ACS Sustainable Chemistry & Engineering
pubs.acs.org/journal/ascecg
Perspective

Catalytic Biomass Upgrading Exploiting Liquid Organic Hydrogen Carriers (LOHCs)

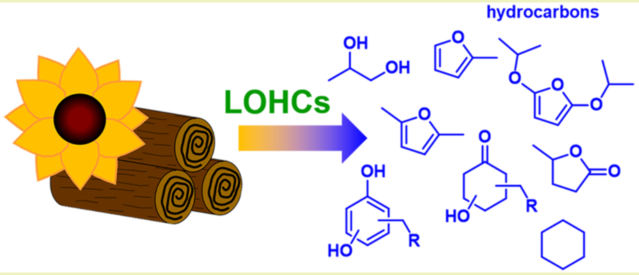
Francesco Ferlin, Federica Valentini, Assunta Marrocchi,* and Luigi Vaccaro*

Cite This: *ACS Sustainable Chem. Eng.* 2021, 9, 9604−9624

Read Online

ACCESS | Metrics & More | Article Recommendations

ABSTRACT: The use of hydrogen at high-pressure is associated with major safety concerns, storage, and high cost. Therefore, the development of reductive chemical processes based on the use of low-pressure hydrogen is very attractive in view of an industrial-scale application. This perspective focuses on the most representative studies reported until 2021 dealing with the reductive manipulation processes of diverse biomass-based feedstock utilizing alternative liquid organic hydrogen carriers (LOHCs). In this context, the research has been dedicated mainly to formic acid and small molecular alcohols, specifically isopropanol. The perspective illustrates the transformations of biobased platform molecules, such as levulinic acid, furfural, and 5-hydroxymethylfurfural, into valuable products, including biofuels. In addition, the lignin upgrading mediated by these H_2 sources is discussed.



KEYWORDS: *Hydrogen production technologies, Liquid organic hydrogen carriers, LOHC, Biomass upgrading, Formic acid, Secondary alcohols, Hydrogen donor*

INTRODUCTION

The urgency of the climate crisis calls for a rapid shift of the existing energy system toward a renewable, climate-neutral one that encompasses economically efficient, socially compatible, environmentally effective global climate protection. Whenever possible, the current infrastructures and technologies should be used, since building/developing entirely new ones is a difficult, time-consuming undertaking.[1]

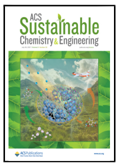
Hydrogen technologies hold the promise of attractive characteristics to face the challenges of a decarbonized energy system. Much of hydrogen is currently obtained through steam-CH_4 reforming and water electrolysis.[1] In steam-CH_4 reforming, high-temperature steam (~700−1000 °C) reacts with methane under a pressure of 3−25 bar in the presence of a catalyst to produce H_2, CO, and a small amount of CO_2. Water electrolysis does not produce any emissions other than H_2 and O_2.

Hydrogen is characterized by a gravimetric energy storage density of 120 MJ kg^{-1} or 33.3 kWh kg^{-1}, which is nearly three times that of gasoline (44 MJ kg^{-1}).[2,3] However, the peculiar physical−chemical nature of H_2 results in a volumetric density under standard temperature and pressure conditions of only 3 Wh L^{-1} or 0.01 MJ L^{-1}.[3] This turns out to be a technical challenge in terms of hydrogen storage. To enhance the volumetric density of hydrogen, well-mature technologies exist,[1] i.e, hydrogen liquefaction, requiring cryogenic temperatures of approximately −253 °C and (near) atmospheric pressure; compressed hydrogen gas involving pressures in the range of 35−70 MPa, which can be reached using advanced pressure tanks made of fiber-reinforced composites; and cryo-compressed hydrogen, which refers to storage at cryogenic temperatures (−253 °C) in tanks that can be pressurized (25−30 MPa). However, these extremes of temperature and/or pressures require costly and technically demanding infrastructures, not yet available in all countries. In addition, they present safety challenges for the material which tanks are made of and in the event of accidental release.

Another less conventional option is to employ hydrogen carrier materials,[4,5] i.e., a technique which immobilizes and stores hydrogen in a solid or liquid state through physisorption and/or[6] chemisorption. Materials-based hydrogen storage technologies are considered safer and more practical compared to the conventional storage approaches due to, for example, low operational barriers, the possibility of an on-demand release, and stable energy states created by hydrogen composites.

For the storage of hydrogen by physisorption, several powerful candidates have been introduced in the past years, exhibiting high porosity combined with very large inner surface areas.[4] The

Received: May 14, 2021
Revised: June 26, 2021
Published: July 14, 2021



https://doi.org/10.1021/acssuschemeng.1c03247

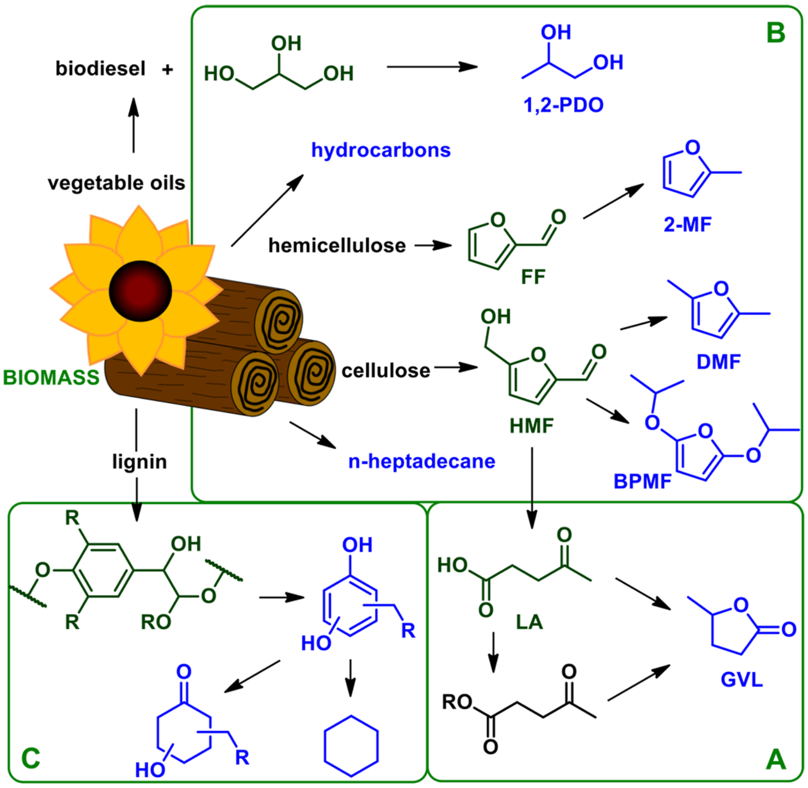


Figure 1. Overview of biomass upgrading processes exploiting LOHCs.

amount of sorbed hydrogen is directly correlated to the surface area of the material, although substantial sorption capacities are possible only at cryogenic temperatures. In fact, because of the weak interaction between nonpolar H_2 and the matrix (less than ~10 kJ/mol), immobilized hydrogen could leak spontaneously at higher temperatures. The most widely investigated systems are nanoporous carbon materials, which can exceed 10 wt % hydrogen storage capacity on a material basis at 77 K and pressures of 60 bar;[7] metal−organic frameworks (MOFs); covalent organic frameworks (COFs); and porous aromatic frameworks (PAFs), exceeding 17 wt % at 77 K and 80 bar.[8]

Chemisorption implies the storage of hydrogen in either a solid or liquid material by chemical bonding or in a complexed form. Chemical carriers offer the option of the highest density of hydrogen storage at low pressures. The hydrogen is released through chemical reactions under specific conditions; however, these processes may have low reversibility and slow reaction kinetics and may require high dehydrogenation temperatures.[9]

Examples of solid chemical hydrogen storage systems are metal hydrides, such as MgH_2, LiH, and AlH_3; complex hydrides (e.g., $NaBH_4$, $NaAlH_4$, Mg_2FeH_6); and chemical hydrides (BH_3NH_3). These families of hydride-based materials often exhibit pyrophoric behavior and may be sensitive to oxygen and water. Moreover, they may suffer from poor reversibility under mild conditions and high thermal stability.

In addition to solid chemical carriers, organic molecules that are liquids at ambient conditions and are able to undergo hydrogen store/release cycles through catalytic hydrogenation/dehydrogenation reactions have been recently receiving increased attention. For these systems, the term "Liquid Organic Hydrogen Carrier" (LOHC) has been coined,[2,10−16] LOHC systems offer the benefits of compatibility with existing transport infrastructures and attractive containment options operating under ambient conditions. In addition, hydrogen handling in the form of liquids reduces the hazard potential and enhances the intrinsic safety.[17]

Several interesting review articles cover different aspects of this topic, including those exploring the economic and energetic feasibility of LOHCs systems.[2,10−21]

Among the many LOHCs proposed as sources of hydrogen, perhydro dibenzyltoluene (H18-DBT) has received particular attention. This compound and the corresponding dehydrogenation product dibenzyltoluene (H0-DBT) are characterized by an excellent theoretical hydrogen storage density of 6.23 wt % (2.05 kW hkg^{-1}),[22] a dehydrogenation enthalpy of 65.4 kJ/molH_2, good cycling stability,[23] favorable safety and toxicological properties, and the ability to be liquid over a broad range of temperatures (−30−360 °C). Although the actual storage capacity of 18H-DBT may be lower than the theoretical one, since incomplete dehydrogenation/hydrogenation steps may occur, depending on process conditions, this LOHC system has been the first to be commercialized.[24]

Other well-studied carbocyclic compounds are cyclohexane (H_2 capacity, 7.2 wt %; enthalpy of dehydrogenation, 68.6 kJ/molH_2), methyl cyclohexane (6.2 wt %; 68.3 kJ/molH_2), decalin (7.3 wt %; 63.9 kJ/molH_2), and bicyclohexyl (7.3 wt %; 62.8 kJ/molH_2). The corresponding dehydrogenation products are, respectively, benzene, toluene, naphthalene, and biphenyl. Note that benzene and toluene are known to pose serious health hazards. Moreover, naphthalene and biphenyl are solid under ambient conditions, which makes it complicated to implement a storage system based on decalin or bicyclohexyl.[10,11]

Among heterocyclic compounds, the most promising LOHC is perhydro-N-ethylcarbazole (12H-NEC). It is characterized by a theoretical hydrogen storage density of 5.8 wt %, which is slightly lower than those achievable for the above carbocyclic systems. This is balanced by a reduced enthalpy of dehydrogenation reaction (62.8 kJ/molH_2), enabling the use of lower temperature conditions. However, it must be considered that the corresponding dehydrogenation product, N-ethyl carbazole, is solid at ambient conditions. Hetero-LOHCs may suffer from side-reactions such as carbon-heteroatom cleavage during hydrogenation/dehydrogenation.[10,11]

Also, other options have been widely investigated as promising LOHC substrates, including alcohols and formic acid.[9,10,25−31] Although a fully closed hydrogenation/dehydrogenation cycle is still difficult to be implemented,[32,33] these systems can be efficiently dehydrogenated to enable hydrogen delivery.

Among the alcohols, a very attractive system for selected applications is represented by isopropanol (IPA). Isopropanol is a secondary alcohol which offers a hydrogen capacity of 3.3 wt %, an energy storage density of 1.11 kWh kg^{-1} (or 0.87 kWh L^{-1}), and a free energy of dehydrogenation (ΔG^0) of -213.2 kJ mol^{-1}. Current isopropanol production is based mainly on three routes, i.e., indirect hydration of propylene, direct hydration of propylene, and hydrogenation of acetone.[34,35] This latter, in particular, is the most recent technology and makes isopropanol a reversible source of hydrogen. Notably, isopropanol can be also produced via vegetal biomass biochemical processing, which makes it a reversible and renewable hydrogen carrier.

Also, formic acid (FA) is gaining ever more attention. It presents a hydrogen capacity as high as 4.4 wt %, an energy storage density of 1.47 kWh kg^{-1}, and a dehydrogenation free energy of -32.9 $kJmol^{-1}$. However, besides dehydrogenation, FA can undergo a competing decomposition via dehydration; therefore, the development of catalytic systems which are selective to the dehydrogenation reaction plays a key role.

The reverse reaction, producing FA through CO_2 hydrogenation, has been widely investigated.[32,33,36−38] Interestingly, Perez-Fortes et al.[36] analyzed FA synthesis employing captured CO_2, under the conditions patented by Schaub et al.,[39] and concluded that a plant is feasible from a technical point of view, although not economically sustainable yet.

Industrially, FA production is based essentially on the carbonylation of methanol and the subsequent hydrolysis of the resulting formate. Beyond this method, FA can be produced, for example, as a byproduct in the manufacturing of chemicals such as acetic acid, formamide, or polyols (pentaerythrol, neopentyl glycol, trimethylolpropane). Notably, it can be prepared via hydrolysis−dehydration of C6 sugars from vegetal biomass.[28]

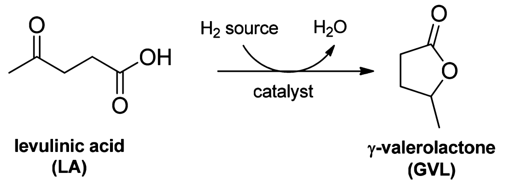
This perspective aims at giving an overview of the representative papers related to the use of LOHCs for biomass upgrading (Figure 1). The topic of biomass upgrading is increasingly taking a hold in the scientific community worldwide as the renewable alternative to fossil raw material to produce a plethora of products. In particular, the chemical processing of biomass is likely to open a wide range of possibilities for fine and bulk chemicals, fuels, pharmaceuticals, and materials. Despite this fact, there are almost no studies exploring the use of carbocyclic or heterocyclic LOHCs as hydrogen sources for biomass upgrading.[40,41] A handful of papers[42−44] report on the use of methanol and ethanol as in situ hydrogen sources, focusing particularly on lignin valorization. On the other hand, IPA and FA as alternative, renewable hydrogen sources for biomass upgrading have been investigated more extensively. Herein, the discussion is restricted to this area. First, an overview on the transformation of levulinic acid (LA) and its esters into high value γ-valerolactone (GVL) is given. LA is one of the “Top 10” biobased chemicals of interest for industrial production, identified by the U.S. Department of Energy,[45] and its significance and potential as a platform chemical is recognized by the International Energy Agency (IEA).[46−48] Note that several contributions have recently appeared in the literature reporting studies on FA-assisted LA conversion into chemicals other than GVL. The reader is referred to the original references for these topics.[49−54] Next, the production of biofuels and biofuel additives from furfural (FF) and 5-hydroxymethylfurfural (HMF) platform chemicals is discussed. The subsequent section gives an overview of possible strategies for the chemical valorization of lignin. Comparative assertions for the most significant catalytic processes using FA or isopropanol as hydrogen donors are provided, for available data.

Some references have been chosen, covering only a part of the many studies carried out during the past decades. A comprehensive overview of all the papers dealing with the conversion of biomass using FA or IPA as in situ hydrogen donors is beyond the scope of this review.

LEVULINIC ACID (AND ITS ESTERS) TO γ-VALEROLACTONE

γ-Valerolactone (GVL) is a five-membered cyclic ester that exists in liquid form at normal conditions and has a high boiling point (208 °C). Also, it is stable, and presents low toxicity ($LD_{50,oral}$ = 8800 mg/kg; $LD_{50,dermal}$ > 5000 mg/kg) and limited flammability risks (vapor pressure = 0.65 kPa; flash point = 96 °C), which make it suitable as a safe alternative solvent. In addition, it is reactive enough to enable the production of a variety of compounds, such as valeric acid, 5-nonanone, and butane, and it is suitable for the production of food additives and perfumes.[55,56] In the past years, there have been significant efforts toward the synthesis of GVL using levulinic acid as substrate. Typically, it is prepared by hydrogenative cyclization[57,58] of LA or its esters (Scheme 1), and the preferred catalytic systems are transition metal catalysts, although more recently some examples of non-noble metal catalysts and noncatalytic protocols have been proposed.[59,60]

Scheme 1. Synthesis of γ-Valerolactone



Formic Acid as Hydrogen Source. The use of FA as a hydrogen donor here is particularly appealing, since LA comes from the production process in an equimolar mixture with FA. Therefore, the direct conversion of the LA−FA mixture into GVL is expected to boost the sustainability credentials of the process both from environmental and economic point of views.

The first report on the selective production of GVL from an equimolar LA−FA mixture was published by Guo et al. in 2009.[61] By using $RuCl_3/PPh_3$ as catalytic systems, in the presence of triethylamine, the authors obtained 90%−95% yields of GVL, and no overreduction byproducts were observed. The base enhances[62] the heterolytic cleavage of H_2. Shortly thereafter,[63] the same authors explored the use of $RuCl_3$ immobilized onto differently functionalized silica, with the aim of efficiently recycling the catalytic system. It was found that FA underwent selective decomposition toward H_2 production, and with high turnover frequencies (TOF, 1428−7357 h^{-1}). Since the hydrogenation of LA by external hydrogen sources showed much lower TOF values, the authors concluded that this was the rate-determining step. The maximum activity (583 h^{-1}) was achieved for Ru-P/SiO_2, which enabled a 96% yield of GVL. Interestingly, a ruthenium leaching as low as 1.4% was detected after reaction completion. However, after three cycles, the yield of GVL dropped, which was attributed to the partial reduction of the Ru(II) to Ru(0) species (XPS analyses). Note that the LA hydrogenation yield was lowered. In the same study, a two-step protocol was also developed, which envisaged first the FA decomposition over Ru-P/SiO_2, the subsequent separation of the catalyst from the reaction mixture, and the selective hydrogenation of LA to GVL over Ru/TiO_2. The overall yield of the process was 88%, and a successful recycling was possible over eight runs.

Darkwa et al.[64] also gained evidence of a higher rate of FA decomposition relative to LA hydrogenation, through the detection of H_2 at a pressure of ∼15 bar generated in the reactor. The solvent-free process was carried out in the presence of pyrazolylphosphinite and pyrazolyl phosphite Ru(II) precatalysts. The authors afforded GVL yields in the range of 50%−96%, with 76%−100% selectivity. The byproduct was 4-hydroxyvaleric acid, derived from the partial hydrogenation of LA.

A representative study has been carried out by Horváth et al.,[65] who demonstrated a selective LA to GVL hydrogenation process using FA only as the hydrogen source, in the presence of a Shvo catalyst,[66] an organoruthenium compound, at 100 °C. A slight excess of FA was used, and the reaction was run quantitatively (>99%). Interestingly, the homogeneous catalyst could be recovered and reused for three subsequent cycles, with a loss of efficiency of ∼2%.

Starting from the observation that the FA:LA mixture is typically produced through hydrolysis−dehydration of glucose or fructose in an aqueous environment, using sulfuric acid as the catalyst, Dumesic et al.[67] disclosed a bimetallic catalyst, i.e. 15 wt % RuRe (3:4) on carbon, showing a stable activity when in the presence of H_2SO_4. More specifically, the RuRe/C catalyst, combining Ru, a typical hydrogenation metal, and Re, a more oxophilic one, proved to be more stable by a factor of 2 under these conditions compared to Ru/C. The proposed system enabled the totally selective conversion of LA to GVL in the presence of sulfuric acid, under flow conditions; the direct conversion of polysaccharides into GVL over the RuRe/C catalyst in flow was also demonstrated.

On the other hand, Heeres et al.[68] demonstrated that by replacing H_2SO_4 with trifluoroacetic acid, the Ru/C catalyst enabled the one-pot processing of C6 sugars, in the presence of sole FA as the hydrogen source, giving a maximum GVL yield of 52%. The byproducts were mainly humins, from the acid-catalyzed C6 to the LA conversion step.

Feng et al.[69] recently used Ru/C (5 wt %) in the presence of triethylamine, based on the observation that a base may enhance the heterolytic cleavage of H_2 (vide supra). Using a 1:3 synthetic mixture of LA−FA, the authors obtained GVL yields up to 81%.

Interestingly, Gao et al.[70] and Ebitani et al.[71] focused on the stability of the support used to anchor a metal catalyst promoting the development of H_2 from FA in water for LA to GVL conversion. Gao et al.[70] compared the activity of different metal catalysts (i.e., Ru, Cu, Ni, Ag) supported on a range of inorganic supports (i.e., ZrO_2, TiO_2, Al_2O_3). It was found that the metals anchored on TiO_2 exhibited a lower efficiency, whereas the Al_2O_3 support tends to dissolve markedly under acidic conditions. The optimal LA conversion was obtained over Ru/ZrO_2 (73%), although it was not possible to recycle the catalytic system. In fact, after one run only, the LA conversion decreased ∼20%, which was attributed to a change in the morphology of ZrO_2 during the ongoing reaction. Doping of the support with 0.1 wt % of SiO_2 enabled the recycling for four runs. In addition, total selectivity toward GVL was achieved.

Ebitani et al.[71] identified Ru and Au as the metals with optimal performance and Au/ZrO_2 as the system showing the highest activity and selectivity in FA-assisted hydrogenation of LA to GVL. Carrying out the reaction in water at 150 °C, GVL was obtained in 77% yield (1:1 FA−LA) or 97% (2:1 FA−LA). In addition, the catalyst was recyclable for at least five times.

The acid tolerability of Au/ZrO_2 was thoroughly investigated by Cao et al.,[72] who demonstrated that at pH ≈ 2 this system enabled the quantitative conversion of a FA−LA equimolar mixture to GVL with 99% selectivity. They also proved that partially neutralized FA−LA mixtures coming from the acid hydrolysis of a range of carbohydrates could be converted into GVL selectively (95%−98%) and in a 33%−60% overall yield using FA as the sole H_2 source. The authors extended the study[73] and developed a protocol for LA−FA reactive extraction using butanol, which allowed one to avoid partial neutralization steps, since the esterification of LA−FA mixtures in acidic water causes the separation of an organic layer comprising butyl levulinate (BL) and butyl formate (BF). A BL−BF mixture could be converted over Au/ZrO_2 to give GVL in 94% yield. Recycling was successful for at least three runs.

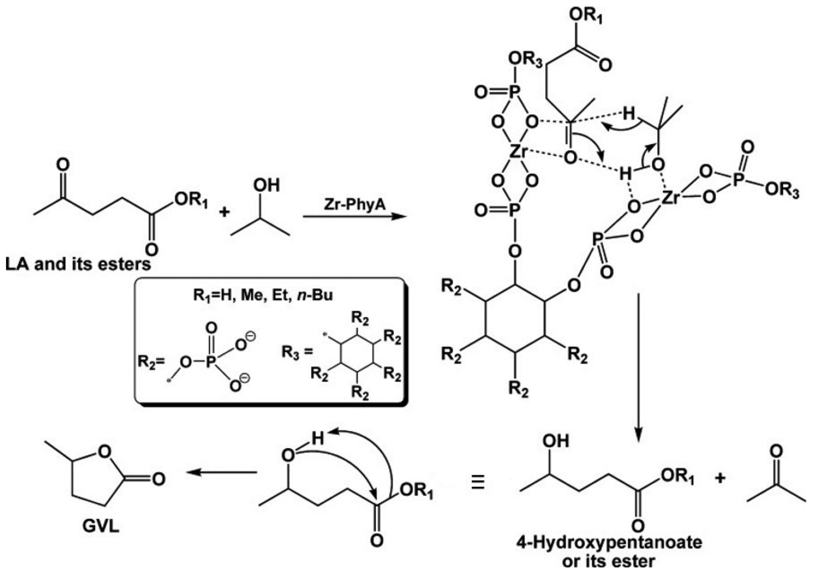
One example of palladium-based catalysts for FA-assisted hydrogenation of LA has been reported by Mondal et al.[74] Specifically, the authors realized a core−shell system (m-SiO_2@Pd@SiO_2) comprising Pd nanoparticles sandwiched between a mesoporous silica shell (m-SiO2) and a nonporous SiO_2 core. The catalyst proved to be very selective and recyclable for 10 cycles, but high yields of GVL were possible only at a FA:LA ratio of 25, which is very far from the ratio of the mixture stream from carbohydrate hydrolysis. Ortiz-Cervantes et al.[75] also experienced issues when dealing with Pd-based catalysts. Although they achieved high GVL conversions (up to 100%) over palladium complexes, for example, [(dtbpe)$PdCl_2$], the formation of a catalytically inactive species, coming from FA concurrent decomposition into CO, was detected, which limited the efficiency of the process.

The catalytic activity of half sandwich iridium complexes was also investigated,[76] although excess FA greater than 1.5 or an additional external H_2 feed was needed.

Lomate et al. explored the effect of different supports (e.g., SiO_2, Al_2O_3, SiO_2−Al_2O_3, TiO_2) on the activity of Cu-based catalysts in the vapor-phase catalytic transfer hydrogenation of aqueous LA−FA mixtures.[77,78] Among these, the optimal activity was shown by the Cu−SiO_2 system, which gave a conversion value of 56% (subsequently improved to 66%) and selectivity of 87%, using excess FA (3 equiv). Interestingly, α-angelica lactone (AL) was detected as the intermediate; the authors hypothesized that the formation of the AL is promoted by the acidic sites of the catalyst support, which helps the cleavage of C−O bonds in LA enol form through dehydration. Next, AL is converted into GVL by Cu-promoted hydrogenation.

Cao et al.[79] also reported on the use Cu-based heterogeneous catalysts, demonstrating a high activity and selectivity for a 20 wt

Scheme 2. Mechanism for the Zr-PhyA-Catalyzed MPV Reaction of LA (and Its Esters) to GVL Proposed by Han et al.[91,a]



[a]Adapted with permission from ref 91. Copyright 2015, John Wiley and Sons.

% Cu/ZrO_2 system in the hydrogenation of an equimolar mixture of FA−LA at 180 °C. GVL, in fact, was obtained quantitatively, and the catalyst could be successfully recycled for subsequent cycles.

Metzker and Burtoloso[80] reported the first example of Fe-catalyzed hydrogenation of a LA-FA aqueous mixture. Note that Fe is particularly interesting to use, since it is a widely available transition metal, and features no toxicity and low costs.[81] The authors specifically investigated the activity of cheap Fe(0) carbonyl complexes, using an imidazole base, and afforded an optimal GVL yield of 92% at 180 °C. They also explored[80] the direct conversion of a liquor derived from sugar cane bagasse hydrolysis under the above conditions and obtained a 50% yield of GVL.

Several bimetallic systems have been also developed to produce GVL through FA-assisted hydrogenation of LA. For example, Rode et al.[82] developed the Ag-Ni/ZrO_2 catalyst and demonstrated its high activity in water at 200 °C. A quantitative yield of GVL was achieved, while monometallic Ag/ZrO_2 and Ni/ZrO_2 gave modest results. Recycling of the catalyst was successful for five cycles. Another example has been reported by Chang et al.,[83] who developed an efficient and stable Ni-promoted Cu/SiO_2 nanocomposite (Ni/Cu 20:60). This system enabled the vapor phase hydrogenation of a FA−LA mixture in continuous flow to produce GVL with conversion and selectivity up to 98% and 92%, respectively. However, the use of 1,4-dioxane solvent was needed. Moreover, Ruppert and co-workers[84,85] developed a set of γ-Al_2O_3 supported bimetallic catalysts and achieved LA conversions up to 89% and selectivities toward GVL up to 89% when using Au−Ni nanoparticles anchored to γ-Al_2O_3. In addition, it was demonstrated that the catalyst activity was far superior than those of the monometallic Au/γ-Al_2O_3 and Ni/γ-Al_2O_3, for which only negligible conversions were obtained; Density functional theory (DFT) calculations supported the evidence of the synergistic action of the two metals by demonstrating the ability of the nanoparticles, featuring isolated Ni atoms within the Au crystal, to decrease the activation energy for the selective FA decomposition into H_2 and, hence, to promote the LA hydrogenation reaction.

Mg−Al hydrotalcite-like catalytic systems with different Mg/Al ratios were investigated under flow conditions by Hussein et al.[86] The authors obtained the optimal results when the reaction was performed over a 3:1 Mg/Al system and employing a 1:5 LA−FA mixture, at very high temperatures (270 °C). A quantitative LA conversion to GVL was possible, with a 98% selectivity. The catalyst system proved to be stable for up to four cycles, with regeneration by flow air in between.

Isopropanol as Hydrogen Source. Since the use of FA may present disadvantages, such as the need for precious metals and/or harsh reaction conditions for both the generation of H_2 from FA and the subsequent hydrogenation of LA to GVL, the catalytic transfer hydrogenation through the Meerwein−Ponndorf−Verley (MPV) reduction, using secondary alcohols (e.g., isopropanol, IPA) as the hydrogen donors, is gaining increasing attention.[87] This reaction pathway begins with the hydrogenation of LA (and its esters), followed by lactonization to afford GVL.

Fu et al.[88] realized the conversion of ethyl levulinate to GVL over an activated homogeneous iron-based Casey's catalyst, using isopropanol as the hydrogen source (100 °C). A 42% GVL yield was obtained, which could be improved up to 95% when a $NaHCO_3$ base was added (5 mol %). Interestingly, under the same conditions, the use of FA gave a 12% GVL yield, whereas supplying hydrogen from an external source (10 bar) led to a 33% yield.

A catalytic transfer hydrogenation (CTH) transfer process for the production of GVL over a Raney Ni catalyst (5 wt %) using ethyl levulinate as the substrate has been reported by Fu et al.[89] The reaction was performed at room temperature, yielding greater than 99% GVL. Note that an Ar atmosphere was required. Recycling of the catalytic system was successful for five cycles.

Chia and Dumesic[90] screened different metal oxides and found that ZrO_2 could efficiently catalyze the conversion of LA butyl ester in a continuous flow reactor (180 °C), affording GVL yields up to 81%. The only byproduct detected was isopropyl levulinate, formed through the transesterification of butyl levulinate with IPA.

Table 1. Representative Syntheses of GVL Using FA as the H_2 Source

Substrate	Catalyst	Conditions	GVL yield (%)	ref
LA	$RuCl_3/PPh_3$ (used for 3 runs)	FA/LA = 1:1 Medium/Additive: H_2O-Et_3N *T* = 150 °C	90	61
LA	Ru/SiO_2-Ru/TiO_2 (used for 8 runs)	FA/LA = 1:1 Medium/Additive: H_2O *T* = 170°	88	63
LA	Ru complex (used for 4 runs)	FA/LA = 1:1 Medium/Additive: – *T* = 120 °C	96	64
LA	Shvo (Ru) (used for 4 runs)	FA/LA = 1.5:1 Medium/Additive: – *T* = 100 °C	>99	65
LA	RuRe/C (flow reactor)	FA/LA = 1:1 Medium/Additive: water-H_2SO_4	99	67
C_6-sugars	Ru/C	FA/LA n.a. Medium/Additive: H_2O-TFA	52	68
LA	Ru/C	FA/LA = 3:1 Medium/Additive: Et_3N	~81	69
LA	Ru/SiO_2-ZrO_2 (used for 4 runs)	FA/LA = 1:1 Medium/Additive: H_2O	~71	70
LA	Au/ZrO_2 (used for 6 runs)	FA/LA = 1:1 Medium/Additive: H_2O *T* = 150 °C	77	71
LA	Au/ZrO_2 (used for 5 runs)	FA/LA = 1:1 Medium/Additive: H_2O	99	72
Butyl levulinate	Au/ZrO_2 (used for 3 runs)	FA/LA = 1:1 Medium/Additive: H_2O-BuOH *T* = 170 °C	94	73
LA	m-SiO_2@Pd@SiO_2 (used for 14 runs)	FA/LA = 25:1 Medium/Additive: –	95	74
LA	Cu/SiO_2 (fixed-bed flow reactor)	FA/LA= 3:1 Medium/Additive: H_2O	54	77, 78
LA	Cu/ZrO_2 (used for 4 runs)	FA/LA= 1:1 Medium/Additive: H_2O *T* = 180 °C	>99	79
LA	$[Fe_3(CO)_{12}]$	FA/LA= 4:1 Medium/Additive: H_2O *T* = 180 °C	92	80
Sugar cane bagasse	$[Fe_3(CO)_{12}]$	FA/LA n.a. Medium/Additive: H_2O *T* = 180 °C	50	80
LA	Ag-Ni/ZrO_2 (used for 5 runs)	FA/LA = 1:1 Medium/Additive: H_2O *T* = 200 °C	99	82

Table 1. continued

Substrate	Catalyst	Conditions	GVL yield (%)	ref
LA	Ni-Cu/ZrO_2 (fixed-bed flow reactor)	FA/LA = 2:1 Medium/Additive: 1,4-dioxane	98	83
LA	Ni-Au/γAl_2O_3 (used for 4 runs)	FA/LA= 1.2:1 Medium/Additive: H_2O	89	84, 85
LA	Mg-Al hydrotalcite (fixed-bed flow reactor)	FA/LA= 5:1 Medium/Additive: − T = 270 °C	98	86

Table 2. Representative Syntheses of GVL Using IPA as the Hydrogen Source

Substrate	Catalyst	Conditions	GVL yield (%)	ref
Ethyl levulinate	Casey (Fe)	Medium/Additive: IPA-$NaHCO_3$ T = 100 °C t = 19 h	95	88
Ethyl levulinate	Raney Ni(used for 5 runs)	Medium/Additive: IPA T = RT (Ar) t = 9 h	>99	89
Butyl levulinate	ZrO_2 (flow reactor)	Medium/Additive: IPA T = 180 °C t = 4 h	81	90
Ethyl levulinate	Zr-PhyA (used for 5 runs)	Medium/Additive: IPA T = 130 °C t = 8 h	95	91
LA	Zr-PhyA	Medium/Additive: IPA T = 130 °C t = 2 h	99	91
Ethyl levulinate	Zr-HA	Medium/Additive: IPA T = 150 °C t = 11 h	85	92
Ethyl levulinate	Zr-LS	Medium/Additive: IPA T = 150 °C t = 8 h	91	93
Ethyl levulinate	Zr-tannin	Medium/Additive: IPA T = 150 °C t = 14 h	93	94
Ethyl levulinate	$ZrO(OH)_2 \cdot xH_2O$ (used for 10 runs)	Medium/Additive: IPA T = 200 °C (N_2) t = 1 h	94	95
LA	Hf-ATMP (used for 5 runs)	Medium/Additive: IPA T = 150 °C t = 7 h	98	105

Most recently, Zr-based metal−organic hybrid catalysts using low-rank natural resources as building blocks have been developed.

For example, Han et al.[91] developed a mesoporous organic−inorganic hybrid catalyst, i.e., Zr-PhyA, by using zirconium phosphonate and phytic acid as building blocks. Zr-PhyA enabled the mild (130 °C, 8h) and selective (97%) MPV reduction of ethyl levulinate into GVL (95% yield). For longer reaction times (24 h), the GVL yield still stands high (75%) by decreasing temperature (100 °C). Note that excellent GVL yields and selectivities were obtained for methyl levulinate (96%) and butyl levulinate (73% and 87%, respectively). The authors also demonstrated that both the Zr (Lewis acidic) and phosphate groups (Lewis basic) contribute significantly to the excellent performance of Zr-PhyA. In addition, LA was quantitatively converted to GVL with 99% yield (99%

selectivity) within 2 h (130 °C). This was ascribed to the inherent acidity of LA which could have improved the lactonization of the 4-hydroxypentanoate intermediate increasing the reaction rate.

The authors also proposed a possible reaction mechanism (Scheme 2), in which isopropanol is first adsorbed on the catalyst. The interaction of IPA with acidic−basic sites results in its dissociation to the corresponding alkoxide and hydrogen. In addition, the carbonyl group in LA (or its esters) is adsorbed on the adjacent catalyst sites (Zr^{4+}). Next, hydrogen transfer occurs between the dissociated IPA and the activated EL via a six-centered intermediate to form 4-hydroxypentanoate and acetone. Finally, GVL is obtained from 4-hydroxypentanoate through intramolecular esterification or transesterification.

Liu et al.[92] subsequently introduced the family of Zr-HAs catalysts, based on low-rank lignite-derived humic acids (HAs). These systems show both acidic (Zr^{4+}) and basic sites (carboxylate and phenate groups), which have been demonstrated[91] essential for the MPV reaction. The MPV reaction of ethyl levulinate (EL) over the Zr-HAs catalyst, carried out at 150 °C (15h), gave an 85% GVL yield. The relatively large structure of EL may create steric hindrance, which may at least in part explain the long reaction times.

Zhou et al.[93] prepared a Zr-lignosulfonate polyphenolic polymer catalyst (Zr-LS) by using paper industry waste lignosulfonate as the building block. Once more, the cooperative role of the acidic−basic sites, $Zr^{4+}-O^{2-}$, revealed to be essential. Ethyl levulinate (EL) was efficiently converted into γ-valerolactone (90%) with a high selectivity of 91% at 150 °C within 8 h. Finally, most recently, Leng et al.[94] used tannins as building blocks to design a heterogeneous zirconium−tannin hybrid catalyst (Zr-tannin). This system enables the selective (96%) MPV reaction of EL to GVL, at 150 °C (14 h), with a conversion value of 93%.

Tang et al. demonstrated the efficiency of the cost-effective $ZrO(OH)_2{\cdot}xH_2O$ catalyst.[95] In fact, EL conversion of 94% and GVL selectivity of 95% were afforded when 2-propanol was used as the sole hydrogen source at 200 °C (1 h). Other examples of Zr-based catalysts which enabled high LA (and/or its esters) conversion values and selectivities toward GVL are Zr-HBA,[96] Zr-β,[97] ZrO2/SBA-15,[98] Ti/Zr,[99] Zr-DTMP,[100] Zr-KIT-5,[101] UiO-66(Zr), MOF-808,[102] Zr-CA (CA = cyanuric acid),[103] and chitosan-Zr.[104]

More recently, Han et al.[105] developed a new porous heterogeneous organic−inorganic hybrid Hf-based catalytic system (Hf-ATMP; ATMP = amino tri(methylene phosphonic acid)) for the IPA-assisted CTH reaction of LA and its esters (methyl, ethyl, butyl) to GVL (150 °C, 7 h). Yields in the range of 80%−98% and 91%−98% selectivities were obtained, with LA giving the best results (98%). Another example of a Hf-based catalyst is FDCA-Hf (FDCA = 2,5-furandicarboxylic acid).[106] Note that the low abundance of hafnium, along with its difficult separation from zirconium minerals, in which it is found in nature, hampers the application of this protocol, particularly on a large scale.

To sum up, some major points can be given on the transformation of LA and its esters into high value γ-valerolactone (GVL) by LOHCs. For example, higher performances can be achieved using noble metal-based catalysts; however, among the possible directions, attention should be payed toward the further development of cost-effective non-noble metal catalysts (e.g., iron-based systems), which have already proven to be promising. Moreover, it has been demonstrated that reduced metal particle size and nonmetallic doping can contribute positively to the efficiency of the catalytic systems. In addition, bimetallic catalysts (e.g., those comprising precious−nonprecious metals) hold the promise of good efficiency and, eventually, present synergistic effects, although they have not been widely explored yet. Acid-tolerable catalytic systems are particularly worth investigating to further enable sequential reactions in a one-pot fashion, which implies more sustainable waste-minimized processes. Finally, for metal-supported heterogeneous systems, the nature of the support can significantly affect their efficiencies; for example, the presence of acidic sites can affect the product distribution. Therefore, the design of new supports should also be pursued.

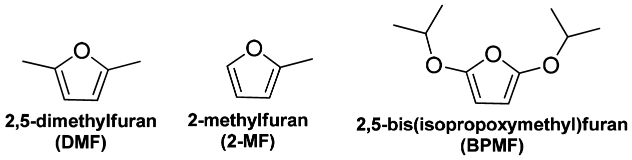
Tables 1 and 2 compare representative syntheses of GVL from LA and its esters using FA and IPA as the hydrogen source, respectively.

BIOFUEL AND BIOFUEL ADDITIVES PRODUCTION

Among the biobased platform chemicals, furfural and 5-hydroxymethylfurfural are attractive for different transformations and can be prepared from pentose (i.e., xylose) and hexose (i.e., glucose or fructose) sugars, respectively. The main difference of these systems relies on their stability and costs. Indeed, although glucose is the most attractive feedstock to access HMF, owing to its abundance and cheap market price compared to fructose, it shows a lower reactivity because of its pyranose ring; in addition, byproducts are typically formed during the conversion process. All this leads to a very high market price for 5-hydroxymethylfurfural. On the other hand, pentose sugars such as D-xylose are easily converted into furfural through dehydration, which ultimately makes furfural cheaper than HMF. In this section, the production of 2,5-dimethylfuran, 2-methylfuran, and 2,5-bis(isopropoxymethyl)furan from furfural and 5-hydroxymethylfurfural is discussed. A brief overview about the synthesis of fuels/additives from oleaginous biomass are also given.

2,5-Dimethyl Furan. 2,5-Dimethylfuran (2,5-DMF) (Chart 1) has become attractive as a biofuel candidate because of its physicochemical properties which are very close to that of conventional fuels.[107] For example, it shows an octane number (119) higher than those of gasoline and ethanol, low water solubility (0.26%), and high boiling point (92−94 °C). The preferred pathway for the synthesis of 2,5-DMF starts at 5-hydroxymethylfurfural (5-HMF), which, analogously to LA, is identified as a biomass-based platform molecule.[45] 5-HMF can be synthesized from fructose, glucose, or polysaccharides through dehydration; the conversion of HMF to DMF proceeds through hydrogenation followed by the hydrogenolysis of the hydroxyl groups of the 2,5-hydroxymethyl furan intermediate.[107]

Chart 1. Chemical Structures of DMF, 2-MF, and BPMF Biofuels



Saha et al.[108] explored the formation of 2,5-dimethylfuran (DMF) from different sources, i.e., fructose, α-cellulose, sugar cane bagasse, and agar, using FA as the hydrogen source. More specifically, the reaction involved two steps: (i) the formation of

5-HMF by dehydration at 150 °C of the feedstock, catalyzed by FA (fructose) or $[DMA]^+[CH_3SO_3]^-$ (other sources) and (ii) the FA-assisted conversion of HMF to DMF into DMF over the Ru/C catalyst. A catalytic amounts of H_2SO_4 and THF as solvent were added in the second step, which, combined with microwave irradiation, enabled DMF yields in the range of 16%−32%. The optimum results were obtained starting from fructose as the biomass source.

Two significant examples demonstrating the efficiency of a Pd/C catalyst have been reported by Rauchfuss and coworkers[109,110] When using 5 mol % Pd/C,[109] an excess of FA (10 equiv), and dioxane as solvent, an HMF conversion value of 95% was achieved (120 °C). Interestingly, no DMF formation was detected when using an external source of H_2, under the same conditions, and the hydrogenation of the furan ring was the preferred reaction pathway. In another contribution,[110] the same authors demonstrated the one-pot DMF synthesis from fructose in the presence of FA. More specifically, a mixture containing mostly HMF and its formate ester, both precursors of DMF, were first afforded from fructose and FA only; next, upon addition of a Pd/C slurry (THF), the mixture underwent hydrogenation and hydrogenolysis to obtain DMF in 51% isolated yield.

Wang et al.[111] realized the HMF conversion to DMF over a 2% nickel−20%cobalt catalyst supported on carbon, using FA, IP,A and molecular H_2 as hydrogen sources (190−230 °C). The optimal results (90% DMF yield) were obtained in the presence of FA, at 190 °C. However, a large excess of FA was required (20 equiv). The use of both IPA and molecular H_2 provided a lower yield (70% and 61%, respectively), and higher temperatures (230 and 210 °C, respectively). Recycling of the catalyst was successful for four runs.

2-Methyl Furan. 2-Methyl furan (2-MF, Chart 1) represents another promising alternative fuel candidate. In fact, it exhibits a high octane number (100.7), water solubility of 3 mg/mL, and boiling point of 63−64 °C.[107] The preferred option for the synthesis of 2-MF starts from the furfural (FF) platform molecule.[45] Furfural can be obtained from xylose through dehydration. The conversion of FF to 2-MF proceeds via hydrogenation followed by the hydrogenolysis of the hydroxyl groups of the furfuryl alcohol intermediate.

Fu et al.[112] recently demonstrated that FF underwent a 91% conversion toward 2-MF over a 10%Ni−10%Cu/C bimetallic catalyst at 200 °C (8 h), by exploiting a synergistic effect of FA and IPA. IPA functioned both as the reaction medium and promoter of the hydrogenation of the aldehyde functional group of FF to afford furfuryl alcohol intermediate. FA played the role to increase the rate of hydrogenolysis of this latter into 2-MF. Under similar conditions, the same group[113] realized a nearly quantitative conversion of FF into 2-MF, employing the a 10% Ni−10%Cu/Al_2O_3 catalytic system.

Very recently, Chilukuri et al.[114] extensively investigated the catalytic transfer hydrogenation of FF to 2-MF by using IPA as hydrogen sources. Several metal catalysts (i.e., Ru, Pd, Au, Pt, Ni, Rh, and Cu) supported on N-doped mesoporous carbons (NMC) were examined. The optimal results were obtained using a 2 wt % Ru-NMC-3 catalyst (with 11.4 wt % N content), which provided an 87% mol yield of 2-MF (140°, 10 h). The correlation between N content, Ru nanoparticle size, and turnover frequency (TOF) of the catalyst was identified and analyzed. The authors concluded that the high N content in the mesoporous framework helps stabilizing the Ru nanoparticles on the support and, consequently, improves the metal−support interaction. On the other hand, increasing the N content favors the formation of small-sized nanoparticles, while improving the CTH activity (higher catalyst basicity). Recycling was successful for four runs. Interestingly, under similar conditions, the CTH of 5-HMF gave an 84% mol yield of DMF.

2,5-Bis(alkoxymethyl)furan. Very recently, Tang et al.[115] realized the synthesis of 2,5-bis(alkoxymethyl)furan (BAMFs, Chart 1) using isopropanol as solvent−hydrogen sources. HMF-derived ethers are attracting ever more attention as biofuel or biofuel additives, since they possess high energy density and favorable blending characteristics in conventional diesel.[116] Since the transformation involves two steps, i.e., hydrogenation (typically promoted by Lewis acids) and etherification (activated by Bronsted acids), Zr-SBA catalysts possessing Lewis−Bronsted acidic sites (L−B) were investigated. A BPMF yield of 94% (150 °C, 4 h) with 95% selectivity was obtained employing the Zr-SBA-UH catalyst (L = 179.7 μmol/g; B = 26.8 μmol/g). Recycling of the catalyst was successful for five runs.

Other contributions in the same direction have appeared in the literature from Jae et al.,[117] who employed Lewis acidic zeolites, i.e., Zr-β and Sn-β, and obtained BAMFs yields in the range of 77%−80%, with an ∼85% selectivity toward the bis-ether at 180 °C (6 h). Note that a marked decrease in yield (and selectivity) was observed over the spent catalyst, due to catalyst fouling. However, after regeneration by calcination (500 °C) in air, its activity was nearly completely recovered. Shinde and Rodes[118] have proposed a combination of $ZrO(OH_2)$ and Zr-montmorillonite as the catalyst, which promoted both the etherification (Zr-mont) and hydrogen transfer ($ZrO(OH_2)$) steps, affording an optimal 95% yield of 2,5-bis(isopropoxymethyl)furan (BPMF) at 150 °C (1 h). Finally, Luo et al.[119] have investigated the effect of oxide acidity on 5-HMF etherification and found that ZrO_2 on SBA-15 mesoporous silica exhibited Lewis acidity as well as a weak Bronsted acidity, promoting the sequential hydrogenation−etherification, although with a low yield (45%, 180 °C, 3 h).

Fuels and Additives from Oleaginous Biomass. Lee et al.[120] reported an interesting use of FA for the hydrodeoxygenation reaction (HDO) of crude Jatropha oil for biofuel production. By performing the reaction at 300 °C over Pd/C with a 30% FA aqueous solution, C15−C17 hydrocarbons were successfully obtained (97%). The authors performed the reaction both in batch and in continuous flow, using a fixed-bed reactor. On the other hand, Lu et al.[121] investigated the hydrodeoxygenation of oleic acid to heptadecane over CuNi/CoOx, using IPA as the hydrogen source. The optimized Cu_1Ni_1/CoO_x enabled an ∼91% *n*-heptadecane yield at 240 °C (8 h). Interestingly, this system could be easily recovered by magnetic separation from the reaction mixture and reused for five cycles. The authors also broadened the scope of the catalysts by using a wide range of fatty acids (e.g., lauric acid, myristic acid, stearic acid, α-linolenic acid), and excellent yields of the corresponding hydrocarbons in the range of ∼88%−91% were obtained.

Also, Güemez et al.[122] reported the conversion of glycerol into 1,2-propanediol over a Ni-Cu/Al_2O_3 bimetallic catalyst, in the presence of FA as hydrogen donor. 1,2-Propanediol is a source of liquid fuels, as well as for fine chemicals and polymers (∼30% yield), also demonstrated was a higher efficiency of FA vs IPA in the hydrogen transfer to glycerol (72% vs 30%). Other catalytic systems for glycerol conversion into 1,2-PDO were developed by Cao et al.[123] using FA as the H source and by Pietropaolo et al.,[124] Zhou et al.,[125] and Zhang et al.[126] employing IPA as the hydrogen donor. Further transformations of glycerol via

Table 3. Representative Processes for Production of Biofuels/Biofuel Additives Using FA or IPA as Hydrogen Source

Substrate	H donor	Catalyst	Conditions	Product	Yield (%)	ref
Fructose	FA	Ru/C	Medium/Additive: THF-H_2SO_4 T = 150 °C; microwave	DMF	32	108
Agar	FA	Ru/C	$[DMA]^+[CH_3SO_3]^-$ Medium/Additive: THF-H_2SO_4 T = 150 °C; microwave	DMF	27	108
α-Cellulose	FA	Ru/C	$[DMA]^+[CH_3SO_3]^-$ Medium/Additive: THF-H_2SO_4 T = 150 °C; microwave	DMF	16	108
HMF	FA	Pd/C	FA/HMF 10:1 Medium/Additive: 1,4-dioxane T = 120 °C t = 15h	DMF	95	109
Fructose	FA	Pd/C	Medium/Additive: THF-H_2SO_4 T = 150 °C (2 h) → 70 °C (15 h)	DMF	51	110
HMF	FA	NiCo/C (used for 4 runs)	FA/HMF 20:1 Medium/Additive: – T = 190 °C	DMF	90	111
HMF	IPA	NiCo/C	Medium/Additive: – T = 230 °C	DMF	70	111
FF	FA	10%Ni–10%Cu/C	Medium/Additive: IPA T = 200 °C T = 8 h	2-MF	91	112
FF	FA	10%Ni–10%Cu/Al_2O_3(used for 5 runs)	Medium/Additive: IPA T = 210 °C T = 7 h	2-MF	92	113
FF	IPA	Ru-NMC-3 (used for 5 runs)	Medium/Additive: – T = 140 °C t = 10h	2-MF	87	114
HMF	IPA	Zr-SBA-UH (used for 6 runs)	Medium/Additive: – T = 150 °C t = 4h	BPMF	94	115
HMF	IPA	Zr-*β* (used for 3 runs)	Medium/Additive: – T = 180 °C t = 6h	BPMF	80%	117
HMF	IPA	$ZrO(OH)_2$/Zr-mont (used for 5 runs)	Medium/Additive: – T = 150 °C t = 1 h	BPMF	95%	118
HMF	IPA	ZrO_2/SBA-15	Medium/Additive: – T = 180 °C t = 3 h	BPMF	45	119
Jatropha oil	FA	Pd/C	Medium/Additive: H_2O T = 300 °C	hydrocarbons	97	120
Oleic acid	IPA	CuNi/CoOx (used for 5 runs)	Medium/Additive: –	*n*-heptadecane	~91	121

Table 3. continued

Substrate	H donor	Catalyst	Conditions	Product	Yield (%)	ref
			T = 240 °C t = 8 h			
Glycerol	FA	Ni-Cu/Al_2O_3	Medium/Additive: H_2O T = 200 °C (N_2) t = 10 h	1,2-PDO	~30	122

hydrogenolysis are treated in detail in a recent review focused on the use of various liquid H donors.[127]

Table 3 summarizes representative results on FA- and IPA-assisted productions of biofuels and biofuel additives.

■ LIGNIN VALORIZATION

Lignin is the second most abundant, renewable, and biodegradable natural resource after cellulose and features many functional groups, thus providing room for chemical modification. This section gives an overview of the most significant studies focusing on the transformation of this feedstock mediated by FA or IPA.[128,129]

Lignin Reductive Depolymerization to Phenols. Currently, many efforts are directed toward lignin valorization by "fragmentation",[42,128,129] which helps in the production of chemicals and fuels. One of the strategies is reductive depolymerization (hydrogenolysis and hydrogenation), targeting the formation of simple aromatics such as phenolic (and nonphenolic) compounds. In a very recent review article by Xu et al.,[44] this conversion route is thoroughly discussed. In this context, the use of formic acid (FA) as a hydrogen source has attracted great interest in the past few years. In the depolymerization process of lignin, the H_2 evolved by FA decomposition combines with oxygen from the alkoxy groups of lignin itself to generate water.[130] Hence, a mixture of phenols along with nonphenolic compounds can be obtained, with an overall decrease in the oxygen content (Scheme 3).

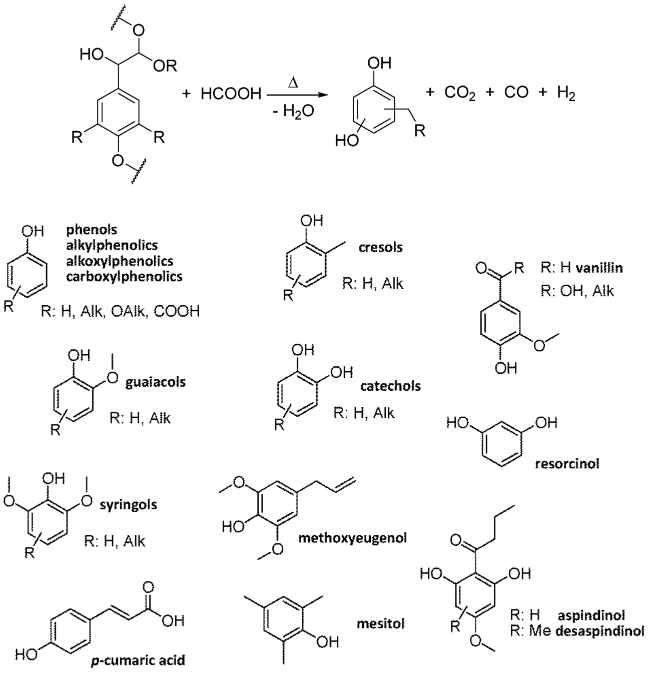
For example, Gasser et al.[131] reported on the FA-assisted depolymerization of a preoxidized lignin. Interestingly, under optimal conditions, it was possible to achieve a 45% lignin depolymerization into monomeric phenolic compounds (e.g., vanillin and its derivatives, syringols) and oligomers. Holmelid et al.[132] proposed a depolymerization protocol in the presence of a FA/water system, which afforded a phenolic fraction (e.g., cresols, catechols, alkylphenolics) in 50% yield.

Oregui-Bengoechea et al.[133] explored the use of several Al_2O_3-supported metal catalysts for the depolymerization of lignin in FA/water, identifying Ru/Al_2O_3 as the best performing system (91% yield). They also highlighted the key role of the Lewis acidic sites in the Al_2O_3 support, which favored the formation of low molecular weight products.

Kim et al.[134] investigated the FA-assisted, catalyst-free protocols for the depolymerization of lignin derived by ethanol production, using supercritical ethanol as the reaction medium. High conversion values were achieved (85%), with high selectivities toward the formation of phenol-rich oils (e.g., alkyl phenolics, alkoxy phenolics, cresols) and very limited production of solid residues. Interestingly, the use of the sole ethanol as both hydrogen donor and reaction medium gave poor results.

Oregui-Bengoechea et al.[135] studied the effect of FA in combination with diverse reaction media (i.e., IPA, ethanol, methanol) on the N-Mo/AA (AA= sulfated γ-Al_2O_3)-catalyzed lignin depolymerization into a phenol-rich oil. Interestingly, they found that the major effect of the medium was the stabilization of the monomers coming from the FA-aided depolymerization, which occurred through formylation, hydrogenation, and hydrogenolysis. The most effective medium was ethanol. Note that the use of sole isopropanol, or of an external H_2 source, rather than FA led to a marked decrease in the yield of lignin oils.

Scheme 3. Degradation−Hydrodeoxygenation of Lignin to Phenolic Monoaromatics Using FA as Hydrogen Source (upper panel). Chemical Structure of Representative Phenolics from Reductive Depolymerization Process of Lignin (lower panel)[a]



[a]Republished with permission from ref 28. Copyright 2019, Royal Society of Chemistry.

The use of a methanol/FA medium was found to be effective in the microwave-assisted catalyst-free depolymerization of alkaline lignin reported by Shao et al.[136] The authors achieved a 72 wt % lignin oil yield at 300 °C (30 min). 2,3-Dihydrobenzofuran, *p*-coumaric acid, guayacol-type, syringol-type, and phenolic compounds were present.

Heeres et al.[137] explored the conversion of Alcell lignin in an IPA/FA mixture (1:1) over a Ru/C catalys, at 400 °C (4h). A good yield of lignin oils was obtained (71% mass yield on lignin input), mainly consisting of catechols, guaiacols, and alkyl phenols, as well as aromatic/aliphatic hydrocarbons deriving from the hydrodeoxygenation reaction of the formers, which are reactive under the adopted conditions. In addition, by replacing isopropanol with methanol (68% mass yield on lignin input), a higher yield in alkylphenolics (11 vs 6 wt % on lignin input) and

Table 4. Representative Lignin FA- or IPA-Mediated Depolymerization Processes

Source	H donor	Catalyst	Conditions	Yield (%)	ref
KL, EL, AL[a]	FA	Ru/Al_2O_3	Medium/Additive: H_2O T = 340−380 °C	91	133
Oak wood CSAHL[b]	FA	–	Medium/Additive: supercritical ethanol T = 350 °C	85	134
Eucalyptus lignin	FA	Ni-Mo/AA	Medium/Additive: ethanol T = 320 °C t = 6 h	38	135
Corn cob lignin	FA	–	Medium/Additive: methanol T = 160 °C, microwave	72	136
Alcell	FA	Ru/C	Medium/Additive: IPA T = 400 °C t = 4 h	71	137
Olive tree pruning lignin	FA	Ni10%Al-SBA-15	Medium/Additive: – T = 150 °C, microwave	29	138
Olive tree clippings lignin	FA	Ni10%Al-SBA-15	Medium/Additive: – T = 150 °C, microwave	37	139
Kraft lignin	IPA	Rh/C	Medium/Additive: – T = 350 °C t = 4 h	94	141
Kraft lignin	IPA	Ni-Cu/H-β (used for 5 runs)	Medium/Additive: – T = 330 °C t = 3 h	99	143
Beech lignin	IPA	$NiAl_2O_3$	Medium/Additive: – T = 170 °C	69	140
Poplar wood lignin	IPA	Raney Ni (used for 8 runs)	Medium/Additive: 30%H_2O T = 180 °C t = 3 h	25	142
Birch lignin	IPA	$Ni_{50}Pd_{50}/SBA-15$	Medium/additive: – T = 245 °C t = 4 h	37	144

[a] KL: low sulfonate alkali lignin. EL: Norway spruce lignin from acid pretreatment. AL: Norway spruce lignin from acid and enzymatic pretreatment. [b] CSHL: concentrated sulfuric acid hydrolysis lignin.

aromatics (19% vs 11% on lignin input), i.e., the most valuable products, was obtained. Also, a reduced O/C value was obtained (0.085 vs 0.09). This was attributed to the possible formation of byproducts when IPA is used from its reaction.

Luque et al.[138] compared the activity of the Ni10%Al-SBA catalyst with various hydrogen-donating media, including FA and IPA. The use of FA gave the best results, avoiding the formation of solid residues. The microwave-assisted hydrogenolytic protocol (150 °C) enabled the formation of a variety of phenols (e.g., mesitol, guaiacol, syringol, vanillin, methoxyeugenol, aspinidol) without any side reaction. On the other hand, these occurred when using isopropanol. In addition, the depolymerization degree was higher for FA, which was attributed to its inherent acidity. The yield was found to be dependent on the pretreatment[139,140] to which lignin sources were subjected (29%−37%).

Over the past few years, the use of IPA in the depolymerization of lignin was most extensively investigated. For example, Zhang et al.[140] recently developed a protocol for the selective hydrogenolysis of the C−O bond in lignin models (i.e., benzylphenyl ether, diphenyl ether, 2-phenylethyl phenyl ether) as well as in beech lignin, using IPA as hydrogen donor, over Ni/Al_2O_3 catalysts. Conversion values up to 100% and high selectivities toward aromatic alkanes and phenol, further reduced to cyclohexanol, were obtained under mild conditions (150 °C).

Wang et al.[141] contributed to the same direction by exploring the use of Rh/C in the IPA-aided depolymerization of Kraft lignin. The authors demonstrated that Rh/C inhibited the IPA self-condensation as well as the formation of oxygenic-chain compounds, compared to other C-supported metals (i.e., Pd, Pt, Ru), enabling the highest phenol conversion value (93%) and the lowest O/C ratio (0.094) at 350 °C (4 h).

Ferrini and Rinaldi[142] demonstrated that, by using IPA as hydrogen donor and Raney Ni as catalyst, lignin from poplar wood can be converted in up to a 25% phenolic-rich oil yield (IPA:H_2O 7:3 v/v; 180 °C, 3 h). Interestingly, the catalyst could be easily recovered by a magnet and reused at least eight times.

Moreover, Kong et al.[143] reported a zeolite-supported bimetallic Ni-Cu/H-β catalyst which enabled high conversion values of Kraft lignin (~99 wt %) and a monomer yield of 50.83 wt % (330 °C, 3 h). The large pore size and acid character of the zeolite support of the Ni-Cu/H-β system, along with the hydrogen transfer ability of IPA, were considered responsible for the efficiency of the hydrodeoxygenation protocol.

Similarly, Hu et al.[144] reported the hydrogenolysis of native lignin from different sources (birch, pine, corn stalk) over a $Ni_{50}Pd_{50}$/SBA-15 bimetallic catalyst, employing IPA as the hydrogen donor. The optimal results were obtained using birch lignin as the source, for which a 37 wt % yield of monophenol was achieved at 245 °C after 4 h. More specifically, 4-propylsyringol reached an approximately19% yield, with a selectivity of 51%. The yield of monophenols from birch lignin was more than 2 times greater than that for native pine lignin (~17%) and 4.6 times greater than that for corn stalk lignin (~8%).

Table 4 summarizes the results on the use of FA and IPA as hydrogen sources for the depolymerization of lignin.

■ LIGNIN-RELATED PHENOLS UPGRADING

Hydrodeoxygenation of Phenols. The upgrading of lignin-related phenols to chemicals and fuels through hydrodeoxygenation protocols is a widely investigated field of research.[129]

Wang et al.[145] explored the hydrodeoxygenation of phenolic compounds using FA as a hydrogen donor and silica-supported Pd-based catalysts, i.e., Pd/SiO_2 and Pd/MCM-41. The reaction was performed at 280 °C, and the major components of the products were cyclohexanol, cyclohexanone, and cyclohexane (~70% yield, Pd/SiO_2). Zeng et al.[146] further investigated the activity of Pd/MCM-41 in the FA-aided hydrodeoxygenation of phenol to cyclohexane and compared it with Pt/MCM-41 and Ru/MCM-41. They demonstrated that Ru/MCM-41 gave the highest conversion value (74%), with a selectivity of 44% toward cyclohexane.

Interestingly, a number of contributions have been directed toward the use of FA or IPA in the dehydrodexygenation of vanillin. The peculiarity of these reactions is the aromatic nature of the product, (2-methoxy-4-methylphenol); that is, the aromatic ring is not hydrogenated by the in situ generated H_2. 2-Methoxy-4-methylphenol is considered a promising biofuel. For example, Kim et al.[147] used a bimetallic PdAg catalyst anchored to Fe_3O_4/N-doped reduced graphene oxide in aqueous medium. A quantitative conversion to 2-methoxy-4-methylphenol was achieved at 130 °C (6 h), with a total selectivity. Nie et al.[148] first explored the use of a Pd/NMC (NMC = nitrogen-enriched mesoporous carbon) for the CTH of vanillin to 2-methoxy-4-methylphenol. Once more, a quantitative conversion and a total selectivity were achieved. Recycling of the catalyst was successful for up to five runs. In a subsequent contribution,[149] the same group explored a different catalyst, i.e., Co metal encapsulated within a NMC structure, and obtained a maximum conversion value of 96% at 180 °C (4 h), using the sole FA as hydrogen source. Note that Co is a non-noble metal. The catalyst could be recycled for five consecutive runs, with no Co leaching in the reaction mixture. Moreover, Tadele et al.[150] proposed a continuous flow protocol employing bimetallic Ag–Pd nanoparticles supported on C_3N_4 as a catalyst (AgPd@g-C_3N_4) and 9:1 methanol:water as a reaction medium; a slight excess of FA (1.5 equiv) was used. They succeeded in obtaining 2-methoxy-4-methylphenol quantitatively at 70 °C (0.1 mL/min flow rate).

On the other hand, Gao et al.[151] used the Cu/$Zn_{15}Al_4Sn_1$-LDH catalyst (LDH = layered double hydroxide) in the hydrodeoxygenation of vanillin to generate 2-methoxy-4-methylphenol, with isopropanol as the in situ hydrogen source. Under relatively moderate conditions (180 °C, 4 h), a nearly quantitative conversion of vanillin (99%) was obtained. Notably, the catalyst could be recovered and reused for five cycles.

Phenol Hydrogenation to Cyclohexanone. Cyclohexanone is a key substrate in the synthesis of many intermediates, including adipic acid and ε-caprolactam, well-known monomers to prepare Nylon-6,6 and Nylon-6, respectively. It is industrially produced by the oxidation of cyclohexane or hydrogenation of phenols, although the former typically lead to the formation of byproducts because of the required drastic pressure and temperature conditions. The hydrogenation of phenol can proceed either via a two-step or a one-step protocol. The two-step process envisages the hydrogenation of phenol, followed by the endothermic dehydrogenation of the cyclohexanol intermediate. The one-step route is a more convenient alternative, since it results in the minimization of the waste associated with the process, operational costs, and increased safety. On the other hand, due to its high reactivity, cyclohexanone can hydrogenate easily to cyclohexanol and other byproducts. The selective hydrogenation of phenol is greatly influenced by the catalyst properties.

Zhao et al.[152] investigated the use of a Pd/C catalyst combined with microwave irradiation (80–90 °C, 15 min) for the hydrogenation of phenol to cyclohexanone using sodium formate as the H_2 source. A complete conversion and a 98% selectivity toward cyclohexanone were observed. Chen et al.[153] employed palladium nanoparticles anchored on a PANI-CNF support (PANI-CNF = polyaniline-functionalized carbon nanofiber), featuring Lewis base sites, targeting a higher process selectivity. Sodium formate was once more used as a hydrogen source at 80 °C in water medium (5 h). Under these conditions, a greater than 99% selectivity toward cyclohexanone was achieved. Recycling of the catalyst was satisfactory over three runs, showing a limited decrease in phenol conversion (~15%). Guan et al.[154] reported on the effect of different solid supports for the palladium catalyst, including activated carbon (AC), metal organic frameworks (MIL-101), and basic oxides (TiO_2, Al_2O_3). The reaction was carried out in the presence of FA as a hydrogen donor and water as a reaction medium at 50 °C (4 h). The optimal results were obtained by using a Pd/AC catalyst system, which was ascribed to its adsorption ability toward both phenol and FA. A quantitative conversion of phenol was obtained, with a 71% selectivity toward cyclohexanone. Catalyst recycling was successful over six runs.

Patil et al.[155] introduced for the first time the use of potassium formate as a hydrogen source for the hydrogenation of phenol. Interestingly, the authors found that when using a slight excess of formate (2.1 equiv), high conversion (92%) and low selectivity toward cyclohexanone (57%) were achieved over a Pd/C catalyst. By increasing potassium formate to 3.5–4.0 equiv, almost complete conversion and selectivity (99%) toward the target compound were observed. These findings indicated that besides being a source of hydrogen, potassium formate behaves as an additive, which increases the selectivity toward cyclo-

Table 5. Overview of representative FA- and IPA- mediated routes for phenols upgrading

Substrate	Catalyst	H source	Conditions	Product	Yield (%)	ref
Phenol	Pd/SiO_2	FA	Medium/Additive: – $T = 280$ °C	cyclohexane	70	145
Phenol	Ru/MCM-41	FA	Medium/Additive: – $T = 280$ °C	cyclohexane	~32	146
Vanillin	$Pd_{50}Ag_{50}/Fe_3O_4$/N-rGO (used for 11 runs)	FA	Medium/Additive: H_2O $T = 130$ °C $t = 6$ h	2-OMe-4-MePhOH[a]	99	147
Vanillin	Pd/NMCs (used for 5 runs)	FA	Medium/Additive: H_2O $T = 150$ °C	2-OMe-4-MePhOH[a]	99	148
Vanillin	Co@NC-700[b] (used for 5 runs)	FA	Medium/Additive: – $T = 180$ °C $t = 4$ h	2-OMe-4-MePhOH[a]	96	149
Vanillin	AgPd@g-C_3N_4 (continuous flow)	FA	Medium/Additive: 9:1 methanol:water $T = 70$ °C	2-OMe-4-MePhOH[a]	>99	150
Vanillin	Cu/$Zn_{15}Al_4Sn_1$-LDH(used for 5 runs)	IPA	Medium/Additive: – $T = 180$ °C $t = 4$ h	2-OMe-4-MePhOH[a]	99	151
Phenol	Pd/C (used for 3 runs)	SF[c]	Medium/Additive: H_2O $T = 80–90°$ (microwave) $t = 15$ min	cyclohexanone	98	152
Phenol	Pd-PANI/CNF (used for 4 runs)	SF[c]	Medium/Additive: H_2O $T = 80$ °C $t = 5$ h	cyclohexanone	99	153
Phenol	Pd/C (used for 6 runs)	FA	Medium/Additive: H_2O $T = 50$ °C $t = 2$ h	cyclohexanone	~80	154
Phenol	Pd/C (used for 4 runs)	PF[d]	Medium/Additive: H_2O $T = 90$ °C $t = 6$ h	cyclohexanone	99	155
Phenol	Pd/C (flow reactor)	SF[c]	Medium/Additive: H_2O; pH 12 $T = 90$ °C Flow rate = 0.5 mL/min	cyclohexanone	93	156
Phenol	POLITAG-Pd(0)-L1 (flow reactor)	SF[c]	Medium/Additive: H_2O; pH 12 $T = 120$ °C Flow rate = 0.26 mL/min	cyclohexanone	87[e]	157
Phenol	Pd-chitin-150 (continuous flow)	SF[c]	Medium/Additive: H_2O $T = 90$ °C Flow rate = 0.2 mL/min	cyclohexanone	99	158

[a] 2-OMe-4-MePhOH: 2-methoxy-4-methylphenol; [b] N-Doped graphitic structures pyrolyzed at 700 °C. [c] SF= sodium formate. [d] PF= potassium formate. [e] Isolated yield.

hexanone. The use of sodium formate, FA, ammonium formate, and molecular hydrogen gave in all cases poorer results. Recycling of the catalyst was successful over four runs.

Vaccaro et al.[156] demonstrated the efficiency of the continuous flow technology combined with a Pd/C heterogeneous catalyst for the selective production of cyclohexanone from phenol. The protocol employed sodium formate as the in situ hydrogen source. Interestingly, the authors investigated the effect of diverse parameters, i.e., the reactant molar ratio, the pH of the reaction mixture, the nature of the base controlling the pH, and the reaction time, on the selectivity toward cyclohexanone. At the optimal pH 12, NaOH resulted as the best choice in terms of conversion and selectivity, among other hydroxides (KOH, Bu_4NOH, NH_4OH), suggesting a "cation size" effect. By feeding a 1:2.5 phenol/sodium formate mixture into the flow reactor packed with 10 wt % Pd/C, it was possible to obtain 80% yield of cyclohexanone (90 °C).

In a subsequent contribution,[157] the same group explored the use of a polymer-supported Pd(0) catalyst (POLITAG-Pd(0)-L1), featuring pincer-type ionic ligands for the metal nanoparticle stabilization. This catalytic system proved to be effective for the sodium formate-assisted selective hydrogenation in water of a range of phenols under continuous flow conditions. An 87% isolated yield of cyclohexanone (100% selectivity) was obtained at a flow rate of 0.26 mL/min (120 °C, pH 12). Notably, more than 100 mmol of substrate was converted using the same reactor without any decrease in conversion/selectivity values, which pointed out the catalyst stability. Such stability was supported by the poor metal leaching (0.01 ppm).

In addition, satisfying results were obtained for substituted phenols. In this case, substrate conversion values in the range of 67%−100% and selectivities toward the corresponding cyclohexanones up to 100% were achieved.

Very recently, Gao et al.[158] reported the use of chitin as a support for palladium nanoparticles (Pd-chitin-150) for the transfer hydrogenation of phenol to cyclohexanone by sodium formate in the presence of H_2O medium. A quantitative phenol conversion and a selectivity toward cyclohexanone of 99% were observed employing a 2.5 formate:phenol mole ratio at 90 °C (3 h). The favorable interaction between Pd nanoparticles and the −OH functional groups of chitin in the Pd−chitin system, leading to a homogeneous dispersion of the metal on the support, was considered responsible for the excellent catalytic activity and stability. Indeed, Pd leaching did not occur during the reaction, and the catalyst could be recycled at least four times, with no significant decrease in conversion/selectivity values. In addition, the Pd-chitin-150 could be fabricated directly into a Teflon tube as a monolith, which enabled the production of cyclohexanone under continuous flow. Under the optimal conditions, the flow system runs for 12 h with 100% phenol conversion and greater than 99% selectivity toward the target compound (flow rate: 0.2 mL/min).

To widen the substrate scope, several substituted phenols were converted over the Pd−chitin system to afford the corresponding cyclohexanones under similar conditions (90 °C, 7−24 h) with good-to-high conversion values (37%−100%) and excellent selectivities (93%−100%).

Recently, the use of FA or formate salts as the H source in the upgrading of phenol to nitrogen-containing useful chemicals via cyclohexanone has been also addressed by different groups.[159,160] The reader is referred to the original papers for further details.

Table 5 summarizes the representative results on the use of FA and IPA as hydrogen sources for lignin-related phenol upgrading.

■ CONCLUSION

In this perspective, representative examples have been discussed demonstrating the potential of formic acid and isopropanol as hydrogen sources in the transformation of different biobased platforms (e.g., levulinic acid, furfural, 5-hydroxymethylfurfural) into value-added products, including biofuels. Also, some examples of processes for lignin upgrading have been considered. Not unexpectedly, the catalyst plays a crucial role in the success of the process. Some correlations have been identified.

Of course, for a trustworthy selective technology, it is equally important to direct further efforts in tuning the reaction conditions (e.g., reaction media, catalyst loading, temperature), as well as increasing the implementation of continuous flow reactors for large-scale applications.

In addition, it is clear that the use of isopropanol as hydrogen donor in biomass valorization is still in its earlier stage, if compared to the FA-assisted conversion processes. This is particularly true for the processes involving LA, since FA comes as an LA byproduct of the conversion of 5-hydroxymethylfurfural, and therefore, the direct conversion of LA−FA mixtures is particularly appealing in terms of costs and sustainability. Moreover, isopropanol, similarly to other small molecular alcohols (methanol, ethanol) is a valuable product as itself; therefore, cost issues are associated with its use. This could be overcome by developing efficient protocols enabling its recover and reuse, particularly for industrial applications. It is noteworthy, however, that many recent reports target the isopropanol-mediated hydrogenation of furfural and, in a less extent, 5-hydroxymethylfurfural platform molecules to the corresponding alcohols, which indicate a fast-growing interest in the field. Further details can be found in the original papers.[161−167] Of particular interest appears to be the use of isopropanol in the depolymerization of lignin. Particularly, isopropanol can have a dual effect as reaction medium and H_2 source.

Finally, it is necessary to point out that a comprehensive techno-economic assessment for biomass upgrading via formic acid or isopropanol-mediated reductive processes has not been carried out yet, neither was it compared to more conventional hydrogen sources. Therefore, it is essential to proceed in this direction, to make large scale applications viable.

■ AUTHOR INFORMATION

Corresponding Authors

Luigi Vaccaro − *Laboratory of Green S.O.C. − Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 Perugia, Italy;* orcid.org/0000-0003-4168-2303; Email: luigi.vaccaro@unipg.it; greensoc.chm.unipg.it

Assunta Marrocchi − *Laboratory of Green S.O.C. − Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 Perugia, Italy;* Email: assunta.marrocchi@unipg.it

Authors

Francesco Ferlin − *Laboratory of Green S.O.C. − Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 Perugia, Italy*

Federica Valentini − *Laboratory of Green S.O.C. − Dipartimento di Chimica, Biologia e Biotecnologie, Università degli Studi di Perugia, 06123 Perugia, Italy*

Complete contact information is available at:
https://pubs.acs.org/10.1021/acssuschemeng.1c03247

Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

Biographies

Francesco Ferlin received his Ph.D. degree in chemical sciences at the University of Perugia in 2019 with Prof. L. Vaccaro. In 2017, he was a visiting Ph.D. student at the Georg-August University in Göttingen in the group of Prof. L. Ackermann. Since 2019, he has been a postdoctoral researcher at the University of Perugia with Prof. L. Vaccaro. His main research interests are focused in the fields of green and sustainable chemistry, C−H functionalizations, flow chemistry, and catalysis.

Federica Valentini is currently a postdoctoral researcher at the University of Perugia in the group of Prof. L. Vaccaro. She obtained her Ph.D. degree in chemical sciences at the University of Perugia in 2020 under the supervision of Prof. L. Vaccaro. During her doctoral studies, she has been visiting the University of Namur (Prof. C. Aprile) and The Hebrew University of Jerusalem (Prof. D. Gelman) to work on joint collaboration programs. Her research focus is the design and development of novel heterogeneous catalytic systems for sustainable processes.

Assunta Marrocchi is currently an Associate Professor at the Department of Chemistry, Biology and Biotechnology of the University of Perugia, and she was habilitated as a Full Professor in 2018. She earned a Ph.D. in chemical sciences at the same institution, working on a research project focusing on the design, synthesis, and characterization of helically shaped polycyclic aromatics. Her research interests include biomass sustainable conversion into high value-added chemicals and fuels, materials design and sustainable synthesis, heterogeneous catalysis, and safe chemicals.

Luigi Vaccaro is a Full Professor of organic chemistry (03/C1) at the University of Perugia where he is leading the Green S.O.C. group. He is currently appointed as an Associate Editor of *RSC Advances* and of the *Beilstein Journal of Organic Chemistry*. His recognitions comprise the Europa Medal from the Society of Chemical Industry − London (2001), the ADP Award from Merck's Chemistry Council for "Creative work in organic chemistry" (2006 and 2007), the G. Ciamician Medal of the Società Chimica Italiana (2007), the Vigevani (2014), and the Lady Davis (2018) Visiting Professorship. His research is currently focused on the development of heterogeneous catalysis, safer media, and flow chemistry toward the definition of novel green/sustainable synthetic tools.

■ ACKNOWLEDGMENTS

The Università degli Studi di Perugia and MUR are acknowledged for financial support for the project AMIS, through the program "Dipartimenti di Eccellenza -2018-2022".

■ ABBREVIATIONS

ATMP =Amino tri(methylene phosphonic acid)
CTH =Catalytic transfer hydrogenation,
COF =Covalent organic framework
DMF =2,5-Dimethylfuran
FA =Formic acid
FDCA =2,5-Furandicarboxylic acid
FF =Furfural
BAMF =2,5-Bis(alkoxymethyl)furan
HMF =5-Hydroxymethylfurfural
IEA =International Energy Agency
IPA =Isopropanol
LDH =Layered double hydroxide
LA =Levulinic acid
LOHC =Liquid organic hydrogen carrier
2-MF =2-Methyl furan
MPV =Meerwein−Ponndorf−Verley
MOF =Metal−organic framework
NMC =Nitrogen-enriched mesoporous carbon
H18-DBT =Perhydro dibenzyltoluene

12H-NEC =Perhydro-N-ethylcarbazole
PAF =Porous aromatic framework
TOF =Turnover frequency
GVL =γ-Valerolactone

REFERENCES

(1) Julianelli, A, Basile, A, Eds.; *Advances in Hydrogen Production, Storage and Distribution*, 1st ed.; Woodhead Publishing, 2014. DOI: 10.1016/C2013-0-16359-3.

(2) Preuster, P.; Papp, C.; Wasserscheid, P. Liquid Organic Hydrogen Carriers (LOHCs): toward a hydrogen-free hydrogen economy. *Acc. Chem. Res.* **2017**, *50*, 74−85.

(3) Haussinger, P.; Lohmueller, R.; Watson, A. M. Hydrogen. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2000.

(4) Hirscher, M.; Yartys, V. A.; Baricco, M.; Bellosta von Colbe, J.; Blanchard, D.; Bowman, R. C.; Broom, D. P.; Buckley, C. E.; Chang, F.; Chen, P.; Cho, Y. W.; Crivello, J. C.; Cuevas, F.; David, W. I. F.; de Jongh, P. E.; Denys, R. V.; Dornheim, M.; Felderhoff, M.; Filinchuk, Y.; Froudakis, G. E.; Grant, D. M.; Gray, E.; Hauback, B. C.; He, T.; Humphries, T. D.; Jensen, T. R.; Kim, S.; Kojima, Y.; Latroche, M.; Li, H. W.; Lototskyy, M. V.; Makepeace, J. V.; Møller, K. T.; Naheed, L.; Ngene, P.; Noréus, D.; Nygård, M. M.; Orimo, S-i.; Paskevicius, M.; Pasquini, L.; Ravnsbæk, D. B.; Sofianos, M. V.; Udovic, T. J.; Vegge, T. J.; Walker, G. S.; Webb, C. J.; Weidenthaler, C.; Zlotea, C. Materials for hydrogen-based energy storage − past, recent progress and future outlook. *J. Alloys Compd.* **2020**, *827*, 153548.

(5) He, T.; Pachfule, P.; Wu, H.; Xu, Q.; Chen, P. Hydrogen carriers. *Nat. Rev. Mater.* **2016**, *1*, 16059.

(6) Ma, L.-J.; Han, T.; Jia, J.; Wu, H.-S. Cooperative physisorption and chemisorption of hydrogen on vanadium-decorated benzene. *RSC Adv.* **2020**, *10*, 37770−37778.

(7) Xu, W.; Takahashi, K.; Matsuo, Y.; Hattori, Y.; Kumagai, M.; Ishiyama, S.; Kaneko, K.; Iijima, S. Investigation of hydrogen storage capacity of various carbon materials. *Int. J. Hydrogen Energy* **2007**, *32*, 2504−2512.

(8) Panella, B.; Hirscher, M.; Pütter, H.; Müller, U. Hydrogen adsorption in Metal−Organic Frameworks: Cu-MOFs and Zn-MOFs compared. *Adv. Funct. Mater.* **2006**, *16*, 520−524.

(9) Dalebrook, A. F.; Gan, W.; Grasemann, M.; Moret, S.; Laurenczy, G. Hydrogen storage: beyond conventional methods. *Chem. Commun.* **2013**, *49*, 8735−8751.

(10) Gianotti, E.; Taillades-Jacquin, M.; Rozière, J.; Jones, D. J. High-purity hydrogen generation via dehydrogenation of organic carriers: a review on the catalytic process. *ACS Catal.* **2018**, *8*, 4660−4680.

(11) Modisha, P. M.; Ouma, C. N. M.; Garidzirai, R.; Wasserscheid, P.; Bessarabov, D. The prospect of hydrogen storage using Liquid Organic Hydrogen Carriers. *Energy Fuels* **2019**, *33*, 2778−2796.

(12) Müller, K.; Thiele, S.; Wasserscheid, P. Evaluations of concepts for the integration of fuel cells in Liquid Organic Hydrogen Carrier systems. *Energy Fuels* **2019**, *33*, 10324−10330.

(13) Sievi, G.; Geburtig, D.; Skeledzic, T.; Boesmann, A.; Preuster, P.; Brummel, O.; Waidhas, F.; Montero, M. A.; Khanipour, P.; Katsounaros, I.; Libuda, J.; Mayrhofer, K. J. J.; Wasserscheid, P. Towards an efficient liquid organic hydrogen carrier fuel cell concept. *Energy Environ. Sci.* **2019**, *12*, 2305−2314.

(14) Rao, P. C.; Yoon, M. Potential Liquid-Organic Hydrogen Carrier (LOHC) systems: a review on recent progress. *Energies* **2020**, *13*, 6040−6063.

(15) Aakko-Saksa, P. T.; Cook, C.; Kiviaho, J.; Repo, T. Liquid Organic Hydrogen Carriers for transportation and storing of renewable energy − Review and discussion. *J. Power Sources* **2018**, *396*, 803−823.

(16) Niermann, M.; Beckendorff, A.; Kaltschmitt, M.; Bonhoff, K. Liquid Organic Hydrogen Carrier (LOHC) - Assessment based on chemical and economic properties. *Int. J. Hydrogen Energy* **2019**, *44*, 6631−6654.

(17) Markiewicz, M.; Zhang, Y. Q.; Bösmann, A.; Brückner, N.; Thöming, J.; Wasserscheid, P.; Stolte, S. Environmental and health impact assessment of Liquid Organic Hydrogen Carrier (LOHC) systems − challenges and preliminary results. *Energy Environ. Sci.* **2015**, *8*, 1035−1045.

(18) Eypasch, M.; Schimpe, M.; Kanwar, A.; Hartmann, T.; Herzog, S.; Frank, T.; Hamacher, T. Model-based techno-economic evaluation of an electricity storage system based on Liquid Organic Hydrogen Carriers. *Appl. Energy* **2017**, *185*, 320−330.

(19) Fikrt, A.; Brehmer, R.; Milella, V. O.; Müller, K.; Bösmann, A.; Preuster, P.; Alt, N.; Schlücker, E.; Wasserscheid, P.; Arlt, W. Dynamic power supply by hydrogen bound to a Liquid Organic Hydrogen Carrier. *Appl. Energy* **2017**, *194*, 1−8.

(20) Wang, H.; Zhou, X.; Ouyang, M. Efficiency analysis of novel Liquid Organic Hydrogen Carrier technology and comparison with high pressure storage pathway. *Int. J. Hydrogen Energy* **2016**, *41*, 18062−18071.

(21) Preuster, P.; Alekseev, A.; Wasserscheid, P. Hydrogen storage technologies for future energy systems. *Annu. Rev. Chem. Biomol. Eng.* **2017**, *8*, 445−471.

(22) Brückner, N.; Obesser, K.; Bösmann, A.; Teichmann, D.; Arlt, W.; Dungs, J.; Wasserscheid, P. Evaluation of industrially applied heat-transfer fluids as Liquid Organic Hydrogen Carrier systems. *ChemSusChem* **2014**, *7*, 229−235.

(23) Jorschick, H.; Preuster, P.; Duerr, S.; Seidel, A.; Mueller, K.; Boesmann, A.; Wasserscheid, P. Hydrogen storage using a hot pressure swing reactor. *Energy Environ. Sci.* **2017**, *10*, 1652−1659.

(24) Hydrogenius. https://www.hydrogenious.net/index.php/en/products-2/ (accessed Apr. 27, 2021).

(25) Jin, X.; Yin, B.; Xia, Q.; Fang, T.; Shen, J.; Kuang, L.; Yang, C. Catalytic transfer hydrogenation of biomass-derived substrates to value-added chemicals on dual-function catalysts, opportunities and challenges. *ChemSusChem* **2019**, *12*, 71−92.

(26) Asefa, T.; Koh, K.; Yoon, C. W. CO_2-Mediated H_2 storage-release with nanostructured catalysts, recent progresses, challenges, and perspectives. *Adv. Energy Mater.* **2019**, *9*, 1901158.

(27) Kar, S.; Goeppert, A.; Prakash, G. K. S. Integrated CO_2 Capture and Conversion to Formate and Methanol, Connecting Two Threads. *Acc. Chem. Res.* **2019**, *52*, 2892−2903.

(28) Valentini, F.; Kozell, V.; Petrucci, C.; Marrocchi, A.; Gu, Y.; Gelman, D.; Vaccaro, L. Formic acid, a biomass-derived source of energy and hydrogen for biomass upgrading. *Energy Environ. Sci.* **2019**, *12*, 2646−2664.

(29) Yu, Z.; Lu, X.; Xiong, J.; Li, X.; Bai, H.; Ji, N. Heterogeneous catalytic hydrogenation of levulinic acid to γ-valerolactone with formic acid as internal hydrogen source. *ChemSusChem* **2020**, *13*, 2916−2930.

(30) Fang, W.; Riisager, A. Recent advances in heterogeneous catalytic transfer hydrogenation/hydrogenolysis for valorization of biomass-derived furanic compounds. *Green Chem.* **2021**, *23*, 670−688.

(31) Nie, R.; Tao, Y.; Nie, Y.; Lu, T.; Wang, J.; Zhang, Y.; Lu, X.; Xu, C. C. Recent advances in catalytic transfer hydrogenation with formic acid over heterogeneous transition metal catalysts. *ACS Catal.* **2021**, *11*, 1071−1095.

(32) Sun, R.; Liao, Y.; Bai, S.-T.; Zheng, M.; Zhou, C.; Zhang, T.; Sels, B. F. Heterogeneous catalysts for CO_2 hydrogenation to formic acid/formate, from nanoscale to single atom. *Energy Environ. Sci.* **2021**, *14*, 1247−1285.

(33) Ra, E. C.; Kim, K. Y.; Kim, E. H.; Lee, H.; An, K.; Lee, J. S. Recycling carbon dioxide through catalytic hydrogenation, recent key developments and perspectives. *ACS Catal.* **2020**, *10*, 11318−11345.

(34) Papa, A. J. Propanols. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH: Weinheim, Germany, 2011.

(35) Dutia, P. Isopropyl alcohol: A techno-commercial profile. https://doczz.net/doc/6463566/i-isopropyl-alcohol--a-techno-commercial-profile-special-... (accessed May 5, 2021).

(36) Pérez-Fortes, M.; Schöneberger, J. C.; Boulamanti, A.; Harrison, G.; Tzimas, E. Formic acid synthesis using CO_2 as raw material: Techno-economic and environmental evaluation and market potential. *Int. J. Hydrogen Energy* **2016**, *41*, 16444−16462.

(37) Kubiak, C. P.; Benson, E. E.; Sathrum, A. J.; Smieja, J. M. Electrocatalytic and homogeneous approaches to conversion of CO_2 to liquid fuels. *Chem. Soc. Rev.* **2009**, *38*, 89−99.

(38) Leitner, W. Carbon dioxide as a raw material, the synthesis of formic acid and its derivatives from CO2. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2207−2221.

(39) Schaub, T.; Fries, D.; Paciello, R.; Mohl, K. Process for preparing formic acid by reaction of carbon dioxide with hydrogen. U.S. Patent US8791297B2, 2014.

(40) Gao, Z.; Li, C.; Fan, G.; Yang, L.; Li, F. Nitrogen-doped carbon-decorated copper catalyst for highly efficient transfer hydrogenolysis of 5-hydroxymethylfurfural to convertibly produce 2,5-dimethylfuran or 2,5-dimethyltetrahydrofuran. *Appl. Catal., B* **2018**, *226*, 523−533.

(41) Shafaghat, H.; Rezaei, P. S.; Daud, W. M. A. W. Using decalin and tetralin as hydrogen source for transfer hydrogenation of renewable lignin-derived phenolics over activated carbon supported Pd and Pt catalysts. *J. Taiwan Inst. Chem. Eng.* **2016**, *65*, 91−100.

(42) Cao, X.; Wei, J.; Liu, H.; Lv, X.; Tang, X.; Zeng, X.; Sun, Y.; Lei, T.; Liu, S.; Lin, L. Hydrogenation of methyl levulinate to γ-valerolactone over Cu—Mg oxide using MeOH as in situ hydrogen source. *J. Chem. Technol. Biotechnol.* **2019**, *94*, 167−177.

(43) Grazia, L.; Bonincontro, D.; Lolli, A.; Tabanelli, T.; Lucarelli, C.; Albonetti, S.; Cavani, F. Exploiting H-transfer as a tool for the catalytic reduction of bio-based building blocks, the gas-phase production of 2-methylfurfural using a $FeVO_4$ catalyst. *Green Chem.* **2017**, *19*, 4412−4422.

(44) Zhao, B.; Hu, Y.; Gao, J.; Zhao, J.; Ray, M. B.; Xu, C. C. Recent advances in hydroliquefaction of biomass for bio-oil production using in situ hydrogen donors. *Ind. Eng. Chem. Res.* **2020**, *59*, 16987−17007.

(45) 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.

(46) Rackemann, D. W.; Doherty, W. O. The conversion of lignocellulosics to levulinic acid. *Biofuels, Bioprod. Biorefin.* **2011**, *5*, 198−214.

(47) Yan, K.; Jarvis, C.; Gu, J.; Yan, J. Production and catalytic transformation of levulinic acid, A platform for speciality chemicals and fuels. *Renewable Sustainable Energy Rev.* **2015**, *51*, 986−997.

(48) Hayes, G. C.; Becer, R. Levulinic acid, a sustainable platform chemical for novel polymer architectures. *Polym. Chem.* **2020**, *11*, 4068−4077.

(49) Huang, Y.-B.; Dai, J.-J.; Deng, X.-J.; Qu, Y.-C.; Guo, Q.-X.; Fu, Y. Ruthenium-catalyzed conversion of levulinic acid to pyrrolidines by reductive amination. *ChemSusChem* **2011**, *4*, 1578−1581.

(50) Metzker, G.; Dias, R. M. P.; Burtoloso, A. C. B. Iron-catalyzed reductive amination from levulinic and formic acid aqueous solutions, an approach for the selective production of pyrrolidones in biorefinery facilities. *Chemistry Select* **2018**, *3*, 368−372.

(51) Amarasekara, A. S.; Lawrence, Y. M. Raney-Ni catalyzed conversion of levulinic acid to 5-methyl-2-pyrrolidone using ammonium formate as the H and N source. *Tetrahedron Lett.* **2018**, *59*, 1832−1835.

(52) Wei, Y.; Wang, C.; Jiang, X.; Xue, D.; Li, J.; Xiao, J. Highly efficient transformation of levulinic acid into pyrrolidinones by iridium catalysed transfer hydrogenation. *Chem. Commun.* **2013**, *49*, 5408−5410.

(53) Wei, Y.; Wang, C.; Jiang, X.; Xue, D.; Liu, Z.-T.; Xiao, J. Catalyst-free transformation of levulinic acid into pyrrolidinones with formic acid. *Green Chem.* **2014**, *16*, 1093−1096.

(54) Ledoux, A.; Kuigwa, L. S.; Framery, E.; Andrioletti, B. A highly sustainable route to pyrrolidone derivatives − direct access to biosourced solvents. *Green Chem.* **2015**, *17*, 3251−3254.

(55) Calvo-Flores, F. G.; Monteagudo-Arrebola, M. J.; Dobado, J. A.; Isac-Garcìa, I. Green and bio-based solvents. *Top. Curr. Chem.* **2018**, *376*, 18.

(56) Alonso, D. M.; Wettstein, S. G.; Dumesic, J. A. Gamma-valerolactone, a sustainable platform molecule derived from lignocellulosic biomass. *Green Chem.* **2013**, *15*, 584−595.

(57) Horváth, I. T.; Mehdi, H.; Fábos, V.; Boda, L.; Mika, L. T. γ-Valerolactone—a sustainable liquid for energy and carbon-based chemicals. *Green Chem.* **2008**, *10*, 238−242.

(58) Mehdi, H.; Fábos, V.; Tuba, R.; Bodor, A.; Mika, L. T.; Horváth, I. T. Integration of homogeneous and heterogeneous catalytic processes for a multi-step conversion of biomass, from sucrose to levulinic acid, γ-valerolactone, 1,4-pentanediol, 2-methyl-tetrahydrofuran, and alkanes. *Top. Catal.* **2008**, *48*, 49−54.

(59) Osatiashtiani, A.; Lee, A. F.; Wilson, K. Recent advances in the production of γ-valerolactone from biomass-derived feedstocks via heterogeneous catalytic transfer hydrogenation. *J. Chem. Technol. Biotechnol.* **2017**, *92*, 1125−1135.

(60) Liguori, F.; Moreno-Marrodan, C.; Barbaro, P. Environmentally friendly synthesis of γ-valerolactone by direct catalytic conversion of renewable sources. *ACS Catal.* **2015**, *5*, 1882−1894.

(61) Deng, L.; Li, J.; Lai, D. M.; Fu, Y.; Guo, Q.-X. Catalytic conversion of biomass-derived carbohydrates into gamma-valerolactone without using an external H_2 supply. *Angew. Chem., Int. Ed.* **2009**, *48*, 6529−6532.

(62) Lu, S. M.; Wang, Z.; Li, J.; Xiao, J.; Li, C. Base-free hydrogenation of CO_2 to formic acid in water with an iridium complex bearing a N,N′-diimine ligand. *Green Chem.* **2016**, *18*, 4553−4558.

(63) Deng, L.; Zhao, Y.; Li, J.; Fu, Y.; Liao, B.; Guo, Q.-X. Conversion of levulinic acid and formic acid into γ-valerolactone over heterogeneous catalysts. *ChemSusChem* **2010**, *3*, 1172−1175.

(64) Amenuvor, G.; Makhubela, B. C. E.; Darkwa, J. Efficient solvent-free hydrogenation of levulinic acid to γ-valerolactone by pyrazolylphosphite and pyrazolylphosphinite ruthenium(II) complexes. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6010−6018.

(65) Fàbos, V.; Mika, L. T.; Horvàth, I. T. Selective conversion of levulinic and formic acids to γ-valerolactone with the Shvo catalyst. *Organometallics* **2014**, *33*, 181−187.

(66) Shvo, Y.; Czarkie, D.; Rahamim, Y.; Chodosh, D. F. A new group of ruthenium complexes, structure and catalysis. *J. Am. Chem. Soc.* **1986**, *108*, 7400.

(67) Braden, D. J.; Henao, C. A.; Heltzel, J.; Maravelias, C. C.; Dumesic, J. A. Production of liquid hydrocarbon fuels by catalytic conversion of biomass-derived levulinic acid. *Green Chem.* **2011**, *13*, 1755−1765.

(68) Heeres, H.; Handana, R.; Chunai, D.; Rasrendra, C. B.; Girisuta, B.; Heeres, H. J. Combined dehydration/(transfer)-hydrogenation of C6-sugars (D-glucose and D-fructose) to γ-valerolactone using ruthenium catalysts. *Green Chem.* **2009**, *11*, 1247−1255.

(69) Feng, J.; Gu, X.; Xue, Y.; Han, Y.; Lu, X. Production of γ-valerolactone from levulinic acid over a Ru/C catalyst using formic acid as the sole hydrogen source. *Sci. Total Environ.* **2018**, *633*, 426−432.

(70) Gao, Y.; Zhang, H.; Han, A.; Wang, J.; Tan, H. R.; Tok, E. S.; Jaenicke, S.; Chuah, G. K. Ru/ZrO_2 Catalysts for transfer hydrogenation of levulinic acid with formic acid/formate mixtures, importance of support stability. *Chemistry Select* **2018**, *3*, 1343−1351.

(71) Son, P. A.; Nishimura, S.; Ebitani, K. Production of γ-valerolactone from biomass-derived compounds using formic acid as a hydrogen source over supported metal catalysts in water solvent. *RSC Adv.* **2014**, *4*, 10525−10530.

(72) Du, X. L.; He, L.; Zhao, S.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. Hydrogen-independent reductive transformation of carbohydrate biomass into γ-valerolactone and pyrrolidone derivatives with supported gold catalysts. *Angew. Chem., Int. Ed.* **2011**, *50*, 7815−7819.

(73) Du, X. L.; Bi, Q. Y.; Liu, Y. M.; Cao, Y.; Fan, K. N. Conversion of biomass-derived levulinate and formate esters into γ-valerolactone over supported gold catalysts. *ChemSusChem* **2011**, *4*, 1838−1843.

(74) Banerjee, B.; Singuru, R.; Kundu, S. K.; Dhanalaxmi, K.; Bai, L.; Zhao, Y.; Reddy, B. M.; Bhaumik, A.; Mondal, J. Towards rational design of core−shell catalytic nanoreactor with high performance catalytic hydrogenation of levulinic acid. *Catal. Sci. Technol.* **2016**, *6*, 5102−5115.

(75) Ortiz-Cervantes, C.; Flores-Alamo, M.; Garcìa, J. J. Hydrogenation of biomass-derived levulinic acid into γ-valerolactone catalyzed by palladium complexes. *ACS Catal.* **2015**, *5*, 1424−1431.

(76) Deng, J.; Wang, Y.; Pan, T.; Xu, Q.; Guo, Q. X.; Fu, Y. Conversion of carbohydrate biomass to γ-valerolactone by using water-soluble and reusable iridium complexes in acidic aqueous media. *ChemSusChem* **2013**, *6*, 1163−1167.

(77) Lomate, S.; Sultana, A.; Fujitani, T. Vapor phase catalytic transfer hydrogenation (CTH) of levulinic acid to γ-valerolactone over copper supported catalysts using formic acid as hydrogen source. *Catal. Lett.* **2018**, *148*, 348−358.

(78) Lomate, S.; Sultana, A.; Fujitani, T. Effect of SiO_2 support properties on the performance of Cu−SiO_2 catalysts for the hydrogenation of levulinic acid to gamma valerolactone using formic acid as a hydrogen source. *Catal. Sci. Technol.* **2017**, *7*, 3073−3083.

(79) Yuan, J.; Li, S. S.; Yu, L.; Liu, Y. M.; Cao, Y.; He, H. Y.; Fan, K. N. Copper-based catalysts for the efficient conversion of carbohydrate biomass into γ-valerolactone in the absence of externally added hydrogen. *Energy Environ. Sci.* **2013**, *6*, 3308−3313.

(80) Metzker, G.; Burtoloso, A. C. B. Conversion of levulinic acid into γ-valerolactone using $Fe_3(CO)_{12}$, mimicking a biorefinery setting by exploiting crude liquors from biomass acid hydrolysis. *Chem. Commun.* **2015**, *51*, 14199−14202.

(81) Frey, P. A.; Reed, G. H. The ubiquity of iron. *ACS Chem. Biol.* **2012**, *7*, 1477−1481.

(82) Hengne, A. M.; Malawadkar, A. V.; Biradar, N. S.; Rode, C. V. Surface synergism of an Ag−Ni/ZrO_2 nanocomposite for the catalytic transfer hydrogenation of bio-derived platform molecules. *RSC Adv.* **2014**, *4*, 9730−9736.

(83) Upare, P. P.; Jeong, M. G.; Hwang, Y. K.; Kim, D. K.; Kim, Y. D.; Hwang, D. W.; Lee, U. H.; Chang, J. S. Nickel-promoted copper-silica nanocomposite catalysts for hydrogenation of levulinic acid to lactones using formic acid as a hydrogen feeder. *Appl. Catal., A* **2015**, *491*, 127−135.

(84) Ruppert, A. M.; Jędrzejczyk, M.; Potrzebowska, N.; Kaźmierczak, K.; Brzezińska, M.; Sneka-Płatek, O.; Sautet, P.; Keller, N.; Michel, C.; Grams, J. Supported gold−nickel nano-alloy as a highly efficient catalyst in levulinic acid hydrogenation with formic acid as an internal hydrogen source. *Catal. Sci. Technol.* **2018**, *8*, 4318−4331.

(85) Soszka, E.; Reijneveld, H.; Jedrzejczyk, M.; Rzeznicka, I. I.; Grams, J.; Ruppert, A. M. Chlorine influence on palladium doped nickel catalysts in levulinic acid hydrogenation with formic acid as hydrogen source. *ACS Sustainable Chem. Eng.* **2018**, *6*, 14607−14613.

(86) Hussain, S. K.; Velisoju, V. K.; Rajan, N. P.; Kumar, B. P.; Chary, K. V. R. Synthesis of γ-valerolactone from levulinic acid and formic acid over Mg-Al hydrotalcite like compound. *Chemistry Select* **2018**, *3*, 6186−6194.

(87) Assary, R. S.; Curtiss, L. A.; Dumesic, J. A. Exploring Meerwein−Ponndorf−Verley reduction chemistry for biomass catalysis using a first-principles approach. *ACS Catal.* **2013**, *3*, 2694−2704.

(88) Dai, N.; Shang, R.; Fu, M.; Fu, Y. Transfer hydrogenation of ethyl levulinate to γ-valerolactone catalyzed by iron complexes. *Chin. J. Chem.* **2015**, *33*, 405−408.

(89) Yang, Z.; Huang, Y. B.; Guo, Q. X.; Fu, Y. RANEY® Ni catalyzed transfer hydrogenation of levulinate esters to γ-valerolactone at room temperature. *Chem. Commun.* **2013**, *49*, 5328−5330.

(90) Chia, M.; Dumesic, J. A. Liquid-phase catalytic transfer hydrogenation and cyclization of levulinic acid and its esters to γ-valerolactone over metal oxide catalysts. *Chem. Commun.* **2011**, *47*, 12233−12235.

(91) Song, J.; Zhou, B.; Zhou, H.; Wu, L.; Meng, Q.; Liu, Z.; Han, B. Porous zirconium−phytic acid hybrid, a highly efficient catalyst for Meerwein−Ponndorf−Verley reductions. *Angew. Chem., Int. Ed.* **2015**, *54*, 9399−9403.

(92) Sha, Y.; Xiao, Z.; Zhou, H.; Yang, K.; Song, Y.; Li, N.; He, R.; Zhi, K.; Liu, Q. Direct use of humic acid mixtures to construct efficient Zr-containing catalysts for Meerwein−Ponndorf−Verley reactions. *Green Chem.* **2017**, *19*, 4829−4837.

(93) Zhou, S.; Dai, F.; Xiang, Z.; Song, T.; Liu, D.; Lu, F.; Qi, H. Zirconium−lignosulfonate polyphenolic polymer for highly efficient hydrogen transfer of biomass-derived oxygenates under mild conditions. *Appl. Catal., B* **2019**, *248*, 31−43.

(94) Leng, Y.; Shi, L.; Du, S.; Jiang, J.; Jiang, P. A tannin-derived zirconium-containing porous hybrid for efficient Meerwein−Ponndorf−Verley reduction under mild conditions. *Green Chem.* **2020**, *22*, 180−186.

(95) Tang, X.; Chen, H.; Hu, L.; Hao, W.; Sun, Y.; Zeng, X.; Lin, L.; Liu, S. Conversion of biomass to γ-valerolactone by catalytic transfer hydrogenation of ethyl levulinate over metal hydroxides. *Appl. Catal., B* **2014**, *147*, 827−834.

(96) Song, J.; Wu, L.; Zhou, B.; Zhou, H.; Fan, H.; Yang, Y.; Meng, Q.; Han, B. A new porous Zr-containing catalyst with a phenate group, an efficient catalyst for the catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone. *Green Chem.* **2015**, *17*, 1626−1632.

(97) 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.

(98) Enumula, S. S.; Gurram, V. R. B.; Kondeboina, M.; Burri, D. R.; Kamaraju, S. R. R. ZrO_2/SBA-15 as an efficient catalyst for the production of γ-valerolactone from biomass-derived levulinic acid in the vapour phase at atmospheric pressure. *RSC Adv.* **2016**, *6*, 20230−20239.

(99) Yang, T.; Li, H.; He, J.; Liu, Y.; Zhao, W.; Wang, Z.; Ji, X.; Yang, S. Porous Ti/Zr microspheres for efficient transfer hydrogenation of biobased ethyl levulinate to γ-valerolactone. *ACS Omega* **2017**, *2*, 1047−1054.

(100) Hu, L.; Li, N.; Dai, X.; Guo, Y.; Jiang, Y.; He, A.; Xu, J. Highly efficient production of 2,5-dihydroxymethylfuran from biomass-derived 5-hydroxymethylfurfural over an amorphous and mesoporous zirconium phosphonate catalyst. *J. Energy Chem.* **2019**, *37*, 82−92.

(101) He, J.; Li, H.; Xu, Y.; Yang, S. Dual acidic mesoporous KIT silicates enable one-pot production of γ-valerolactone from biomass derivatives via cascade reactions. *Renewable Energy* **2020**, *146*, 359−370.

(102) Valekar, A. H.; Cho, K. H.; Chitale, S. K.; Hong, D. Y.; Cha, G. Y.; Lee, U. H.; Hwang, D. W.; Serre, C.; Chang, J. S.; Hwang, Y. K. Catalytic transfer hydrogenation of ethyl levulinate to γ-valerolactone over zirconium-based metal−organic frameworks. *Green Chem.* **2016**, *18*, 4542−4552.

(103) Xue, Z.; Jiang, J.; Li, G.; Zhao, W.; Wang, J.; Mu, T. Zirconium−cyanuric acid coordination polymer, highly efficient catalyst for conversion of levulinic acid to γ-valerolactone. *Catal. Sci. Technol.* **2016**, *6*, 5374−5379.

(104) Wang, T.; Xu, H.; He, J.; Zhang, Y. MPV reduction of ethyl levulinate to γ-valerolactone by the biomass-derived chitosan-supported Zr catalyst. *New J. Chem.* **2020**, *44*, 14686−14694.

(105) Xie, C.; Song, J.; Zhou, B.; Hu, J.; Zhang, Z.; Zhang, P.; Jiang, Z.; Han, B. Porous hafnium phosphonate, novel heterogeneous catalyst for conversion of levulinic acid and esters into γ-valerolactone. *ACS Sustainable Chem. Eng.* **2016**, *4*, 6231−6236.

(106) Li, H.; Yang, T.; Fang, Z. Biomass-derived mesoporous Hf-containing hybrid for efficient Meerwein-Ponndorf-Verley reduction at low temperatures. *Appl. Catal., B* **2018**, *227*, 79−89.

(107) Boot, M., Ed.; *Biofuels from Lignocellulosic Biomass: Innovations beyond Bioethanol*; Wiley-VCH: Weinheim, Germany, 2016.

(108) De, S.; Dutta, S.; Saha, B. One-pot conversions of lignocellulosic and algal biomass into liquid fuels. *ChemSusChem* **2012**, *5*, 1826−1833.

(109) Mitra, J.; Zhou, X.; Rauchfuss, T. Pd/C-catalyzed reactions of HMF, decarbonylation, hydrogenation, and hydrogenolysis. *Green Chem.* **2015**, *17*, 307−313.

(110) Thananatthanachon, T.; Rauchfuss, T. Efficient production of the liquid fuel 2,5-dimethylfuran from fructose using formic acid as a reagent. *Angew. Chem., Int. Ed.* **2010**, *49*, 6616−6618.

(111) Yang, P.; Xia, Q.; Liu, X.; Wang, Y. Catalytic transfer hydrogenation/hydrogenolysis of 5-hydroxymethylfurfural to 2,5-dimethylfuran over Ni-Co/C catalyst. *Fuel* **2017**, *187*, 159−166.

(112) Fu, Z.; Wang, Z.; Lin, W.; Song, W. Conversion of furan derivatives for preparation of biofuels over Ni−Cu/C catalyst. *Energy Sources, Part A* **2017**, *39*, 1176−1181.

(113) Fu, Z.; Wang, Z.; Lin, W.; Song, W.; Li, S. High efficient conversion of furfural to 2-methylfuran over Ni-Cu/Al_2O_3 catalyst with formic acid as a hydrogen donor. *Appl. Catal., A* **2017**, *547*, 248−255.

(114) Nagpure, A. S.; Gogoi, P.; Lucas, N.; Chilukuri, S. V. Novel Ru nanoparticle catalysts for the catalytic transfer hydrogenation of biomass-derived furanic compounds. *Sustainable Energy Fuels* **2020**, *4*, 3654−3667.

(115) Wei, J.; Wang, T.; Liu, H.; Li, M.; Tang, X.; Sun, Y.; Zeng, X.; Hu, L.; Lei, T.; Lin, L. Highly efficient reductive etherification of 5-hydroxymethylfurfural to 2,5-bis(alkoxymethyl)furans as biodiesel components over Zr-SBA catalyst. *Energy Technol.* **2019**, *7*, 1801071.

(116) Tian, M.; McCormick, R. L.; Luecke, J.; de Jong, E.; van der Waal, J. C.; van Klink, G. P. M.; Boot, M. D. Anti-knock quality of sugar derived levulinic esters and cyclic ethers. *Fuel* **2017**, *202*, 414−425.

(117) Jae, J.; Mahmoud, E.; Lobo, R. F.; Vlachos, D. G. Cascade of liquid-phase catalytic transfer hydrogenation and etherification of 5-hydroxymethylfurfural to potential biodiesel components over Lewis acid zeolites. *ChemCatChem* **2014**, *6*, 508−513.

(118) Shinde, S.; Rode, C. Cascade reductive etherification of bioderived aldehydes over Zr-Based Catalysts. *ChemSusChem* **2017**, *10*, 4090.

(119) Luo, J.; Yu, J.; Gorte, R. J.; Mahmoud, E.; Vlachos, D. G.; Smith, M. A. The effect of oxide acidity on HMF etherification. *Catal. Sci. Technol.* **2014**, *4*, 3074−3081.

(120) Hwang, K. R.; Choi, I. H.; Choi, H. Y.; Han, J. S.; Lee, K. H.; Lee, J. S. Biofuel production from crude Jatropha oil, addition effect of formic acid as an in-situ hydrogen source. *Fuel* **2016**, *174*, 107−113.

(121) Wang, J.; Xu, L.; Nie, R.; Lyu, X.; Lu, X. Bifunctional CuNi/CoOx catalyst for mild-temperature in situ hydrodeoxygenation of fatty acids to alkanes using isopropanol as hydrogen source. *Fuel* **2020**, *265*, 116913.

(122) Gandarias, I.; Arias, P. L.; Fernandez, S. G.; Requies, J.; El Doukkali, M.; Güemez, M. B. Hydrogenolysis through catalytic transfer hydrogenation, Glycerol conversion to 1,2-propanediol. *Catal. Today* **2012**, *195*, 22−31.

(123) Yuan, J.; Li, S.; Yu, L.; Liu, Y.; Cao, Y. Efficient catalytic hydrogenolysis of glycerol using formic acid as hydrogen source. *Chin. J. Catal.* **2013**, *34*, 2066−2074.

(124) Musolino, M. G.; Scarpino, L. A.; Mauriello, F.; Pietropaolo, R. Selective transfer hydrogenolysis of glycerol promoted by palladium catalysts in absence of hydrogen. *Green Chem.* **2009**, *11*, 1511−1513.

(125) Zhou, C. H.; Deng, K.; Di Serio, M.; Xiao, S.; Tong, D. S.; Li, L.; Lin, C. X.; Beltramini, J.; Zhang, H.; Yu, W. H. Cleaner hydrothermal hydrogenolysis of glycerol to 1,2-propanediolover Cu/oxide catalysts without addition of external hydrogen. *Mol. Catal.* **2017**, *432*, 274−284.

(126) Cai, F.; Pan, D.; Ibrahim, J. J.; Zhang, J.; Xiao, G. Hydrogenolysis of glycerol over supported bimetallic Ni/Cu catalysts with and without external hydrogen addition in a fixed-bed flow reactor. *Appl. Catal., A* **2018**, *564*, 172−182.

(127) Liu, X.; Yin, B.; Zhang, W.; Yu, X.; Du, Y.; Zhao, S.; Zhang, G.; Liu, M.; Yan, H.; Abbotsi-Dogbey, M.; Al-Absi, S. T.; Yeredil, S.; Yang, C.; Shen, J.; Yan, W.; Jin, X. Catalytic Transfer Hydrogenolysis of Glycerol over Heterogeneous Catalysts: AShort Review on Mechanistic Studies. *Chem. Rec.* **2021**, *21*, 1−20.

(128) Laurichesse, S.; Averous, L. Chemical modification of lignins, Towards biobased polymers. *Prog. Polym. Sci.* **2014**, *39*, 1266−1290.

(129) Beckham, G. T. *Lignin Valorization, Emerging Approaches*; Energy and Environmental Science Series; Royal Society of Chemistry, 2018.

(130) Løhre, C.; Barth, T.; Kleinert, M. The effect of solvent and input material pretreatment on product yield and composition of bio-oils from lignin solvolysis. *J. Anal. Appl. Pyrolysis* **2016**, *119*, 208−216.

(131) Gasser, C. A.; Čvančarová, M.; Ammann, E. M.; Schäffer, A.; Shahgaldian, P.; Corvini, P. F. X. Sequential lignin depolymerization by combination of biocatalytic and formic acid/formate treatment steps. *Appl. Microbiol. Biotechnol.* **2017**, *101*, 2575−2588.

(132) Holmelid, B.; Barth, T.; Brusletto, R.; Kleinert, M. Production of monomeric phenols by formic acid assisted hydrous liquefaction of lignin. *Biomass Bioenergy* **2017**, *105*, 298−309.

(133) Oregui-Bengoechea, M.; Hertzberg, A.; Miletic, N.; Arias, P. L.; Barth, T. Simultaneous catalytic de-polymerization and hydrodeoxygenation of lignin in water/formic acid media with Rh/Al_2O_3, Ru/Al_2O_3 and Pd/Al_2O_3 as bifunctional catalysts. *J. Anal. Appl. Pyrolysis* **2015**, *113*, 713−722.

(134) Riaz, A.; Kim, C. S.; Kim, Y.; Kim, J. High-yield and high-calorific bio-oil production from concentrated sulfuric acid hydrolysis lignin in supercritical ethanol. *Fuel* **2016**, *172*, 238−247.

(135) Oregui-Bengoechea, M.; Gandarias, I.; Arias, P. L.; Barth, T. Unraveling the role of formic acid and the type of solvent in the catalytic conversion of lignin, a holistic approach. *ChemSusChem* **2017**, *10*, 754.

(136) Shao, L.; Zhang, Q.; You, T.; Zhang, X.; Xu, F. Microwave-assisted efficient depolymerization of alkaline lignin in methanol/formic acid media. *Bioresour. Technol.* **2018**, *264*, 238−243.

(137) Kloekhorst, A.; Shen, Y.; Yie, Y.; Fang, M.; Heeres, H. J. Catalytic hydrodeoxygenation and hydrocracking of Alcell (R) lignin in alcohol/formic acid mixtures using a Ru/C catalyst. *Biomass Bioenergy* **2015**, *80*, 147−161.

(138) Toledano, A.; Serrano, L.; Labidi, J.; Pineda, A.; Balu, A. M.; Luque, R. Heterogeneously catalysed mild hydrogenolytic depolymerisation of lignin under microwave irradiation with hydrogen-donating solvents. *ChemCatChem* **2013**, *5*, 977−985.

(139) Toledano, A.; Serrano, L.; Balu, A. M.; Luque, R.; Pineda, A.; Labidi, J. Fractionation of organosolv lignin from olive tree clippings and its valorization to simple phenolic compounds. *ChemSusChem* **2013**, *6*, 529−536.

(140) Jiang, L.; Guo, H.; Li, C.; Zhou, P.; Zhang, Z. Selective cleavage of lignin and lignin model compounds without external hydrogen, catalyzed by heterogeneous nickel catalysts. *Chem. Sci.* **2019**, *10*, 4458.

(141) Yang, J.; Zhao, L.; Liu, S.; Wang, Y.; Dai, L. High-quality bio-oil from one-pot catalytic hydrocracking of Kraft lignin over supported noble metal catalysts in isopropanol system. *Bioresour. Technol.* **2016**, *212*, 302−310.

(142) Ferrini, P.; Rinaldi, R. Catalytic Biorefining of Plant Biomass to Non-Pyrolytic Lignin Bio-Oil and Carbohydrates through Hydrogen Transfer Reactions. *Angew. Chem., Int. Ed.* **2014**, *53*, 8634−8639.

(143) Kong, L.; Liu, C.; Gao, J.; Wang, Y.; Dai, L. Efficient and controllable alcoholysis of Kraft lignin catalyzed by porous zeolite supported nickel-copper catalyst. *Bioresour. Technol.* **2019**, *276*, 310−317.

(144) Hu, J.; Zhao, M.; Jiang, B.; Wu, S.; Lu, P. Catalytic transfer hydrogenolysis of native lignin to monomeric phenols over a Ni−Pd bimetallic catalyst. *Energy Fuels* **2020**, *34* (8), 9754−9762.

(145) Zeng, Y.; Wang, Z.; Lin, W.; Song, W.; Christensen, J. M.; Jensen, A. D. Hydrodeoxygenation of phenol over Pd catalysts by in-situ generated hydrogen from aqueous reforming of formic acid. *Catal. Commun.* **2016**, *82*, 46−49.

(146) Zeng, Y.; Wang, Z.; Lin, W.; Song, W. In situ hydrodeoxygenation of phenol with liquid hydrogen donor over three supported noble-metal catalysts. *Chem. Eng. J.* **2017**, *320*, 55−62.

(147) Singh, A. K.; Jang, S.; Kim, J. Y.; Sharma, S.; Basavaraju, K.; Kim, M. G.; Kim, K. R.; Lee, J. S.; Lee, H. H.; Kim, D. P. One-pot defunctionalization of lignin-derived compounds by dual-functional $Pd_{50}Ag_{50}/Fe_3O_4$/N-rGO catalyst. *ACS Catal.* **2015**, *5*, 6964−6972.

(148) Nie, R.; Peng, X.; Zhang, H.; Yu, X.; Lu, X.; Zhou, D.; Xia, Q. Transfer hydrogenation of bio-fuel with formic acid over biomass-derived N-doped carbon supported acid-resistant Pd catalyst. *Catal. Sci. Technol.* **2017**, *7*, 627−634.

(149) Yang, H.; Nie, R.; Xia, W.; Yu, X.; Jin, D.; Lu, X.; Zhou, D.; Xia, Q. Co-embedded within biomass-derived mesoporous N-doped carbon as an acid-resistant and chemoselective catalyst for transfer hydrodeoxygenation of biomass with formic acid. *Green Chem.* **2017**, *19*, 5714−5722.

(150) Tadele, K.; Verma, S.; Gonzalez, M. A.; Varma, R. S. A sustainable approach to empower the bio-based future: upgrading of biomass via process intensification. *Green Chem.* **2017**, *19*, 1624−1627.

(151) Gao, Z.; Liu, F.; Wang, L.; Luo, F. Highly efficient transfer hydrodeoxygenation of vanillin over Sn4+-induced highly dispersed Cu-based catalyst. *Appl. Surf. Sci.* **2019**, *480*, 548.

(152) Cheng, H.; Liu, R.; Wang, Q.; Wu, C.; Yu, Y.; Zhao, F. Selective reduction of phenol derivatives to cyclohexanones in water under microwave irradiation. *New J. Chem.* **2012**, *36*, 1085−1090.

(153) Chen, A.; Li, Y.; Chen, J.; Zhao, G.; Ma, L.; Yu, Y. Selective Hydrogenation of Phenol and Derivatives over Polymer-Functionalized Carbon-Nanofiber-Supported Palladium Using Sodium Formate as the Hydrogen Source. *ChemPlusChem* **2013**, *78*, 1370−1378.

(154) Zhang, D.; Ye, F.; Xue, T.; Guan, Y.; Wang, Y. M. Transfer hydrogenation of phenol on supported Pd catalysts using formic acid as an alternative hydrogen source. *Catal. Today* **2014**, *234*, 133−138.

(155) Patil, R. D.; Sasson, Y. Selective transfer hydrogenation of phenol to cyclohexanone on supported palladium catalyst using potassium formate as hydrogen source under open atmosphere. *Appl. Catal., A* **2015**, *499*, 227−231.

(156) Valentini, F.; Santillo, N.; Petrucci, C.; Lanari, D.; Petricci, E.; Taddei, M.; Vaccaro, L. Continuous-Flow Palladium-Catalyzed Synthesis of Cyclohexanones from Phenols using Sodium Formate as a Safe Hydrogen Source. *ChemCatChem* **2018**, *10*, 1277−1281.

(157) Trombettoni, V.; Ferlin, F.; Valentini, F.; Campana, F.; Silvetti, M.; Vaccaro, L. POLITAG-Pd(0) catalyzed continuous flow hydrogenation of lignin-derived phenolic compounds using sodium formate as a safe H-source. *Mol. Catal.* **2021**, *509*, 111613.

(158) Zhao, C.; Zhang, Z.; Liu, Y.; Shang, N.; Wang, H.-J.; Wang, C.; Gao, Y. Palladium Nanoparticles Anchored on Sustainable Chitin for Phenol Hydrogenation to Cyclohexanone. *ACS Sustainable Chem. Eng.* **2020**, *8*, 12304−12312.

(159) Chen, Z.; Zeng, H.; Gong, H.; Wang, H.; Li, C.-J. Palladium-catalyzed reductive coupling of phenols with anilines and amines: efficient conversion of phenolic lignin model monomers and analogues to cyclohexylamines. *Chem. Sci.* **2015**, *6*, 4174−4178.

(160) Jumde, V. R.; Petricci, E.; Petrucci, C.; Santillo, N.; Taddei, M.; Vaccaro, L. Domino Hydrogenation−Reductive Amination of Phenols, a Simple Process To Access Substituted Cyclohexylamines. *Org. Lett.* **2015**, *17*, 3990−3993.

(161) Zhang, J.; Liu, Y.; Yang, S.; Wei, J.; He, L.; Peng, L.; Tang, X.; Ni, Y. Highly selective conversion of furfural to furfural alcohol or levulinate ester in one-pot over Zr_2@SBA-15 and its kinetic behaviour. *ACS Sustainable Chem. Eng.* **2020**, *8*, 5584−5594.

(162) Valekar, A. H.; Lee, M.; Yoon, W.; Kwak, J.; Hong, D. Y.; Oh, K. R.; Cha, G. Y.; kwon, Y. U.; Jung, J.; Chang, J. S.; Hwang, Y. K. Catalytic transfer hydrogenation of furfural to furfuryl alcohol under mild conditions over Zr-MOFs: Exploring the role of metal node coordination and modification. *ACS Catal.* **2020**, *10*, 3720−3732.

(163) Naguib, M.; Tang, W.; Browning, K.; Veith, G. M.; Maliekkal, V.; Neurock, M.; Villa, A. Catalytic activity of Ti-Based M-Xenes for the hydrogenation of furfural. *ChemCatChem* **2020**, *12*, 5733−5742.

(164) He, J.; Li, H.; Riisager, A.; Yang, S. Catalytic transfer hydrogenation of furfural to furfuryl alcohol with recyclable Al-Zr@Fe mixed oxides. *ChemCatChem* **2018**, *10*, 430−438.

(165) Ma, M.; Hou, P.; Zhang, P.; Cao, J.; Liu, H.; Yue, H.; Tian, G.; Feng, S. Magnetic Fe_3O_4 nanoparticles as easily separable catalysts for efficient catalytic transfer hydrogenation of biomass derieved furfural to furfuryl alcohol. *Appl. Catal., A* **2020**, *602*, 117709.

(166) Wang, T.; Zhang, J.; Xie, W.; Tang, Y.; Guo, D.; Ni, Y. Catalytic transfer hydrogenation of bio-based HMF to 2,5-bis(hydroxymethyl)-furan over Ru/CO_3O_4. *Catalysts* **2017**, *7*, 92.

(167) Song, J.; Hua, M.; Huang, X.; Visa, A.; Wu, T.; Fan, H.; Hou, M.; Zhang, Z.; Han, B. Highly efficient Meerwein-Ponndorf-Verley reductions over a robust zirconium-organoboronic acid hybrid. *Green Chem.* **2021**, *23*, 1259−1265.