Short Review

# Catalytic transfer hydrogenolysis as an efficient route in cleavage of lignin and model compounds

Jiaguang Zhang

*School of Chemistry, University of Lincoln, Joseph Banks Laboratories, Lincoln LN6 7DL, United Kingdom*

## Abstract

Cleavage of aromatic ether bonds through hydrogenolysis is one of the most promising routes for depolymerisation and transformation of lignin into value-added chemicals. Instead of using pressurized hydrogen gas as hydrogen source, some reductive organic molecules, such as methanol, ethanol, isopropanol as well as formates and formic acid, can serve as hydrogen donor is the process called catalytic transfer hydrogenolysis. This is an emerging and promising research field but there are very few reports. In this paper, a comprehensive review of the works is presented on catalytic transfer hydrogenolysis of lignin and lignin model compounds aiming to breakdown the aromatic ethers including α-O-4, β-O-4 and 4-O-5 linkages, with focus on reaction mechanisms. The works are organised regarding to different hydrogen donors used, to gain an in-depth understanding of the special role of various hydrogen donors in this process. Perspectives on current challenges and opportunities of future research to develop catalytic transfer hydrogenolysis as a competitive and unique strategy for lignin valorisation are also provided.

## 1. Introduction

Lignin is a main component of lignocellulosic biomass, which accounts for 15−30% by weight and 40% by energy [1]. Valorisation of lignin and its derived compounds by transformation into value-added chemicals and fuels is important for a sustainable future [2–6]. Unlike cellulose [7] and chitin [8], the top two biopolymers in nature—that contain only one monomer linking together primarily by 1,4-glycosidic bond in a liner form, lignin is composed of three types of substituted phenols connected by a number of C−O and C−C bonds, forming a three-dimensional amorphous, irregular polymer. Lignin and its derived compounds contain various kinds of aromatic ether bonds in their molecular structures. Therefore, efficient cleavage of aromatic ether bonds is a key step for the valorisation of lignin and its derived compounds. However, cleavage of these aromatic ether bonds is difficult due to their high strength and stability.

Lignin depolymerisation via hydrogenolysis [9–26], oxidation [27–32], hydrolysis [33–39], thermal [40–43], photo- [44,45] and electro-chemical [46] transformations have been intensively and extensively studied in the past decade. Among various strategies, hydrogenolysis is one of the most promising routes because of its high atom-economy of the overall reaction. In particular, some homogeneous or heterogeneous catalytic systems have been developed for hydrogenolysis cleavage of aromatic ether bonds in the presence of $H_2$, including $Ni(COD)_2$ complex [47,48], $Ni/SiO_2$ [49], Cu-based porous metal oxide [50], and Ni-based bimetallic catalysts [19–21,51–54], etc. However, the high pressure $H_2$ in the reaction system does not only cause more energy input and higher equipment requirement, but also lead to the competitive undesired hydrogenation of aromatic rings. Thus, exploration of efficient

*E-mail address:* jizhang@lincoln.ac.uk.

catalytic routes for hydrogenolysis cleavage of aromatic ether bonds under milder condition is highly desirable.

Reductive organic molecules, such as alcohols, formic acid and formates, can serve as hydrogen source in biomass conversion. If the reaction involved is saturation of C=C or C=O bonds, the process is called catalytic transfer hydrogenation. If the target reaction is cleavage of C–C or C–O bonds, the process is called catalytic transfer hydrogenolysis (Scheme 1). Both processes can be shortened as CTH process. Although CTH was firstly reported more than a century ago, when Knoevenagel employed Pd black as catalyst for the disproportionation of methyl terephthalate [55], it has been largely overshadowed by the success of hydrogenation and hydrogenolysis directly using $H_2$ as hydrogen source. In the last few decades, the development of novel and more efficient catalytic systems has significantly broadened the scope of CTH chemistry. A recent review has highlighted the application of CTH in biomass conversion as an attractive alternative pathway to the conventional high pressure $H_2$ processes [56]. In this paper, the particular applications of catalytic transfer hydrogenolysis in lignin depolymerisation are reviewed (Table 1), to get a more close view into this specific reaction.

## 2. Alcohols as hydrogen source

Alcohols such as methanol, ethanol and isopropanol are widely used as (co-)solvent in the extraction of organosolv lignin from raw lignocellulosic biomass [75]. Although in general alcohols are reductive organic molecules, their performance as hydrogen donors in the transfer hydrogenolysis of lignin is quite different due to their different reactivity. In general, methanol and ethanol dehydrogenated at high temperature (in most case supercritical conditions) and the dehydrated products are not clear, while isopropanol is normally selectively dehydrogenated into acetone under much milder reaction conditions.

Ford and co-workers studied the conversion of a lignin model compound dihydrobenzofuran (DHBF) in supercritical methanol using Cu-doped porous metal oxide (Cu-PMO) as catalyst (Scheme 2) [57]. They were inspired by a noncatalytic process for degradation of lignin and lignin model compounds in the presence of stoichiometric excess amount of KOH [76]. Transition metal doped PMOs, which were

reported as strong solid bases finding applications in $CO_2$ adsorption or catalysing the transesterification for bio-diesel production [77], were employed as catalysts to promote the transfer of hydrogen from methanol to DHBF. A Cu-PMO prepared by calcining Cu-doped hydrotalcites was effective and reusable catalysts for the reaction. The Cu-PMOs turned from green to red after reaction, accompanied by reduction of Cu(II) to Cu(I) and/or Cu(0). The low-valent red Cu-PMO showed a lower activity, and the reactivity could be recovered by calcination which brought Cu to high valent again. The reaction was conducted at 300 °C, where hydrogenolysis product 2-ethylphenol was dominant at the initial 1 h, and then the aromatic ring was slowly hydrogenated to 2-ethylcyclohexanol and methylethylcyclohexanols [57]. The same group then further evaluated the system for the reductive depolymerisation of organosolv lignin. After reaction in supercritical methanol at 300 °C, Cu-PMO could catalyse the depolymerisation of lignin, hydrogenation of aromatic rings, and hydrodeoxygenation of the monomeric products, resulting in a mixture of monomeric products with virtually no aromatics and greatly reduced oxygen content [58].

Chmely et al. reported the use of earth-abundant FeNiB alloy as catalyst for the transfer hydrogenolysis of organosolv lignin using supercritical ethanol as the hydrogen donor and reaction solvent. The system also possesses the ability of the hydrogenation of ketones to alcohols as well as the hydrogenolysis removal of hydroxyl groups, resulting alkylphenols as product [59]. Singh reported the catalytic transfer hydrogenolysis of the lignin-rich residue obtained from an ionic liquid process. The yield of low molecular weight products in the liquid fraction was 65.5 wt% with isopropanol as the hydrogen donor and with Ru/C as the catalyst [60].

Rinaldi et al. developed a Raney-Ni + isopropanol system for lignin and bio-oil conversion [61−63]. The reactions were conducted under very mild reaction conditions, at 60−160 °C in isopropanol using Raney-Ni as catalyst. 32 model compounds, including substituted phenols as well as ones representing 4-O-5, α-O-4 and β-O-4 linkages, were tested in the system. At lower temperatures around 60−80 °C, the transfer hydrogenation of ketone, aldehyde groups and C=C bonds took place, while the aromatic rings remained untouched. The cleavage of the aryl ether linkages also happened at around 80 °C via transfer hydrogenolysis. The conversion of a
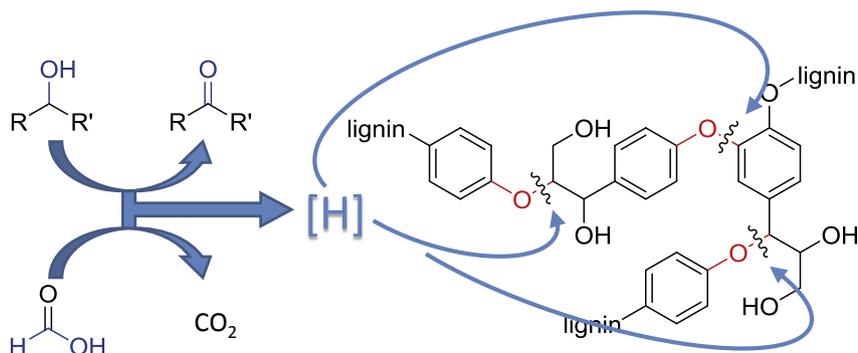


Scheme 1. Transfer hydrogenolysis of lignin ether bonds with alcohols or formic acid as hydrogen donor.

Table 1
Catalytic transfer hydrogenolysis of various lignin/lignin model compounds reported in literatures.

| Substrate | Catalyst | Solvent | Hydrogen donor | Temperature | Ref. |
|---|---|---|---|---|---|
| Dihydrobenzofuran | Cu-PMO | Supercritical methanol | Methanol | 300 °C | [57] |
| Organosolv lignin | Cu-PMO | Supercritical methanol | Methanol | 300 °C | [58] |
| Organosolv lignin | FeNiB | Supercritical ethanol | Ethanol | 320 °C | [59] |
| Lignin-rich residue | Ru/C | Isopropanol | Isopropanol | 300 °C | [60] |
| Model compounds | Raney-Ni | Isopropanol | Isopropanol | 60−80 °C | [61] |
| Bio-oil | Raney-Ni | Isopropanol | Isopropanol | 120−160 °C | [61] |
| Bio-oil or organosolv lignin | Raney-Ni + H-BEA-35 | Isopropanol | Isopropanol | 160−240 °C | [62] |
| Woody biomass | Raney-Ni | Isopropanol/water | Isopropanol | 160−220 °C | [63] |
| Benzyl phenyl ether | Pd/Fe$_3$O$_4$ | Isopropanol | Isopropanol | 240 °C | [64] |
| Diphenyl ether | Ru/C | Isopropanol | Isopropanol | 120 °C | [65] |
| β-O-4 ketone | TiO$_2$ | Ethanol | Ethanol | Photocatalytic | [66,67] |
| β-O-4 alcohol or organosolv lignin | ZnIn$_2$S$_4$ | Acetone or acetonitrile | Intramolecular hydroxyl group | Photocatalytic | [68] |
| β-O-4 alcohol or organosolv lignin | Pd$_1$Ni$_4$/MIL-100(Fe) | Water | Intramolecular hydroxyl group | 130 °C | [69] |
| Bark | Pd/C | Methanol/water | Carbohydrates | 200 °C | [70] |
| Lignin | Ni-SBA-15 | Formic acid | Formic acid | Microwave | [71] |
| β-O-4 model compounds or organosolv lignin | Pd/C | Ethanol/water | Ammonium formate | 80 °C | [72] |
| Pine or birch | Pd/C | Ethanol/water | Ethanol or formic acid | 195 °C | [73] |
| β-O-4 model compounds | Pd/C | Ethyl acetate/water | Intramolecular hydroxyl group | 80 °C | [74] |
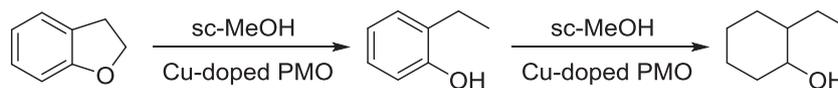


Scheme 2. Cu-PMO catalysed transfer hydrogenolysis and hydrogenation of DHBF in supercritical methanol.

lignocellulose derived bio-oil was carried out in this system at 120−160 °C under autogenous pressure, with substituted phenols and cyclohexanols as products [61]. By incorporating of a solid acid H-BEA-35, the reactivity of the system was altered to the production of arenes. The proposed reaction pathways of phenol conversion in this system are shown in Scheme 3. The initial step is the transfer hydrogenation of phenol to cyclohexanol/cyclohexanone. Then H-BEA-35 catalyses the dehydration of cyclohexanol to cyclohexene.
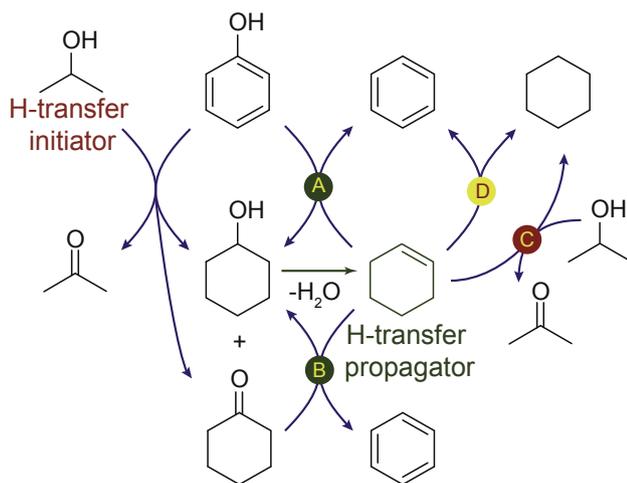


Scheme 3. Proposed pathways of phenol conversion in the Raney-Ni/H-BEA-35/isopropanol system. Arrows in blue indicate the reactions catalysed by Raney-Ni, and arrow in green indicates the dehydration step catalysed by H-BEA-35. Reproduced with permission [62]. Copyright 2013, John Wiley and Sons.

Cyclohexene then acts as H-transfer propagator, yielding benzene as dehydrogenation product. The addition of solid acid also affected the products of the aryl ether model compounds. With tandem transfer hydrogenolysis, transfer hydrogenation, and dehydration reactions, the cleavage of aryl ethers yielded arenes as main products, with very few oxygen containing or saturated products. By slightly increase the reaction temperature, the Raney-Ni + H-BEA-35 catalysed conversion of bio-oil or organosolv lignin was carried out in *n*-pentane at 160−240 °C, using isopropanol as hydrogen source, which also successfully afforded mixed arenes as products [62]. Later on, the system was tested with raw lignocellulosic biomass as starting material, where the reactions were conducted in a 7:3 isopropanol/water mixture at 160−220 °C in the presence of Raney-Ni. This biorefining method is able to convert lignin into a phenolic bio-oil while providing pulp susceptible to enzymatic hydrolysis [63].

Mauriello and co-workers reported the use of Pd/Fe$_3$O$_4$ as catalyst for transfer hydrogenolysis cleavage of benzyl phenyl ether (α-O-4 model compound) using isopropanol as the hydrogen donor. The reactions were carried out under 10 bar N$_2$ at 240 °C for 90 min, achieving 100% yield of phenol and toluene. The unwanted hydrogenation reactions of the aromatic rings were totally avoided over this catalyst. Different alcohols including C$_1$ to C$_4$ primary and secondary alcohols were evaluated as the hydrogen donor, where isopropanol delivered the best performance, in terms of H-donor ability (0.120 mol L$^{-1}$) and benzyl phenyl ether conversion. In the proposed reaction mechanism shown in Scheme 4, the Fe−Pd interface formed during the co-precipitation preparation of the

catalyst was believed to be responsible for the adsorption and activation of the phenyl ether, while the H-donor alcohol was dehydrogenated over the adjacent Pd surface and the α-H and hydroxyl-H were transferred into toluene and phenol, respectively [64].

For 4-O-5 linkage possessing higher bonding energy than α-O-4 and β-O-4 linkages, there are very few reports on cleavage of 4-O-5 model compounds through transfer hydrogenolysis. Han's group recently found that commercial Ru/C could efficiently catalyse the cleavage of 4-O-5 compounds via transfer hydrogenolysis using isopropanol as hydrogen donor. However, due to the high hydrogenation activity of the Ru/C catalyst, aromatic ring saturation was also observed in the reaction system [65].

Wang et al. reported a tandem method for cleaving the β-O-4 linkages by photocatalytic oxidation-hydrogenolysis. For the first step the Pd/ZnIn$_2$S$_4$ catalyst catalyses the aerobic oxidation of the hydroxyl group to a carbonyl group on the α position with 455 nm light, which is known to reduce the bond energy of the adjacent β-O-4 C−O bond; In the second step, a TiO$_2$−NaOAc system is used for cleaving the β-O-4 C−O bond neighbouring the α carbonyl group through a transfer hydrogenolysis reaction using ethanol as the hydrogen source by switching to 365 nm light. The tandem reaction can be carried out in a one pot manner with a dual light wavelength switching (DLWS) strategy, yielding acetophenones and phenols as product with up to 90% selectivity (Fig. 1). In-depth investigations elucidate that the in situ formed $Ti^{3+}$ is responsible for the photocatalytic transfer hydrogenolysis, activating the oxidised β-O-4 bonds by electron transfer from $Ti^{3+}$ to the β-O-4 ketones [66]. Similar to the second step, Li et al. reported the transfer hydrogenolysis of the β-O-4 ketones in ethanol under UV irradiation employing TiO$_2$ as catalyst. Pd/TiO$_2$ and Cu/TiO$_2$ were also investigated in their system, where hydrogenation of ketone groups in the starting material and the acetophenone product, resulting the formation of corresponding alcohols [67].

## 3. Lignin or carbohydrates as hydrogen source

It is a good strategy to use the intramolecular C$_\alpha$H-OH as hydrogen donor for at least two reasons: (a) reducing the β-O-4 bonding energy to facilitate the cleavage; and (b) no need for additional hydrogen source so that offering a more economical choice for the large-scale operations of lignin
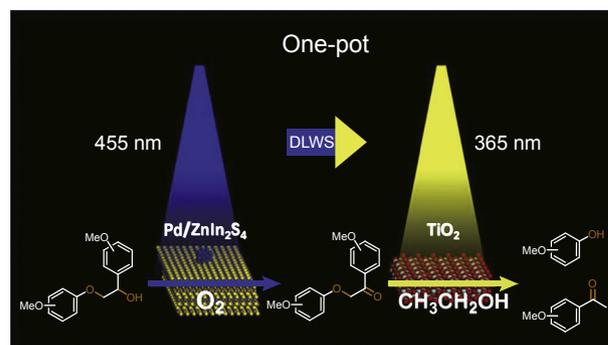


Fig. 1. Oxidation-hydrogenolysis tandem reaction strategy via DLWS for cleaving β-O-4 linkages. Reproduced with permission [66]. Copyright 2016, American Chemistry Society.

depolymerisation. Wang's group recently reported another transfer hydrogenolysis system for β-O-4 cleavage using ZnIn$_2$S$_4$ driven by visible light. In this system, hydroxyl groups of lignin act as hydrogen donors. 71−91% yields of phenols in the conversion of lignin β-O-4 model compounds are achieved, and dioxanesolv poplar lignin is photocatalytically converted to *p*-hydroxyl acetophenone derivatives with 10% yield. In this process, the hydrogen of C$_\alpha$H-OH is transferred to ZnIn$_2$S$_4$ surface to form a "hydrogen pool", and then the hydrogen species in the "hydrogen pool" is used to breakdown the β-O-4 C−O− bond. The dehydration and hydrogenolysis reactions undergo in one-pot manner over a single photocatalyst with lignin itself as the hydrogen donor [68].

The intramolecular transfer hydrogenolysis is also achievable with thermal catalysis. Cai et al. reported a MIL-100(Fe) supported PdNi bimetallic nanoparticles catalyst catalysed intramolecular transfer hydrogenolysis of lignin β-O-4 model compounds as well as organosolv lignin. The reaction was conducted in water at 130 °C under Ar for 6 h, and Pd$_1$Ni$_4$/MIL-100(Fe) demonstrated the best performance. The synergistic effects between the two active metals as well as between the bimetallic nanoparticles and the MOFs support include (a) MIL-100(Fe) can serve as co-catalyst to promote the C$_\alpha$-OH bond cleavage and dehydration to form the "hydrogen pool"; (b) the electron transfer between Pd and Ni in bimetallic nanoparticles together with the interfacial electron transfer effect between the bimetallic nanoparticles and MIL-100(Fe) result in more electron-enriched metal centre, which may
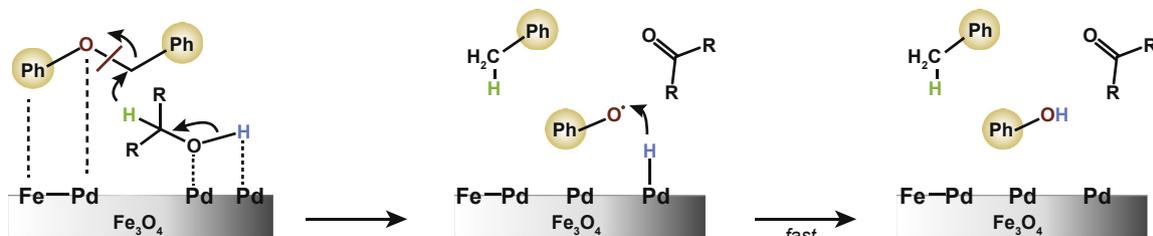


Scheme 4. Proposed reaction mechanism for transfer hydrogenolysis of benzyl phenyl ether over Pd/Fe$_3$O$_4$ catalyst. Reproduced with permission [64]. Copyright 2016, Royal Society of Chemistry.

spur the conversion from $H^+$ to $H^-$ in the "hydrogen pool"; (c) MIL-100(Fe) can enrich the hydrogen molecules around the active sites, speeding up the hydrogenolysis reaction; and (d) the nanoparticles are encapsulated in the micropores of MIL-100(Fe), preventing the potential agglomeration and enhancing the recyclability [69].

In principle, carbohydrates are also reductive which may serve as hydrogen donor in the transfer hydrogenolysis. Kumaniaev and Samec developed a reductive fractionation process for the valorisation of bark. In the first step, transfer hydrogenolysis of lignin takes place where the carbohydrates serve as an inherent hydrogen donor using Pd/C as catalyst. After distillation, 4-ethylguaiacol is isolated with 90% purity and 2.6% yield [70].

## 4. Formic acid/formates as hydrogen source

Formic acid has been regarded as a good candidate for chemically hydrogen storage, since the formation and decomposition is reversible and very easily achieved. Luque et al. have studied lignin depolymerisation in a series of hydrogen-donating solvents under microwave irradiation with 10% Ni-SBA-15 as catalyst. Among the selected solvents (tetralin, isopropanol, glycerol and formic acid), formic acid showed the best performance, yielding around 30 wt% phenolic bio-oil and no biochar under microwave irradiation for 30 min [71].

Samec et al. developed a Pd/C catalysed redox neutral cleavage of lignin β-O-4 type ether bonds via transfer hydrogenolysis [72–74]. The reactions were conducted at 80 °C in ethanol/water in the presence of 1 equivalent of ammonium formate. Different β-O-4 model compounds were tested, and it was found that both the hydroxyl group and

proton on the α-position play a critical role, substrates without either of which cannot undergo any reactions in this system. The presence of at least of one proton on the β-position is necessary too, because the substrate with two methyl substitution on the β-position also cannot be converted. Based on these findings and results from isotope kinetic experiments, a reaction mechanism was proposed as shown in Scheme 5. The substrate **1** is dehydrogenated to ketone **9** in the initial step, which is a slow step. After desorption of hydride facilitated by molecular oxygen in air, ketone **9** adsorbs to Pd surface to form intermediate **A**. A formate ion adsorbs on the surface and provides hydride for the formation and desorption of products aryl ketone **3** and phenol **4**. Encouraged by the results, organosolv lignin from *Pinus sylverstris* was also depolymerised in this system. However, after 24 h reaction with ammonium formate and 12 h reaction with formic acid, there was no significant monomer production, although 73% β-O-4 linkages were cleaved [72]. This should be due to the formation of additional C–C linkages during the organosolv process [10]. The conversion of raw woody biomass including pine and birch gave better results. By a tandem organosolv-transfer hydrogenolysis process, 10% of aryl propene and aryl propane monomers were obtained in ethanol/water solution at 195 °C for 1 h with 5 mol% Pd/C as catalyst, where ethanol acted as the hydrogen source. Addition of 2 equivalent of formic acid in the reaction system led to the increase of monomer yield to 30% [73]. It was also found that by changing the solvent to ethyl acetate/water, the transfer hydrogenolysis cleavage of β-O-4 model compounds would undergo well in the presence of less amount (0.1 equivalent) of hydrogen donor such as formic acid or $NaBH_4$. It was proposed that the hydrogen donors were used for remove the surface oxygen on the Pd catalyst, and the hydrogen for the
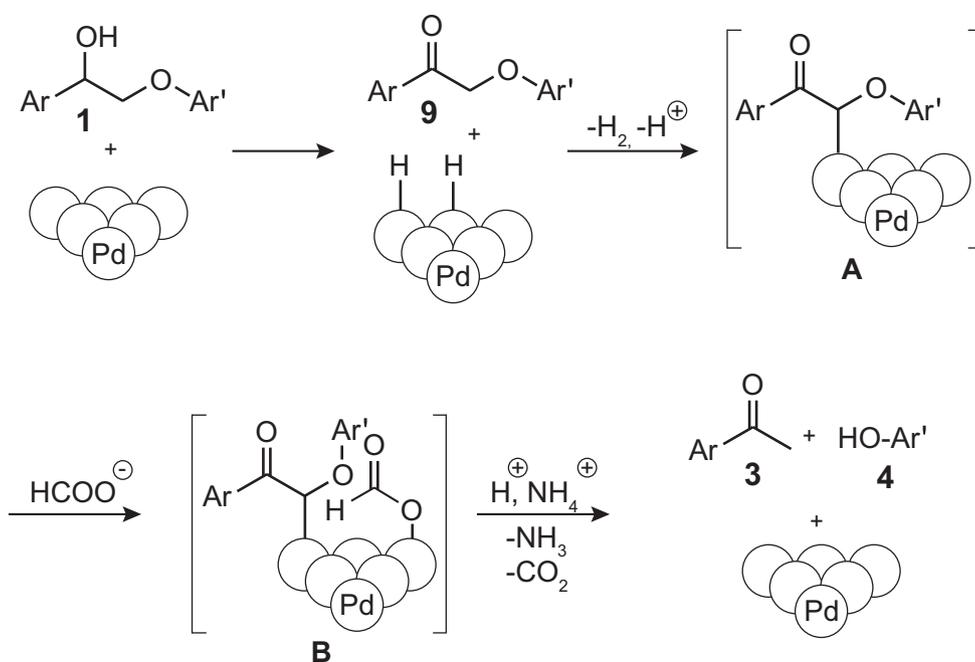


Scheme 5. Proposed mechanism for the transformation of **1** to **3** and **4**. Reproduced with permission [72]. Copyright 2013, John Wiley and Sons.

hydrogenolysis of the linkage was from the model compound by dehydrogenation of the α-hydroxyl group [74].

Samec et al. has recently further developed the system into a flow-through system in which pulping and transfer hydrogenolysis steps were separated in time and space. This approach results in a high yield of phenolic monomers at 37 wt %, which is 83% of the maximum theoretical yield based on the empirical estimation [78] method. This flow through system has shown advantage in preserve the cellulose fraction as it has not been contaminated by the catalyst and thereby is easily enzymatically hydrolysed to glucose (87 wt% yield) without prior purification, which is usually not possible in the direct catalytic conversion of woody biomass. On the other hand, although the pulping and transfer hydrogenolysis steps are separated in time and space, the distance in time and space is well controlled so that the extracted lignin would not undergo major re-condensation reactions, leading to a high phenolic monomers yield [79].

## 5. Perspectives

The various reactions and catalytic systems discussed in Sections 2–4 have revealed the emerging applications of catalytic transfer hydrogenolysis in lignin depolymerisation. The different hydrogen donors, e.g., methanol, ethanol, isopropanol, formates/formic acid, and intramolecular hydrogen donors, require different catalyst and reaction conditions, and realise the transformation through different reaction pathways and with different performances. The works, which are not only using organic molecules as alternative hydrogen source but also taking advantages from the unique reaction mechanism where the hydrogen donors react directly with substrate to afford new reaction pathways, are particularly interesting. This type of work is making full use of the nature of transfer hydrogenolysis, and it is the future trend in application of transfer hydrogenolysis in lignin depolymerisation. The versatility of hydrogen donors, catalysts, and reaction realisation manners afford the possibility of developing highly efficient process; on the other hand, a better understanding of the following aspects in future research is crucial to push forward the application of transfer hydrogenolysis in lignin depolymerisation.

### 5.1. Reaction mechanism at molecular level

In transfer hydrogenolysis of aromatic ether bonds, the reaction mechanisms are typically the fusion of two catalytic cycles, which are the dehydrogenation or activation of the hydrogen donors and the reaction on the aromatic ether bonds. In some cases, the two cycles are even merging into one new cycle where an intermediate is formed between the hydrogen donor and the substrate. In situ characterisations, isotopic labelling and theoretical calculation should be combined together with conventional kinetics study and substrate scope study, to get a clearer reaction mechanism at molecular level, which is helpful to achieve an in-depth understanding of the reaction pathway and the role of the catalyst and hydrogen donor.

### 5.2. Other role of hydrogen donors in the reaction

Alcohols as hydrogen donors are normally also used as (part of) reaction solvent. As a solvent, its properties of acidity, polarity, and hydrogen bonding ability also play vital roles in the reactivity of the whole catalytic system. These solvent properties should also be taken into consideration as additional aspect when selecting the hydrogen donors.

Moreover, formic acid as reaction mediate is offering strong acidity and can react with the hydroxyl groups through esterification reaction, which offers unique reaction pathways for deoxygenation and dehydrogenation [80]. It can be anticipated that use of formic acid as reaction solvent in the transfer hydrogenolysis may lead to new and efficient depolymerisation mechanism.

### 5.3. Catalyst design

As mentioned above, the transfer hydrogenolysis typically involves two catalytic cycles. Either a single catalytic centre compatible for the two cycles or bifunctional catalyst is desired for the process. However, in the published papers, very limited works are focused on the catalyst design. Thus, it is important to intentionally design catalyst suitable for the transfer hydrogenolysis of lignin aromatic ether bonds with a certain hydrogen donor.

## Conflict of interest

There is no conflict of interest.

## References

[1]  K. Sanderson, Nature 474 (2011) S12–S14.
[2]  C. Li, X. Zhao, A. Wang, G.W. Huber, T. Zhang, Chem. Rev. 115 (2015) 11559–11624.
[3]  M. Saidi, F. Samimi, D. Karimipourfard, T. Nimmanwudipong, B.C. Gates, M.R. Rahimpour, Energy Environ. Sci. 7 (2014) 103–129.
[4]  P. Azadi, O.R. Inderwildi, R. Farnood, D.A. King, Renew. Sustain. Energy Rev. 21 (2013) 506–523.
[5]  J. Zakzeski, P.C.A. Bruijnincx, A.L. Jongerius, B.M. Weckhuysen, Chem. Rev. 110 (2010) 3552–3599.
[6]  Y. Wang, S. De, N. Yan, Chem. Commun. 52 (2016) 6210–6224.
[7]  L.T. Mika, E. Cséfalvay, Á. Németh, Chem. Rev. 118 (2018) 505–613.
[8]  N. Yan, X. Chen, Nature 524 (2015) 155–157.
[9]  Y. Shao, Q. Xia, L. Dong, X. Liu, X. Han, S.F. Parker, Y. Cheng, L.L. Daemen, A.J. Ramirez-Cuesta, S. Yang, Y. Wang, Nat. Commun. 8 (2017) 16104.
[10] L. Shuai, M.T. Amiri, Y.M. Questell-Santiago, F. Héroguel, Y. Li, H. Kim, R. Meilan, C. Chapple, J. Ralph, J.S. Luterbacher, Science 354 (2016) 329–333.
[11] Q. Xia, Z. Chen, Y. Shao, X. Gong, H. Wang, X. Liu, S.F. Parker, X. Han, S. Yang, Y. Wang, Nat. Commun. 7 (2016) 11162.
[12] M. Zaheer, R. Kempe, ACS Catal. 5 (2015) 1675–1684.
[13] S. Van den Bosch, W. Schutyser, R. Vanholme, T. Driessen, S.F. Koelewijn, T. Renders, B. De Meester, W.J.J. Huijgen, W. Dehaen, C.M. Courtin, B. Lagrain, W. Boerjan, B.F. Sels, Energy Environ. Sci. 8 (2015) 1748–1763.
[14] V. Molinari, C. Giordano, M. Antonietti, D. Esposito, J. Am. Chem. Soc. 136 (2014) 1758–1761.
[15] K. Barta, G.R. Warner, E.S. Beach, P.T. Anastas, Green Chem. 16 (2014) 191–196.

[16] X. Huang, T.I. Korányi, M.D. Boot, E.J.M. Hensen, ChemSusChem 7 (2014) 2276–2288.

[17] R. Ma, W. Hao, X. Ma, Y. Tian, Y. Li, Angew. Chem. Int. Ed. 53 (2014) 7310–7315.

[18] P. Ferrini, R. Rinaldi, Angew. Chem. Int. Ed. 53 (2014) 8634–8639.

[19] J. Zhang, H. Asakura, J.v. Rijn, J. Yang, P. Duchesne, B. Zhang, X. Chen, P. Zhang, M. Saeys, N. Yan, Green Chem. 16 (2014) 2432–2437.

[20] H. Konnerth, J. Zhang, D. Ma, M.H.G. Prechtl, N. Yan, Chem. Eng. Sci. 123 (2015) 155–163.

[21] J. Zhang, J. Teo, X. Chen, H. Asakura, T. Tanaka, K. Teramura, N. Yan, ACS Catal. 4 (2014) 1574–1583.

[22] Y. Hu, G. Jiang, G. Xu, X. Mu, Mol. Catal. 445 (2018) 316–326.

[23] Z. Luo, Z. Zheng, L. Li, Y.-T. Cui, C. Zhao, ACS Catal. 7 (2017) 8304–8313.

[24] B. Ma, H. Cui, D. Wang, P. Wu, C. Zhao, Nanoscale 9 (2017) 5986–5995.

[25] J. Chen, F. Lu, X. Si, X. Nie, J. Chen, R. Lu, J. Xu, ChemSusChem 9 (2016) 3353–3360.

[26] H. Guo, B. Zhang, Z. Qi, C. Li, J. Ji, T. Dai, A. Wang, T. Zhang, ChemSusChem 10 (2017) 523–532.

[27] C.S. Lancefield, O.S. Ojo, F. Tran, N.J. Westwood, Angew. Chem. Int. Ed. 127 (2015) 260–264.

[28] R. Ma, M. Guo, X. Zhang, ChemSusChem 7 (2014) 412–415.

[29] Y. Gao, J. Zhang, X. Chen, D. Ma, N. Yan, ChemPlusChem 79 (2014) 825–834.

[30] R. Lu, F. Lu, J. Chen, W. Yu, Q. Huang, J. Zhang, J. Xu, Angew. Chem. Int. Ed. 55 (2016) 249–253.

[31] W. Deng, H. Zhang, X. Wu, R. Li, Q. Zhang, Y. Wang, Green Chem. 17 (2015) 5009–5018.

[32] M. Wang, X. Zhang, H. Li, J. Lu, M. Liu, F. Wang, ACS Catal. 8 (2018) 1614–1620.

[33] P.J. Deuss, M. Scott, F. Tran, N.J. Westwood, J.G. de Vries, K. Barta, J. Am. Chem. Soc. 137 (2015) 7456–7467.

[34] T.D.H. Nguyen, M. Maschietti, T. Belkheiri, L.-E. Åmand, H. Theliander, L. Vamling, L. Olausson, S.-I. Andersson, J. Supercrit. Fluids 86 (2014) 67–75.

[35] L. Yang, Y. Li, P.E. Savage, Ind. Eng. Chem. Res. 53 (2014) 2633–2639.

[36] J.A. Onwudili, P.T. Williams, Green Chem. 16 (2014) 4740–4748.

[37] A. Toledano, L. Serrano, J. Labidi, Fuel 116 (2014) 617–624.

[38] J. Pan, J. Fu, S. Deng, X. Lu, Energy Fuels 28 (2013) 1380–1386.

[39] J. Hu, D. Shen, S. Wu, H. Zhang, R. Xiao, Energy Fuels 28 (2014) 4260–4266.

[40] S. Adhikari, V. Srinivasan, O. Fasina, Energy Fuels 28 (2014) 4532–4538.

[41] G.T. Neumann, B.R. Pimentel, D.J. Rensel, J.C. Hicks, Catal. Sci. Technol. 4 (2014) 3953–3963.

[42] G. Jiang, Y. Hu, G. Xu, X. Mu, H. Liu, ACS Sustain. Chem. Eng. 6 (2018) 5772–5783.

[43] M.P. Pandey, C.S. Kim, Chem. Eng. Technol. 34 (2011) 29–41.

[44] J.D. Nguyen, B.S. Matsuura, C.R.J. Stephenson, J. Am. Chem. Soc. 136 (2013) 1218–1221.

[45] H. Liu, H. Li, J. Lu, S. Zeng, M. Wang, N. Luo, S. Xu, F. Wang, ACS Catal. 8 (2018) 4761–4771.

[46] D. Shao, J. Liang, X. Cui, H. Xu, W. Yan, Chem. Eng. J. 244 (2014) 288–295.

[47] A.G. Sergeev, J.F. Hartwig, Science 332 (2011) 439–443.

[48] A.G. Sergeev, J.D. Webb, J.F. Hartwig, J. Am. Chem. Soc. 134 (2012) 20226–20229.

[49] J. He, C. Zhao, J.A. Lercher, J. Am. Chem. Soc. 134 (2012) 20768–20775.

[50] T.D. Matson, K. Barta, A.V. Iretskii, P.C. Ford, J. Am. Chem. Soc. 133 (2011) 14090–14097.

[51] S. De, J. Zhang, R. Luque, N. Yan, Energy Environ. Sci. 9 (2016) 3314–3347.

[52] S. Bulut, S. Siankevich, A.P. van Muyden, D.T.L. Alexander, G. Savoglidis, J. Zhang, V. Hatzimanikatis, N. Yan, P.J. Dyson, Chem. Sci. 9 (2018) 5530–5535.

[53] J. Zhang, N. Yan, Part. Part. Syst. Charact. 33 (2016) 610–619.

[54] J. Zhang, M. Ibrahim, V. Collière, H. Asakura, T. Tanaka, K. Teramura, K. Philippot, N. Yan, J. Mol. Catal. A: Chem. 422 (2016) 188–197.

[55] G. Brieger, T.J. Nestrick, Chem. Rev. 74 (1974) 567–580.

[56] M.J. Gilkey, B. Xu, ACS Catal. 6 (2016) 1420–1436.

[57] G.S. Macala, T.D. Matson, C.L. Johnson, R.S. Lewis, A.V. Iretskii, P.C. Ford, ChemSusChem 2 (2009) 215–217.

[58] K. Barta, T.D. Matson, M.L. Fettig, S.L. Scott, A.V. Iretskii, P.C. Ford, Green Chem. 12 (2010) 1640–1647.

[59] Y.N. Regmi, J.K. Mann, J.R. McBride, J. Tao, C.E. Barnes, N. Labbé, S.C. Chmely, Catal. Today 302 (2018) 190–195.

[60] K.H. Kim, B.A. Simmons, S. Singh, Green Chem. 19 (2017) 215–224.

[61] X. Wang, R. Rinaldi, Energy Environ. Sci. 5 (2012) 8244–8260.

[62] X. Wang, R. Rinaldi, Angew. Chem. Int. Ed. 52 (2013) 11499–11503.

[63] F. Paola, R. Roberto, Angew. Chem. Int. Ed. 53 (2014) 8634–8639.

[64] E. Paone, C. Espro, R. Pietropaolo, F. Mauriello, Catal. Sci. Technol. 6 (2016) 7937–7941.

[65] H. Wu, J. Song, C. Xie, C. Wu, C. Chen, B. Han, ACS Sustain. Chem. Eng. 6 (2018) 2872–2877.

[66] N. Luo, M. Wang, H. Li, J. Zhang, H. Liu, F. Wang, ACS Catal. 6 (2016) 7716–7721.

[67] J. Fang, P. Ye, M. Wang, D. Wu, A. Xu, X. Li, Catal. Commun. 107 (2018) 18–23.

[68] N. Luo, M. Wang, H. Li, J. Zhang, T. Hou, H. Chen, X. Zhang, J. Lu, F. Wang, ACS Catal. 7 (2017) 4571–4580.

[69] J.-w. Zhang, G.-p. Lu, C. Cai, Green Chem. 19 (2017) 4538–4543.

[70] I. Kumaniaev, J.S.M. Samec, ACS Sustain. Chem. Eng. 6 (2018) 5737–5742.

[71] A. Toledano, L. Serrano, J. Labidi, A. Pineda, A.M. Balu, R. Luque, ChemCatChem 5 (2013) 977–985.

[72] M.V. Galkin, S. Sawadjoon, V. Rohde, M. Dawange, J.S.M. Samec, ChemCatChem 6 (2014) 179–184.

[73] M.V. Galkin, J.S.M. Samec, ChemSusChem 7 (2014) 2154–2158.

[74] M.V. Galkin, C. Dahlstrand, J.S.M. Samec, ChemSusChem 8 (2015) 2187–2192.

[75] F. Xu, J.-X. Sun, R. Sun, P. Fowler, M.S. Baird, Ind. Crops Prod. 23 (2006) 180–193.

[76] J.E. Miller, L. Evans, A. Littlewolf, D.E. Trudell, Fuel 78 (1999) 1363–1366.

[77] G.S. Macala, A.W. Robertson, C.L. Johnson, Z.B. Day, R.S. Lewis, M.G. White, A.V. Iretskii, P.C. Ford, Catal. Letters 122 (2008) 205–209.

[78] N. Yan, C. Zhao, P.J. Dyson, C. Wang, L.-t. Liu, Y. Kou, ChemSusChem 1 (2008) 626–629.

[79] I. Kumaniaev, E. Subbotina, J. Savmarker, M. Larhed, M.V. Galkin, J.S.M. Samec, Green Chem. 19 (2017) 5767–5771.

[80] J. Zhang, N. Yan, Green Chem. 18 (2016) 5050–5058.