

Review

Catalytic Transfer Hydrogenolysis as an Effective Tool for the Reductive Upgrading of Cellulose, Hemicellulose, Lignin, and Their Derived Molecules

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Abstract: Lignocellulosic biomasses have a tremendous potential to cover the future demand of bio-based chemicals and materials, breaking down our historical dependence on petroleum resources. The development of green chemical technologies, together with the appropriate eco-politics, can make a decisive contribution to a cheap and effective conversion of lignocellulosic feedstocks into sustainable and renewable chemical building blocks. In this regard, the use of an indirect H-source for reducing the oxygen content in lignocellulosic biomasses and in their derived platform molecules is receiving increasing attention. In this contribution we highlight recent advances in the transfer hydrogenolysis of cellulose, hemicellulose, lignin, and of their derived model molecules promoted by heterogeneous catalysts for the sustainable production of biofuels and biochemicals.

Keywords: lignocellulosic biomasses; H-donor molecules; hydrogenolysis; catalytic transfer hydrogenolysis reactions; heterogeneous catalysis; cellulose; hemicellulose; lignin; glycerol; polyols; furfural; levulinic acid; aromatic ethers

1. Introduction

The hegemony of fossil resources is declining by now. In the last few decades, industrial chemistry has accepted the challenge for the sustainable production of chemicals and energy by using renewable biomasses as starting supplies [1]. Moreover, the changes in consumer attitudes towards “green” products, as well as government initiatives for sustainable development programs and regulations, are surely the key driving factors for the development of the bio-based chemical industries and refineries [2–6].

While many criticisms have been raised towards the first generation of bio-energies and biofuels since they are in direct competition with human and animal food, reducing the land availability [7], we have recently achieved significant progress in the production of chemical building blocks and intermediates from lignocellulosic wastes and residues [8–20]. This is because their use in the chemical industry presents several advantages including: (i) the production of less toxic by-products and lower environmental risks, (ii) the reduction of CO₂ emissions, (iii) a minor dependence on fossil resources and/or foreign commodities, and (iv) the use of indigenous raw materials that can add value in many agriculture products or processes.

Three different approaches have been used, so far, by the bio-based refineries: (i) the production of the identical petrochemical building block starting from the lignocellulosic platform molecules, (ii) the use of platform molecules to produce the first petrochemical intermediates, and (iii) to synthesize new products alternative to the petrochemical ones starting from the platform molecules and/or their intermediates. It is expected that the market relative to all bio-based chemicals and materials will increase at an annual growth rate of 16.53% in the forecast period 2018–2026 [21] with a total product value of about 103 billion euros by 2050 [22].

Natural abundance, renewability, and recyclability of non-edible lignocellulose-based wastes and residues make them one of the most eco-attractive and alternative candidates to replace unrenewable petroleum-based resources in modern industrial chemistry.

The chemical structure of lignocellulosic biomasses allows the production of a wide spectra of platform chemicals (Figure 1) [23].

Cellulose and hemicellulose allow the production of C5–C6 sugars that can be easily converted into aliphatic acids, ethers, esters, polyols, and alcohols [24–29], while lignin is a source of aromatic compounds [30–33].

Cellulose is a linear glucosidic-based polymer with a degree of polymerization of around 100,000 units containing 49 wt% of oxygen [23,34]. Hemicellulose has a heterogeneous architecture based on pentoses, hexoses, and sugar acids with a degree of polymerization ranging from 100 to 200 units in which anhydrous sugars alternate with five- and six-carbon atoms and an overall oxygen content of 54 wt% is present [23,34]. Lignin is a branched polymer mainly consisting of phenols whose oxygen content is between 12 and 29 wt% [23,34].

In order to lower the oxygen content in cellulose, hemicellulose, and lignin—as well as in their relative derived molecules—three different chemical ways can be followed: (i) the removal of small molecules of oxidized carbon (CO_2 , formaldehyde, and formic acid), (ii) the elimination of water through dehydration processes, and (iii) the direct “lysis” of the C–O bond by molecular H_2 with the concurrent formation of a molecule of water.

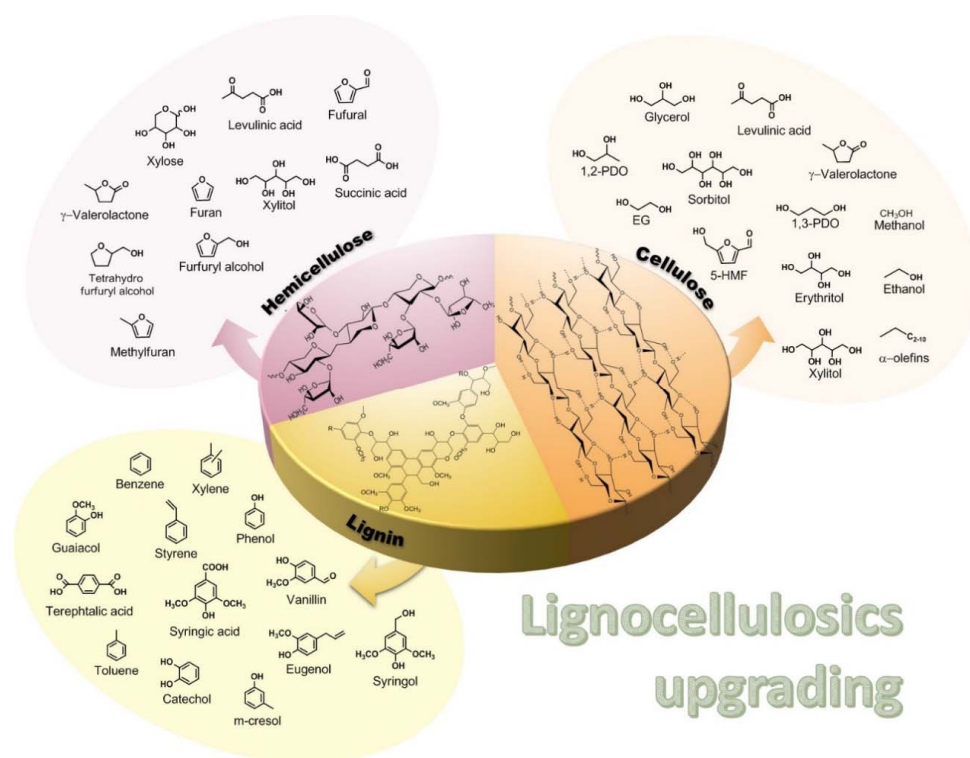


Figure 1. Chemical structure of cellulose, hemicellulose, lignin, and their relative derived molecules.

Hydrogenolysis is a very well-known reaction in which carbon–carbon or carbon–heteroatom bonds are cleaved, generally in the presence of a homogeneous or heterogeneous catalyst, that has been efficiently adopted for the reduction of the oxygen content in lignocellulosic components and in their derived platform chemicals [35–37].

The reductive valorization of lignocellulosic biomasses and their relative derived molecules are generally conducted in the presence of a solvent in order to limit their thermal decomposition. As a consequence, due to the well-known poor solubility of H₂ in most solvents, hydrogenolysis processes require the direct use of high-pressure molecular hydrogen with all concurrent problems that this entails, including purchase, transport, costly infrastructures, and safety hazards.

Simple organic molecules represent a valid green alternative to the direct use of molecular H₂ in reductive processes [38–40]. The ability of alcohols as potential sources of hydrogen in catalytic transfer hydrogenolysis (CTH) reactions can be correlated with their reduction potentials (defined as the difference of the standard molar free energy of formation between the alcohol and the corresponding carbonyl compound).

In CTH reactions, the use of H-donor molecules as solvent reduces the safety problems of handling high-pressure and explosive hydrogen gas, reducing, at the same time, costs and complexity of bio-based industrial chemical plants. Moreover, at present, many H-donor molecules can be easily produced from renewable feedstocks [41]. Nonetheless of importance, H-donor molecules, due to their lower hydrogenation ability with respect to molecular H₂, generally allow a higher production of aromatic compounds.

Formic acid was also efficiently used as a potential liquid storage medium capable of releasing H₂ under mild conditions via catalytic decomposition [42,43]. Formic acid can be formed by renewable technologies, namely from the lignocellulosic biomass or from electrochemical reduction of CO₂, which makes it an environmentally friendly source for both high-purity hydrogen production and hydrogen donor for CTH reactions [44].

In this review, we examine the recent progress in the CTH of cellulose, hemicellulose, lignin, and their relative derived molecules promoted by heterogeneous catalysts, focusing our attention in the C–O and C–C bond breaking. The overall aim is to offer a complete overview of the huge potential offered by the catalytic transfer hydrogenolysis reaction in the upgrading lignocellulosic resources for the sustainable production of biofuels and biochemicals.

2. Catalytic Transfer Hydrogenolysis Applied to Cellulose and to Cellulose Derivable Molecules

2.1. Glycerol and Other Polyols

Among the family of cellulose derived molecules, C₆–C₃ polyols are of particular interest, being used as a starting resource for several building block chemicals.

Glycerol is the main by-product in biodiesel manufacture and, at the same time, it is easily derivable from cellulose thus being a promising renewable molecule to obtain, among others, 1,2-propanediol (1,2-PDO) which is an important polymer precursor. Therefore, the conversion of glycerol into 1,2-PDO, through the catalytic transfer hydrogenolysis, becomes an interesting tool. The main results present in literature concerning several catalytic substrates, applied to the CTH of glycerol, are summarized in Table 1.

The catalytic transfer hydrogenolysis (CTH) of glycerol, was performed for the first time by Pietropaolo and co-workers, using 2-propanol (2-PO) as a hydrogen donor and solvent [45]. The investigation started by using the unreduced bimetallic catalyst PdO/Fe₂O₃ and reaches complete conversion of glycerol and a high selectivity of 94% towards 1,2-propanediol (1,2-PDO), after 24 h of reaction at 180 °C. Ethanol was also used showing slightly lower selectivity to 1,2-PDO (90%) in the same operating conditions.

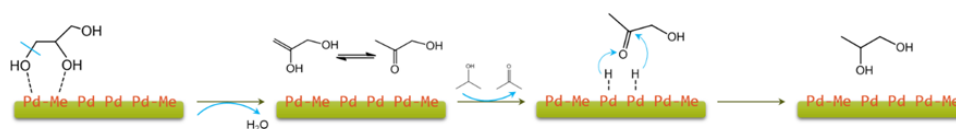
The transfer hydrogenolysis of glycerol into 1,2-propanediol, catalyzed by bimetallic Pd/Fe₃O₄ and Pd/Co₃O₄ catalysts, enlightens a mechanism in which the glycerol (i) adsorbs over the bimetallic sites

giving dehydration through the breaking a C–OH of the primary alcoholic group, and (ii) thanks to the hydrogen supplied from the 2-propanol dehydrogenation, the intermediate acetol can be hydrogenated into 1,2-propanediol (Scheme 1) [46]. Furthermore, a close correlation between the ability of catalysts towards the dehydrogenation of 2-propanol and the ability to perform CTH reactions was found [46].

Table 1. Catalytic transfer hydrogenolysis of glycerol to 1,2-propanediol.

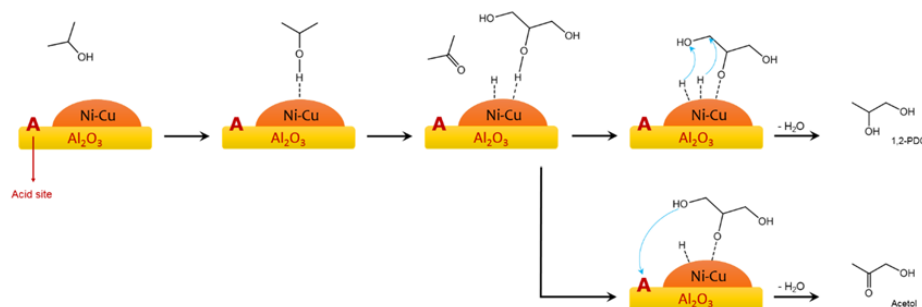
Entry	Catalyst	H-Donor ¹	Cat/Gly ²	Temp (°C)	Time (h)	Conv. (%)	1,2-PDO Select. (%)	Ref.
1	PdO/Fe ₂ O ₃	EtOH	0.237	180	24	100	90	[45]
2	PdO/Fe ₂ O ₃	2-PO	0.237	180	24	100	94	[45]
3	PdO/Fe ₂ O ₃	2-PO	0.237	180	8	96	87	[45]
4	Pd/Fe ₃ O ₄	2-PO	0.237	180	8	100	84	[45]
5	Pd/Fe ₃ O ₄	2-PO	0.207	180	24	100	56	[46]
6	Pd/Co ₃ O ₄	2-PO	0.207	180	24	100	64	[46]
7	Ni-Cu/Al ₂ O ₃	-	0.166	220	24	70.5	66.9	[47]
8	Ni-Cu/Al ₂ O ₃	2-PO	0.166	220	24	60.4	64.6	[47]
9	Ni-Cu/Al ₂ O ₃	2-PO	0.166	220	10	28.2	77.4	[48]
10	Ni-Cu/Al ₂ O ₃	MeOH	0.120	220	10	26.2	51.2	[48]
11	Ni-Cu/Al ₂ O ₃	FA	0.120	220	10	33.5	85.9	[48]
12	Ni-Cu/Al ₂ O ₃	FA	0.498	220	24	90	82	[49]
13	70Cu30Al	2-PO	-	220	5	69	90	[50]
14	20Cu/ZrO ₂	FA	-	220	18	97	95	[51]

¹ Abbreviations: EtOH: ethanol; 2-PO: 2-propanol; MeOH: methanol; FA: formic acid; ² Ratio of Cat/Gly (g/g).



Scheme 1. Mechanism of CTH of glycerol over Pd/Fe₃O₄ and Pd/Co₃O₄ catalysts. Adapted from Ref. [46]. Copyright Year 2015, Elsevier.

Gandarias et al. have deeply studied the reactivity of bimetallic catalysts Ni-Cu/Al₂O₃, prepared through the sol-gel technique, giving the best performances when pretreated at 450 °C [47–49]. At the beginning, the hydrogenolysis of glycerol was studied either in presence of molecular hydrogen or in conditions in which the hydrogen is produced in situ, through the aqueous phase reforming (APR) or through the catalytic transfer hydrogenolysis (CTH) by means of 2-propanol [47]. Results suggest that 2-propanol is a more effective hydrogen source than the aqueous-phase reforming, for the glycerol hydrogenolysis process. However, CTH of 2-propanol data are comparable to those obtained in the presence of molecular hydrogen. Two different mechanisms are involved when the hydrogenolysis of glycerol is performed in the presence of molecular hydrogen or in that of 2-PO (Scheme 2). Moreover, the deactivation of the catalyst occurs more rapidly in the presence of 2-PO, because adjacent sites are required for the donor and the acceptor processes relative to the transfer reaction, during the hydrogenation [47].



Scheme 2. Mechanism of CTH of glycerol over Ni-Cu/Al₂O₃ catalyst. Adapted from Ref. [47]. Copyright Year 2011, Elsevier.

On the other hand, by changing the hydrogen donor molecule, it is possible to improve the performance of the CTH of glycerol on using the bimetallic Ni-Cu/Al₂O₃ catalyst [49]. Gandarias et al. performed a study on the effect of the hydrogen donor molecule, by comparing methanol (MeOH), formic acid (FA) and 2-propanol [48]. Formic acid appears to be the most effective hydrogen donor molecule. The scale of efficiency, per donor molecule, follows this order: formic acid > 2-propanol > methanol. With the aim to further improve the reactivity of the Ni-Cu/Al₂O₃ catalyst, it is necessary to add formic acid and molecular hydrogen in order to obtain a conversion of glycerol of 43.9% and a selectivity to 1,2-PDO of almost 90% [48]. The kinetic study enables to understand that the hydroxyl groups of glycerol and the target product 1,2-PDO adsorb over the same acidic sites of the Al₂O₃ support. Therefore, in order to overcome this problem, it is necessary to increase the amount of catalyst and high conversion (90%) and selectivity (82%), within 24 h of reaction, were obtained [49].

Furthermore, the higher prevalence of the C–O bond cleavage is produced by a Cu-Ni alloy, whereas active Ni ensembles are responsible for both the C–C and the C–O bond cleavage, and the Cu ensembles favor mainly the C–O breaking but not the C–C one. Therefore, in the case of the reduced Ni-Cu/Al₂O₃ catalyst, the C–C bond cleavage is limited, while the activity to the C–O bond cleavage is significantly promoted [49].

Rasika et al. performed a study on the dehydration and the hydrogenolysis of glycerol by using both water and 2-propanol and screening the reactivity of Cr-based and Cu-Al catalysts [50]. Considering the hydrogenolysis of glycerol, the co-precipitated Cu-Al catalysts have shown a better performance, particularly in conditions of the CTH promoted by 2-propanol. Indeed, the 70Cu30Al catalyst reaches 69% of conversion and 90% of selectivity in 1,2-PDO within 5h of reaction. The evidence of different performances in the presence of 2-propanol instead of water indicates that the two processes are ruled by two different reaction pathways [50].

Yuan et al. investigated a series of Cu/ZrO₂-based catalysts, particularly the 20%Cu/ZrO₂, synthesized by co-precipitation, and found they can be used to convert glycerol to 1,2-PDO in high yields with formic acid as a hydrogen source. They found that the production of 1,2-PDO can be optimized using a FA/glycerol molar ratio (1:1) and a temperature of 200 °C. In this case, a yield of 1,2-PDO (94%) after 18 h is obtained [51]. Furthermore, this catalyst is also pretty stable, and reusable at least five times without losing any appreciable reactivity and selectivity [51].

In the literature, some works that report the conversion of glycerol in traditional hydrogenolysis conditions (with addition of molecular hydrogen), but operating in a solvent that can donate hydrogen, like ethanol and 2-propanol, are present (Table 2).

A bimetallic Pd-Cu/solid-base catalyst was prepared via thermal decomposition of Pd_xCu_{0.4}Mg_{5.6-x}Al₂(OH)₁₆CO₃. The hydrogenolysis of glycerol was easier on bimetallic Pd-Cu/solid-base catalysts than over separated Pd and Cu catalysts. On performing the hydrogenolysis of glycerol on Pd_{0.04}Cu_{0.4}/Mg_{5.5}Al₂O_{8.5}, at 180 °C for 10 h and 20 bar of H₂, both in ethanol and methanol solutions, conversion and selectivity to 1,2-PDO are particularly efficient [52]. Authors suggest that the performances are better than in water, and stem from the minor interaction between ethanol and the catalyst surface making more surface available for the conversion of glycerol [52,53].

Table 2. Hydrogenolysis of glycerol in presence of H-donor solvents.

Entry	Catalyst	Solvent ¹	Cat/Gly ²	Temp (°C)	Gas (bar)	Time (h)	Conv. (%)	Desired Prod. Select. (%) ³	Ref.
1	Pd _{0.04} Cu _{0.4} /Mg _{5.5} Al ₂ O _{8.5}	MeOH	0.125	180	H ₂ (20)	10	89.5	1,2-PDO (98)	[52]
2	Pd _{0.04} Cu _{0.4} /Mg _{5.5} Al ₂ O _{8.5}	EtOH	0.125	180	H ₂ (20)	10	88.0	1,2-PDO (99)	[52]
3	Rh _{0.02} Cu _{0.4} /Mg _{5.6} Al _{1.9} O _{8.6}	EtOH	0.167	180	H ₂ (20)	10	91.0	1,2-PDO (99)	[54]
4	Pd/Fe ₃ O ₄	2-PO	0.237	180	H ₂ (5)	24	100	1,2-PDO (71)	[55]
5	2Pt/20WO ₃ /ZrO ₂	EtOH	0.250	170	H ₂ (55)	12	45.7	1,3-PDO (21)	[56]

¹ Abbreviations: EtOH: ethanol; 2-PO: 2-propanol; ² Ratio of Cat/Gly (g/g); ³ Abbreviations: 1,2-PDO: 1,2-propanediol; 1,3-PDO: 1,3-propanediol.

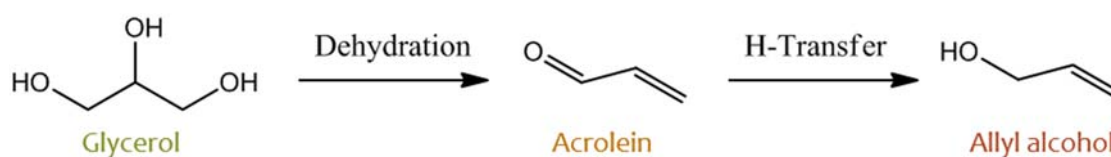
On using analogous catalysts based on Rh (Rh_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.6}), the hydrogenolysis of glycerol, in the presence of ethanol, leads to high conversion and selectivity to 1,2-PDO respectively, 91.0% and 98.7%, at 2.0 MPa H₂ and 180 °C. Moreover, this catalyst was found to be stable for five

consecutive hydrogenolysis tests in ethanol, even if the conversion decreases from 91% to 56.7% in the third cycle and then it remains constant until the fifth cycle [54]. Similarly, for the Pd-Cu/solid-base catalyst, the improved performance was attributed to a less strong interaction of the solvent with the catalytic surface [54].

Also, the bimetallic Pd/Fe₃O₄ catalyst was tested for the hydrogenolysis of glycerol using 2-propanol, as a solvent, and in mild operating conditions, such as 180 °C and only 5 bar of molecular hydrogen [55].

Gong et al. have found that it is possible to guide the selectivity of glycerol towards 1,3-propanediol using a 2Pt/20WO₃/ZrO₂ catalyst, in ethanol as solvent medium [56].

Another interesting route to valorize glycerol, like a potential biorefinery feedstock, is to obtain allyl alcohol by using H-donor molecules as a catalyst and/or solvent, through the dehydration of glycerol to acrolein followed by reductive H-transfer to allyl alcohol (Scheme 3).



Scheme 3. Schematic representation of the dehydration/H-transfer of glycerol into allyl alcohol.

Schüth and coworkers investigated the conversion of glycerol into allyl alcohol, through an initial dehydration to acrolein, by using iron oxide as a catalyst [57]. Among the operating conditions investigated, it was found that at 320 °C, it is possible to obtain an almost full conversion of glycerol and a yield to allyl alcohol of 20–25%. Particularly, the selectivity in the transfer hydrogenation to allyl alcohol, is close to 100%. This evidence has never been observed before for iron oxide catalysts, which were scarcely considered active in hydrogen transfer reactions. In this case the hydrogen donor species could be the glycerol itself and some intermediates bearing hydroxy groups [57].

Furthermore, Masuda and coworkers carried out the conversion of glycerol into allyl alcohol using iron oxide-based catalysts at 350 °C [58]. The dehydration of glycerol takes place on acid sites of catalysts, while the allyl alcohol formation occurs through a hydrogen transfer mechanism. Several alkali metals (Na, K, Rb, and Cs) were supported on the ZrO₂-FeO_x substrate and all of them give higher allyl alcohol yield suppressing glycerol dehydration due to the reduced catalyst acidic property. Particularly, the K-supported catalyst (K/ZrO₂-FeO_x) affords an allyl alcohol yield of 27 mol%. Also, in this case, the hydrogen transfer mechanism seems to take place between glycerol and hydrogen atoms deriving from the formic acid formed during the reaction, or active hydrogen species produced from the decomposition of H₂O by ZrO₂. Furthermore, the addition of Al₂O₃ (K/Al₂O₃-ZrO₂-FeO_x) enables an improvement of the stability of the catalyst during the glycerol conversion, also making the K/Al₂O₃-ZrO₂-FeO_x catalyst applicable directly to the crude glycerol (which is the waste solution obtained from biodiesel production), reaching a yield of 29% in allyl alcohol after 4–6 h of reaction [58].

Another kind of approach was followed by Bergman and coworkers, by using formic acid either as acid catalyst or solvent, with the aim to deoxygenate the glycerol into an allyl compound through the mediation of formic acid (230–240 °C) [59]. This method allows for the conversion of the 1,2-dihydroxy group to a carbon–carbon double bond. The same procedure was applied to erythritol that has been converted into 2,5-dihydrofuran at 210–220 °C [59]. During the dehydration step, formic acid acts as acid catalyst and, in the reductive step, as hydrogen donor [60].

A similar approach was followed by Fristrup and co-workers and allows for the reduction of two vicinal diols into an alkene group [61]. In this work the deoxydehydration (DODH) of glycerol and erythritol is performed with the commercially available (NH₄)₆Mo₇O₂₄·4H₂O catalyst, in the presence of 2-propanol, acting both as solvent and reductant agent. Following this approach, the total yield of reduced species (such as alkene and alcohols) can be as high as 92% at 240–250 °C. The DODH of erythritol can reach a yield of 39% to 2,5-dihydrofuran [60].

2.2. Glucose and Carbohydrates

Deng et al. have investigated the conversion of the biomass derived cellulose, starch, and glucose into γ -valerolactone without using any external hydrogen source. The first step implies the dehydration of biomass carbohydrates into levulinic and formic acids, whereas in the second step the formic acid furnishes the hydrogen necessary to the reduction of levulinic acid into γ -valerolactone [61]. The authors hydrolyzed carbohydrates (microcrystalline cellulose, α -cellulose and starch) using a solution of 0.8 M HCl at 220 °C in order to obtain levulinic acid and formic acid. In this step it is very important that the yield to formic acid has to be high enough (in excess or in equimolar amount with respect to levulinic acid) to enable the subsequent reduction to levulinic acid. In this work, the recyclable and cheap $\text{RuCl}_3/\text{PPh}_3/\text{pyridine}$ catalyst was used. In a model experiment, performed using glucose, γ -valerolactone was produced with a yield of 48% [61].

Another example of combined dehydration and transfer-hydrogenation to produce γ -valerolactone, starting from glucose or fructose, was given by Heeres [62]. In this case the process was performed in water using the trifluoroacetic acid (TFA) coupled with a heterogeneous hydrogenation catalyst (Ru/C), and also molecular hydrogen or formic acid as hydrogen donor were added [62].

Au-based catalysts were investigated by Fan and co-workers [63] and the Au/ZrO₂ catalyst shows interesting results in converting efficiently glucose into levulinic and formic acids in high yield, 54% and 58% respectively. Under the same reaction conditions also cellulose, starch, and fructose were converted [63].

Scholz et al. applied co-precipitated Cu-Ni-Al catalysts to the hydrogenation of glucose by using 1,4-butanediol as a hydrogen source to obtain sorbitol. A sorbitol yield of 67% was obtained from glucose with the catalyst remaining stable within 48 h of reaction. Similarly, several other substrates (i.e., fructose, mannose, xylose, arabinose) can be used to obtain the corresponding polyols [64].

Finally, there is also an example, given by Van Hengstum et al., where glucose is applied as H-donor substrate [65]. An equimolar mixture of glucose and fructose was employed to obtain gluconic acid and hexitols, such as sorbitol and mannitol. On using Pt/C and Rh/C catalysts, it is possible to obtain equal amounts of gluconic acid and hexitols, operating at room temperature in an aqueous alkaline medium, under nitrogen atmosphere. The general mechanism that occurs in this reaction starts from the generation of hydrogen from the dehydrogenation of glucose; the hydrogen generated is chemisorbed on the metallic surface of the catalyst and it is subsequently consumed by the co-adsorbed fructose [65].

2.3. Cellulose

At present, the work of Fukuoka and coworkers is the only example of the catalytic transfer hydrogenation applied to cellulose to obtain hexitols, such as sorbitol and mannitol, without using high molecular hydrogen pressures, but only hydrogen producing in situ molecules, such as 2-propanol (Table 3). A screening of several Ru-based catalysts was carried out by using milled cellulose in aqueous solution at 25 vol% of 2-propanol at 190 °C for 18 h [66] showing that the support plays a crucial role for the reactivity of the catalysts. Indeed, supported Ru/carbons appears the more reactive, and in particular Ru/C-Q10, Ru/CMK-3 and Ru/AC(N) show high conversion (74–81%) and high yields to sorbitol and mannitol (sum of C6-polyols 42.5–45.8%). Other supports, such as Al₂O₃, TiO₂, and ZrO₂, were found inactive. Characterization measurements, show also that the reactivity stems from the presence of highly dispersed cationic ruthenium species, which are active for the transfer hydrogenolysis [66].

Beltramini, in collaboration with Fukuoka, carried out further studies using catalysts of Ru supported on activated carbon applied to the CTH of cellulose, with the scope of optimizing the operating conditions for reactions performed in batch mode, overcoming the problem deriving from the long reaction time, in order to carry on the process with a continuous set-up in a fixed bed reactor [67]. In particular, glucose gives 82% of conversion and a 79.7% yield in hexitols at 180 °C after only 20 min of reaction, using water and 2-propanol in equal volume. The optimized conditions

were subsequently applied to the transfer hydrogenation of cellulose oligomers, which were obtained through a process of milling of crystalline cellulose impregnated with sulfuric acid. This pre-treatment was necessary in order to facilitate the solubilization of the reacting substrate, used in a continuous process, and to reduce the time of reaction. In this way, within 20 min of reaction at 180 °C, the highest yield of 35.3% to hexitols, was obtained. Furthermore, on performing the reaction in a continuous set-up, a hexitols yield of 36.4%, constant for 12 h of reaction, was obtained with a liquid hourly space velocity (LHSV) of 4.7 h⁻¹. The mechanism that enables the transfer of hydrogen from 2-propanol to glucose seems to be the di-hydride mechanism [67].

Table 3. Catalytic transfer hydrogenolysis of cellulose performed in batch conditions.

Entry	Substrate ¹	Catalyst	H-Donor ²	Temp (°C)	Time (h)	Conv. (%)	Yield Sorbitol (%)	Yield Mannitol (%)	Ref.
1	MC	Ru/C-Q10	2-PO	190	18	80.2	36.8	9.0	[66]
2	MC	Ru/CMK-3	2-PO	190	18	81.2	35.7	9.3	[66]
3	MC	Ru/AC(N)	2-PO	190	18	74.4	33.5	9.0	[66]
4	Glucose	Ru/AC(N)	2-PO	180	0.33	82	77.0	2.7	[67]
5	ACO	Ru/AC(N)	2-PO	180	0.33	100	32.2	3.1	[67]

¹ Abbreviations: MC: milled cellulose; ACO: acidified cellulose oligomers; ² Abbreviations: 2-PO: 2-propanol.

3. Catalytic Transfer Hydrogenolysis (CTH) Reactions of Hemicellulose Derived Molecules

3.1. Furfural Derivatives

Furfural (FU) is an important building block for biorefineries and chemical industries and it became a subject of interest for both academic and industrial research [68,69]. It is commercially produced by the acid-catalysed reaction of biomass containing pentose sugars [70], and it is the starting molecule for several bio-based chemical intermediates (Figure 2).

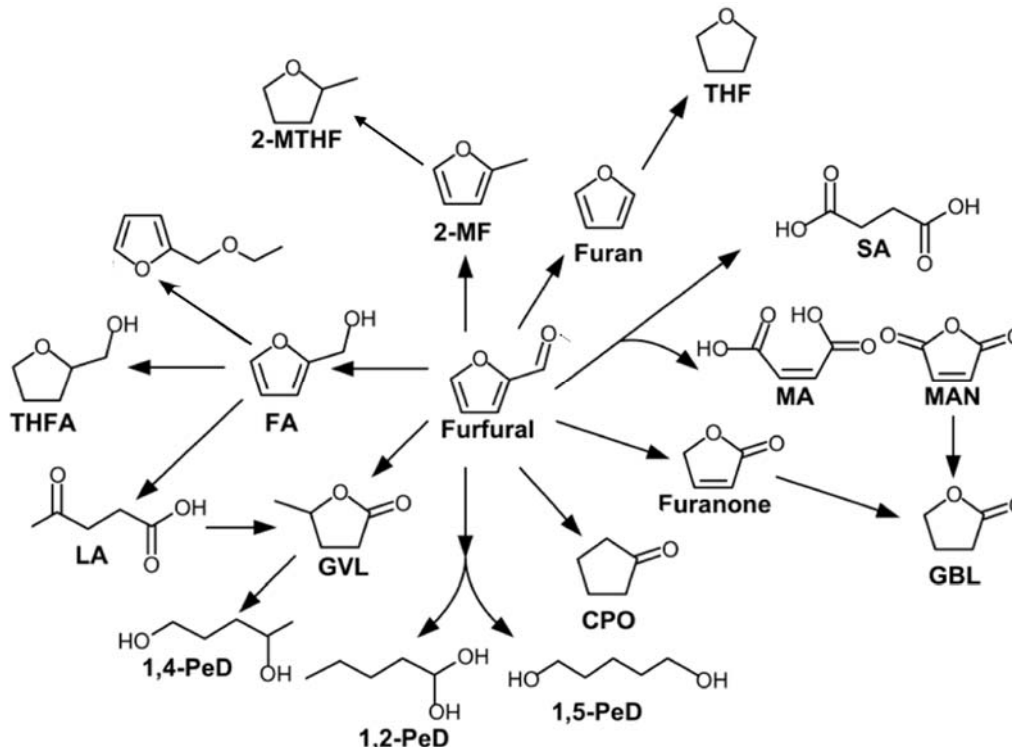


Figure 2. Examples of furfural-derived chemicals and biofuels. Adapted from Ref. [70]. Copyright Year 2016, American Chemical Society.

Among all possible reaction pathways, the hydrogenation/hydrogenolysis of FU to 2-methylfuran (MF) and 2-methyltetrahydrofuran (MTHF) gained much attention recently because of their fuel properties [70–72]. Many works were also directed to the use of alcohols as a H-source in CTH reactions of FU and an overview referring to heterogeneous metal catalysts used in the CTH of FU is presented in Table 4.

Table 4. A literature overview of the examples of metal catalysts used in CTH of FU.

Entry	Catalyst	H-Donor ¹	Reaction Conditions ² (Temperature, Time, Solvent)	Conv. (%)	Main Product ³	Yield (%)	Ref.
1	Ru/RuO ₂ /C	2-PE, 2-BU	180 °C, 10 h, 2-PE, 2-BU	100.0	MF	76.0	[73]
2	Ru/RuO _x /C	2-BU	180 °C, 10 h, TU	100.0	MF	76.0	[74]
3	Ru/C	2-PO	180 °C, 10 h, 2-PO	100.0	MF	61.0	[75]
4	Ru/NiFe ₂ O ₄	2-PO	180 °C, 10 h, 2-PO	>97.0	MF	83.0	[76]
5	Cu-Ni/Al ₂ O ₃	2-PO	230 °C, 4 h, 2-PO	>97.0	MF, MTHF	82.5	[77]
6	Cu/C	2-PO	200 °C, 5 h, 2-PO	96.3	MF	84.0	[78]
7	Cu-Pd/C	2-PO	200 °C, 4 h, 2-PO	100.0	MF, MTHF	83.9	[79]
8	Cu ₃ Al-A	MeOH	240 °C, 1.5 h, MeOH	>97.7	MF	88.2	[80]
9	Pd/Fe ₂ O ₃	2-PO	180 °C, 7.5 h, 2-PO	95.0	MF, MTHF	62.0	[81]

¹ Abbreviations: 2-PE: 2-pentanol; 2-BU: 2-butanol; 2-PO: 2-propanol; MeOH: 2-methanol; ² Abbreviations: TU: toluene; ³ Abbreviations: MF: 2-methylfuran; MTHF: 2-methyltetrahydrofuran.

Vlacos and co-workers deeply investigated the CTH of FU [73–75]. As an example, they showed the effect of alcohols, both as a solvent and hydrogen donor, in the CTH of FU to MF over the Ru/RuO₂/C catalyst [73]. The correlation between the type of alcohol and the yield to MF was proposed. MF yield increases from 0 to 68% at 180 °C according to the following order: 2-methyl-2-butanol < tert-butanol < ethanol < 1-propanol ≈ 2-propanol < 2-butanol ≈ 2-pentanol. The highest yield was obtained on using 2-butanol and 2-pentanol.

Liang research group presented a very stable Ru/NiFe₂O₄ catalyst for the CTH of FU into MF in high yield (83%) at relative mild conditions (180 °C, 10 h, 2.1 MPa N₂) by using 2-PO as H-donor [76].

Zhang et al. reported the CTH of FU with 2-propanol used as a hydrogen donor. The Cu-Ni/Al₂O₃ bimetallic catalyst, synthesized using the coprecipitation method, shows an improved activity in the mixed production of MF and MTHF compared to monometallic catalysts, with a yield of 82.5% [77].

Gong et al. [78] reported on the catalytic results related to a Cu/C catalyst with different Cu loadings (10.4; 17.1; 22.9 wt%), prepared by the ultrasound-assisted impregnation method, performed in the CTH of FU. The highest conversion of FU and the selectivity to MF were observed with a Cu loading of 17.1 wt% (96.3% FU conversion and 58.8% MF selectivity) and 2-propanol as hydrogen source. The effect of the hydrogen donor ability in the on CTH of FU to MF was also investigated. The selectivity to MF increases from 8.9% to 78.5% following the trend: 2-propanol > 2-pentanol > 2-butanol > ethanol > methanol > n-butanol > n-pentanol (180 °C, 5 h). The highest selectivity of 91.6% to MF was obtained in presence of 2-propanol and was completed within 5 h at 200 °C. This effect was attributed to the dispersing effect of the support that prevents aggregation of Cu nanoparticles.

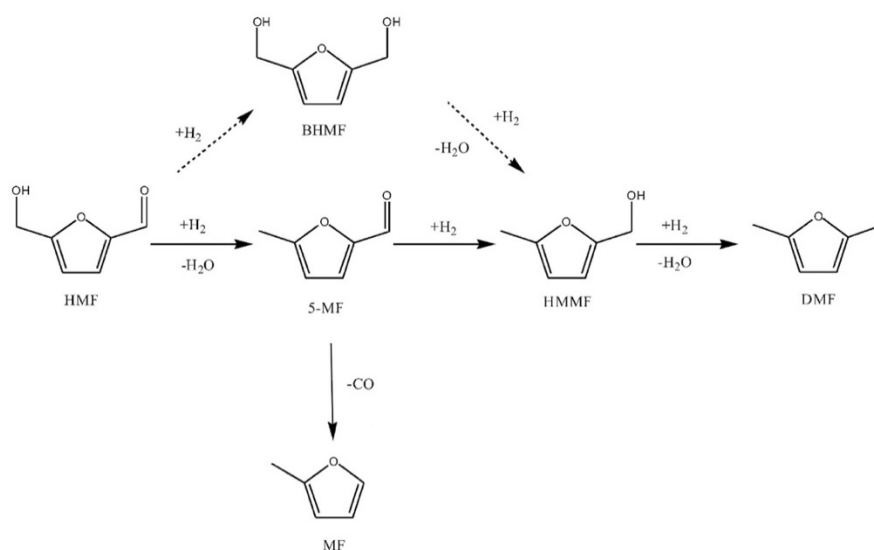
The CTH of FU into 2-MF and 2-MTHF, promoted by several bimetallic catalysts in presence of 2-propanol as H-donor, was investigated by Huang [79]. The best performances were obtained with the bimetallic Cu-Pd catalyst. Moreover, authors demonstrated that selectivity toward 2-MF or 2-MTHF can be driven by changing the Pd ratios in the Cu-Pd system.

Zhang and Chen [80] investigated a series of copper-based catalysts Cu_xAl-A (where x refers to the Cu/Al molar ratio and -A means that the catalyst was activated in H₂/N₂ flow) obtained from hydrotalcite precursors in the CTH of HMF to 2,5-dimethylfuran (DMF) with methanol both as a solvent and hydrogen source. The Cu₃Al-A catalysts showed the best catalytic activity and good recycling performances were also observed.

Scholz and co-workers [81] used monometallic Cu/Fe₂O₃, Ni/Fe₂O₃ and Pd/Fe₂O₃ with different metal loading (1–10 wt%), synthesised by the coprecipitation method, in the CTH of FU in presence of 2-propanol. The hydrogenolysis selectivity highly depends both on the metal nature and its

loading. The highest activity was observed with the 2 wt% Pd/Fe₂O₃ and was attributed to a strong metal-support interaction. A significant enhancement of the MF and MTHF yield to 62.0% was observed under continuous flow conditions.

Yang et al. compared the CTH of FU using three different hydrogen sources: 2-propanol, formic acid (FA), and molecular hydrogen in the presence of a 2%Ni-20%Co/C catalyst [82]. It has been observed that with 2-propanol, the conversion of FU was 51% at 190 °C (24 h) with the main product being furfuryl alcohol (FUA) with traces of MF. Increasing of the temperature to 210 °C causes the increasing of the conversion to 99%, but the yield to MF remains low, about 5%. When formic acid was used as an H-donor (210 °C, 24 h) the conversion was 99% and a strong increase of the yield to MF up to 79.2% was observed. This result is even better if compared to that obtained by using molecular hydrogen (33.2% yield of MF at 210 °C and 1.5 MPa for 24 h). Authors propose a relative reaction pathway (Scheme 4) [82].

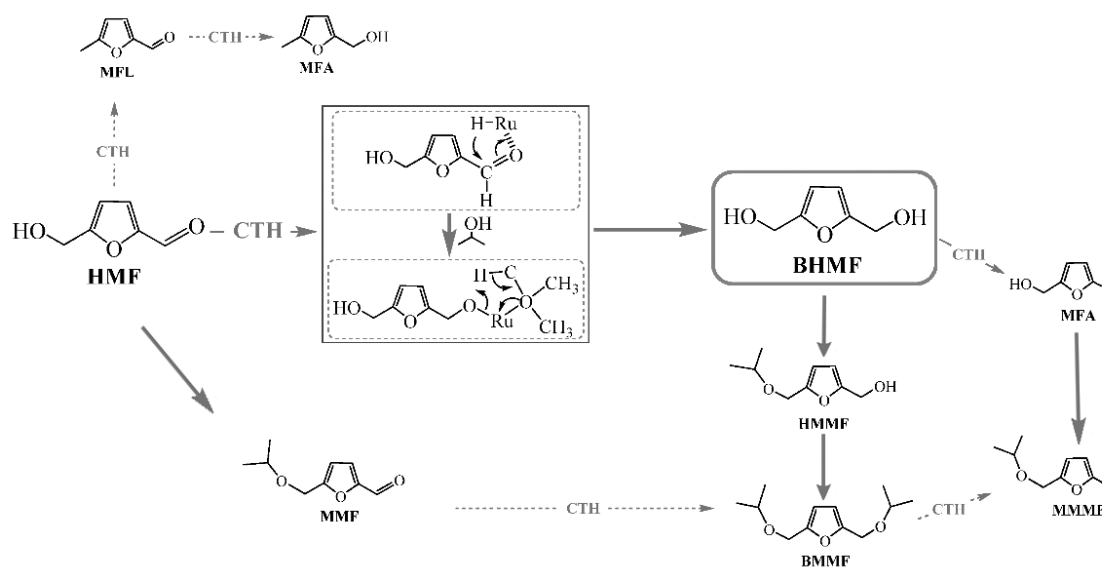


Scheme 4. Proposed reaction pathway for the CTH of HMF. Adapted from Ref. [82]. Copyright Year 2017, Elsevier.

5-hydroxymethylfurfural (HMF) can be synthesized by dehydration of hemicellulose and cellulose and it is one of the most promising feedstocks because of its abundance. In the biorefinery area, HMF is regarded as a “sleeping giant” in the field of value-added and renewable resources [83]. HMF possesses, in fact, two functional groups and can be converted to valuable compounds useful in chemical manufacturing and industrial applications.

Jae and co-workers [84] investigated the catalytic performance of a 5% Ru/C catalyst in the presence of 2-propanol. It was shown that the selectivity towards MF increases with increasing reaction temperatures. At low temperatures (100–130 °C) the primary product is 2,5-bis(hydroxymethyl)furan (BHMF) after 5 h of reaction. On increasing the temperature to 190 °C, BHMF is completely converted into MF with a selectivity up to 81%.

Wang et al. [85] used Ru/Co₃O₄ catalysts (prepared via the co-precipitation method) in the CTH of HMF to BHMF. It was found that the effect of reaction temperature and time is critical and a simplified reaction pathway from HMF to BHMF was proposed (Scheme 5).



Scheme 5. Simplified reaction pathways in the CTH of HMF to BHMF using 2-propanol and the Ru/Co₃O₄ catalyst. Adapted from Ref. [86].

Aelig et al. tested some Cu/AlO_x catalysts in the CTH of HMF to BHMF in presence of 1,4-butanediol as an H-source and 1,4-dioxane as a solvent in continuous flow reactions [86]. It has been observed that the highest conversion of HMF with a BHMF selectivity of 93% was obtained at 220 °C.

Hansen et al. [87] reported the catalytic performance of Cu-PMO (porous metal oxide) catalysts in the CTH of HMF to DMF with the supercritical methanol. The highest conversion (>99%) was obtained at 320 °C with a selectivity of 32% to DMF (3 h reaction time).

The CTH of HMF to BHMF and the following etherification to BMF were investigated by Jae et al. [88]. Reactions were catalysed by Lewis acid zeolites, Zr-Beta and Sr-Beta in the presence of 2-propanol (170 °C, 6 h). More than 80% of yield towards 5-bis(alkoxymethyl)furan (BMF) was obtained. Catalytic results showed that the etherification of HMF and BHMF with the alcohol is the fast reaction and the Meerwein–Ponndorf–Verley conversion of HMF to BHMF is the rate-determining step.

Hao et al. [89] reported that the low-cost ZrO(OH)₂ was effective in CTH of HMF to BHMF in the presence of ethanol (the HMF conversion of 94%, and an almost 89% selectivity to BHMF was obtained at 150 °C in 2.5 h).

A CTH transformation of HMF to BHMF over various magnetic zirconium hydroxides (MZH) in the presence of 2-butanol as a hydrogen source was also recently reported by Hu et al. [90]. An excellent catalytic activity was observed over MZH with Zr/Fe = 2 molar ratio, resulting in 98.4% HMF conversion and 89.6% DHMF yield at 150 °C for 5 h. A reaction mechanism for the CTH of HMF to DHMF was also proposed where the hydroxyl groups, with the aid of zirconium metal centres, were responsible for the hydride transfer via a ring structure.

Methanol as a clean and useful H-source was reported by Prof. Cavani's research group in the CTH of HMF to BHMF in the presence of MgO as a catalyst [91]. A superior 100% conversion of HMF and 100% selectivity to BHMF at 160 °C in 3 h was observed and the only methanol deriving products were CO, CO₂, and CH₄, whereas partially hydrogenated or dimerized compounds, such as formaldehydes, hemiacetals, and acetals, were not detected. Recovery experiments also showed that MgO can be recovered by filtration and re-used, but a thermal treatment is required to regenerate the partially deactivated catalyst.

Studies with FA as an H-source in the CTH of HMF were carried out to a considerably lesser extent compared to that of alcohols. In the reaction of HMF with the participation of FA as a hydrogen source (the reaction was carried out in an organic solvent (THF) with the addition of H₂SO₄ in the presence of Pd/C at 80 °C), Thananattanachon and Rauchfuss obtained a DMF yield of 94% [92]. The disadvantage of

this approach is the formation of esters as by-products. The same authors also studied some homogeneous noble metal catalysts in the CTH with FA as hydrogen source and THF as solvent [93].

Tuteja and co-workers [94] reported the CTH process of HMF to 1,6-hexanediol (HDO) under atmospheric pressure in the presence of Pd/ZrP (zirconium phosphate) with FA as a hydrogen source. A 43% yield of HDO at 140 °C in 21 h was obtained. This effect was correlated with the specific Brønsted acidity of the ZrP support.

Gao et al. report a high DMF and 2,5-dimethyltetrahydrofuran (DMTHF) yield of 96.1% and 94.6%, respectively by using a nitrogen carbon doped-Cu/MgAlO catalyst in the CTH of HMF with cyclohexanol as a hydrogen source (220 °C, 0.5 h) and suggest that highly dispersed Cu⁰ nanoparticles and electrophilic Cu⁺ species promote the hydrogen transfer and activation of both the carbonyl and hydroxyl groups in the HMF molecule [95].

3.2. Levulinic Acid

The upgrading of biomass-derived levulinic acid (LA) and its esters to γ -valerolactone (GVL) is a very important issue in the development of a sustainable and economical route to chemicals and liquid fuels. LA has attracted much attention because it is one of the top biomass derived platform molecules that can be made by the transformation of the lignocellulosic biomass followed by hydration and dehydration of hexose sugars [96,97]. The different chemical products that can be derived from LA are collected in Figure 3.

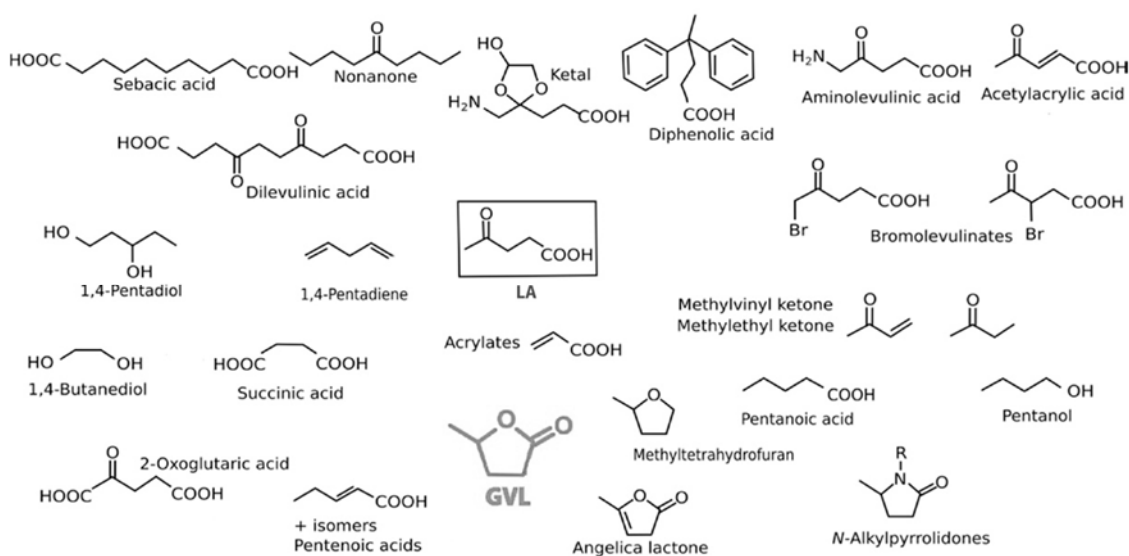


Figure 3. Chemical products derived from LA. Adapted from Ref. [98].

The CTH of LA can be an alternative way to the typical reduction of the molecule to GVL by means of molecular hydrogen and an increasing interest for this type of reactions is growing in the literature. Some of the most representative heterogeneous catalysts for the CTH of LA in the presence of alcohols as an H-source are collected in Table 5.

The CTH of LA promoted by heterogeneous Ni catalysts (Al₂O₃, ZnO, MMT and SiO₂) was reported by Rode and co-workers. GVL was obtained in very high yield (~99%) over the Ni/MMT catalyst within 1 h [98].

Yang et al. referred to a CTH process for the production of GVL from EL and 2-propanol as an H-donor [99]. The process was performed at room temperature over a RANEY[®] Ni catalyst with a yield of GVL of 99.0%.

Song and co-workers studied some porous Zr-containing catalysts bearing a phenate group in the CTH of EL to GVL [100]. The results show that Zr-HBA is very active for the conversion of EL and the GVL yield of 95.9% can be achieved in the presence of 2-butanol as an H-donor.

Tang et al. synthesised low cost and eco-friendly metal hydroxides and examined their behaviour as catalysts in the production of GVL from biomass-derived EL via CTH in the presence of 2-propanol [101,102]. A 93.6% conversion of EL and 94.5% yield to GVL was achieved at 250 °C in 1 h with 2-propanol.

Table 5. Representative heterogeneous catalysts in the CTH of LA and its derivatives using different alcohols as hydrogen donors.

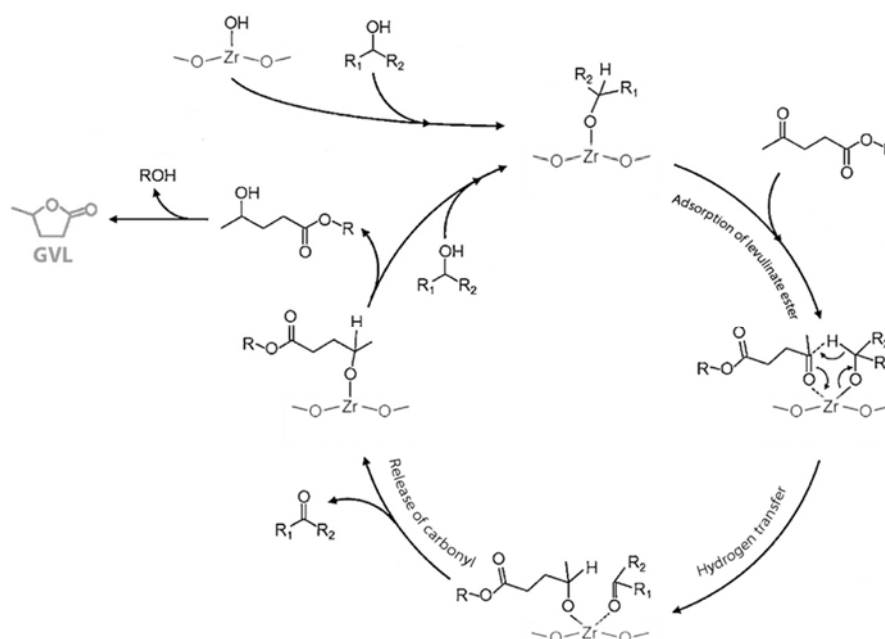
Entry	Substrate ¹	Catalyst ²	H-Donor ³	Reaction Conditions (Temperature, Time, Solvent)	Conv. (%)	GVL Yield (%)	Ref.
1	LA	Ni/MMT	2-PO	200 °C, 1 h, 2-PO	99.0	99.0	[98]
2	EL	Raney [®] Ni	2-PO	25 °C, 9 h, 2-PO	-	99.0	[99]
3	EL	Zr-HBA	2-BU	150 °C, 4 h, 2-BU	100.0	95.9	[100]
4	EL	ZrO ₂	EtOH	250 °C, 3 h, EtOH	95.5	81.5	[101]
5	EL	ZrO(OH) ₂	2-PO	200 °C, 1 h, 2-PO	93.6	94.5	[102]
6	BL	ZrPO-1.00	2-PO	210 °C, 2 h, 2-PO	98.1	95.7	[103]
7	ML	ZrO ₂ /SBA-15	2-PO	150 °C, 6 h, 2-PO	99.9	95.0	[104]
8	LA	Zr-Beta	2-PO	250 °C, vap. phase, 2-PO	100.0	>99.0	[105]
9	LA	ZrO ₂	2-BU	150 °C, 16 h, 2-BU	>99.9	84.7	[106]
10	FU	Zr-Beta + Al-MFI-ns	2-BU	120 °C, 48 h, 2-BU	-	78.0	[107]
11	EL	UiO66(Zr)	2-PO	200 °C, 2 h, 2-PO	>98.0	92.7	[108]

¹ Abbreviations: LA: levulinic acid; EL: methyl levulinate; FU: furfural; BL: n-butyl levulinate; ML: methyl levulinate;

² Abbreviations: MMT: montmorillonite; ³ Abbreviations: 2-PO: 2-propanol; 1,4-BU: 1,4-butadienol; 2-BU: 2-butanol
EtOH: ethanol.

Li studied the efficient production of GVL from LA and its esters via the CTH using different hydrogen donors [103]. Zirconium phosphate catalysts (ZrPO-X, where X is the molar ratio of Zr to PO) were tested and a 98.1% of BL conversion and a 95.7% GVL yield were obtained using ZrPO-1.00 system.

Kuwahara and co-workers investigated a series of ZrO₂ catalysts supported on SBA-15 silica in the synthesis of GVL from LA and its esters via CTH using different alcohols as hydrogen donors [104]. The highest yield of GVL (95.0%) was obtained from methyl levulinate (ML) in the presence of 2-propanol (150 °C, 6 h, conv. 99.9%). A reaction mechanism of the CTH was also proposed (Scheme 6).



Scheme 6. Proposed reaction mechanism of the CTH of levulinate esters over silica-supported ZrO₂ catalysts. Adapted from Ref. [106]. Copyright Year 2017, Elsevier.

Accordingly, Zr-Beta zeolite was proved to be a very efficient catalyst in the CTH of LA to GVL via Meerwein–Ponndorf–Verley reduction [105].

Chia et al. examined different metal oxides (MgO/Al₂O₃, MgO/ZrO₂, ZrO₂) in the presence of different alcohols used as hydrogen donors [106]. ZrO₂ turned out to be the most active and selective catalyst when 2-butanol was used as a hydrogen source.

Bui reported the one-pot conversion of FU to GVL through the CTH process catalysed by zeolites containing Lewis and Brønsted acid sites (Zr-Beta + Al-MFI-ns). The best GVL yield was 78.0% at 120 °C in 48 h using 2-butanol as a hydrogen source [107].

Valekar and co-workers studied zirconium-based metal organic frameworks catalysts for the CTH of EL to GVL in the presence of 2-propanol: a yield of 98.7% to GVL with the conversion of EL almost of 100.0% at 200 °C within 2 h was reported [108].

Taking into account that formic acid is co-produced along with LA during the biomass conversion, it seems very interesting to also use this molecule in CTH reactions of LA and its esters [109]. Catalytic systems for the CTH of LA and its esters to GVL using FA as an H-source are summarised in Table 6.

Table 6. Catalytic systems for the production GVL from LA and derivatives using FA as a hydrogen source.

Entry	Catalyst	Reaction Conditions (Temperature, Time, Solvent) ¹	Conv. (%)	GVL Yield (%)	Ref.
1	Ru NPs	130 °C, 42 h, FA + triethylamine + water	100.0	100.0	[110]
2	Ru-P/SiO ₂ + Ru/TiO ₂	150 °C, 6 h, LA	100.0	30.0	[111]
3	Ru/C	150 °C, 5 h, water	100.0	90.0	[112]
4	Cu/SiO ₂	250 °C, vap. phase, -, FA + water	48.0	90.0	[113]
5	Cu/ZrO ₂	200 °C, 5 h, water	100.0	100.0	[114]
6	Ag-Ni/ZrO ₂	220 °C, 5 h, water	100.0	99.0	[115]

¹ Abbreviations: FA: formic acid.

Ortiz-Cervantes and García synthesised free Ru nanoparticles from the Ru₃Co₁₂ for the CTH process of LA to GVL in presence of formic acid [110]. A complete conversion of LA and 100.0% yield to GVL were obtained at 130 °C in 42 h.

Deng and co-workers used immobilised Ru-P/SiO₂ + Ru/TiO₂ to carry out the reaction of LA to GVL showing that the two-step process implies the decomposition of FA and the CTH of LA through parallel routes [111].

Son et al. reported a 90.0% GVL yield in the CTH process using FA as hydrogen source and Ru/C in optimised reaction conditions (150 °C, 5 h) [112].

Cu-supported catalysts were also tested in the CTH of the LA conversion to GVL by Lomate et al. [113]. Results indicate that Cu/SiO₂ leads to a conversion of 48.0% and a 90.0% yield to GVL. Additionally, Cu/SiO₂ shows a remarkable stability and re-utilization that indicates minimal losses of Cu particles during the reaction.

Yuan et al. described the successful utilization of Cu/ZrO₂ in the CTH process of LA to GVL by optimising the reaction conditions (200 °C, 5 h) in order to get a complete conversion of LA and a 100.0% GVL yield [114].

Finally, Hengne reported the total conversion of LA to GVL in the CTH process in the presence of (10% Ag, 20% Ni) Ag-Ni/ZrO₂. The synergistic effect between Ag and Ni is responsible of the decomposition of FA and the in-situ hydrogenation of LA precedes smoothly to GVL with a 99.0% yield [115].

4. Catalytic Transfer Hydrogenolysis (CTH) of Lignin and Its Derived Molecules

4.1. CTH of Lignin Derived Molecules

Prof. Ford's research group can be surely considered one the first that studied the transfer hydrogenolysis of dihydrobenzofuran (DHBf), a lignin model compound (α -O-4 C-O bond), using the Cu-doped PMO as a catalyst and MeOH as a hydrogen source/solvent, in a microreactor, for 2 h at 300 °C, in the presence of KOH. DHBf was fully converted to methylated 2-ethylphenols (63%), 2-ethylphenol (22%) and phenol (11%) [116].

Besse and co-workers investigated the catalytic transfer hydrogenolysis of eight model compounds with peculiar lignin linkages at 275–350 °C in a batch reactor, using the Pt/C catalyst and EtOH/H₂O as a hydrogen source solvent. They demonstrated that the lignin linkage cleavage follows the energy bond order showing that methoxyl and phenolic hydroxyl model molecules are unreactive, while α -1 model compounds are fully converted [117].

Han and co-workers recently demonstrated the performing catalytic activity of the commercial Ru/C in CTH reactions of aromatic ethers using a variety of 4-O-5 type lignin model compounds using 2-propanol as a solvent/H-donor under mild conditions (at 120 °C for 10–26 h) [118].

Samec and co-workers report that the commercial Pd/C can be a good catalyst in the C–O bond cleavage of the β -O-4' ether as a model lignin molecule using formic acid and 2-propanol as H-donors. They also tested other heterogeneous catalysts (Ir/C, Ni/C, Pd/C, Re/C, Rh/C) and Pd/C showed the higher reactivity in the cleavage of the β -O-4' C–O bond, allowing an efficient transformation to the corresponding aryl ketones and phenols in high yield, at 80 °C for 1–24 h. They proposed a reaction mechanism in which the first key step is the dehydrogenation of the α -CHO group followed by formation of a Pd-enolate complex, that undergoes a transfer hydrogenolysis process [119,120].

Wang et al., encouraged by the catalytic performance of Pd catalysts under hydrogenation conditions, studied the CTH of phenol in the presence of formic acid under mild reaction conditions: a good selectivity of 80% to cyclohexanone was observed [121].

In 2012, Rinaldi and co-workers reported, for the first time, the use of the bimetallic RANEY[®] Ni catalyst in the H-transfer reactions of lignin model molecules. 2-propanol was used as reaction solvent and hydrogen source and 32 model substrates at temperatures from 80 °C to 120 °C for 3 h were explored: the RANEY[®] Ni catalyst shows a high performance under CTH conditions and a good stability in the recycling tests [122]. In the course of years, his research group deeply investigated the CTH of other lignin model molecules (including phenol) in the presence of different heterogeneous catalysts, also elucidating the role of the catalyst's surface on the H-transfer mechanism [123,124].

Recently, a Pd/Ni catalyst was found to be very efficient also in the CTH of other model molecules, such as diphenyl ether (DPE), 2-phenethyl phenyl ether (PPE), and benzyl phenyl ether (BPE), leading to an arene derivative [125]. Interestingly, authors found that the hydrogenation of an aromatic ring in the CTH of DPE, PPE, and BPE is influenced by the nature of aryl groups that compose the aromatic ether (Figure 4).

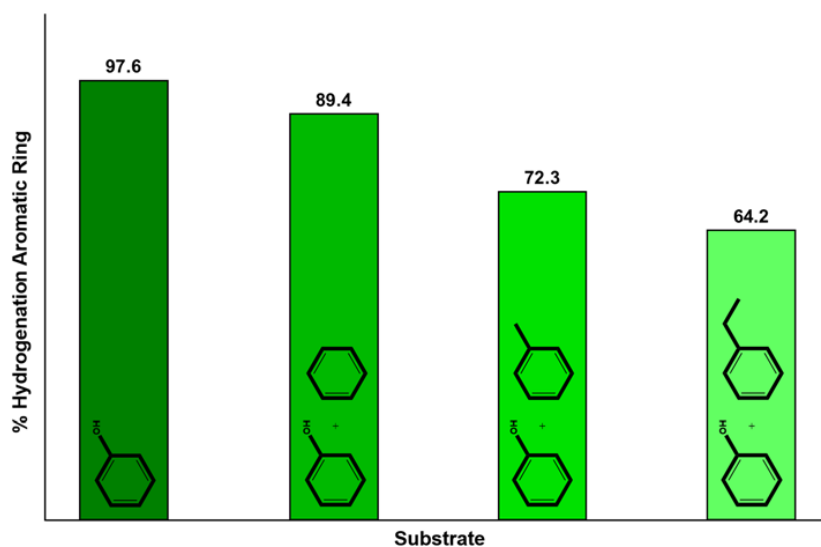
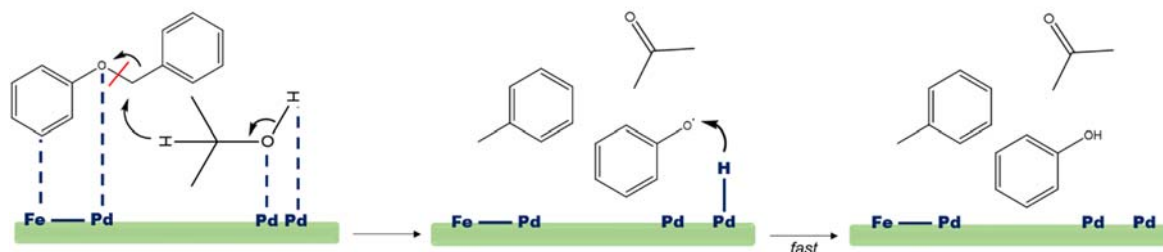


Figure 4. Competitive catalytic hydrogenation of phenol and phenol/benzene, phenol/toluene and phenol/ethylbenzene equimolar mixtures at 210 °C under CTH conditions. Adapted from Ref. [125]. Copyright Year 2018, American Chemical Society.

The same authors previously presented the bimetallic Pd/Fe₃O₄ system as a very efficient catalyst in the cleavage of the C–O bond in aromatic ethers and esters for the production of arene derivatives in presence of 2-propanol as a solvent/H-donor [126,127]. In the case of benzyl phenyl ether (BPE), authors proposed that the CTH process is very sensitive to the steric hindrance of the involved H-donor system, postulating a reaction mechanism in which the H-transfer from the alcoholic solvent and the C–O bond cleavage occur in a single step (Scheme 7).



Scheme 7. CTH mechanism of BPE promoted by Pd/Fe₃O₄ catalyst in presence of 2-propanol as H-donor/solvent. Adapted from Ref. [127]. Copyright Year 2016, Royal Society of Chemistry

Kim and co-workers explored the CTH of guaiacol, another important lignin model compound, to cyclohexane (>70% yield) using the bimetallic RuRe/C catalytic system and 2-propanol as a hydrogen source/solvent, demonstrating that the bimetallic catalyst is very efficient both in the dehydrogenation of solvent and the hydrogenation of guaiacol, and that the presence of Re increases the rate of the C–O hydrogenolysis, allowing a higher selectivity to cyclohexane (≈60%) [128].

Wang and co-workers proposed a strategy for the direct deoxygenation of *p*-cresol to toluene (84% yield) via the catalytic transfer hydrogenolysis, promoted by the Ru/Nb₂O₅-SiO₂ catalyst using 2-propanol as a hydrogen source/solvent at 230 °C. Authors demonstrated the influence of the *p*-cresol/2-propanol molar ratio on the toluene yield in order to limit hydrogenation of the aromatic rings. Furthermore, the efficiency of Ru/Nb₂O₅-SiO₂ catalyst on the CTH of other complex lignin model compounds (β -O-4 and α -O-4 linkages) was also studied [129].

4.2. CTH of Lignin

Lignin was efficiently converted into dimeric and monomeric compounds via the CTH approach by several research groups. The main obtained results are reported in Table 7.

Ford and co-workers demonstrated the occurrence of a single step process in the hydrogenolysis-depolymerization of the bio-oligomer organosolv lignin (obtained from sanded poplar sawdust) using a Cu-doped porous metal oxide (PMO) catalyst and supercritical MeOH (sc-MeOH) as a H-source/solvent at 300 °C for 24 h. A mixture of aromatics and monomeric substituted cyclohexyl derivatives with a low oxygen content was formed together with a gas phase mainly composed of H₂ (79% mol), CH₄ (8%), CO (9%), and CO₂ (4%) [130].

Barta and co-workers reported the walnut lignin depolymerization using triflic acid as a catalyst in 1,4-dioxane at 140 °C for 4 h. The main reaction products were C2-aldehyde fragments [131].

Samec and co-workers reported also the transfer hydrogenolysis of Pine sawdust using the Pd/C catalyst and only an endogenous hydrogen source at 195 °C for 1 h converting its lignin content into aryl propene monomers. Formic acid generated from the organosolv process is the H-source used for the CTH reaction [132]. The same authors also propose the direct use of a hemicellulose fraction as an H-donor source to carry out CTH reactions [133]. Phenol, and saturated and unsaturated propylphenols were obtained as the main reaction products and their selectivity can be efficiently tuned by changing (i) the solvent biomass ratio and (ii) reaction temperatures/times.

Table 7. A literature overview on the CTH of lignin promoted by heterogeneous catalysts.

Entry	Lignin Type ¹	Catalyst	H-Source	Temp. [°C]	Time [h]	Conversion [%]	Main Products	Ref.
1	OL	Cu-MPO	MeOH	300	24	100	Cyclohexyl derivatives	[130]
2	DWL	Trifilic acid	1,4-dioxane	140	4	100	C2-aldehyde fragments	[131]
3	PS	Pd/C	Formic acid	195	1	100	Aryl propene monomers	[132]
4	OL	Pd/C	Hemicellulose	210	15	100	Phenols and propylphenols	[133]
5	OL	Pd/C	Carbohydrate fractions	200	2	100	4-ethylguaiaicol	[134]
6	OL	Pd/C	Hemicellulose	160–220	3–6	100	Monophenolic products	[135]
7	OL	Pd/C	MeOH	250	3	90	4-n-propanolguaiaicol and 4-n-propanolsyringol	[136]
8	OL	Ru/C	MeOH	250	3	85	para-propyl phenolics	[137]
9	OL	Ru/C	2-PO	300	1–3	100	4-ethyl phenol, 2-methoxy phenol and phenol	[137]
10	BVL	Ni/C	Aliphatic alcohols	200	6	50	4-propylguaiaicol and 4-propylsyringol	[138]
11	OL	Al-SBA-15	Tetraline/FA	140	1/2	100	Mesitol and syringaldehyde	[139]
12	OL	RANEY® Ni	Hemicellulose	160–220	3	100	Monocyclic products	[140]
13	OL	RANEY® Ni	2-PO/H ₂ O	160–220	18	100	Alkenes and arenes	[141]
14	KL	TiN-Ni and TiO ₂ -Ni	MeOH, EtOH, 2-PO, THF	150	4.5 min	100	Guaiaicol products	[142]
15	OL	Pd ₁ Ni ₄ /MIL-100(Fe)	H ₂ O	180	6	100	Phenol and guaiaicol derivatives	[143]
16	OL	FeB, NiB and FeNiB	EtOH	320	2	100	21 depolymerization products	[144]
17	KL	Fe on Rh/La ₂ O ₃ /CeO ₂ -ZrO ₂	2-PO/H ₂ O	373	2	100	C _{12–26} aliphatic, C _{6–16} aromatic and C _{7–10} hydrogenated cycles compounds	[145]
18	OL	Cu-Mg-Al oxides	EtOH	340	4	100	C _{6–12} aromatics, C _{3–8} alcohols, C _{3–12} esters	[146]

¹ Abbreviation: OL: Organosolv Lignin; DVL: Dioxolv walnut Lignin; PS: Pine sawdust; BVL: Birch-wood Lignin; KL: Kraft Lignin.

In another recent contribution, the same research group presented a three-step process to convert lignin obtained from the *quercus suberin* to monomeric phenolic compounds and hydrocarbons by using the Pd/C catalyst in the CTH with carbohydrate fractions serving as hydrogen donors under mild alkaline conditions. The lignin was converted with a delignification (wt%) of 90%. [134].

In 2017, the same authors presented for the first time a method to fractionate the lignin in high yield to monophenolic products by a flow system in CTH conditions using the Pd/C catalyst and hemicellulose as an internal H-source and reducing agent at 160–220 °C for 3–6 h. Furthermore, the cellulose fraction was found as solid residue in 92 wt% [135].

Also, Sels and co-workers demonstrated that commercial Pd/C and Ru/C catalysts can be used in the CTH of lignin fractions (obtained from birch wood) using MeOH as an H-donor solvent [136]. They showed that Pd/C and Ru/C obtained different lignin products (4-n-propanolguaiacol and 4-n-propanolsyringol) at 250 °C for 3 h. The Ru/C catalyst favors the formation of para-propyl phenolics, while the Pd/C catalyst preferentially forms para-propanol phenol derivatives with a remarkable selectivity (91%) to 4-n-propanolguaiacol (PohG) and 4-n-propanolsyringol (PohS). Finally, they demonstrated that the Pd/C catalyst is preferred when a high OH-content lignin oil is present.

Moreover, Kim and co-workers explored the potential efficiency of CTH using 2-propanol as a solvent/H-donor to valorize the lignin-rich residue obtained from an ionic liquid conversion process, using Ru/C (5% wt on C) as a catalyst. Monomeric and alkyl-substituted phenols (4-ethyl phenol, 2-methoxy phenol, and phenol) were the main reaction products in the liquid oil, suggesting that the lignin residue can be efficiently depolymerized under CTH conditions [137].

Song's research group proposed a successful method using the Ni/C catalyst in the presence of simple aliphatic alcohols as a hydrogen source. Under mild reaction conditions (200 °C, for 6 h, 1 MPa Ar), the birch-wood lignin was converted into 4-propylguaiacol (M7G) and 4-propylsyringol (M7S) with a selectivity of 97% and 54% yield referred to all monomers. They proposed that the lignin is first fragmented into smaller lignin species by alcoholysis reactions and then the Ni/C catalyst converts oligomers to monomeric phenols [138].

Toledano and Luque published a microwave hydrogenolytic method (400 W at 140 °C for 30 min) to depolymerise organosolv lignin, isolated from tree pruning, into simple phenolic compounds, including mesitol and syringaldehyde by mild hydrogen-free conditions, using a range of bifunctional catalysts based on metal supported nanoparticles (Ni, Ru, Pd, and Pt) on the mesoporous acidic aluminosilicate support (Al-SBA-15) with tetraline or formic acid as the H-donor/solvents. Among all catalysts, the Ni10%AlSBA gave the best degree of lignin depolymerization after only 30 min of reaction with the main products being bio-oil, bio-char, and residual lignin [139].

Raney Ni can favor the organosolv separation, promoting the upgrading of the liquor by means of an H-transfer process [140,141]. Similar to studies conducted by the Samec research group, the hemicellulose fraction acts as an H-donor substrate.

Conversely, Esposito et al. compared the effect of two different Ni-based systems (TiN-Ni and TiO₂-Ni) in the reductive depolymerization of Kraft lignin to substituted guaiacol products without molecular H₂ in a flow-reactor system (150 °C for ≈4.5 min) [142]. TiN-Ni shows a better catalytic performance than TiO₂-Ni as a consequence of the major dispersion of Ni in the TiN phase. At the same time, the TiN-Ni system presents a better stability than the well-known Raney Ni and Pd/C catalysts.

Cai and co-workers reported the excellent catalytic performance of the Pd₁Ni₄/MIL-100(Fe) catalyst in the self-hydrogenolysis of organosolv lignin, using water as solvent, at 180 °C for 6 h. A 17% monomer yield and a set of reaction products including substituted phenol and guaiacol derivatives were registered. The catalyst shows a highly porous structure, strong Lewis acid properties, and water stability. Furthermore, the catalytic system can be recycled up to five times [143].

Chmely and co-workers, examined the catalytic activity of three different nanomaterial, amorphous B-containing FeNi alloys (FeB, NiB and FeNiB) in the transfer hydrogenolysis reaction of organosolv lignin using supercritical ethanol as an H-source/solvent. FeNiB shows the best

reactivity (74% conversion) and selectivity (84%) among the three catalysts, affording 21 different depolymerization products [144].

Jin and co-workers described the depolymerization of the Kraft lignin using a 2-propanol/water mixture system as solvent/hydrogen source over Fe on Rh/La₂O₃/CeO₂-ZrO₂ catalyst at 373 °C for 2 h. The main products obtained were C_{12–26} aliphatic, C_{6–16} aromatic, and C_{7–10} hydrogenated cycles compounds [145].

Hensen et al. investigated the role of different Cu-Mg-Al mixed oxides as catalysts, prepared by varying the Cu content and the (Cu+Mg)/Al ratio, in the depolymerization of lignin in CTH conditions by using supercritical ethanol as a solvent and H-donor at 340 °C for 4 h. The optimum performance was given by the mixture containing 20 wt% Cu and having a (Cu+Mg)/Al ratio of 4. Cu₂₀MgAl₄ affords the highest monomers yield and the least amount of repolymerization products during the lignin conversion [146].

5. Conclusions and Perspectives

In this review we summarize recent reports concerning the conversion of cellulose, hemicellulose and lignin promoted by heterogeneous catalysts by using the transfer hydrogenolysis (CTH) approach. A lot of attention has been paid in the CTH of their relative derived molecules with polyols, furan derivatives, levulinic acid, and aromatic ethers being the most investigated in order to get a chemical insight in the cleavage of C–O and C–C bond cleavage by alternative H-sources. At present, two main H-donor molecules have mainly been used: simple primary-secondary alcohols (methanol, ethanol, and 2-propanol) and formic acid.

Surely, lignin depolymerization—through transfer hydrogenolysis processes—has been more investigated with respect to other components of lignocellulosic biomasses due to the possibility to produce more aromatic compounds with respect to analogous catalytic processes that traditionally use high-pressure hydrogen gas. At the same time, only a few examples are present in the CTH of cellulose in the literature, whereas hemicellulose has been proposed mainly as an H-source itself in the direct upgrading of woods via tandem organosolv-transfer hydrogenolysis reactions.

In summary, the CTH seems to have all the potential to be a valid alternative to the use of molecular hydrogen for the reductive upgrading of lignocellulosic biomasses; however, a better understanding of catalysts' active sites, together with the molecular level of both C–O and C–C bond-breaking mechanism, is still needed. In particular, although the development of several heterogeneous catalysts has made significant progress in widening the choice of the transfer hydrogenolysis chemistry allowing also an increase of reaction rates and yields that has for a long time hindered the CTH application in recent years, the role of active metal sites and acid-base sites also remains to be clarified. In order to define correct structure–activity relationships, a comprehensive knowledge of the nature of the active sites (metal, Brønsted or Lewis acid, or base site) is necessary, as well as their strength and density. The development of catalytic systems characterized by tailored site compositions and sharp structures, employed in investigative model reactions, will be useful in revealing the synergistic effects of the different types of active sites, also contributing in outlining the kinetic behavior and mechanistic features of the title reactions. A comprehensive understanding of the reaction pathway at the molecular level of the C–O and C–C bond-breaking mechanism, could be attained by using computational studies, isotopic labeling, and combined kinetic measurements. The use of innovative approaches, such as in situ and interfacial sensitive spectroscopic tools, capable of elucidating the active hydrogen species involved in the hydrogen transfer step, the reaction intermediates at solid/liquid interfaces, and probing how the presence of solvent affects the interaction between reactants and active sites, would be desirable. Furthermore, in order to make CTH processes competitive with high pressure hydrogen gas conventional procedures and also to have the possibility of getting a real outcome in biomass transformation, basic studies on the role of a solvent as an H-source, as well as the practical application of transfer hydrogenolysis processes in the one-pot direct conversion of real lignocellulosic biomasses, are still necessary tasks.

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