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

Claudia Espro 1, Bianca Gumina 1, Tomasz Szumelda 2, Emilia Paone 3 and Francesco Mauriello 3,*

1 Dipartimento di Ingegneria, Università di Messina, Contrada di Dio–Vill. S. Agata, I-98166 Messina, Italy; espro@unime.it (C.E.); bianca.gumina@unime.it (B.G.)
2 Jerzy Haber Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, Niezapominajek 8, 30-239 Krakow, Poland; ncszumel@cyf-kr.edu.pl
3 Dipartimento DICEAM, Università Mediterranea di Reggio Calabria, Loc. Feo di Vito, I-89122 Reggio Calabria, Italy; emilia.paone@unirc.it
* Correspondence: francesco.mauriello@unirc.it; Tel.: +39-0965-169-2278

Received: 9 July 2018; Accepted: 28 July 2018; Published: 31 July 2018

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 (CO2, formaldehyde, and formic acid), (ii) the elimination of water through dehydration processes, and (iii) the direct “lysis” of the C–O bond by molecular H2 with the concurrent formation of a molecule of water.

![Figure 1](image-url). 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 H$_2$ 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 H$_2$ 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 H$_2$, generally allow a higher production of aromatic compounds.

Formic acid was also efficiently used as a potential liquid storage medium capable of releasing H$_2$ 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 CO$_2$, 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/Fe$_2$O$_3$ 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/Fe$_3$O$_4$ and Pd/Co$_3$O$_4$ 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 | Cat/Gly | Temp (°C) | Time (h) | Conv. (%) | 1,2-PDO Select. (%) | Ref. |
|-------|----------|---------|---------|-----------|----------|-----------|---------------------|------|
| 1     | PdO/Fe2O3 | EtOH    | 0.237   | 180       | 24       | 100       | 90                  | [45] |
| 2     | PdO/Fe2O3 | 2-PO    | 0.237   | 180       | 24       | 100       | 94                  | [45] |
| 3     | PdO/Fe2O3 | 2-PO    | 0.237   | 180       | 8        | 96        | 87                  | [45] |
| 4     | Pd/Fe2O3  | 2-PO    | 0.237   | 180       | 8        | 100       | 84                  | [45] |
| 5     | Pd/Fe2O3  | 2-PO    | 0.207   | 180       | 24       | 100       | 56                  | [46] |
| 6     | Pd/CeO2   | 2-PO    | 0.207   | 180       | 24       | 100       | 64                  | [46] |
| 7     | Ni-Cu/Al2O3 | -      | 0.166   | 220       | 24       | 70.5      | 66.9                | [47] |
| 8     | Ni-Cu/Al2O3 | 2-PO  | 0.166   | 220       | 24       | 60.4      | 64.6                | [47] |
| 9     | Ni-Cu/Al2O3 | 2-PO  | 0.166   | 220       | 10       | 28.2      | 77.4                | [48] |
| 10    | Ni-Cu/Al2O3 | MeOH  | 0.120   | 220       | 10       | 26.2      | 51.2                | [48] |
| 11    | Ni-Cu/Al2O3 | FA    | 0.120   | 220       | 10       | 33.5      | 85.9                | [48] |
| 12    | Ni-Cu/Al2O3 | FA    | 0.498   | 220       | 24       | 90        | 82                  | [49] |
| 13    | 7Cu30Al  | 2-PO   | -       | 220       | 5        | 69        | 90                  | [50] |
| 14    | 20Cu/ZrO2 | 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/CoO2 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 PdₓCu₀.₄Mg₅.₆–ₓAl₂O₃(OH)₆CO₃. 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 Pd₀.₀₆Cu₀.₄/Mg₅.₅Al₂O₃, 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 | Cat/Gly | Temp (°C) | Gas (bar) | Time (h) | Conv. (%) | Desired Prod. | Select. (%) | Ref. |
|-------|----------|---------|---------|-----------|-----------|----------|-----------|--------------|------------|-----|
| 1     | Pd₀.₀₆Cu₀.₄/Mg₅.₅Al₂O₃ | MeOH     | 0.125   | 180       | H₂ (20)   | 10       | 89.5      | 1,2-PDO (98) |            | [52]|
| 2     | Pd₀.₀₆Cu₀.₄/Mg₅.₅Al₂O₃ | EtOH     | 0.125   | 180       | H₂ (20)   | 10       | 88.0      | 1,2-PDO (99) |            | [52]|
| 3     | Rh₀.₀₂Cu₀.₄/Mg₅.₅Al₂O₃ | EtOH     | 0.167   | 180       | H₂ (20)   | 10       | 91.0      | 1,2-PDO (99) |            | [54]|
| 4     | Pd/Fe/Cu | 2/PO    | 0.237   | 180       | H₂ (5)    | 24       | 100       | 1,2-PDO (71) |            | [55]|
| 5     | 2Pt/20WO₃/ZrO₂ | EtOH | 0.250   | 170       | H₂ (55)   | 12       | 45.7      | 1,2-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 (Rh₀.₀₂Cu₀.₄/Mg₅.₆Al₁.₉₈O₈.₆), 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.](image)

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–FeOₓ 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–FeOₓ) 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–FeOₓ) enables an improvement of the stability of the catalyst during the glycerol conversion, also making the K/Al₂O₃–ZrO₂–FeOₓ 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 RuCl₃/PPh₃/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     | 82.2      | 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.](image-url) 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 | Reaction Conditions 2 (Temperature, Time, Solvent) | Conv. (%) | Main Product 3 | Yield (%) | Ref. |
|-------|----------|---------|---------------------------------------------------|-----------|----------------|-----------|-----|
| 1     | Ru/RuO₂/C | 2-PE, 2-BU | 180 °C, 10 h, 2-PE, 2-BU | 100.0 | MF | 76.0 | [73] |
| 2     | Ru/RuO₂/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/NiFeO₄ | 2-PO | 180 °C, 10 h, 2-PO | >97.0 | MF | 83.0 | [76] |
| 5     | Cu-Ni/Al₂O₃ | 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     | Cu₃Al-A | MeOH | 240 °C, 1.5 h, MeOH | >97.7 | MF | 88.2 | [80] |
| 9     | Pd/Fe₂O₃ | 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/NiFeO₄ 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 > n-propanol > 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 Cu₃Al-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%), synthesized 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/Fe$_2$O$_3$ 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/Co$_3$O$_4$ 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).
Aelig et al. tested some Cu/AlO₃ 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 BMHMF in the presence of MgO as a catalyst [91]. A superior 100% conversion of HMF and 100% selectivity to BMHMF 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), Thanathanthanachon 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.

![Chemical Products Derived from LA](image)

**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 RANNEY® 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 | Catalyst | H-Donor | 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        | ZrO₂     | EtOH    | 250 °C, 3 h, EtOH                              | 95.5     | 81.5          | [101]|
| 5     | EL        | Zr(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        | ZrO₂/SBA-15| 2-PO   | 150 °C, 6 h, 2-PO                              | 99.9     | 95.0          | [104]|
| 8     | LA        | ZrBeta   | 2-PO    | 250 °C, vap. phase, 2-PO                        | 100.0    | >99.9         | [105]|
| 9     | LA        | ZrO₂     | 2-BU    | 150 °C, 16 h, 2-BU                             | >99.9    | 84.7          | [106]|
| 10    | FU        | ZrBeta + Al-MFI-ns| 2-BU | 120 °C, 48 h, 2-BU                             | 78.0     | 78.0          | [107]|
| 11    | EL        | Li(366/2Zr)| 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-butanediol; 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) | Conv. (%) | GVL Yield (%) | Ref. |
|-------|----------|--------------------------------------------------|-----------|---------------|------|
| 1     | Ru NPs   | 130 °C, 42 h, FA + triethylamine + water         | 100.0     | 100.0         | [110]|
| 2     | Ru-P/SiO₂ + Ru/TiO₂ | 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/SiO₂  | 250 °C, vap. phase, - FA + water                 | 48.0      | 90.0          | [113]|
| 5     | Cu/ZrO₂  | 200 °C, 5 h, water                               | 100.0     | 100.0         | [114]|
| 6     | Ag-Ni/ZrO₂ | 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 loses 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 DPE is influenced by the nature of aryl groups that compose the aromatic ether (Figure 4).

![Figure 4](https://example.com/fig4.png)

**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](image)

Kim and co-workers explored the CTH of guaiacol, another important lignin model compound, to ciclohexane (>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 derivates 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 propyphenols 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 | Catalyst | H-Source | Temp. [°C] | Time [h] | Conversion [%] | Main Products | Ref. |
|-------|-------------|----------|----------|------------|----------|----------------|---------------|------|
| 1     | OL          | Cu-MPO   | MeOH     | 300        | 24       | 100            | Cycloexyl derivates | [130] |
| 2     | DWL         | Triflic 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-ethylguaiacol | [134] |
| 6     | OL          | Pd/C     | Hemicellulose | 160–220    | 3–6      | 100            | Monophenolic products | [135] |
| 7     | OL          | Pd/C     | MeOH     | 250        | 3        | 90             | 4-n-propanolguaiacol and 4-n-propanolsyringol | [136] |
| 8     | OL          | Ru/C     | MeOH     | 250        | 3        | 85             | 4-ethyl phenol, 2-methoxy phenol and phenol | [137] |
| 9     | OL          | Ru/C     | 2-PO     | 300        | 1-3      | 100            | 4-propylguaiacol and 4-propylsyringol | [138] |
| 10    | BVL         | Ni/C     | Aliphatic alcohols | 200        | 6        | 50             | Mesitol and syrangaldehyde | [139] |
| 11    | OL          | Al-SBA-15 | Tetraline/FA | 140        | 1/2      | 100            | Monocyclic products | [140] |
| 12    | OL          | RANEY® Ni | Hemicellulose | 160-220    | 3        | 100            | Guaiacol products | [141] |
| 13    | OL          | RANEY® Ni | 2-PO/H2O | 160-220    | 18       | 100            | Guaiacol products | [142] |
| 14    | KL          | TiNi-Ni and TiO2-Ni | MeOH, EtOH, 2-PO, THF | 150        | 4.5 min   | 100            | Phenol and guaiacol derivates | [143] |
| 15    | OL          | PdNi/MIL100Fe | H2O     | 180        | 6        | 100            | Phenol and guaiacol derivatives | [144] |
| 16    | OL          | FeNi and FeNiB | EtOH    | 320        | 2        | 100            | 21 depolymerization products | [145] |
| 17    | KL          | Fe on Rh/La2O3/CeO2-ZrO2 | 2-PO/H2O | 373        | 2        | 100            | C22-26 aliphatic, C6-12 aromatic and C5-12 hydrogenated cycles compounds | [146] |
| 18    | OL          | Cu-Mg-Al oxides | EtOH    | 340        | 4        | 100            | C6-12 aromatics, C3-8 alcohols, C5-12 esters | [147] |

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 TiO$_2$-Ni) in the reductive depolymerization of Kraft lignin to substituted guaiacol products without molecular H$_2$ in a flow-reactor system (150 °C for ≈4.5 min) [142]. TiN-Ni shows a better catalytic performance than TiO$_2$-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 Pd$_4$Ni$_{14}$/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/La$_2$O$_3$/CeO$_2$–ZrO$_2$ 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. Cu$_{20}$MgAl$_4$
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.
Author Contributions: All authors contributed equally to this review.

Funding: This publication was supported from Università Mediterranea di Reggio Calabria and PON (“ACQUASYSTEM” and “MEL” projects).

Acknowledgments: Authors thanks Pietropaolo and Signorino Galvagno for fruitful discussions.

Conflicts of Interest: The authors declare no conflict of interest.

References
1. Klass, D.L. Biomass for Renewable Energy, Fuels, and Chemicals; Academic Press: San Diego, CA, USA, 1998.
2. The White House-Washington. National Bio-economy Blueprint; The White House: Washington, DC, USA, 2012; pp. 1–43. Available online: https://obamawhitehouse.archives.gov/sites/default/files/microsites/ostp/national_bioeconomy_blueprint_april_2012.pdf (accessed on 30 June 2018).
3. European Commission. Innovating for Sustainable Growth: A Bioeconomy for Europe; European Commission: Brussels, Belgium, 2012; pp. 1–9. Available online: http://ec.europa.eu/research/bioeconomy/pdf/official-strategy_en.pdf (accessed on 30 June 2018).
4. European Commission. A Roadmap for Moving to a Competitive Low Carbon Economy in 2050; European Commission: Brussels, Belgium, 2011; Available online: http://eur-lex.europa.eu/legal-content/EN/ALL/?uri=CELEX:52011DC0112 (accessed on 30 December 2016).
5. Lee, D.-H. Bio-based economies in Asia: Economic analysis of development of bio-based industry in China, India, Japan, Korea, Malaysia and Taiwan. Int. J. Hydrogen Energy 2016, 41, 4333–4346. [CrossRef]
6. Dey, S. Asian bioeconomy and biobusiness: Current scenario and future prospects. New Biotechnol. 2014, 31, S34. [CrossRef]
7. Ignaciuk, A.; Vöhringer, F.; Ruijs, A.; Van Ierland, E.C. Competition between biomass and food production in the presence of energy policies: A partial equilibrium analysis. Energy Policy 2006, 34, 1127–1138. [CrossRef]
8. Somerville, C.; Youngs, H.; Taylor, C.; Davis, S.C.; Long, S.P. Feedstocks for lignocellulosic biofuels. Science 2010, 329, 790–792. [CrossRef] [PubMed]
9. Tuck, C.O.; Pérez, E.; Horváth, I.T.; Sheldon, R.A.; Poliakoff, M. Valorization of biomass: Deriving more value from waste. Science 2012, 337, 695–699. [CrossRef] [PubMed]
10. Yan, K.; Yang, Y.; Chai, J.; Lu, Y. Catalytic reactions of gamma-valerolactone: A platform to fuels and value-added chemicals. Appl. Catal. B Environ. 2015, 179, 292–304. [CrossRef]
11. Hu, L.; Lin, L.; Wu, Z.; Zhou, S.; Liu, S. Chemocatalytic hydrolysis of cellulose into glucose over solid acid catalysts. Appl. Catal. B Environ. 2015, 174–175, 225–243. [CrossRef]
12. Negahdar, L.; Delidovich, I.; Palkovits, R. Aqueous-phase hydrolysis of cellulose and hemicelluloses over molecular acidic catalysts: Insights into the kinetics and reaction mechanism. Appl. Catal. B Environ. 2016, 184, 285–298. [CrossRef]
13. Sheldon, R.A. Green and sustainable manufacture of chemicals from biomass: State of the art. Green Chem. 2014, 16, 950–963. [CrossRef]
14. Zhang, Z.; Song, J.; Han, B. Catalytic transformation of lignocellulose into chemicals and fuel products in ionic liquids. Chem. Rev. 2016, 117, 6834–6880. [CrossRef] [PubMed]
15. Li, C.; Zhao, X.; Wang, A.; Huber, G.H.; Zhang, T. Catalytic transformation of lignin for the production of chemicals and fuels. Chem. Rev. 2015, 115, 11559–11624. [CrossRef] [PubMed]
16. Lange, J.P. Lignocellulose conversion: An introduction to chemistry, process and economics. Biofuels Bioprod. Biorefin. 2007, 1, 39–48. [CrossRef]
17. Stöcker, M. Biofuels and biomass-to-liquid fuels in the biorefinery: Catalytic conversion of lignocellulosic biomass using porous materials. Angew. Chem. Int. Ed. 2008, 47, 9200–9211. [CrossRef] [PubMed]
18. Espro, C.; Gumina, B.; Paone, E.; Mauriello, F. Upgrading Lignocellulosic Biomasses: Hydrogenolysis of Platform Derived Molecules Promoted by Heterogeneous Pd-Fe Catalysts. Catalysts 2017, 7, 78. [CrossRef]
19. Sun, Z.; Fridrich, B.; De Santi, A.; Elangovan, S.; Barta, K. Bright Side of Lignin Depolymerization: Toward New Platform Chemicals. Chem. Rev. 2018, 118, 614–678. [CrossRef] [PubMed]
20. Schutyser, W.; Renders, T.; Van den Bosch, S.; Koelewijn, S.-F.; Beckham, G.T.; Sels, B.F. Chemicals from lignin: An interplay of lignocellulose fractionation, depolymerisation, and upgrading. Chem. Soc. Rev. 2018, 47, 852–908. [CrossRef] [PubMed]
21. Global Bio-Based Chemical Market Forecast 2018–2026. Available online: https://www.reportlinker.com/p05001382/Global-Bio-Based-Chemicals-Market-Forecast.html (accessed on 30 June 2018).

22. Dornburg, V.; Hermann, B.G.; Patel, M.K. Scenario Projections for Future Market Potentials of Biobased Bulk Chemicals. Environ. Sci. Technol. 2008, 42, 2261–2267. [CrossRef] [PubMed]

23. Chen, H. Chemical composition and structure of natural lignocellulose. In Biotechnology of Lignocellulose: Theory and Practice; Springer Science + Business Media B.V.: Dordrecht, The Netherlands, 2014; pp. 25–71.

24. Klemm, D.; Heublein, B.; Fink, H.-P.; Bohn, A. Cellulose: Fascinating biopolymer and sustainable raw material. Angew. Chem. Int. Ed. 2005, 44, 3358–3393. [CrossRef] [PubMed]

25. Kobayashi, H.; Fukuoka, A. Synthesis and utilisation of sugar compounds derived from lignocellulosic biomass. Green Chem. 2013, 15, 1740–1763. [CrossRef]

26. Isikgor, F.H.; Becer, C.R. Lignocellulosic Biomass: A sustainable platform for production of bio-based chemicals and polymers. Polym. Chem. 2015, 6, 4497–4559. [CrossRef]

27. Besson, M.; Gallezot, P.; Pinel, C. Conversion of biomass into chemicals over metal catalysts. Chem. Rev. 2014, 114, 1827–1870. [CrossRef] [PubMed]

28. Corma, A.; Iborra, S.; Velty, A. Chemical routes for the transformation of biomass into chemicals. Chem. Rev. 2007, 107, 2411–2502. [CrossRef] [PubMed]

29. Binder, J.B.; Raines, R.T. Simple Chemical Transformation of Lignocellulosic Biomass into Fuars for Fuels and Chemicals. J. Am. Chem. Soc. 2009, 131, 1979–1985. [CrossRef] [PubMed]

30. Xu, C.; Arancon, R.A.D.; Labidi, J.; Luque, R. Lignin depolymerisation strategies: Towards valuable chemicals and fuels. Chem. Soc. Rev. 2014, 43, 7485–7500. [CrossRef] [PubMed]

31. Deuss, P.J.; Barta, K. From models to lignin: Transition metal catalysis for selective bond cleavage reactions. Coord. Chem. Rev. 2016, 306, 510–532. [CrossRef]

32. Zakzeski, J.; Bruijnincx, P.C.A.; Jongerius, A.L.; Weckhuysen, B.M. The Catalytic Valorization of Lignin for the Production of Renewable Chemicals. Chem. Rev. 2010, 110, 3552–3599. [CrossRef] [PubMed]

33. Galkin, M.V.; Samec, J.S.M. Lignin Valorization through Catalytic Lignocellulose Fractionation: A Fundamental Platform for the Future Biorefinery. ChemSusChem 2016, 9, 1544–1558. [CrossRef] [PubMed]

34. Bridgewater, A.V.; Meierb, D.; Radlein, D. An overview of fast pyrolysis of biomass. Org. Geochem. 1999, 30, 1479–1493. [CrossRef]

35. De, S.; Saha, B.; Luque, R. Hydrodeoxygenation processes: Advances on catalytic transformations of biomass-derived platform chemicals into hydrocarbon fuels. Bioresour. Technol. 2015, 178, 108–118. [CrossRef] [PubMed]

36. Ruppert, A.M.; Weinberg, K.; Palkovits, R. Hydrogenolysis goes bio: From carbohydrates and sugar alcohols to platform chemicals. Angew. Chem. Int. Ed. 2012, 51, 2564–2601. [CrossRef] [PubMed]

37. Li, N.; Wang, W.; Zheng, M.; Zhang, T. General Reaction Mechanisms in Hydrogenation and Hydrolysis for Biorefining. In Catalytic Hydrogenation for Biomass Valorization; Rinaldi, R., Ed.; Royal Society of Chemistry: Cambridge, UK, 2015; pp. 22–50.

38. Wang, D.; Astruc, D. The Golden Age of Transfer Hydrogenation. Chem. Rev. 2015, 115, 6621–6686. [CrossRef] [PubMed]

39. Gilkey, M.J.; Xu, B. Heterogeneous Catalytic Transfer Hydrogenation as an Effective Pathway in Biomass Upgrading. ACS Catal. 2016, 6, 1420–1436. [CrossRef]

40. Muzart, J.P. Catalyzed Hydrogen-Transfer Reactions from Alcohols to C=C, C=O and C=N Bonds. Eur. J. Org. Chem. 2015, 5693–5707. [CrossRef] [PubMed]

41. Barta, K.; Ford, P.C. Catalytic Conversion of Nonfood Woody Biomass Solids to Organic Liquids. Acc. Chem. Res. 2014, 47, 1503–1512. [CrossRef] [PubMed]

42. Mellmann, D.; Sponholz, P.; Junge, H.; Beller, M. Formic acid as a hydrogen storage material–development of homogeneous catalysts for selective hydrogen release. Chem. Soc. Rev. 2016, 45, 3954–3988. [CrossRef] [PubMed]

43. Loges, B.; Boddien, A.; Gärtner, F.; Junge, H.; Beller, M. Catalytic Generation of Hydrogen from Formic acid and its Derivatives: Useful Hydrogen Storage Materials. Top. Catal. 2010, 53, 902–914. [CrossRef]

44. Grasemann, M.; Laurenczy, G.; Hirose, T.; Raspail, P.; Liu, S.L.; Wu, Y.P.; Guo, Q.-X.; Ludwig, R.; Beller, M. Formic acid as a hydrogen source–recent developments and future trends. Energy Environ. Sci. 2012, 5, 8171–8181. [CrossRef]
45. 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. [CrossRef]
46. Mauriello, F.; Ariga, H.; Musolino, M.G.; Pietropaolo, R.; Takakusagi, S.; Asakura, K. Exploring the catalytic properties of supported palladium catalysts in the transfer hydrogenolysis of glycerol. Appl. Catal. B Environ. 2015, 166–167, 121–131. [CrossRef]
47. Gandarias, I.; Arias, P.L.; Requies, J.; El Doukkali, M.; Güemez, M.B. Liquid-phase glycerol hydrogenolysis to 1,2-propanediol under nitrogen pressure using 2-propanol as hydrogen source. J. Catal. 2011, 282, 237–247. [CrossRef]
48. Gandarias, I.; Arias, P.L.; Fernández, 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. [CrossRef]
49. Gandarias, I.; Requies, J.; Arias, P.L.; Armbruster, U.; Martin, A. Liquid-phase glycerol hydrogenolysis by formic acid over Ni-Cu/Al₂O₃ catalysts. J. Catal. 2012, 290, 79–89. [CrossRef]
50. Mane, R.B.; Rode, C.V. Continuous Dehydration and Hydrogenolysis of Glycerol over Non-Chromium Copper Catalyst: Laboratory-Scale Process Studies. Org. Process Res. Dev. 2012, 16, 1043–1052. [CrossRef]
51. 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. [CrossRef]
52. Heeres, H.; Handana, R.; Rasrendra, C.B.; Girisuta, B.; Heeres, H.J. Combined dehydration/(transfer)-hydrogenation of biomass-derived carbohydrates into diols and biomass-derived polyols glycerol and erythritol. Mechanistic studies of a formic acid-mediated dehydration/(transfer)-hydrogenation of C₆-sugars (D-glucose and D-fructose) to γ-valerolactone and pyrrolidone derivatives with supported gold catalysts. Angew. Chem. Int. Ed. 2009, 48, 6529–6532. [CrossRef] [PubMed]
53. Gandarias, I.; Arias, P.L.; Requies, J.; El Doukkali, M.; Güemez, M.B. Hydrogenolysis through catalytic transfer hydrogenation: Glycerol conversion to 1,2-propanediol. Catal. Today 2011, 166–167, 121–131. [CrossRef]
54. Gandarias, I.; Arias, P.L.; Fernández, 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. [CrossRef]
55. Gandarias, I.; Requies, J.; Arias, P.L.; Armbruster, U.; Martin, A. Liquid-phase glycerol hydrogenolysis by formic acid over Ni-Cu/Al₂O₃ catalysts. J. Catal. 2012, 290, 79–89. [CrossRef]
56. Mane, R.B.; Rode, C.V. Continuous Dehydration and Hydrogenolysis of Glycerol over Non-Chromium Copper Catalyst: Laboratory-Scale Process Studies. Org. Process Res. Dev. 2012, 16, 1043–1052. [CrossRef]
57. 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. [CrossRef]
58. Xia, S.; Yuan, Z.; Wang, L.; Chen, P.; Hou, Z. Hydrogenolysis of glycerol on bimetallic Pd-Cu/solid-base catalysts prepared via layered double hydroxides precursors. Appl. Catal. A Gen. 2011, 403, 173–182. [CrossRef]
59. Gandarias, I.; Arias, P.L.; 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. [CrossRef]
60. Mane, R.B.; Rode, C.V. Continuous Dehydration and Hydrogenolysis of Glycerol over Non-Chromium Copper Catalyst: Laboratory-Scale Process Studies. Org. Process Res. Dev. 2012, 16, 1043–1052. [CrossRef]
61. 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. [CrossRef]
62. Heeres, H.; Handana, R.; Rasrendra, C.B.; Girisuta, B.; Heeres, H.J. Combined dehydration/(transfer)-hydrogenation of biomass-derived carbohydrates into diols and biomass-derived polyols glycerol and erythritol. Mechanistic studies of a formic acid-mediated dehydration/(transfer)-hydrogenation of C₆-sugars (D-glucose and D-fructose) to γ-valerolactone and pyrrolidone derivatives with supported gold catalysts. Angew. Chem. Int. Ed. 2009, 48, 6529–6532. [CrossRef] [PubMed]
63. Heeres, H.; Handana, R.; 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. [CrossRef]
64. Scholz, D.; Aellig, C.; Mondelli, C.; Perez-Ramirez, J. Continuous transfer hydrogenation of sugars to alditols with bioderived donors over Cu-Ni-Al catalysts. ChemCatChem 2015, 7, 1551–1558. [CrossRef]
65. Van Hengstum, A.J.; Kieboom, A.P.G.; van Bekkum, H. Catalytic transfer hydrogenation of glucose-fructose syrups in alkaline solution. *Starch* 1984, 36, 317–320. [CrossRef]
66. Kobayashi, H.; Matsuhashi, H.; Komanoya, T.; Hara, K.; Fukuoka, A. Transfer hydrogenation of cellulose to sugar alcohols over supported rhenium catalysts. *Chem. Commun.* 2011, 47, 2366–2368. [CrossRef] [PubMed]
67. Shroti, A.; Kobayashi, H.; Tanksale, A.; Fukuoka, A.; Beltramini, J. Transfer Hydrogenation of Cellulose-based Oligomers over Carbon-supported Ruthenium Catalyst in a Fixed-bed Reactor. *ChemCatChem* 2014, 6, 1349–1356. [CrossRef]
68. Dalvand, K.; Rubin, J.; Gunukula, S.; Clayton Wheeler, M.; Hunt, G. Economics of biofuels: Market potential of furfural and its derivatives. *BioMass Bioenergy* 2018, 115, 56–63. [CrossRef]
69. Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; López Granados, M. Furfural: A renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energy Environ. Sci.* 2016, 9, 1144–1189. [CrossRef]
70. Li, X.; Jia, P.; Wang, T. Furfural: A Promising Platform Compound for Sustainable Production of C4 and C5 Chemicals. *ACS Catal.* 2016, 6, 7621–7640. [CrossRef]
71. Li, J.; Liu, J.; Zhou, H.; Fu, Y. Catalytic Transfer Hydrogenation of Furfural to Furfuryl Alcohol over Nitrogen-Doped Carbon-Supported Iron Catalysts. *ChemSusChem* 2016, 9, 1339–1347. [CrossRef] [PubMed]
72. Tang, X.; Wei, J.; Ding, N.; Sun, Y.; Zeng, X.; Hu, L.; Liu, S.; Lei, T.; Lin, L. Chemoselective hydrogenation of biomass derived 5-hydroxymethylfurfural to diols: Key intermediates for sustainable chemicals, materials and fuels. *Renew. Sustain. Energy Rev.* 2017, 77, 287–296. [CrossRef]
73. Panagiotopoulou, P.; Martin, N.; Vlachos, D.G. Effect of hydrogen donor on liquid phase catalytic transfer hydrogenation of furfural over a Ru/RuO2/C catalyst. *J. Mol. Catal. A Chem.* 2014, 392, 223–228. [CrossRef]
74. Gilkey, M.J.; Panagiotopoulou, P.; Mironenko, A.V.; Jenness, G.R.; Vlachos, D.G.; Xu, B. Mechanistic Insights into Metal Lewis Acid-Mediated Catalytic Transfer Hydrogenation of Furfural to 2-Methylfuran. *ACS Catal.* 2015, 5, 3988–3994. [CrossRef]
75. Panagiotopoulou, P.; Vlachos, D.G. Liquid phase catalytic transfer hydrogenation of furfural over a Ru/C catalyst. *Appl. Catal. A Gen.* 2014, 480, 17–24. [CrossRef]
76. Wang, B.; Li, C.; He, B.; Qi, J.; Liang, C. Highly stable and selective Ru/NiFe2O4 catalysts for transfer hydrogenation of biomass-derived furfural to 2-methylfuran. *J. Energy Chem.* 2017, 26, 799–807. [CrossRef]
77. Zhang, Z.; Pei, Z.; Chen, H.; Chen, K.; Hou, Z.; Lu, X.; Ouyang, P.; Fu, J. Catalytic in-Situ Hydrogenation of Furfural over Bimetallic Cu-Ni Alloy Catalysts in Isopropanol. *Ind. Eng. Chem. Res.* 2018, 57, 4225–4230. [CrossRef]
78. Gong, W.; Chen, C.; Fan, R.; Zhang, H.; Wang, G.; Zhao, H. Transfer-hydrogenation of furfural and levulinic acid over supported copper catalyst. *Fuel* 2018, 231, 165–171. [CrossRef]
79. Chang, X.; Liu, A.-F.; Cai, B.; Luo, J.-Y.; Pan, H.; Huang, Y.-B. Catalytic Transfer Hydrogenation of Furfural to 2-Methylfuran and 2-Methyltetrahydrofuran over Bimetallic Copper-Palladium Catalysts. *ChemSusChem* 2016, 9, 3330–3337. [CrossRef] [PubMed]
80. Zhang, J.; Chen, J. Selective Transfer Hydrogenation of Biomass-Based Furfural and 5-Hydroxymethylfurfural over Hydrotalcite-Derived Copper Catalysts Using Methanol as a Hydrogen Donor. *ACS Sustain. Chem. Eng.* 2017, 5, 5982–5993. [CrossRef]
81. Scholz, D.; Aellig, C.; Hermans, I. Catalytic Transfer Hydrogenation/Hydrogenolysis for Reductive Upgrading of Furfural and 5-(Hydroxymethyl)furfural. *ChemSusChem* 2014, 7, 268–275. [CrossRef] [PubMed]
82. Yang, P.; Xia, Q.; Liu, X.; Wang, Y. Catalytic transfer hydrogenation/hydrogenolysis of 5-hydroxymethylfurfural to 2,5dimethylfuran over Ni-Co/C catalyst. *Fuel* 2017, 187, 159–166. [CrossRef]
83. Qi, L.; Mui, Y.F.; Lo, S.W.; Lui, M.Y.; Akien, G.R.; Horváth, I.T. Catalytic conversion of fructose, glucose, and sucrose to 5-(hydroxymethyl)furfural and levulinic and formic acids in γ-valerolactone as a green solvent. *ACS Catal.* 2014, 4, 1470–1477. [CrossRef]
84. Jae, J.; Zheng, W.; Lobo, R.F.; Vlachos, D.G. Production of dimethylfuran from hydroxymethylfurfural through catalytic transfer hydrogenation with rhenium supported on carbon. *ChemSusChem* 2013, 6, 1158–1162. [CrossRef] [PubMed]
85. Wang, T.; Zhang, J.; Xie, W.; Tang, Y.; Guo, D.; Ni, Y. Catalytic Transfer Hydrogenation of Biobased HMF to 2,5-Bis-(Hydroxymethyl)Furan over Ru/Co3O4. *Catalysts* 2017, 7, 92. [CrossRef]
Aellig, C.; Jenny, F.; Scholz, D.; Wolf, P.; Giovinazzo, I.; Kollhoff, F.; Hermans, I. Combined 1,4-butanediol lactonization and transfer hydrogenation/hydrogenolysis of furfural-derivatives under continuous flow conditions. *Catal. Sci. Technol.* 2014, 4, 2326–2331. [CrossRef]

Hansen, T.S.; Barta, K.; Anastas, P.T.; Ford, P.C.; Riisager, A. One-pot reduction of 5-hydroxymethylfurfural via hydrogen transfer from supercritical methanol. *Green Chem.* 2012, 14, 2457–2461. [CrossRef]

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. [CrossRef]

Hao, W.; Li, W.; Tang, X.; Zeng, X.; Sun, Y.; Liu, S.; Lin, L. Catalytic transfer hydrogenation of biomass-derived 5-hydroxymethyl furfural to the building block 2,5-bis(hydroxymethyl) furan. *Green Chem.* 2016, 18, 1080–1088. [CrossRef]

Hu, L.; Yang, M.; Xu, N.; Xu, J.; Zhou, S.; Chu, X.; Zhao, Y. Selective transformation of biomass-derived 5-hydroxymethylfurfural into 2,5-dihydroxymethylfuran via catalytic transfer hydrogenation over magnetic zirconium hydroxides. *Korean J. Chem. Eng.* 2018, 35, 99–109. [CrossRef]

Pasini, T.; Lolli, A.; Albonetti, S.; Cavani, F.; Mella, M. Methanol as a clean and efficient H-transfer reactant for carbonyl reduction: Scope, limitations, and reaction mechanism. *J. Catal.* 2014, 317, 206–219. [CrossRef]

Thananatthanachon, T.; Rauchfuss, T.B. 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. [CrossRef] [PubMed]

Thananatthanachon, T.; Rauchfuss, T.B. Efficient route to hydroxymethylfurans from sugars via transfer hydrogenation. *ChemSusChem* 2010, 3, 1139–1141. [CrossRef] [PubMed]

Tuteja, J.; Choudhary, H.; Nishimura, S.; Ebinti, K. Direct Synthesis of 1,6-Hexanediol from HMF over a Heterogeneous Pd/ZrP Catalyst using Formic Acid as Hydrogen Source. *ChemSusChem* 2014, 7, 96–100. [CrossRef] [PubMed]

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 Environ.* 2018, 226, 523–533. [CrossRef]

Bozell, J.J.; Moens, L.; Elliott, D.; Wang, Y.; Neuenschwander, G.; Fitzpatrick, S.; Bilski, R.; Jarnefeld, J. Production of levulinic acid and use as a platform chemical for derived products. *Resour. Conserv. Recycl.* 2000, 28, 227–239. [CrossRef]

Antonetti, C.; Licursi, D.; Pulignati, S.; Valentini, G.; Raspolli Galletti, A. New Frontiers in the Catalytic Synthesis of Levulinic Acid: From Sugars to Raw and Waste Biomass as Starting Feedstock. *Catalysts* 2016, 6, 196. [CrossRef]

Hengne, A.M.; Kadu, B.S.; Biradar, N.S.; Chikate, R.C.; Rode, C.V. Transfer hydrogenation of biomass-derived levulinic acid to γ-valerolactone on Ni catalysts. RSC Adv. 2016, 6, 59753–59761. [CrossRef]

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. [CrossRef] [PubMed]

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. [CrossRef]

Tang, X.; Hu, L.; Sun, Y.; Zhao, G.; Hao, W.; Lin, L. Conversion of biomass-derived ethyl levulinate into γ-valerolactone via hydrogen transfer from supercritical ethanol over a ZrO₂ catalyst. *RSC Adv.* 2013, 3, 10277–10284. [CrossRef]

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 Environ.* 2014, 147, 827–834. [CrossRef]

Li, F.; France, L.J.; Cai, Z.; Li, Y.; Liu, S.; Lou, H.; Long, J.; Li, X. Catalytic transfer hydrogenation of butyl levulinate to γ-valerolactone over zirconium phosphates with adjustable Lewis and Brønsted acid sites. *Appl. Catal. B Environ.* 2017, 214, 67–77. [CrossRef]

Kuwahara, Y.; Kaburagi, W.; Osada, Y.; Fujitani, T.; Yamashita, H. Catalytic transfer hydrogenation of biomass-derived levulinic acid and its esters to γ-valerolactone over ZrO₂ catalyst supported on SBA-15 silica. *Catal. Today* 2017, 281, 418–428. [CrossRef]
Catalysts 2018, 8, 313

105. 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. [CrossRef]

106. 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. [CrossRef] [PubMed]

107. Bui, L.; Luo, H.; Gunther, W.R.; Román-Leshkov, Y. Domino Reaction Catalyzed by Zeolites with Brønsted and Lewis Acid Sites for the Production of γ-Valerolactone from Furfural. Angew. Chem. Int. Ed. 2013, 52, 8022–8025. [CrossRef] [PubMed]

108. 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. [CrossRef]

109. Tang, X.; Zeng, X.; Li, Z.; Hu, L.; Sun, Y.; Liu, S.; Lei, T.; Lin, L. Production of γ-valerolactone from lignocellulosic biomass for sustainable fuels and chemicals supply. Renew. Sustain. Energy Rev. 2014, 40, 608–620. [CrossRef]

110. Ortiz-Cervantes, C.; Garcia, J.J. Hydrogenation of levulinic acid to γ-valerolactone using ruthenium nanoparticles. Inorg. Chim. Acta 2013, 397, 124–128. [CrossRef]

111. 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. [CrossRef] [PubMed]

112. 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. [CrossRef]

113. 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. [CrossRef]

114. 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. [CrossRef]

115. Hengne, A.M.; Malawadkar, A.V.; Biradar, N.S.; Rode, C.V. Surface synergism of an Ag–Ni/ZrO₂ nanocomposite for the catalytic transfer hydrogenation of bio-derived platform molecules. RSC Adv. 2014, 4, 9730–9736. [CrossRef]

116. Mascala, S.M.; Matson, T.D.; Johnson, C.L.; Lewis, R.S.; Iretskii, A.V.; Ford, P.C. Hydrogen Transfer from Supercritical Methanol over a Solid Base Catalyst: A Model for Lignin Depolymerization. ChemSusChem 2009, 2, 215–217. [CrossRef] [PubMed]

117. Besse, X.; Schuerman, Y.; Guilhame, N. Reactivity of lignin model compounds through hydrogen transfer catalysis in ethanol/water mixtures. Appl. Catal. B 2017, 209, 265–272. [CrossRef]

118. Wu, H.; Song, J.; Xie, C.; Wu, C.; Chen, C.; Han, B. Efficient and Mild Transfer Hydrogenolytic Cleavage of Aromatic Ether Bonds in Lignin-Derived Compounds over Ru/C. ACS Sustain. Chem. Eng. 2018, 6, 2872–2877. [CrossRef]

119. Galkin, M.V.; Sawadjoon, S.; Rohde, V.; Dawange, M.; Samec, J.S.M. Mild Heterogeneous Palladium-Catalyzed Cleavage of β-O-4'-Ether Linkages of Lignin Model Compounds and Native Lignin in Air. ChemCatChem 2014, 6, 179–184. [CrossRef]

120. Sawadjoon, S.; Lundstedt, A.; Samec, J.S.M. Pd-Catalyzed Transfer Hydrogenolysis of Primary, Secondary, and Tertiary Benzylic Alcohols by Formic Acid: A Mechanistic Study. ACS Catal. 2013, 3, 635–642. [CrossRef]

121. 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. [CrossRef]

122. Wang, X.; Rinaldi, R. Exploiting H-transfer reactions with RANEY® Ni for upgrade of phenolic and aromatic biorefinery feeds under unusual, low-severity conditions. Energy Environ. Sci. 2012, 5, 8244–8260. [CrossRef]

123. Wang, X.; Rinaldi, R. A Route for Lignin and Bio-Oil Conversion: Dehydroxylation of Phenols into Arenes by Catalytic Tandem Reactions. Angew. Chem. Int. Ed. 2013, 52, 11499–11503. [CrossRef] [PubMed]

124. Kennema, M.; de Castro, I.B.D.; Meemken, F.; Rinaldi, R. Liquid-Phase H-Transfer from 2-Propanol to Phenol on Raney Ni: Surface Processes and Inhibition. ACS Catal. 2017, 7, 2437–2445. [CrossRef]
125. Mauriello, F.; Paone, E.; Pietropaolo, R.; Balu, A.M.; Luque, R. Catalytic transfer hydrogenolysis of lignin derived aromatic ethers promoted by bimetallic Pd/Ni systems. ACS Sustain. Chem. Eng. 2018, 6, 9269–9276. [CrossRef]

126. Cozzula, D.; Vinci, A.; Mauriello, F.; Pietropaolo, R.; Müller, T.E. Directing the Cleavage of Ester C–O Bonds by Controlling the Hydrogen Availability on the Surface of Coprecipitated Pd/Fe₃O₄. ChemCatChem 2016, 8, 1515–1522. [CrossRef]

127. Paone, E.; Espro, C.; Pietropaolo, R.; Mauriello, F. Selective arene production from transfer hydrogenolysis of benzyl phenyl ether promoted by a co-precipitated Pd/Fe₃O₄ catalyst. Catal. Sci. Technol. 2016, 6, 7937–7941. [CrossRef]

128. Kim, M.; Ha, J.-M.; Lee, K.-Y.; Jae, J. Catalytic transfer hydrogenation/hydrogenolysis of guaiacol to cyclohexane over bimetallic RuRe/C catalysts. Catal. Commun. 2016, 86, 113–118. [CrossRef]

129. Guo, T.; Xia, Q.; Shao, Y.; Liu, X.; Wang, Y. Direct deoxygenation of lignin model compounds into aromatic hydrocarbons through hydrogen transfer reaction. Appl. Catal. A 2017, 547, 30–36. [CrossRef]

130. Barta, K.; Matson, T.D.; Fettig, M.L.; Scott, S.L.; Iretskii, A.V.; Ford, P.C. Catalytic disassembly of an organosolv lignin via hydrogen transfer from supercritical methanol. Green Chem. 2010, 12, 1640–1647. [CrossRef]

131. Deuss, P.J.; Scott, M.; Tran, F.; Westwood, N.J.; de Vries, J.G.; Barta, K. Aromatic Monomers by in Situ Conversion of Reactive Intermediates in the Acid-Catalyzed Depolymerization of Lignin. J. Am. Chem. Soc. 2015, 137, 7456–7467. [CrossRef] [PubMed]

132. Galkin, M.V.; Samec, J.S.M. Selective Route to 2-Propenyl Aryls Directly from Wood by a Tandem Organosolv and Palladium-Catalysed Transfer Hydrogenolysis. ChemSusChem 2014, 7, 2154–2158. [CrossRef] [PubMed]

133. Galkin, M.V.; Smit, A.T.; Subbotina, E.; Artenenko, K.A.; Bergquist, J.; Huijgen, W.J.; Samec, J.S.M. Hydrogen-free catalytic fractionation of woody biomass. ChemSusChem 2016, 9, 3280–3287. [CrossRef]

134. Kumaniaev, I.; Samec, J.S.M. Valorization of Quercus suber Bark toward Hydrocarbon Bio-Oil and 4-Ethylguaiaicol. ACS Sustain. Chem. Eng. 2018, 6, 5737–5742. [CrossRef]

135. Kumaniaev, I.; Subbotina, E.; Savmarker, J.; Larhed, M.; Galkin, M.V.; Samec, J.S.M. Lignin depolymerization to monophenolic compounds in a flow-through system. Green Chem. 2017, 19, 5767–5771. [CrossRef]

136. Van den Bosch, S.; Schutyser, W.; Koelewijn, S.-F.; Renders, T.; Courtin, C.M.; Sels, B.F. Tuning the lignin oil OH-content with Ru and Pd catalysts during lignin hydrogenolysis on birch wood. Chem. Commun. 2015, 51, 13158–13161. [CrossRef] [PubMed]

137. Kim, K.H.; Simmons, B.A.; Singh, S. Catalytic transfer hydrogenolysis of ionic liquid processed biorefinery lignin to phenolic compounds. Green Chem. 2017, 19, 215–224. [CrossRef]

138. Song, Q.; Wang, F.; Cai, J.; Wang, Y.; Zhang, J.; Yu, W.; Xu, J. Lignin depolymerization (LDP) in alcohol over nickel-based catalysts via a fragmentation–hydrogenolysis process. Energy Environ. Sci. 2013, 6, 994–1007. [CrossRef]

139. Teodano, A.; Serrano, L.; Pineda, A.; Romero, A.A.; Luque, R.; Labidi, J. Microwave-assisted depolymerisation of organosolv lignin via mild hydrogen-free hydrogenolysis: Catalyst screening. Appl. Catal. B 2014, 145, 43–55. [CrossRef]

140. Ferrini, P.; Rezende, C.A.; Rinaldi, R. Catalytic Upstream Biorefining through Hydrogen Transfer Reactions: Understanding the Process from the Pulp Perspective. ChemSusChem 2016, 9, 3171–3180. [CrossRef] [PubMed]

141. 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. [CrossRef] [PubMed]

142. Molinari, V.; Clavel, G.; Graglia, M.; Antonietti, M.; Esposito, D. Mild Continuous Hydrogenolysis of Kraft Lignin over Titanium Nitride–Nickel Catalyst. ACS Catal. 2016, 6, 1663–1670. [CrossRef]

143. Zhang, J.-W.; Lu, G.-P.; Cai, C. Self-hydrogen transfer hydrogenolysis of β-O-4 linkages in lignin catalyzed by MIL-100(Fe) supported Pd-Ni BMNPs. Green Chem. 2017, 19, 4538–4543. [CrossRef]

144. Remi, Y.N.; Mann, J.K.; McBride, J.R.; Tao, J.; Barnes, C.E.; Labbè, N.; Chmel, S.C. Catalytic transfer hydrogenolysis of organosolv lignin using B-containing FeNi alloyed catalysts. Catal. Today 2018, 302, 190–195. [CrossRef]
145. Luo, L.; Yang, J.; Yao, G.; Jin, F. Controlling the selectivity to chemicals from catalytic depolymerization of kraft lignin with in-situ H$_2$. *Bioresour. Technol.* **2018**, *264*, 1–6. [CrossRef] [PubMed]

146. Huang, X.; Atay, C.; Korányi, T.I.; Boot, M.D.; Hensen, E.J.M. Role of Cu–Mg–Al Mixed Oxide Catalysts in Lignin Depolymerization in Supercritical Ethanol. *ACS Catal.* **2015**, *5*, 7359–7370. [CrossRef]