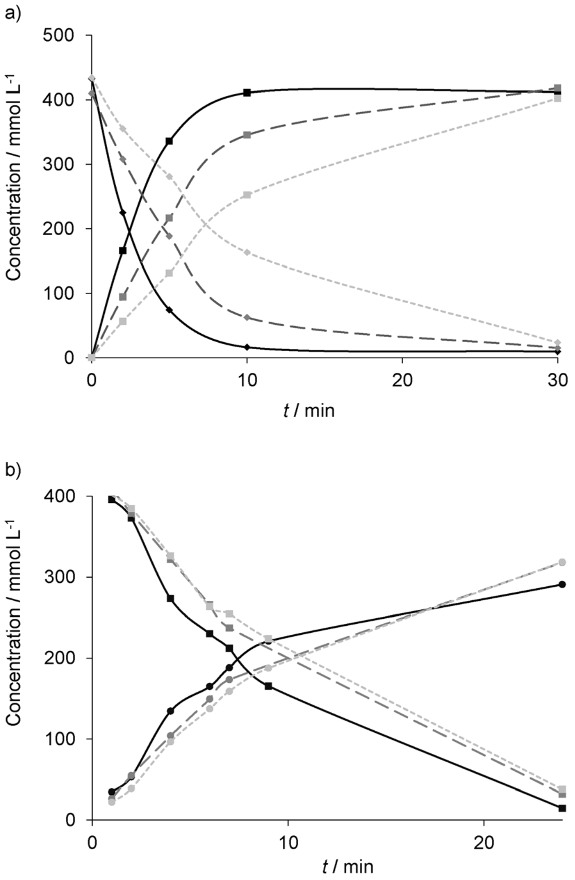


Figure 9. Influence of the *x* Re % in the 1.9 % Ru–*x* % Re/C catalysts [*x* = 1.8 (——), 3.6 (– – –), and 4.6(-----)] on the conversion of a) LevA (◆) and b) GVL (●) to PDO (■). Reaction conditions: [LevA] = 430 mmol L^{-1}, 140 °C, 150 bar. In parentheses: Re wt %.

Conclusions

Noble-metal (Ru, Pd, or Pt) supported catalysts and the corresponding Re-promoted catalysts exhibit a high activity for the hydrogenation of biobased carboxylic acids. Both LevA and SucA are converted into the corresponding lactones or diols depending on the nature of the catalyst and the reaction conditions. Although the reactivity of LevA and SucA is significantly different because of the nature of the first functional group to be hydrogenated (carbonyl or carboxyl group), the behavior of intermediate lactones (GBL and GVL) is similar regardless of the catalyst. A maximum selectivity to 1,4-PDO of 82 % was achieved at 140 °C in the presence of 1.9 % Ru–3.6 % Re/C as catalyst. Further studies are in progress to optimize the preparation of the bimetallic catalyst and to reach the highest diol yield.

Experimental Section

Catalysts preparation

Active carbon (Acticarbon L3S, 900 $m^2 g^{-1}$) was used as supporting material after oxidation with 15 % NaOCl for 24 h to introduce carboxylic groups.[20] The oxidation procedure did not significantly affect the textural properties of the support [Figure 1 a, S_{BET} = 850 $m^2 g^{-1}$ (BET = Brunauer–Emmett–Teller)].

The monometallic catalysts were prepared through cationic exchange at room temperature. To a suspension of the oxidized support in NH_4OH (1 mol L^{-1}), an aqueous solution of the metallic salt ($[Ru(NH_3)_6Cl_3]$, $[Pt(NH_3)_4Cl_2]$ or $[Pd(NH_3)_4Cl_2]$ was added to obtain 2–4 wt % metal and the suspension was stirred for 24 h. After filtration, washing, and drying, the solid was reduced under H_2 at 300 °C for 3 h and finally passivated in 1 % O_2/N_2 gas flow. The bimetallic catalysts were prepared by impregnation of the monometallic Ru and Pd solids by using an aqueous solution of NH_4ReO_4, evaporation of water, drying under vacuum at 100 °C, reduction at 450 °C for 3 h, and passivation (1 % O_2/N_2 flow). The nominal loading was 4 wt % Re.

The catalysts were characterized by elemental analysis (inductively coupled plasma optical emission spectrometry), XRD analysis by using a Siemens Bruker D5005 diffractometer with CuK_α radiation, and by transmission electron microscopy (TEM, JEOL 2010) equipped with an energy dispersive X-ray detector (EDX).

Hydrogenation reaction

SucA and LevA were of reagent grade (Aldrich).

All experiments were conducted in a 300 mL Hastelloy Parr 4560 high pressure reactor equipped with an electrically heated jacket, a turbine stirrer with a variable speed magnetic driver, and a liquid sampling line. In a typical reaction, the reactor was loaded with LevA (7.5 g), water (142 g), and catalyst (1 g). After purging with Ar, the reactor was heated to the desired temperature (typically 160 °C), and a H_2 pressure (150 bar) was used to initiate the reaction. The liquid samples taken from the reactor at regular intervals were analyzed by using both HPLC chromatography equipped with UV and refractive index detectors (ICSep Coregel 107H column, 0.005 N H_2SO_4 as mobile phase at a flow rate of 0.5 mL min^{-1}) and gas chromatography (FFAP column, 30 m, 0.25 mm using He as carrier gas). Acids, lactones, diols (1,4-pentanediol and 1,4-butanediol), cyclic ethers, and by-products (propionic, butyric, and acetic acids; *n*-butanol and *n*-propanol) could be quantified. GC–MS analysis was used for identification of the different products. TOC was also measured by using a Shimadzu TOC-VCHS analyzer. Comparison of the measured TOC with the TOC calculated from chromatography analysis verified the material balance based on the initial concentration of the acid and yielded an estimation of gaseous products formed by cracking. The products contained in the gas phase were analyzed (butane, propane, ethane, methane, carbon monoxide, etc.) at the end of the reaction by using a μGC–MS (see the Supporting Information).

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Keywords: biomass · carboxylic acids · diols · heterogeneous catalysis · hydrogenation

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