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The Role of the Hydrogen Source on the Selective Production of γ-Valerolactone and 2-Methyltetrahydrofuran from Levulinic Acid

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A mechanistic study of the hydrogenation reaction of levulinic acid (LA) to 2-methyltetrahydrofuyran (MTHF) was performed using three different solvents under reactive H_2 and inert N_2 atmospheres. Under the applied reaction conditions, catalytic transfer hydrogenation and hydrogenation with molecular H_2 were effective at producing high yields of γ-valerolactone. However, the conversion of this stable intermediate to MTHF required the combination of both hydrogen sources (the solvent and the H_2 atmosphere) to achieve good yields. The reaction system with 2-propanol as solvent and Ni–Cu/Al_2O_3 as catalyst allowed full conversion of LA and a MTHF yield of 80% after 20 h reaction time at 250 °C and 40 bar of H_2 (at room temperature). The system showed the same catalytic activity at LA feed concentrations of 5 and up to 30 wt%, and also when high acetone concentration at the beginning of the reaction were added, which confirmed the potential industrial applications of this solvent/catalyst system.

Concerns about fossil fuel shortage and the environment have triggered intensive research to find environmentally benign alternatives for the non-renewable energy resources that are currently used. Although other renewable energy sources, such as solar or wind power, are expected to fulfill the future electricity demand,[1] biomass-derived liquid fuels have arisen as the only sustainable short-term alternative for the transportation sector.[2]

To achieve this goal, the biorefinery concept has been proposed as an integrated industrial complex in which biomass-derived feedstocks are converted into fuels and value-added chemicals.[1] In the petrochemical industry, the addition of oxygen to unfunctionalized feedstocks is typically performed in the gas phase.[3] In contrast, most biorefinery processes involve the removal of oxygen from highly oxygenated raw materials for the production of higher added-value chemicals.[2,4] Economic considerations and thermal limitations of biomass-derived building blocks have resulted in the need for liquid phase processes in future biorefineries. The use of solvents for these reactions is common[5] and may serve different purposes such as enhancing the catalytic activity,[6] switching the selectivity,[7] improving heat and mass transfer, and facilitating product separation.[7]

The US Department of Energy published a list of the “Top 10” building blocks for use in future biorefineries.[8] Levulinic acid (LA) was included in this list according to criteria, such as i) direct substitution of existing petrochemicals, ii) strong potential as a platform chemical, and iii) underway state of the scale-up of the production to pilot, demo, or full scale. 2-Methyltetrahydrofuran (MTHF), which can be derived from LA or its intermediate γ-valerolactone (GVL) (Figure 1), is considered as an ideal biofuel or fuel additive for currently used gasoline formulations and for new oil-free fuel formulations.[9] Interesting features such as hydrophobicity, suitable octane number, and a similar energy density as gasoline make the use of this molecule straightforward in conventional engines without any mechanical modifications.[10–13] The production of MTHF from LA is summarized in Figure 1, along with the main side reactions.

LA can be transformed into GVL by a sequence of dehydrogenation–hydrogenation or vice versa, depending on the reaction conditions.[14] GVL can then be hydrogenated into different molecules such as 1,4-pentanediol (PDO), valeric acid (VA), or 2-butanol (2-BuOH) via 4-hydroxypentanal. Intramolecular etherification of PDO yields MTHF whereas hydrogenolysis of PDO can produce either 1-pentanol (1-PeOH) or 2-pentanol (2-PeOH). The first step of the reaction, LA to GVL, can be achieved under a wide range of conditions. Although the solvent may interfere to a certain extent,[15] it does not seem to play a determining role on this step of the reaction because the reaction proceeds at high yields under hydrogen atmosphere in different media such as water,[16,17] 1,4-dioxane,[15,18] tetrahydrofuran,[19] alcohols,[20,21] or even under solvent-free conditions.[15,22] This reaction is also reported to occur by catalytic transfer hydrogenation (CTH) over metal oxides or supported

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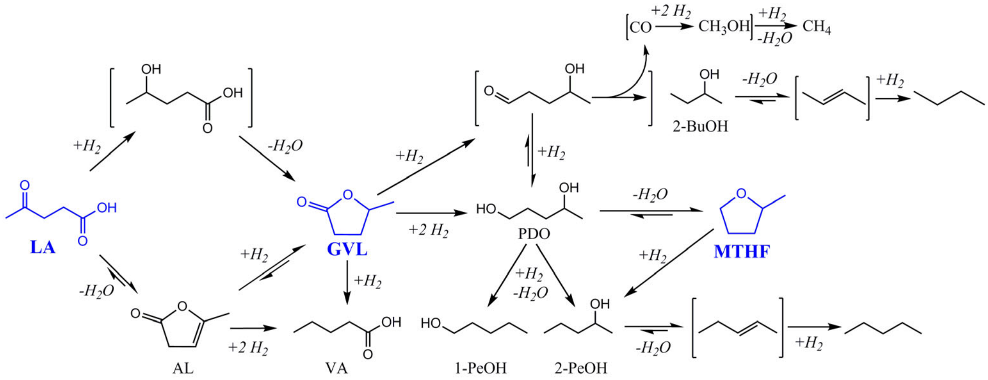

Figure 1. Synthesis of MTHF from LA.[26,28,33]

metal catalysts using alcohols[23] or formic acid[24,25] (FA) as hydrogen donor molecules.

The second step of the reaction, GVL to MTHF, is more challenging owing to the high thermodynamic stability of GVL.[14] Hence, this step requires harsher reaction conditions. Previous investigations have shown the paramount importance of the H_2 pressure on the GVL conversion. Hydrogen pressures below 80 bar (at room temperature, then heated up to 190 °C) were insufficient for the solvent-free hydrogenation of GVL over Ru/C,[26] whereas 50–100 bar of H_2 were required at 150–200 °C to produce MTHF starting from LA using homogenous Ru catalysts with several additives.[27–29] Additionally, in the scarce literature reports of this reaction, the important role of the solvent is evident. The most used solvent for this step is 1,4-dioxane, under 100 bar H_2[30] or in the vapor phase.[31] The transformation of GVL is reported to be strongly inhibited by water,[26,32] and the selectivity towards MTHF appears to be limited by a mechanism that is still unclear. The reports of aqueous phase GVL dehydrogenation into α-angelica lactone[33] and LA[34] suggest that the reversibility of these reactions is a factor in the inhibition by water. The MTHF yield significantly improves if alcohols are used as solvents instead of water.

The results in ethanol were similar to those in water (<1% MTHF yield). However, 10% MTHF yield was obtained in 1-butanol (1-BuOH), and nearly complete GVL conversion and 46% MTHF yield were obtained in 2-propanol (2-PrOH).[33] Conversely, high PDO[35,36] and MTHF[37] yields were reported in aqueous reactions using noble metal based catalysts, emphasizing that further studies are required to fully understand this complex reaction. The production of MTHF utilizing FA as hydrogen source has also been reported. An MTHF yield of 72% was obtained under microwave conditions when LA was fed with a 170% excess of FA in the presence of Pd(5%)/C.[38]

It is evident that the presence of a hydrogen donor in the reaction medium, either an alcohol or FA, enhances the yield of MTHF. To investigate the effects of the two possible hydrogen sources (molecular hydrogen and CTH) on the hydrogenation of LA, this work presents a systematic study of the reaction with a set of three solvents (1,4-dioxane, 1-BuOH, and 2-PrOH) and three catalysts (Ru(5%)/C, Ni(35%)/Al_2O_3, and Ni(23%)–Cu (12%)/Al_2O_3). These catalysts and solvents were selected according to their interest and reported use in the literature; either for hydrogenation using molecular hydrogen or for CTH reactions. 1,4-Dioxane, as an aprotic solvent, shows no ability to serve as a hydrogen donor in the absence of degradation reactions. Nonetheless, the highest reported MTHF yields starting from LA were achieved in this solvent in the gas phase.[31] 1-BuOH is an interesting solvent for this reaction as recent reports have shown a simple and effective method to separate LA from the aqueous phases through the formation of butyl levulinate in the presence of butene or butanol and the use of an acid catalyst to cause spontaneous separation of the aqueous/organic phases.[25,39] These LA esters have shown similar reactivity towards GVL as neat LA.[20,25] 2-PrOH was selected as the third solvent owing to its high capacity for hydrogen donation. 2-PrOH was also reported to enable high MTHF yields using Ni–Cu based catalysts.[33]

The commercial Ru(5%)/C catalyst and our previously reported Ni(23%)–Cu(12%)/Al_2O_3 and Ni(35%)/Al_2O_3 catalysts were selected based on their reported utilization in these reactions and the significant MTHF yields achieved previously.[26,33]

Two different atmospheres were chosen for the experiments, namely, N_2 and H_2. In the activity tests performed under N_2 pressure, the CTH was the principal source of hydrogen for the reaction. In the reactions performed under H_2 pressure, the required hydrogen could come from both molecular hydrogen and CTH.

Results and Discussion

The catalytic activities of the three catalysts in the solvents and reaction atmospheres are summarized in Figure 2. For clarity, the results of the experiments under N_2 will be discussed based on GVL yields, whereas the results under H_2 atmosphere will be discussed based on MTHF yields. The reason for this consideration is that under H_2 atmosphere, the reaction of LA to GVL is very fast and reaches full conversion in all cases, making activity comparisons impossible. Under N_2 atmosphere, as previously discussed, CTH reactions are the principal source of hydrogen for the transformation of LA into GVL. However, this in situ-generated hydrogen alone is insufficient to convert

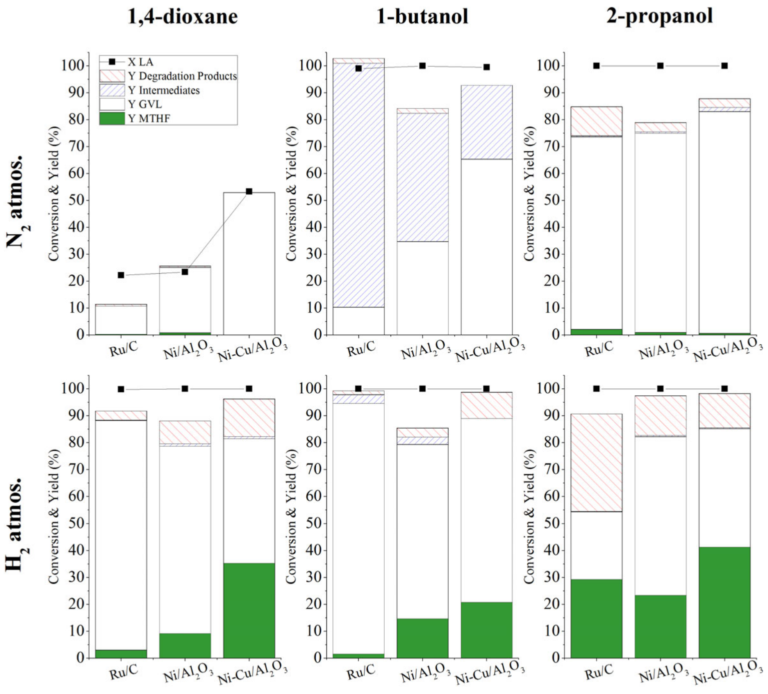

Figure 2. LA conversion and product distribution for different catalysts, solvents, and reaction atmospheres. Reaction conditions: 5 wt% LA in solvent, LA/Cat. 10 g g^{-1}, 250 °C, 40 bar initial pressure and 5 h reaction time. The intermediates considered in this graph are AL, PDO, and LA esters. Quantified degradation products are VA, 2-BuOH, 1-PeOH, and 2-PeOH. Other detected but not quantified degradation products: pentane, butane, methanol, and methane. The corresponding carbon balances are shown in Table S2.

the highly stable GVL into MTHF. These results are discussed in detail in the following sections.

Activity tests under a N_2 atmosphere

Low hydrogen availability provided by a poor hydrogen donor (1,4-dioxane) and a N_2 atmosphere resulted in relatively low LA conversions for the three tested catalysts. The Ru-based catalyst allowed up to 20 % LA conversion with GVL as the main product. Interestingly, significantly higher LA conversions and GVL yields (up to 53 %) were achieved with Ni and Ni–Cu based catalysts. The hydrogen required for the transformation of LA to GVL was most probably provided by solvent degradation. Indeed, 1,4-dioxane derivatives (e.g., ethanol, 2-ethoxyethanol, and ethanol 2-ethoxy methoxy) were detected among the liquid reaction products using GC–MS. Additionally, neat 1,4-dioxane degradation experiments under N_2 atmosphere showed the presence of molecular hydrogen in the gas phase, confirming the production of hydrogen by degradation of the solvent or solvent derivatives. According to these data, it is reasonable to argue that the low catalytic activity of Ru/C under the reaction conditions can be related to its lower activity for 1,4-dioxane degradation and the use of the in situ-generated hydrogen in the conversion of LA to GVL.

A similar GVL yield (up to 10 %) was obtained using Ru/C and 1-BuOH, which is a moderate hydrogen donor molecule,[40] whereas the use of Ni–Cu/Al_2O_3 resulted in a GVL yield of 65 %. In this solvent, full conversion of LA was achieved over the three tested catalysts but with 27–90 % yield of butyl levulinate, a by-product caused by esterification.

The performance of all the three catalysts improved with 2-PrOH as the solvent, which is a well-known hydrogen donor.[40] Complete conversion of LA was achieved and only trace amounts of 2-propyl levulinate were detected in all cases. The most noticeable change was observed for the Ru/C catalyst, which achieved a 71 % yield of GVL. The production of GVL with the non-noble metal catalysts also increased, delivering 74–82 % GVL yields and VA as the main by-product (3 %). The VA yield is expressed as the sum of free VA and VA esters.

Notably, none of the experiments that were performed under N_2 atmosphere produced significant amounts of MTHF (< 2 %). To confirm these results, additional experiments using GVL as substrate were performed in 2-PrOH under N_2 atmosphere with the Ru/C and Ni–Cu/Al_2O_3 catalysts. The results were consistent and showed low MTHF yields. As shown in Table 3, very low (≈ 10 %) GVL conversions were achieved along with low MTHF yields (≈ 2 %) for both catalysts. The main difference was the higher VA yield obtained by using Ni–Cu/Al_2O_3 and the higher 2-BuOH yield achieved by using Ru/C, in good agreement with the well-known decarbonylation activity of Ru catalysts.[26]

The conversion of LA and the GVL yields were higher for each catalyst when a better hydrogen donor solvent was used, and for each solvent when a more CTH-active catalyst was used. These results clearly indicate that under the applied reaction conditions in situ-generated hydrogen alone is insufficient to convert the highly stable GVL into MTHF even if a high excess of active hydrogen donor molecules is used. In contrast with the presented results, significant MTHF yields were reported using FA as a hydrogen donor molecule both under microwave irradiation and fixed bed reactor conditions, however, the catalyst lost its activity after a short reaction time.[38]

Activity tests under a H_2 atmosphere

Full LA conversion was achieved by using Ru/C in 1,4-dioxane, with a GVL yield of 85.3 % and a MTHF yield of 3 %. Similar GVL and MTHF yields were observed using 1-BuOH as solvent. The use of 2-PrOH as solvent triggered the production of MTHF with a yield of 29 %. However, up to 36 % yield of degradation products (mainly 2-BuOH and VA) were obtained using this reaction system, which showed a lack of selectivity towards the desired product. The large differences in the MTHF yield obtained with each solvent under H_2 atmosphere are in good agreement with the results under N_2 atmosphere. In addition, significant concentrations of solvent dehydrogenation products (acetone and butanal) were detected in the experiments under 100 bar H_2 (Table 1). Similar to the experiments under N_2, solvent dehydrogenation produced no measurable increase in the total reaction pressure, thus, keeping the dissolved H_2 concentration constant for each solvent.

Analogous conclusions were drawn from the results using non-noble metal catalysts. Similar to the results under N_2 atmosphere, the general trend was as follows: for each catalyst, the better the hydrogen donating capacity of the solvent, the higher the MTHF yield; and, for each solvent, the higher the CTH activity of the catalyst, the higher the obtained MTHF yield. However, two exceptions were found under H_2 atmosphere. First, a higher MTHF yield was obtained using Ni–Cu/Al_2O_3 in 1,4-dioxane than in 1-BuOH. Second, a higher MTHF yield was observed using Ru/C in comparison to Ni/Al_2O_3 in 2-PrOH as solvent. This different behavior is indicative of more complex interactions and reaction mechanisms in the presence of a high H_2 pressure. Nevertheless, for all the catalysts, the highest MTHF yields were obtained when the best hydrogen donor, 2-PrOH, was used as a solvent.

Table 1. Butanal and acetone concentrations for the different catalysts and reaction atmospheres.

Entry	Product	Atmosphere	Concentration[a] [mg g^{-1}] Ru/C	 Ni/Al_2O_3	 Ni–Cu/Al_2O_3
1	butanal	N_2	15.6	29.5	30.4
2	butanal	H_2	1.7	1.1	1.6
3	acetone	N_2	179.5	135.3	128.1
4	acetone	H_2	34.9	35.0	37.3

[a] Equilibrium concentrations (for pure alcohol dehydrogenation reactions) were calculated using Aspen Plus software (see the Supporting Information for details).

In terms of the carbon balances of these experiments, those under N_2 atmosphere showed a higher deviation (79.6–104.3) than those obtained under a H_2 atmosphere (88.6–99.3), as shown in Table S2 (Supporting Information). This difference can be associated with sufficient availability of hydrogen for the reduction of the secondary reactions.

Hydrogenation mechanism

In view of the important role of the CTH in the reaction under N_2 and H_2 atmospheres, a direct correlation between the amount of dehydrogenation products (acetone or butanal) resulting from the solvent and the yield of the desired product was expected. Although such a trend could not be found in Figure 3 (left) some remarks are worth noting. As expected, acetone and butanal were present at lower concentrations under H_2 atmosphere than under N_2 atmosphere (Table 1). Under H_2 atmosphere, all the catalysts showed very similar concentrations of the dehydrogenated donor near the thermodynamic equilibrium conditions, which indicates that the reaction Solvent$-H_2 \rightleftarrows H_2 +$Solvent reached equilibrium. Conversely, underN_2 atmosphere, different concentrations of dehydrogenation products were measured depending on the catalysts used, which, considering the reaction atmosphere, suggests possible kinetic control in the solvent dehydrogenation reaction. Nevertheless, considerable differences in the product yields can be observed with similar solvent dehydrogenation product concentrations. This implies that it is important for the catalyst to effectively use the in situ produced hydrogen atoms for the hydrogenation reactions, and to reduce their combination and desorption as hydrogen molecules.

A linear trend can be observed between the hydrogenation performance (plotted as MTHF yield) under H_2 atmosphere versus CTH performance of the system (plotted as GVL yield) under N_2 atmosphere, as shown in Figure 3 (right). This correlation suggests that a catalyst that shows a high CTH performance combined with a good hydrogen donor solvent promotes the production of MTHF.

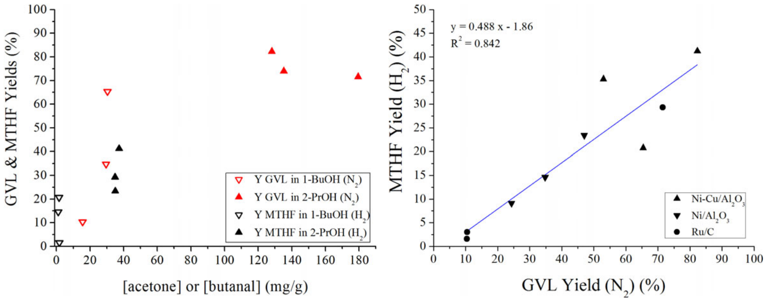

Figure 3. Correlation between the solvent dehydrogenation product concentration (mg g^{-1} of reaction media) and desired product yields (left) and correlation between GVL yields under a N_2 atmosphere and MTHF yields under a H_2 atmosphere (right).

In this study, the maximum MTHF yield was obtained with the combination of Ni–Cu/Al_2O_3 catalyst and 2-PrOH as solvent. Nonetheless, in addition to the mentioned CTH active catalyst/solvent system, a H_2 atmosphere is necessary to convert the stable GVL into MTHF. Based on this evidence, we suggest that both sources of hydrogen, molecular hydrogen and the hydrogen donor, play a significant and synergetic role in the reaction. The dynamic hydrogenation–dehydrogenation chemical equilibrium of the donor increases the amount of adsorbed hydrogen atoms on the catalyst surface. Meanwhile, a high molecular hydrogen pressure increases the H_2 dissolved in the reaction medium, which in turn promotes the adsorption of hydrogen atoms and reduces their desorption rate. This improved hydrogen availability seems necessary for the slow and high-hydrogen-demanding reaction (2 mol H_2 per mol GVL) of GVL to PDO and MTHF (Figure 1). The two possible hydrogen sources are illustrated in Figure 4, which shows the LA to GVL and GVL to MTHF reactions under a N_2 and H_2 atmosphere, respectively.

Characterization of the catalyst was conducted to determine the origin of the observed differences in the performance. Considering that the reaction is composed of hydrogenation and dehydrogenation steps, both hydrogenating and acidic functionalities are expected to play a role. It is well known that the CTH mechanism (the metal-hydride route) requires close proximity of both functionalities.[40] Therefore, the concentrations of the metal and acid sites on the catalyst surface were determined.

It appears likely that a higher concentration of active metal sites in the catalyst could be the reason for the improved catalytic performance of Ni–Cu/Al_2O_3. Therefore, CO chemisorption measurements of the three fresh catalysts were performed (Table 2). Ni/Al_2O_3 contained the largest amount of active metal sites, followed by Ru/C; surprisingly Ni–Cu/Al_2O_3 showed the lowest amount of sites, two times less than Ni/Al_2O_3. These results showed significant activity differences related to the active metal sites of each catalyst. Normalized productivities using 2-PrOH as a solvent under N_2 and H_2 atmospheres were used for comparison purposes. Under a N_2 atmosphere, the Ru metal sites were 1.4 times more active than the Ni sites, whereas the active sites in the Ni–Cu catalyst were 2.6 times more active. These differences increased under a H_2 atmosphere,

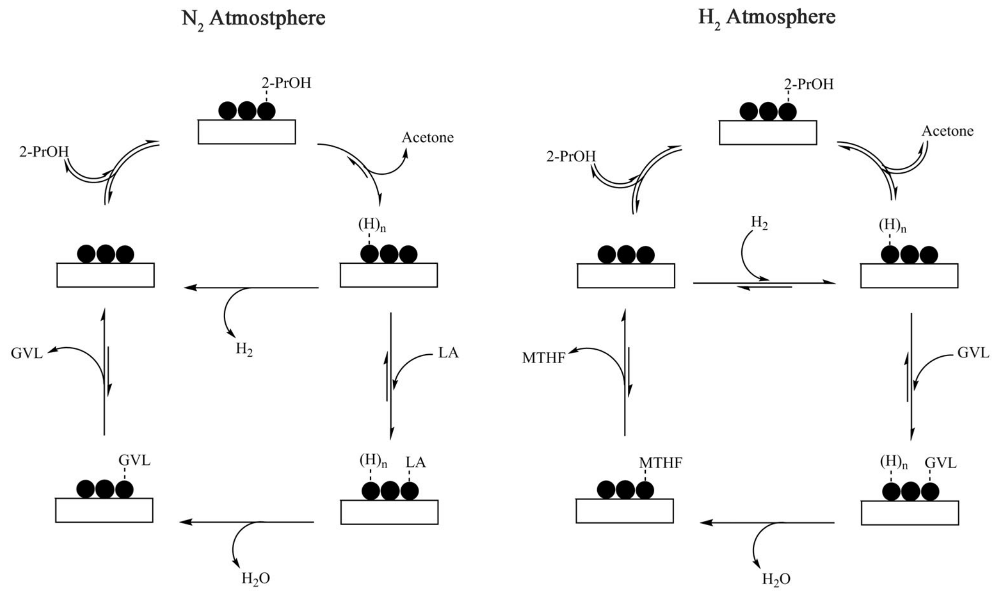

Figure 4. Proposed reaction mechanism of hydrogen adsorption, 2-PrOH dehydrogenation, and LA to GVL reaction under N_2 (left) and GVL to MTHF reaction under H_2 (right) atmosphere.

Table 2. Surface characterization of the fresh catalyst and normalized productivities.

Entry	Catalyst	Amt. CO [$mmol_{CO}\,g_{Cat.}^{-1}$]	Acidity[a] [$mmol_{NH_3}\,g_{Cat.}^{-1}$] Weak	Medium	Strong	Normalized productivity[c] [h^{-1}] GVL (N_2)	MTHF (H_2)
1	Ru/C	0.0614	0.147 (310 °C)	–[b]	–[b]	201	82
2	Ni/Al_2O_3	0.0895	0.380 (325 °C)	0.242 (564 °C)	0.179 (785 °C)	142	45
3	Ni–Cu/Al_2O_3	0.0375	0.297 (364 °C)	0.245 (537 °C)	0.275 (742 °C)	378	189

[a] The strength of the acidity was assessed by peak fitting. The maximum of the peaks is expressed in brackets. [b] Ru/C catalyst is decomposed during the TPD analysis for temperatures above 400 °C, hence, its acidity cannot be determined above this temperature [c] Normalized productivities are calculated by dividing the produced GVL or MTHF mol by the amount of metallic active sites (g Cat. xCO mol g^{-1} Cat.) and reaction time (5 h).

Table 3. PDO, GVL, and MTHF conversion and product distribution for different catalysts and reaction atmospheres.

Entry	Solvent	Gas	Catalyst	Conv. [%]	Yields [%]						CB[a]
				PDO	MTHF	VA	2-BuOH	1-PeOH	2-PeOH	Others	[%]
1	2-PrOH	H_2	-	2.3	1.5	0.0	0.0	traces	0.0	0.0	99.2
2	2-PrOH	H_2	Ni–Cu/Al_2O_3	99.4	99.0	0.0	0.0	0.4	0.0	0.8	100.8
				GVL	MTHF	VA	2-BuOH	1-PeOH	2-PeOH	Others	
3	2-PrOH	N_2	Ru/C	12.6	1.9	3.3	3.0	0.0	0.4	0.7	96.7
4	2-PrOH	N_2	Ni–Cu/Al_2O_3	5.4	2.5	4.6	0.5	0.1	0.0	0.0	102.3
5	2-PrOH	H_2	Ru/C	97.4	14.9	1.8	37.3	0.0	18.9	9.2	84.7
6	2-PrOH	H_2	Ni–Cu/Al_2O_3	44.1	30.3	8.5	2.5	1.1	0.5	0.5	99.3
				MTHF	–	VA	2-BuOH	1-PeOH	2-PeOH	Others	
7	2-PrOH	H_2	Ru/C	98.5	–	0.0	5.4	0.0	51.8	15.8	74.5
8	2-PrOH	H_2	Ni–Cu/Al_2O_3	10.3	–	0.0	1.0	0.1	3.8	0.3	94.9

[a] Carbon balances over 100 % are probably caused by experimental or analytical errors.

whereby the Ru sites were 2 times more active and the Ni–Cu catalyst were 4.2 times more active than the Ni sites.

The superior performance of the active sites on Ni–Cu/Al_2O_3, as compared to Ni/Al_2O_3, is indicative of a significant promotion effect by the addition of Cu, considering that Cu was found to be a less active metal than Ni for this reaction.[33] The lower concentration of metal sites on the surface of Ni–Cu/Al_2O_3 reveals that Cu promotion effect was not caused by metal dispersion enhancement, but rather by a bimetallic effect produced by an especially active Ni–Cu mixed phase. This bimetallic effect has previously been detected in this catalyst, which showed incorporation of Cu in the Ni crystal structure.[33] The presented evidence is consistent with the literature data, which shows improved CTH activity of Ni–Cu bimetallic catalysts compared to Ni or Cu monometallic catalysts.[41,42] Acidity measurements revealed that Ni/Al_2O_3 and Ni–Cu/Al_2O_3 had a similar total acidity ($\approx$0.8 mmol g^{-1}). Conversely, the NH_3 temperature programmed desorption (TPD) profiles showed that Ni had a higher amount of weak acid sites whereas the Ni–Cu catalyst had more strong acid sites (Table 2). The TPD profile of Ru/C was difficult to analyze as further contributions (including decomposition) could not be excluded. The profile showed some weak acidity on this catalyst but, for temperatures above 400 °C, carbon is expected to decompose and, hence, the measurements allowed no direct interpretation. The low acidity of the Ru/C catalysts was emphasized in CTH studies in which partial oxidation of Ru was necessary to provide the required acidity for the reaction mechanism. This catalyst was partially deactivated by in situ reduction,[43] showing both metallic and acid sites to be necessary for CTH reactions.[40] Hence, the better performance of the Ni–Cu/Al_2O_3 catalyst as compared to Ru/C under the applied reaction conditions can be ascribed to a balance amount of adjacent acidic and metal active sites.

Additionally, the reactivity of PDO, GVL, and MTHF in 2-PrOH was analyzed to gain a deeper insight into the reaction mechanism. PDO was found to be stable in the absence of a catalyst. However, when using a catalyst, full conversion to MTHF was achieved in less than 90 min with trace amounts of 2-BuOH, 1-PeOH, 2-PeOH, and GVL. As shown in Table 3, Ru/C showed a high activity with almost full conversion of GVL in 2-PrOH, with MTHF, 2-BuOH, and 2-PeOH as the main products in yields of 15, 37, and 19%, respectively. Similarly, MTHF was fully converted over Ru/C in 2-PrOH with 2-PeOH as the main product and small quantities of 2-BuOH. These experiments (Table 3, Entries 5 and 7) clearly differentiate the origin of the degradation products if Ru/C is used: The high yields of 2-BuOH observed in the LA hydrogenation experiments were mainly produced from the conversion of GVL rather than the degradation of MTHF, as MTHF degradation produced mainly 2-PeOH. Conversely, using Ni–Cu/Al_2O_3 in 2-PrOH, 44 % conversion of GVL was achieved with a MTHF yield of 30 % and VA as the main by-product (8 %). Under the same conditions, in the presence of this catalyst, MTHF conversion only reached 10 % with 2-PeOH as the main product. This catalyst, which showed a significant activity for the challenging GVL conversion, also showed high selectivity towards MTHF. Its low activity for the degradation of MTHF makes it a suitable catalyst for selective production of MTHF. Meanwhile, Ru/C is also a very active catalyst for the conversion of GVL in the presence of 2-PrOH. However, the selectivity towards MTHF is considerably lower owing to the formation of 2-BuOH from GVL and the high activity of this catalyst for the degradation of MTHF (mainly to 2-PeOH).

Taking into consideration the presented activity results and the features of the studied catalysts and solvents, the most active and selective system was chosen for a more in-depth analysis. Ni–Cu/Al_2O_3 was found to produce the highest MTHF yields (35–40 %) after 5 h reaction time in both 2-PrOH and 1,4-dioxane under a H_2 atmosphere. As discussed above, these superior results are derived from a high efficiency of the catalyst for CTH alongside high selectivity for the conversion of GVL to MTHF and a very low activity for the degradation of MTHF. 2-PrOH was selected as a green solvent alternative to 1,4-dioxane,[44] which was not stable under the applied reaction conditions.

The time evolution profile in Figure 5 showed complete conversion of LA in less than one hour in 2-PrOH using Ni–Cu/Al_2O_3 under H_2 atmosphere. The MTHF yield continuously increased from 16 % after the first hour to 80 % after a 20 h reaction time. GVL was the main product after short reaction times

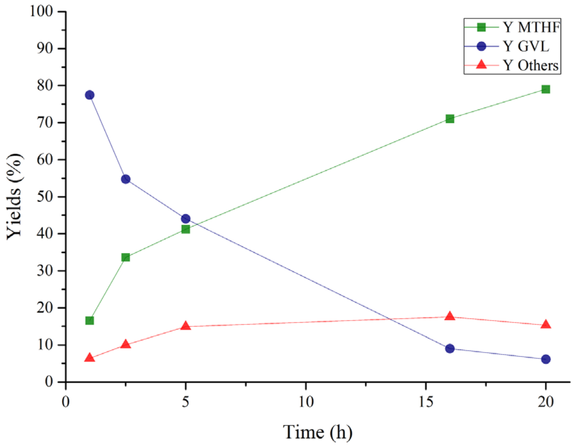

Figure 5. Time evolution profile of the reaction in 2-PrOH with Ni–Cu/Al_2O_3. Reaction conditions: 5 wt% LA in 2-PrOH, LA/Cat. 10 $g\,g^{-1}$, 250 °C, 40 bar H_2 initial pressure. The term "others" includes VA (up to 9.9 % yield), 2-BuOH (up to 2.3 %), and 1-PeOH (up to 2.9 %).

and steadily decreased from 77 % after 1 h to 6 % after 20 h. The main by-product detected was VA, which reached 10 % yield after 20 h. Minor amounts of 2-BuOH and 1-PeOH were also detected, reaching 2 % and 3 %, respectively, at the end of the experiment.

Additional experiments were performed to show the potential applicability of this reaction system. As 2-PrOH readily dehydrogenates and produces acetone as part of the CTH mechanism, the activity of the system may decrease if acetone builds up in the reaction mixture. This was investigated by performing an activity test with 5 wt% LA in a mixture of 2-PrOH and acetone (up to 4:1 weight ratio). The results showed that even at this high initial acetone loading there was no decrease in the activity of the system, which reached complete conversion of LA with MTHF, GVL, and VA yields of 40, 39, and 6 %, respectively, after 5 h of reaction with 91 % carbon balance. Furthermore, the acetone concentration in the reaction mixture decreased from 190 to 55 $mg\,g^{-1}$ at the end of the reaction, only slightly above the concentration in the experiment without acetone addition (37 $mg\,g^{-1}$). This fact, along with comparable LA hydrogenation results, indicates that the 2-PrOH$\rightleftarrows$acetone + H_2 reaction occurs much faster than the conversion of LA to GVL and MTHF. Consequently, the kinetics of the transformation of 2-PrOH do not affect the conversion of LA. This would be an important advantage for a possible scale-up of the process since no ex situ acetone hydrogenation would be required for solvent recycling in the reactor.

The use of more concentrated solutions is of paramount importance for possible industrial application. Hence, an experiment was performed with a 30 wt% LA solution in 2-PrOH, keeping the LA/catalysts weight ratio constant at 10. The results were in good agreement with the results using the 5 wt% feed and showed that full LA conversion was facilitated after 5 h of reaction time with MTHF, GVL, and VA yields of 47, 43, and 6 % at 98 % carbon balance.

Conclusions

The two possible sources of hydrogen (catalytic transfer hydrogenation (CTH) and molecular hydrogen) for the conversion of LA to MTHF were studied using three different catalysts. Although hydrogenation through CTH or molecular H_2 alone was able to produce GVL yields of up to 82–93 %, only trace amounts of MTHF (< 3 %) were detected under these conditions. The combination of both sources of hydrogen was indispensable to achieve significant yields. Furthermore, the linear relationship found between the results under N_2 and H_2 atmospheres indicates the important role of CTH in the hydrogenation of LA to MTHF even under a high H_2 pressure. Hydrogen pressure is considered to contribute to the reaction by increasing the hydrogen dissolved in the reaction medium and, as a consequence, by reducing hydrogen desorption from the catalyst surface. This enhanced hydrogen availability allows an efficient conversion of GVL and results in a high yield of MTHF. Provided that the solvent was a good hydrogen donor, Ru/C also proved to be a very active catalyst for the conversion of LA and GVL. However, its selectivity towards MTHF from GVL is low, and it is further hampered owing to the high activity for the degradation of MTHF. In contrast, Ni–Cu/Al_2O_3 showed the best results, even using a poor hydrogen donor solvent such as 1,4-dioxane. This catalyst was very active for the conversion of the highly stable GVL into MTHF and showed very low activity for further transformations of MTHF, resulting in high MTHF selectivity. Notably, this bimetallic catalyst, which produced the highest MTHF yields, has the lowest active site concentration among the tested catalysts. This confirmed the bimetallic promotion effect of the catalyst, which produced less active sites with much higher activity instead of improving the dispersion of the metal. Overall, the use of Ni–Cu/Al_2O_3 resulted in MTHF yields as high as 80 % using a good hydrogen donor solvent, 2-PrOH, under a H_2 atmosphere after 20 h reaction time.

Experimental Section

A commercial Ru(5 %)/C catalyst was purchased from Sigma–Aldrich and used without further modifications. The catalyst was always preserved under a N_2 atmosphere. Ni(35 %)/Al_2O_3 and Ni(23 %)–Cu(12 %)/Al_2O_3 catalysts were prepared using a simple wet impregnation procedure reported previously.[16] Briefly, the desired amounts of γ-Al_2O_3 (Alfa-Aesar) were mixed with deionized water in a 1:9 weight ratio and the appropriate amounts of metal precursor salts ($Ni(NO_3)_2{\cdot}6\,H_2O$, Sigma–Aldrich and $Cu(NO_3)_2{\cdot}5/2\,H_2O$, Alfa-Aesar) were added and stirred overnight at 90 rpm. Water was removed by heating the solution to 60 °C under vacuum. The catalysts were then dried overnight at 110 °C, crushed, and calcined at 300 °C for 2 h (2 $K\,min^{-1}$ ramp). Prior to the activity tests, the catalysts were reduced at 450 °C (10 $K\,min^{-1}$ heating ramp) for 1 h under H_2 flow and cooled down under Ar flow.

Activity tests were performed in 50 mL Hastelloy autoclaves. The typical reaction mixtures consisted of 5.3 g of a 5 wt% substrate in solvent solution with a substrate/catalyst weight ratio of 10. The autoclaves were fed with the reduced catalysts and the reaction mixture, sealed, flushed three times with the appropriate gas, loaded with 40 bar H_2 or N_2, placed in preheated heating plates, and stirred at 500 rpm for 5 h. The autoclaves were cooled down, and the pressure in the autoclaves was slowly released. The reaction products were analyzed by GC-FID in an Agilent HP6890 series device equipped with a CP-WAX-52-CB column (60 m × 0.25 mm × 0.25 μm), and 1-hexanol was used as external standard.

Reaction conversion (*X*), yields (*Y*), and carbon balance (*CB*) were calculated according to Equations 1–3:

$$X = 100\left(1-\frac{n^{t}_{\mathrm{React}}\times\vartheta^{C}_{\mathrm{React}}}{n^{t=0}_{\mathrm{React}}\times\vartheta^{C}_{\mathrm{React}}}\right) = 100\left(1-\frac{n^{t}_{\mathrm{React}}}{n^{t=0}_{\mathrm{React}}}\right) \tag{1}$$

$$Y_i = 100\frac{n^{t}_{i}\times\vartheta^{C}_{i}}{n^{t=0}_{\mathrm{React}}\times\vartheta^{C}_{\mathrm{React}}} \tag{2}$$

$$\mathrm{CB} = 100\frac{\sum_{\forall i}\left(n^{t}_{i}\times\vartheta^{C}_{i}\right)}{n^{t=0}_{\mathrm{React}}\times\vartheta^{C}_{\mathrm{React}}} = 100 - X + \sum_{\forall i,\ i\neq \mathrm{React}} Y_i \tag{3}$$

where n_i^t is the moles of the product "*i*" at reaction time "*t*", ϑ_i^C is the number of carbon atoms in the product "*i*", "React" stands for reactant and "$t=0$" means at the beginning of the reaction.

CO chemisorption was performed in an AutoChem (Micromeritics) device equipped with a calibrated thermal conductivity detector . The samples were placed in a U-shaped quartz cell, reduced (except for Ru/C which is supplied in a reduced state) with the same temperature program, flushed with He, and cooled down to 35 °C. At this temperature, CO pulses were injected in the sample until saturation was observed.

NH_3 TPD was performed in an AutoChem (Micromeritics) device. The samples were placed in a U-shaped quartz cell, reduced (except for Ru/C, which is supplied in a reduced state) with the temperature program used in the activity tests, saturated with 50 mL min^{-1} using 10 vol% NH_3 in He gas flow for 30 min at 100 °C, and flushed with He at 150 °C for 60 min to remove the physically adsorbed NH_3. The samples were then heated to 450 °C by a 10 K min^{-1} ramp, and the release of NH_3 was monitored using a calibrated TCD detector.

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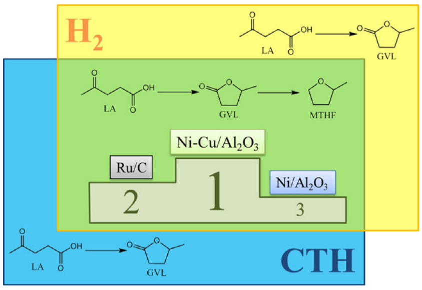

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The Role of the Hydrogen Source on the Selective Production of γ-Valerolactone and 2-Methyltetrahydrofuran from Levulinic Acid