Hydrodeoxygenation processes: advances on catalytic transformations of biomass-derived
platform chemicals into hydrocarbon fuels

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Abstract

Lignocellulosic biomass provides an attractive source of renewable carbon that can be sustainably converted into chemicals and fuels. Hydrodeoxygenation (HDO) processes have recently received considerable attention to upgrade biomass-derived feedstocks into liquid transportation fuels. The selection and design of HDO catalysts plays an important role to determine the success of the process. This review has been aimed to emphasize recent developments on HDO catalysts in effective transformations of biomass-derived platform molecules into hydrocarbon fuels with reduced oxygen content and improved H/C ratios. Liquid hydrocarbon fuels can be obtained by combining oxygen removal processes (e.g. dehydration, hydrogenation, hydrogenolysis, decarbonylation etc.) as well as by increasing the molecular weight via C–C coupling reactions (e.g. aldol condensation, ketonization, oligomerization, hydroxyalkylation etc.). Fundamentals and mechanistic aspects of the use of HDO catalysts in deoxygenation reactions will also be discussed.

Keywords: Biorefinery, Hydrogenation, Hydrodeoxygenation, C–C coupling, Liquid hydrocarbon.

1. Introduction

Declining fossil fuel resources, along with the increased petroleum demand by emerging economies, drives our society to search for new sources of liquid fuels. With decreasing crude-oil reserves, increased political and environmental concerns about the use of fossil-based energy carriers, the focus has recently turned towards an improved utilization of renewable energy resources. Biomass is a highly abundant and carbon-neutral renewable energy resource, being an ideal alternative option for the production of biofuels using different catalytic technologies from conventional petroleum refinery processing. During the last decade, innovative protocols have been developed for the production of biofuels from sustainable resources. Several fuel components have been identified and tested by means of biomass valorization. The results have been already summarized in recent overviews in past years (Huber and Corma, 2007; Alonso et al., 2010; Climent et al., 2014).^{1,2,3} Based on the aforementioned premises, the proposed contribution has been aimed to emphasize the critical and fundamental role of innovative and newly reported catalytic systems in the HDO process. The role of active catalyst functions has been discussed with their interconnected mechanistic insights.

Lignocellulose is the major non-food component of biomass comprising three main fractions, namely cellulose (40–50%), hemicellulose (25–35%) and lignin (15–20%). Cellulose is a polymer of glucose units linked by β -glycosidic bonds which can lead to important building blocks (e.g. levulinic acid, 5-hydroxymethylfurfural) upon pretreatment via hydrolysis followed by dehydration. Hemicellulose is comparably composed of C₅ and C₆ sugar monomers including D-xylose, D-galactose, D-arabinose, D-glucose and D-mannose as major compounds. Lignin is the most complex and recalcitrant fraction, having a three-dimensional randomised aromatic structure responsible for the structural rigidity of plants.

Three main existing routes for lignocellulosic processing into fuels and chemicals include gasification, pyrolysis and pretreatment/hydrolysis. Gasification and pyrolysis are pure thermal routes aimed to convert lignocellulose into syngas and liquid fractions (bio-oils) which are valuable intermediates for the production of fuels and chemicals. However, the harsh temperature conditions employed in these routes difficult a proper control of reaction chemistries producing intermediate fractions with high degrees of impurities that require deep cleaning and/or conditioning prior to upgrading to valuable products.

Pretreatment/hydrolysis routes allow separation/fractionation of lignin and carbohydrate fractions of lignocellulose. The sugar fraction can be subsequently processed to fuels and chemicals using (bio)chemical and biological routes whereas lignin is typically burnt to provide heat and electricity for various processes. Separate catalytic treatments of the different fractions (namely hemicellulose and cellulose) can provide access to different platform chemicals. Following the production of platform chemicals, various catalytic strategies have been developed for their upgrading into fuels.

Biomass-derived platform molecules are generally highly oxygenated compounds and their conversion into liquid hydrocarbon fuels needs oxygen removal reactions. New catalytic routes and mechanistic insights are required to develop advanced methods for a chemically controllable disassembly of biopolymers as well as subsequent selective deoxygenation of resulting feedstocks (Rinaldi and Schuth, 2009; Huber et al., 2006).^{4,5} Different methods including dehydration, hydrogenolysis, hydrogenation, decarbonylation, decarboxylation have been reported to remove oxygen functionalities. Diesel range hydrocarbons can also be obtained by increasing the carbon number via C–C coupling reactions through different chemistries including aldol-condensation, ketonization, oligomerization and hydroxyalkylation. A major challenge in converting biomass into hydrocarbon fuels relates to

an efficient cleavage of ubiquitous ether and alcoholic C–O linkages within the feedstock molecules to reduce both the oxygen content and degree of polymerization.

Hydrodeoxygenation (HDO) can be currently considered as most effective method for bio-oil upgrading which improves the effective H/C ratio, eventually leading to hydrocarbons. The key challenge of HDO processes is to achieve a high degree of oxygen removal with minimum hydrogen consumption, for which catalysts need appropriate and careful designed. Up to now, several classes of catalysts have been reported for HDO, with various advantages and disadvantages (He and Wang, 2012).⁶ Precious metal catalysts (e.g., Pd, Pt, Re, Rh, and Ru) and non-precious metal catalysts (e.g., Fe, Ni and Cu) have exhibited good activities in hydrogenation/hydrogenolysis reactions. However, the proposed systems require high hydrogen pressures that result in excessive hydrogen consumption, leading to complete hydrogenation of double bonds in some systems (Bykova et al., 2012).⁷

Industrial catalysts based on Co–Mo–Ni formulations can provide a comparatively superior HDO performance but these undergo rapid deactivation due to coke formation and water poisoning (Badawi et al., 2011).⁸ Since HDO reactions generally require high pressures of hydrogen, a selective HDO catalyst is highly desirable in order to prevent complete hydrogenation of unsaturated compounds as well as to prevent over-utilisation of expensive hydrogen. In the light of these premises, cost effective and simple catalytic routes combined with advanced highly active and stable (nano) catalytic systems are required for a large scale commercial development of lignocellulosic biofuels.

This contribution summarizes recent advances in HDO processes for the transformation of biomass-derived feedstocks into liquid transportation fuels (Scheme S1).

2. HMF platform for hydrocarbon fuels

5-hydroxymethylfurfural (HMF) is a highly reactive biomass-derived compound with a challenging hydrogenation/hydrogenolysis profile due to the presence of several functionalities in its structure including double bonds, hydroxyl and carbonyl groups (Nakagawa et al., 2013).⁹ HMF reductive chemistries include C=O bond reduction, hydrogenation of the furan ring as well as C–O hydrogenolysis. In this section, we will mainly discuss a number of key proposed catalytic technologies for hydrogenation and C–C coupling reactions followed by HDO to upgrade HMF into higher energy hydrocarbons.

2.1. Hydrogenation of HMF

2,5-dimethylfuran (DMF) has received increasing attention in recent years as promising liquid transportation biofuel. DMF can be obtained via selective hydrogenation of biomass-derived HMF. Compared to current market-leading bioethanol, DMF possesses a higher energy density, higher boiling point and a higher octane number, being also immiscible with water. Studies on selective hydrogenation of HMF into DMF are becoming highly relevant in the field of bioenergy. Production strategies of DMF from HMF have been recently reviewed by Hu *et al.* (Hu et al., 2014).¹⁰

The Dumesic group studied and evaluated the different possible strategies to upgrade HMF into liquid fuels (Alonso et al., 2010). The breakthrough of deriving DMF from biomass-derived fructose was firstly reported in a two-step process (Roman-Leshkov et al., 2007).¹¹ The first step involved an acid-catalyzed dehydration of fructose (30 wt%) in a biphasic reactor to produce HMF, followed by subsequent hydrogenation over a supported bimetallic Cu-Ru/C catalyst using molecular hydrogen (H₂) in 1-butanol. The initial

hydrogenation reactions were carried out in the presence of copper chromite (CuCrO_4) catalysts. This catalyst was however shown to be easily deactivated by chloride ions even at ppm level. The low melting point and high surface mobility of Cu(I) chloride species were observed to accelerate Cu catalysts sintering. To overcome this problem, a chloride-resistant carbon-supported copper-ruthenium (Cu-Ru/C) catalyst was developed. Based on literature reports, copper has a comparably lower surface energy to that of ruthenium and their combination generates a two-phase system in which the copper phase coats the ruthenium surface as confirmed by electron spectroscopy. The designed Carbon-supported Ru catalyst is resistant to deactivation by chloride ions, while Cu shows the predominant role in hydrogenolysis over Ru. Cu-Ru/C catalyst consequently exhibits copper-like hydrogenolysis behaviour combined with ruthenium-like chlorine resistance. The liquid-phase hydrogenation of HMF using Cu-Ru/C catalyst provided quantitative conversion of HMF with a maximum 71% DMF selectivity under 6.8 bar H_2 in 1-butanol (Table 1). The authors demonstrated no deactivating effect of chloride ions when the reaction was repeated in the presence of 1.6 mmol/L chloride ions. After this pioneering work, many groups have attempted DMF synthesis using different approaches.

The same catalytic system (Cu-Ru/C, hydrogen and 1-butanol) was also explored for the selective hydrogenation of crude biomass-derived HMF from corn stover (Binder and Raines, 2009).¹² A 49% DMF yield from HMF was achieved at 220 °C after 10 h, which further proved a wide applicability of Cu-Ru/C in the selective hydrogenation of HMF to DMF, although the activity of the Cu-Ru/C catalyst in the later reaction was much lower than that reported by Dumesic et al.

A two-step approach for the conversion of glucose into DMF was also attempted in ionic liquids (ILs) in combination with acid catalysts (Chidambaram and Bell, 2010).¹³ This process involved glucose dehydration to HMF in [EMIM]Cl and acetonitrile using

12-molybdophosphoric acid (12-MPA) as catalyst, followed by subsequent conversion of HMF into DMF using Pd/C in a one-pot method. This method provided only 19% conversion of HMF with a poor DMF selectivity (13%). One of the major drawbacks of the proposed protocol related to the requirement of very high hydrogen pressures (62 bar) owing to its low solubility in ILs.

In a very recent report, a novel catalytic strategy for the selective hydrogenation of HMF using supercritical carbon dioxide and water as reaction medium has been developed in the presence of Pd/C (Chatterjee et al., 2014).¹⁴ The most interesting finding of this work relates to the possibility to switch the selectivity to various key compounds by simply tuning CO₂ pressure. Quantitative DMF yields could be achieved at 10 MPa CO₂ and 1 MPa H₂ and 80 °C for 2 h. At the lower pressure region (4–6 MPa), tetrahydro-5-methyl-2-furanmethanol (MTHFM) was formed with a comparatively higher selectivity (57.8%) whereas complete hydrogenation of DMF was observed (selectivity dropped to 27%) with an increase in 2,5-dimethyltetrahydrofuran (DMTHF) selectivity at higher CO₂ pressures (>12 MPa). DMF selectivity was found to be dependent on CO₂ to H₂O molar ratio, with an excessive CO₂ or H₂O concentration reducing such selectivity. An optimum mole ratio of CO₂ to H₂O = 1:0.32 was necessary to achieve high DMF selectivity.

Owing to the different functionalities in HMF, several by-products are typically formed in HMF conversion processes which lead to a low DMF yield and increase the costs of product purification. One of the proposed approaches to improve DMF yield relates to the exploration of bimetallic catalysts. In bimetallic systems, the incorporation of a second metal creates a number of possibilities to modify the surface structure and composition of metal catalysts towards the design of advanced materials. In general, the properties of bimetallic catalysts have been shown to be significantly different from their monometallic analogues due to geometric and electronic effects between the two metals (Tao et al., 2012).¹⁵

The catalytic activity of these catalysts can be easily tuned by changing their size and composition. PtCo bimetallic nanoparticles have been reported as effective catalysts for selective C=O bond hydrogenation in the presence of C=C bonds (Tsang et al., 2008).¹⁶ This is achieved via minimisation of unselective low coordination sites and optimization in the electronic environment of Pt nanoparticles of appropriate size upon Co decoration. Pt (111) surfaces preferentially adsorb α,β -unsaturated aldehyde in a terminal di- σ_{Co} mode which leads to a preferential terminal aldehyde reduction to unsaturated alcohol. In contrast, low coordination sites favor π interactions with C=C bonds, which account for unselective products. In this way, PtCo bimetallic nanoparticles encapsulated in hollow carbon spheres were reported to achieve quantitative HMF conversion with an 98% DMF yield in 2 h (Wang et al., 2014).¹⁷ A soft-templating method was used to generate such uniform hollow carbon sphere structures and Pt nanoparticles were incorporated inside the spheres by *in-situ* impregnation during the carbonization process. Cobalt nanoparticles were introduced in a subsequent step using as-synthesized Pt@HPS, with final PtCo@HCS material obtained upon Pt@HPS-Co⁺² pyrolysis under H₂/Ar atmosphere. Using PtCo@HCS-500 as a catalyst, 2,5-di(hydroxymethyl)furan was obtained as main product (70%) at 120 °C, which indicates the effectiveness of PtCo@HCS-500 for the selective hydrogenation of the formyl group in HMF. Almost quantitative DMF yield (96%) was obtained when the reaction temperature was raised to 160 °C, confirming that PtCo@HCS-500 can also catalyze the hydrogenolysis of the hydroxyl group at high temperature. A further increase of reaction temperature and time did not significantly affect DMF yields. The kinetics of hydrogenation and hydrogenolysis steps as well as the effect of other catalysts were also studied in this work. A rapid increase of DMF yield (from 44% to 95% after 6 min) indicates that the hydrogenolysis step is the rate-determining step for the formation of DMF. Using crushed PtCo@HCS as a control, comparable DMF yield was achieved to that of PtCo@HCS within 40 min, indicating

a negligible mass transfer limitation induced by the hollow shells. For comparative purposes, the authors utilised activated carbon-supported platinum (Pt/AC) and graphitized carbon-supported platinum (Pt/GC) catalysts under the same reaction conditions. However, only 9% and 56% DMF yields were respectively obtained. Interestingly, the conversion of HMF and the yield of DMF were increased to 100% and 98%, respectively, when catalysts were modified with cobalt to form PtCo/AC and PtCo/GC. These results demonstrate the pivotal role of bimetallic alloy systems for the selective hydrogenolysis of HMF to DMF. The overall outstanding catalytic performance of the catalyst in the hydrogenolysis of HMF to DMF was due to the small particle size and the homogeneous alloying of two metals.

Comparatively, a highly efficient non-noble bimetallic catalyst based on nickel-tungsten carbide for the hydrogenolysis of HMF to DMF with excellent yields was recently reported (Huang et al., 2014).¹⁸ Using different catalysts, metal ratios and reaction conditions, a maximum DMF yield of 96% was obtained. To understand the role of Ni and W₂C components in the hydrogenolysis reaction, Ni/AC and W₂C were prepared and individually tested. Results suggested two different different roles for metals: Ni particles mainly contributed to hydrogenation activity while tungsten carbide (W₂C) offers an additional deoxygenation activity. W₂C particles have already been reported as a bifunctional catalyst containing both acidic and metallic sites, and can therefore catalyze both deoxygenation and hydrogenation reactions. However, the addition of a second metal center (Ni) was proved to be essential to increase the active hydrogen concentration to improve hydrogenation rates. Higher Ni loadings were also shown to promote a remarkably improvement in hydrogenolysis reaction upon increasing the hydrogenation ability.

A carbon supported PdAu bimetallic catalyst has been recently reported by Ebitani *et al.* for the selective hydrogenation of HMF to DMF (Nishimura et al., 2014).¹⁹ Pd_xAu_y/C catalysts with various Pd/Au molar ratios (x/y) were prepared and tested in the presence of

hydrochloric acid (HCl) under atmospheric hydrogen pressure. Almost quantitative yields to DMF were achieved. Results showed that the bimetallic Pd_xAu_y/C catalysts exhibited a significantly higher activity as compared to monometallic Pd/C and Au/C catalysts. To clarify the novelty of the catalyst, the authors claimed the existence of a charge transfer phenomenon from Pd to Au atoms which was proved by XPS and X-ray absorption near-edge structure (XANES) analyses. Au atoms gain electrons from Pd atoms as a result of alloy formation and negatively charged Au atoms are produced with the co-existence of Pd atoms in PdAu/C, which significantly enhanced the hydrogenation activity.

A remarkable synergy between Pd and Ir has also been observed in bimetallic Pd-Ir alloy particles supported on SiO₂ for the hydrogenation of furfural and HMF in water (Nakagawa et al., 2014).²⁰ Higher H₂ pressure and lower reaction temperatures made the hydrogenation process selective by suppressing side reactions. Incorporation of Ir showed a remarkably higher TOF to that achieved using monometallic Pd catalysts with similar particle size, particularly for C=O hydrogenation. Ir atoms on the surface were found to promote the adsorption at C=O site, whereas the Pd surface strongly interacts with the furan ring.

Hydrogen donor solvents (e.g. formic acid, alcohols, etc.) have been comparably utilised in replacement of molecular H₂ as hydrogenating agent in HMF conversion to DMF. A successful one-pot conversion of sugar into DMF was developed using formic acid (FA) as hydrogen carrier (Thananattathanachon and Rauchfuss, 2010).²¹ FA played multiple roles in the conversion of fructose into DMF; i.e. dehydrating agent (acid catalyst) to remove water from sugar to produce HMF and key roles in subsequent steps of hydrogenation and hydrogenolysis. In these steps, FA could be a hydrogenating agent on supported catalysts and a deoxygenating agent in the presence of catalytic amounts of concentrated H₂SO₄, thereby turning the process into a one-pot conversion. The conversion is believed to proceed via formation of 5-formyloxymethylfurfural (FMF), 2-hydroxymethyl-5-methylfuran (HMMF)

and 2-formyloxymethyl-5-methylfuran (FMMF) intermediates. This method produced 51% DMF yield from fructose and 95% DMF yield from HMF.

A similar catalytic strategy was proposed for the conversion of HMF and a range of substrates (including fructose, cellulose, sugarcane bagasse, and agar) to DMF (De et al., 2012).²² Both oil-bath and microwave-assisted reactions were conducted in the presence of Ru/C as hydrogenation catalyst. Conversion values around 30% DMF were obtained from fructose without any significant differences between conventional and microwave heating. The difference in HMF yield as compared to previous protocols however proves that Pd/C is a more effective hydrogenation catalyst as compared to Ru/C under similar reaction conditions. The main drawback of using formic acid relates to the need to add a Bronsted mineral acid to achieve high DMF yields during HMF hydrogenation. Mineral acids are corrosive hence special corrosion-resistant equipment is needed which increases the cost of the process and restricts wide applications of FA in HMF conversion.

Hansen *et al.* reported an alternative approach for the selective hydrogenation of HMF via catalytic transfer hydrogenation (CTH), in which supercritical methanol was used as a hydrogen donor and reaction medium (Hansen et al., 2012).²³ A Cu-doped porous metal oxide (Cu-PMO) was utilised as catalyst which produced a mixture of products including dimethylfuran (DMF), dimethyltetrahydrofuran (DMTHF) and 2-hexanol in good yields. Reaction conditions were tunable which offered a degree of flexibility to the process. DMF yield reached 41% and 48% after 3 h at 240 and 260 °C, respectively. A combined yield (DMF + DMTHF) of 58% was achieved after 3 h at 260 °C. Compared to H₂ and FA, production costs were reduced using supercritical MeOH as hydrogen donor, an alternative and promising direction towards a renewable chemical industry. However, the critical temperature of methanol is very high in this process (300 °C) and the selectivity of DMF is very low (ca. 34%) at this temperature. Methanol was replaced by isopropyl alcohol to

overcome these issues (critical temperature = 235 °C) (Jae et al., 2013).²⁴ 81% DMF yield at complete HMF conversion was achieved at 190 °C for 6 h using a Ru/C catalyst in isopropyl alcohol. Unfortunately, the efficiency of the recovered Ru/C catalyst dropped in the second cycle, leading to 13% DMF at 47% conversion. The considerable deactivation of Ru/C might be due to the formation of high molecular weight by-products on ruthenium surfaces.

Isopropyl alcohol was also employed as hydrogen donor in the sequential transfer hydrogenation/hydrogenolysis of furfural and HMF over *in situ* reduced, Fe₂O₃-supported Cu, Ni, and Pd catalysts (Scholz et al., 2014).²⁵ Pd/Fe₂O₃ exhibited an extraordinary activity in comparison to Cu and Ni catalysts but ring-hydrogenation and decarbonylation compounds were observed as reaction side products. Pd nanoparticles strongly coordinate with the π -system of the furfural ring which causes ring hydrogenation. However, the formation of ring-hydrogenated products could be reduced by decreasing Pd loading (specific activity decreases due to an increased metal dispersion). The observed higher hydrogenolysis activity of Pd/Fe₂O₃ catalysts could be correlated to the morphology and size of Pd particles and their strong interaction with the hematite (Fe₂O₃) support. The oxophilic nature of Fe along with the intimate contact between Pd and Fe species promoted the activation of O–H bonds which readily underwent hydrogenolysis in the presence of active hydrogen generated over Pd surfaces. In comparison to methanol, isopropyl alcohol can provide a better selectivity in the hydrogenation of HMF via catalytic transfer hydrogenation due to a decrease in reaction temperature. The process has however several drawbacks including the reversibility of the hydrogen transfer reaction and the need of high-pressure nitrogen for a feasible process.

All hydrogen donors discussed above including molecular hydrogen, formic acid, methanol or isopropyl alcohol, require higher temperature (over 60 °C and in some cases up to 300 °C) for HMF hydrogenation. Nilges and Schröder recently reported an electrocatalytic hydrogenation approach at room-temperature and atmospheric pressure for the selective

hydrogenation of HMF into DMF, where water acts as hydrogen donor (Nilges and Schroder, 2013).²⁶ The reaction proceeds through a series of consecutive 2-electron/2-proton reduction steps which require a total of six electrons and six protons to produce DMF as final product. Different electrodes were proposed in the system including copper, nickel, platinum, carbon, iron, lead, and aluminum. Copper electrodes showed a comparably improved efficiency. Beside the proper selection of electrodes, electrolyte solutions had a significant impact on the success of the hydrogenation process. Acetonitrile or ethanol were utilised as organic co-solvents in the experiments to suppress the formation of molecular hydrogen which improved DMF yields and the coulombic efficiency of the electrocatalytic hydrogenation. The highest DMF selectivity (35.6%) was achieved under a combination of copper electrodes and 0.5 M H₂SO₄ in a 1:1 water/ethanol mixture. Side products such as 2,5-bis(hydroxymethyl)furan (33.8%), 5-methylfurfuryl alcohol (11.1%) and 5-methylfuran-2-carbaldehyde (0.5%) were also formed together with DMF. The authors claimed that the above intermediate side products can be further transformed into DMF by extending the reaction time. This method was also successfully extended to the hydrogenation of furfural into 2-methylfuran.

2.2. HMF upgrading via C–C coupling

C–C coupling reactions constitute another set of relevant strategies to upgrade HMF into liquid alkane fuels using external carbonyl-containing molecules followed by HDO processes. The Dumesic group developed a process to obtain high quality diesel fuels from condensation of furan aldehydes (HMF or furfural) with acetone involving aldol condensations followed by hydrogenation and dehydrodeoxygenation (Huber et al., 2005; West et al., 2008).^{27, 28} In a biphasic reactor system, the aqueous NaOH catalyzed condensation of HMF with acetone produced C₉ and C₁₅ unsaturated intermediates depending

on utilised HMF/acetone molar ratio. Aldol compounds were subsequently subjected to hydrogenation/dehydration/ring opening processes in the presence of bifunctional catalysts such as Pd/Al₂O₃ and Pt/NbPO₅, producing a mixture of linear C₉ and C₁₅ alkanes in high yields.

Chatterjee *et al.* employed the same protocol with Pd/Al-MCM-41 as dehydration/hydrogenation catalyst in supercritical carbon dioxide at 80 °C, P (CO₂) = 14 MPa, P (H₂) = 4 MPa. The process resulted in >99% selectivity for C₉ linear alkanes (Chatterjee et al., 2010).²⁹

From the viewpoint of organic synthesis, metal trifluoromethanesulfonate (triflate, OTf) complexes have also been demonstrated to be highly effective Lewis acid catalysts, offering acidity, moisture and air stability as well as recyclability (Li et al., 2014).³⁰ These catalysts are able to promote C–O bond heterolysis to cationic species which subsequently form C–C or C–O bonds with nucleophiles. Results showed that higher-valent metal triflates (e.g. Hf(OTf)₄) exhibited higher activity through hydrogenolysis of both ether and alcoholic C–O bonds for a variety of biomass-related substrates. The use of such Lewis acids along with a hydrogenating catalyst can generate saturated hydrocarbons as major products which does not result in any skeletal rearrangements by isomerization. Metal triflates have been successfully utilised in a recent report which describes the selective production of linear alkanes with carbon chain lengths between eight and sixteen carbons from biomass-derived molecules upon catalytic removal of functional groups including olefins, furan rings and carbonyl groups (Sutton et al., 2013).³¹ The novelty of this work is based on the use of common reagents and catalysts under mild reaction conditions to provide *n*-alkanes in high yields and selectivities. The first step elongates carbon chains (up to C₁₅) by reacting furfural based compounds with acetone via aldol condensation pathways. The second step comprises removal of oxygen functionalities from aldol products using HDO processes. HDO reactions

take place in either a stepwise process or a one-pot process (Figure S1). Removal of the exocyclic unsaturation in C₉ compound (**1**) was carried out under 1 atm H₂ pressure in presence of palladium (0.16 mol%) at 65 °C in a 50% aqueous acetic acid solution. The use of other solvents (e.g. THF or MeOH) results in complete hydrogenation of the furan ring due to their higher hydrogen solubility and faster reaction kinetics. Upon saturation of the furan ring (compound **3**), ring opening to linear carbon chains becomes highly challenging even at higher palladium loading and higher hydrogen pressures. For this reason, acidic medium is used, which allows acid-promoted ring-opening to occur in a faster rate to that of furan hydrogenation, resulting in 2,5,8-nonanetrione (**4**) as sole product. Subsequent oxygen removal from **4** is carried out using La(OTf)₃ as Lewis acid which facilitates HDO via reduction and dehydration pathways. The resulting unsaturation is then reduced under H₂ (3.45 MPa) using a suitable hydrogenation catalyst i.e. Pd/C at 200 °C to give *n*-nonane as final product (**5**). The method described above provides a facile general strategy for the production of *n*-alkane from any polyketones using HDO chemistry.

The extended application of metal triflates was recently reported for the production of C₁₂ alkane fuels from HMF (Liu and Chen, 2013; Liu and Chen, 2014).^{32,33} The integrated catalytic process comprises three different steps: (i) semicontinuous organocatalytic conversion of biomass (fructose and glucose) to high-purity HMF, (ii) N-Heterocyclic carbene (NHC) catalyzed self-coupling (Umpolung) of C₆ HMF to 5,5'-dihydroxymethyl furoin (DHMF), and finally (iii) conversion of DHMF to linear alkanes via metal-acid tandem catalyzed hydrodeoxygenation. In the second step, a 91% isolated yield DHMF could be obtained using an NHC catalyst loading of 0.10 mol% at 60 °C for 3 h under solvent-free conditions. The bifunctional catalytic system consisting of Pd/C + La(OTf)₃ + acetic acid converted DHMF into liquid hydrocarbon fuels at 250 °C and 300 psi H₂ (16 h reaction).

Alkanes were produced in 78% yields, with a 64% selectivity to $n\text{-C}_{12}\text{H}_{26}$ and an overall C/H/O % ratio of 84/11/5.

Another bifunctional catalytic system ($\text{Pt/C}+\text{TaOPO}_4$) showed improved alkane selectivity (96% linear C_{10-12} alkanes) comprising 27.0% n -decane, 22.9% n -undecane, and 45.6% n -dodecane. The methods described above have several potential advantages: (i) DHMF is obtained from HMF self-coupling, which does not require any other petrochemicals for cross-condensation; (ii) NHC catalyzed HMF self-coupling can be carried out under solvent-free conditions at 60 °C after 1 h reaction, affording DHMF in near quantitative isolated yields; (iii) as DHMF is soluble in water, HDO processes can be carried out directly in water, which allows for a spontaneous separation of hydrocarbons from the aqueous phase; and (iv) DHMF hydrodeoxygenation achieves high conversion and near quantitative selectivity towards linear C_{10-12} alkanes with a narrow alkane distribution.

3. Furfural platform for hydrocarbon fuels

3.1. Hydrogenation of furfural

Similar to HMF, furfural can also be hydrogenated to 2-methylfuran (2-MF) and 2-methyltetrahydrofuran (MTHF), both potentially useful in gasoline blends. Different metal based catalysts including Cu, Ni, Fe have been reported for the selective production of 2-MF in the liquid or vapor phase (Burnett et al., 1948; Zheng et al., 2006; Sitthisa et al., 2011).^{34,35,36} Different Cu-based catalysts and catalyst carriers were initially studied in the vapor phase hydrogenation of furfural to 2-MF. Copper chromite dispersed on activated charcoal was found to be the most efficient catalyst in the reaction (90–95% 2-MF yield

obtained at 1 atm hydrogen and 200–230 °C) (Table 2). Unfortunately, yields and catalyst life were somewhat lower in a large unit due to catalyst deactivation.

Sitthisa *et al.* investigated SiO₂-supported Ni and Ni–Fe bimetallic catalysts for the conversion of furfural under 1 bar H₂ in the 210–250 °C temperature range. Furfuryl alcohol and furan were primary products over monometallic Ni/SiO₂, resulting from hydrogenation and decarbonylation of furfural. Comparatively, 2-MF yields greatly increased with reduced yields of furan and C₄ products using Fe–Ni bimetallic catalysts. Results proved that the addition of Fe suppressed the decarbonylation activity of Ni while promoting C=O hydrogenation (at low temperatures) and C–O hydrogenolysis (at high temperatures). A detailed DFT analysis was conducted to better understand possible surface species on mono- and bimetallic surfaces, which proved that selectivity differences displayed by these two catalysts were dependent on the stability of η^2 -(C,O) surface species. These η^2 -(C,O) species were found to be comparatively more stable on Ni–Fe to those on pure Ni. Furfural could then be readily hydrogenated to furfuryl alcohol and subsequently hydrogenolyzed to 2-MF. The strong interaction between O (from the carbonyl group) and the oxyphilic Fe atoms supports a preferential hydrogenolysis reaction on the bimetallic alloy. On the other hand, the Ni surface initiates the decomposition of η^2 -(C,O) species to produce furan and CO.

The vapor phase hydrodeoxygenation of furfural was recently reported using Mo₂C catalysts at low temperature (150 °C) and ambient pressure (Lee et al., 2014).³⁷ Under the investigated reaction conditions, the selectivity for C=O bond cleavage (~50–60%) was far higher as compared to that of C–C bond cleavage (<1%). 2-methylfuran was obtained as major product instead of furan. The high selectivity towards C=O bond cleavage could be due to the strong interaction between Mo₂C and C=O bond as revealed by DFT calculations and high-resolution electron energy loss spectroscopy (HREELS) experiments (Xiong et al., 2014).³⁸

In another report, vapor phase furfural hydrogenation studies were performed on a series of silica supported monodisperse Pt nanoparticle catalysts where the extent of decarbonylation and hydrogenation of carbonyl group was highly dependent on the size and shape of Pt NPs (Pushkarev et al., 2012).³⁹ Small particles were found to predominantly give furan as major product (via decarbonylation) while larger sized particles yielded both furan and furfuryl alcohol (carbonyl hydrogenation product). Octahedral particles were found to be highly selective towards furfuryl alcohol, while cube-shaped particles produced an equal amount of furan and furfuryl alcohol. Furan and furfuryl alcohol were further converted to propylene and 2-methylfuran via decarbonylation and hydrogenolysis, respectively. Authors claim that the aromatic ring hydrogenation reactions for both furfural and furan based compounds do not readily occur on Pt under the investigated conditions, most probably due to the poisoning of Pt surface with chemisorbed CO produced during furfural decarbonylation.

A comparative study for furfural hydrodeoxygenation using three different metal catalysts, Cu, Pd and Ni supported on SiO₂, revealed that products distribution was strongly dependent on the metal catalyst. A high selectivity to furfuryl alcohol was obtained for Cu/SiO₂ (with a small amount of 2-MF) as compared to furan decarbonylation observed followed by further hydrogenation to form THF in the case of Pd/SiO₂. Comparatively, Ni/SiO₂ promoted ring opening reactions to form butanal, butanol and butane in significant quantities.

3.2. Furfural upgrading via C–C coupling

Aldol condensations and hydroxyalkylation-alkylation (HAA) reactions are two effective methods to extend the carbon chain length for furfural upgrading to fuels. Similar to HMF, furfural can also undergo aldol condensation with external carbonyl-containing molecules having an α -hydrogen (e.g. ketones) in the presence of a base or an acid catalyst. Further hydrogenation of aldol products can produce high-quality longer-chain alkanes.

The Dumesic group developed a sequential aldol-condensation and hydrogenation strategy for furfural upgrading in the aqueous phase using a bifunctional Pd/MgO-ZrO₂ catalyst (Barrett et al., 2006).⁴⁰ The cross aldol-condensation of furfural with acetone results in water-insoluble monomer and dimer products, which are subsequently hydrogenated to give products with high overall carbon yields (>80%).

HAA combined with HDO is a comparatively promising route for the synthesis of renewable high-quality diesel or jet fuel. Taking advantage of this combined process, 2-MF (Sylvan) can be used in the Sylvan diesel process where it serves as starting material (Corma et al., 2011; Corma et al., 2012).^{41,42} The process consists of two consecutive steps, namely (i) hydroxyalkylation/alkylation and (ii) hydrodeoxygenation. In the hydroxyalkylation/alkylation step, two Sylvan molecules are reacted with an aldehyde or a ketone to yield oxygenated intermediate molecules. Butanal is chosen as most promising molecular linker for two Sylvan molecules because (i) it is a biomass-derived molecule that can be obtained by selective oxidation of 1-butanol (produced from biomass fermentation) and (ii) the final hydrogenated product contains fourteen carbon atoms and fits perfectly within the boiling point range of diesel fuel. The second hydrodeoxygenation step is a hydrogenolysis process to remove oxygen atoms from oxygen-containing compounds at moderate temperatures and high H₂ pressures.

Further implementation of HAA-HDO was reported by Zhang *et al.* where different types of resins (such as, Nafion, Amberlyst etc.) were utilised to couple 2-MF and furfural (Li *et al.*, 2012; Li *et al.*, 2013).^{43,44} Nafion-212 resin demonstrated the highest activity and stability. HDO steps were performed using Pd/C, Pt/C and Ni-WxC/C catalysts where Ni-WxC/C catalyst exhibited excellent catalytic performance and good stability for HDO of hydroxyalkylation/alkylation products. A 94% carbon yield of diesel and 75% carbon yield of C₁₅ hydrocarbons (with 6-butylundecane as major component) was achieved using a 4% Pt/ZrP catalyst.

Different solid acid catalysts including Nafion-212 were studied for the alkylation of 2-MF with mesityl oxide (Li *et al.*, 2014).⁴⁵ HDO steps were conducted using Ni-Mo₂C/SiO₂ and Ni-W₂C/SiO₂ catalysts. Ni-Mo₂C/SiO₂ exhibited a higher selectivity to diesel range alkanes (77% yield) at 573 K and 6.0 MPa H₂. Using the same strategy, C₁₀ and C₁₁ branched alkanes, with low freezing points, were synthesized in high overall yields (~90 %) under solvent-free condition through the aldol condensation of furfural and methyl isobutyl ketone (Yang *et al.*, 2013).⁴⁶

4. Levulinic acid platform for hydrocarbon fuels

Levulinic acid (LA) is considered one of the most important biomass derived platform compounds due to its reactive nature along with the fact that it can be produced from lignocellulosic waste at low cost. Due to its high functionality (a ketone and an acid function), LA can be converted into a variety of valuable chemicals as well as advanced biofuels (Climent *et al.*, 2014). Shell recently reported a new platform of LA derivatives, the so-called *valeric biofuels*, which can deliver both gasoline and diesel components fully compatible with current transportation fuels (Lange *et al.*, 2010).⁴⁷

The first step of the manufacturing method involves the acid hydrolysis of lignocellulosic materials to LA. In subsequent steps, LA is hydrogenated to γ -valerolactone and valeric acid (VA) and finally esterified to alkyl (mono/di) valerate esters. In this section, we will discuss different processes to upgrade levulinic acid to biofuels mainly via hydrogenation processes.

4.1. Hydrogenation of levulinic acid to γ -valerolactone (GVL)

Several LA derivatives have been proposed for fuel applications including ethyl levulinate (EL), γ -valerolactone (GVL), and methyl-tetrahydrofuran (MTHF) (Geilen et al., 2010).⁴⁸ GVL was identified as a potential intermediate for the production of fuels and chemicals based on renewable feedstocks. GVL can be used as a fuel additive to current fuels derived from petroleum due to a combustion energy similar to ethanol (35 MJ L⁻¹) (Horvath et al., 2008).⁴⁹ Comparative evaluation of GVL and ethanol was performed. A mixture of 90 v/v% gasoline with 10 v/v% GVL or EtOH shows that at similar octane numbers, the mixture with GVL has improved combustion properties due to its lower vapor pressure.

GVL is generally produced from levulinic acid via two main routes: (i) hydrogenation of levulinic acid to gamma-hydroxyvaleric acid followed by an intramolecular esterification through cyclisation to produce GVL and (ii) acid catalyzed dehydration of levulinic acid to angelica-lactone followed by hydrogenation. Both homogeneous and heterogeneous catalysts have been used for GVL production in vapor-phase as well as liquid-phase conditions. However, homogeneous systems are not suitable as the high boiling point of GVL (207-208 °C) makes product/catalyst separation economically unfeasible by means of distillation. For further reading on different heterogeneous catalytic systems for the

conversion of levulinic acid to GVL, readers are kindly referred to the recent overview of the topic by Wright and Palkovits (Wright and Palkovits, 2012).⁵⁰

In the 1950s, Quaker Oats firstly developed a continuous process for the vapor-phase commercial-scale production of GVL via LA hydrogenation (Dunlop and Madden, 1957).⁵¹ Quantitative yields to GVL could be achieved using a mixture of metal oxide catalysts (CuO and Cr₂O₃) at 200 °C. Later on, hydrogenation of levulinic acid has been typically performed in the presence of H₂ using various metal catalysts such as Ru, Pd, Pt, Ni, Rh, Ir, Au on different supports.

Ru based catalysts have shown high performance to reduce levulinic acid or its esters to GVL (Hengne et al., 2012).⁵² XPS studies revealed that a higher extent of Ru⁰ species in case of carbon supported Ru could account for its higher hydrogenation activity as compared to Ru on other supports. Bourne *et al.* described a new approach for GVL production which combines the use of water as co-solvent with phase manipulation using supercritical CO₂ to integrate reaction and separation into a single process with reduced energy requirements as compared to conventional distillation (Bourne et al., 2007).⁵³ Reactions were performed at 10 MPa H₂ pressure with Ru/SiO₂ and almost quantitative yield (>99%) of GVL was achieved at 200 °C (Table 3).

The Dumesic group designed a biphasic reaction system for the transformation of cellulose to GVL using an aqueous-phase solution containing a phase modifier (e.g., salt and sugars) and GVL as solvent. Main advantages of the proposed system include (i) no need for a filtration step after cellulose deconstruction and, (ii) no need for a step to separate product and solvent (Wettstein et al., 2012).⁵⁴ Levulinic acid, produced upon HCl catalyzed dehydration, was subsequently converted to GVL over a carbon-supported Ru-Sn catalyst.

The *in-situ* production of hydrogen by decomposition of formic acid (a by-product concomitantly produced from cellulose hydrolysis and dehydration to levulinic acid) is an interesting integrated process for the production of GVL. Taking advantage of this strategy, the production of GVL from different carbohydrates using Ru based homogeneous catalysts has been reported (Deng et al., 2009).⁵⁵ An inexpensive, recyclable $\text{RuCl}_3/\text{PPh}_3/\text{pyridine}$ catalyst system converted a 1:1 aqueous mixture of levulinic acid and formic acid into GVL. Results showed that an appropriate tuning of base and ligand in Ru-based catalytic systems could selectively reduce LA to GVL instead of 1,4-pentanediol. The hydrogen transfer mechanism in this process was not clearly proved, but it was claimed to proceed via two possible routes: (i) formic acid decomposition into H_2 and CO_2 (with hydrogen being the reducing agent) and (ii) formation of a metal-formate which decomposes into CO_2 and a metal-hydride that reduces levulinic acid to GVL.

Another alternative route to produce GVL from levulinic acid is the catalytic transfer hydrogenation (CTH) of levulinic acid through the Meerwein–Ponndorf–Verley (MPV) reaction using secondary alcohols as hydrogen donors in which expensive noble metal catalysts are not required. Following this approach, the hydrogenation of levulinic acid and its esters to GVL using various secondary alcohols as hydrogen donors and solvents was recently reported (Chia and Dumesic, 2011).⁵⁶ Different heterogeneous metal oxides including ZrO_2 , $\text{MgO}/\text{Al}_2\text{O}_3$, MgO/ZrO_2 , CeZrO_x and $\gamma\text{-Al}_2\text{O}_3$ were tested, among which ZrO_2 was most active (92% GVL) using 2-butanol at 150 °C.

Recent advances on GVL production using various advanced strategies have also been recently reported. An advanced integrated catalytic process for the efficient production of GVL from furfural through sequential CTH and hydrolysis reactions catalyzed by zeolites with Brønsted and Lewis acid sites recently emerged as interesting alternative to conventional GVL production processes (Bui et al., 2013).⁵⁷ In the first step, furfural is converted into

furfuryl alcohol and butyl furfuryl ether via CTH promoted by a Lewis acid catalyst. Furfuryl alcohol and butyl furfuryl ether are subsequently converted into LA and butyl levulinate through hydrolytic ring-opening reactions using a Brønsted acid, which finally undergo a second CTH step to produce 4-hydroxypentanoates followed by lactonization to GVL.

Another interesting approach to produce GVL relates to an electrocatalytic hydrogenation (ECH) of levulinic acid using non-precious Pb electrodes (Xin et al., 2013).⁵⁸ This is an effective approach by means of storing electric energy into biofuels. Valeric acid (VA) and GVL were obtained as main products depending on the applied potential and electrolyte pH values. Lower overpotentials favored the production of GVL, whereas higher overpotentials facilitated VA formation. A 95% VA selectivity was achieved when an acidic electrolyte (pH 0) was used as compared to complete selectivity to GVL under neutral electrolyte conditions (pH 7.5). The method showed a high Faradaic efficiency (>86 %) and promising electricity storage efficiency (70.8 %) giving almost quantitative yields of VA (>90 %).

4.2. Levulinic acid upgrading into liquid fuels

Levulinic acid can be transformed into hydrocarbon fuels by different catalytic routes involving deoxygenation reactions combined with C–C coupling. The Dumesic group extensively worked on the conversion of GVL to kerosene- and diesel-range hydrocarbons (Serrano-Ruiz and Dumesic, 2011).⁵⁹

A series of catalytic approaches were developed to convert aqueous solutions of levulinic acid into different types of liquid hydrocarbon transportation fuels. The catalytic pathways involved oxygen removal via dehydration/hydrogenation and decarboxylation

reactions combined with C–C coupling processes through ketonization, isomerization, and oligomerization that are required to increase the molecular weight as well as to adjust the structure of the final hydrocarbon product. Aqueous levulinic acid is firstly hydrogenated to water-soluble GVL over non-acidic catalysts (e.g., Ru/C) at low temperatures. Water soluble GVL was subsequently upgraded to liquid hydrocarbon fuels following two main pathways: C₉ route and C₄ route (Figure S2).

In the C₉ route, GVL was converted to 5-nonanone via pentanoic acid over a water-tolerant multifunctional Pd/Nb₂O₅. Subsequently, 5-nonanone was transformed into its corresponding alcohol that was further converted to C₉ alkanes through hydrogenation/dehydration cycles using the same bifunctional Pt/Nb₂O₅ catalyst. Comparatively, GVL was first decarboxylated in the C₄ route using a silica/alumina catalyst at elevated pressure to give butene followed by oligomerization over acidic catalysts (e.g., H-ZSM5, Amberlyst 70), resulting in different C₁₂ alkanes.

A stepwise pathway to produce branched C₇–C₁₀ gasoline-like hydrocarbons in high yields has also been recently reported by Mascal and co-workers (Mascal et al., 2014).⁶⁰ The three-step process proceeds through the formation of an angelica lactone dimer which serves as a novel feedstock for hydrodeoxygenation. LA is converted using a solid acid catalyst (e.g. montmorillonite clay, K10) into angelica lactone, which dimerises in the presence of catalytic amounts of K₂CO₃. This dimer product is eventually hydrodeoxygenated to gasoline range hydrocarbons using a combination of oxophilic metal and noble metal catalysts under mild conditions. Different catalysts were screened in HDO reactions of angelica lactone dimers. Ir-ReOx/SiO₂ catalyst exhibited the highest activity, with quantitative conversion producing 88% total hydrocarbon yield. Pt-ReOx/C catalysts were also effective in providing analogous hydrocarbon yields but their C₁₀ hydrocarbon selectivity was comparatively inferior to that of Ir-ReOx/SiO₂.

5. Lignin derived hydrocarbons

Biomass-derived lignin has significant potential as source for the sustainable production of fuels and bulk chemicals. Biomass contains a significant percentage of lignin rigidly bound to cellulose and hemicellulose. To improve carbon utilization and economic competitiveness of biomass refineries, biomass-derived lignin can be partially utilised for the production of fuels and chemicals. Various catalytic processes have already been developed to selectively depolymerize lignin and remove oxygen via HDO reactions. However, most studies relate to the conversion of lignin model compounds rather than organosolv lignin.

Research groups of Gates^{61,62} (Runnebaum et al., 2012; Saidi et al., 2014) and Resasco⁶³ (Crossley et al., 2010) have extensively studied HDO chemistries to upgrade different model compounds from lignin-derived bio-oils including anisole, guaiacol, vanillin, eugenol, phenol and cresol. Their findings indicate that noble metals (e.g. Pt, Pd, Ru etc.) in combination with an acidic support (such as Al₂O₃, SiO₂, zeolites) can offer most effective catalytic systems for selective HDO processes. Different bimetallic systems including noble combined with a transition metals (e.g. Fe, Ni, Cu, Zn or Sn) have also been identified as highly selective for oxygen removal even under mild HDO conditions. For more information, readers are kindly referred to recently reported overviews related to catalysts design, selection of catalyst supports, HDO mechanisms and catalysts deactivation (Saidi et al., 2014; Dutta et al., 2014).⁶⁴

Noble metals normally show optimum hydrogenation activities and have been shown to catalyse HDO reactions with monomeric lignin model compounds at lower hydrogen pressures and temperatures (Zhao et al., 2009).⁶⁵ HDO processes have been studied using guaiacol (a monomeric lignin model compound) with both noble metal-based (Rh) and

sulfide (CoMo and NiMo) catalysts at 300–400 °C and 5.0 MPa H₂ under batch conditions (Lin et al., 2001).⁶⁶ Rh catalysts provided optimum catalytic activities as compared to CoMo and NiMo catalysts under analogous reaction conditions. Reactions catalysed using Rh-based catalysts involved two consecutive reaction steps, namely aromatic ring hydrogenation from guaiacol followed by demethoxylation and dehydroxylation. Guaiacol conversion started with demethylation, demethoxylation, and deoxygenation, followed by benzene ring saturation for sulfided CoMo and NiMo catalysts. Gates and co-workers studied HDO reaction for the conversion of different lignin model compounds as well as lignin-derived bio-oils using Pt/ γ -Al₂O₃ as catalyst (Runnebaum et al., 2012). The proposed bifunctional system served two different roles in the reaction; the metallic function offered enhanced HDO kinetics, while the acidic support played a key role in the transalkylation reaction for the effective cleavage of ether linkages from the lignin structure. Experimental facts were able to provide information on the occurrence of an extensive number of reactions including hydrodeoxygenations, transalkylations, hydrogenolysis and hydrogenations. The reaction network clearly accounted the formation of primary products on the basis of selectivity-conversion plots for the conversion of individual reactants (guaiacol, anisole, 4-methylanisole, and cyclohexanone).

Understanding the interaction between bio-oils (or raw lignin) with the catalyst surface as well as the design of optimum catalytic surfaces are essential in order to achieve high conversion of lignin-derived bio-oils to fuels via HDO. The alcoholic fractions of lignin bio-oils are water soluble while alkylated phenolic compounds lead to water/oil emulsions. An easily recoverable catalytic system that simultaneously stabilizes emulsions will be highly advantageous for HDO technologies in a biphasic reaction set-up.

Resasco et al. designed a hybrid catalytic system consisting of deposited Pd nanoparticles on a carbon nanotube–inorganic oxide (SiO₂) hybrid that can stabilize water-oil

emulsions and catalyze reactions at the liquid/liquid interface (Crossley et al., 2010). The hybrid solid nanoparticles were reported to be capable of catalyzing reactions in both aqueous and organic phases. Pd deposited on the hydrophilic interface catalyzes aqueous reactions, whereas its deposition on its hydrophobic counterpart favors reactions in the organic solvent.

Bifunctional catalysts (Ru supported on zeolite HZSM-5) have also been designed, exhibiting an excellent hydrodeoxygenation activity towards the conversion of lignin-derived phenolic monomers and dimers to cycloalkanes in aqueous solution at 150 °C (Zhang et al., 2014).⁶⁷ Initially, a series of noble metals supported on HZSM-5 (Si/Al = 38) were tested in the aqueous-phase hydrodeoxygenation of phenol at 150 °C. Ru was shown to be most active and selective for the production of cyclohexane as compared to Pd and Pt. The protocol discloses the removal of oxygen functionalities through C–O bond cleavage in phenolics, followed by an integrated metal- and acid-catalyzed hydrogenation and dehydration. The separate role of Brønsted acid sites from the zeolite (promotes dehydration reactions) and Ru (catalyses hydrogenation processes) make this system ideal for alkanes formation from lignin-derived phenolics. In addition to metallic sites, the Si/Al ratio had a crucial role in determining the acid strength as well as the catalyst hydrophobicity. Although phenol conversions did not depend on Si/Al ratios and topology of the zeolite, the selectivity to cyclohexane remarkably increased with decreased Si/Al ratios in HZSM-5. Experiments revealed that Ru/HZSM-5 with the lowest Si/Al ratio in HZSM-5 (Si/Al = 25) was most selective to cycloalkanes production. These findings indicate that the presence of a larger concentration of acid sites in the zeolite favored cyclohexanol dehydration during HDO, which leads to a higher selectivity to hydrocarbons, in good agreement with recent studies showing that the integration of acid functionality with noble metal catalysts can provide useful bifunctional catalytic systems to achieve fast oxygen removal (Zhao et al., 2011).⁶⁸ Kinetic studies of the catalytic hydrodeoxygenation of phenol and substituted phenols was

studied on a dual-functional Pd/C and H₃PO₄ system in order to better understand the elementary steps of the overall reaction.

The actual reaction proceeds via different steps namely, (i) hydrogenation of the aromatic ring followed by transformation of the cyclic enol to the corresponding ketone, (ii) cycloalkanone hydrogenation to cycloalkanol (iii) cycloalkanol dehydration to cycloalkene and finally (iv) cycloalkene hydrogenation to cycloalkane. The metal function promotes the hydrodeoxygenation step in bifunctional catalysts, while the acid function catalyses hydrolysis, dehydration and isomerization steps. The dehydration reaction was found to have significantly reduced reaction rates as compared to hydrogenation and keto/enol transformations. Turnover frequencies of the acid-catalyzed dehydration reactions are about half of the rates of metal-catalyzed hydrogenation. Due to this reason, catalysts having significantly larger concentration of Brønsted acid sites compared to available metal sites are required for hydrogenation.

Acidic zeolites such as H-Beta and H-ZSM-5 have been proved as effective supports to design bi-functional catalysts to convert monomeric lignin compounds (guaiacol) to cyclohexane derivatives (Zhao and Lercher, 2012a,b).^{69,70} A bifunctional Ni/HZSM-5 catalyst (Si/Al = 45 and Ni = 20 wt%) exhibited high activity and selectivity for the hydrodeoxygenation of various C–O and C=O bonds in furans, alcohols, ketones, and phenols. The same catalyst was also able to convert a series of alkyl-, ketone-, or hydroxy-substituted phenols and guaiacols, alkyl-substituted syringol to produce cycloalkanes (73–92%) as major products along with some aromatics (5.0–15%) and methanol (0–17%).

A two-step hydrodeoxygenation process was comparatively established for benzyl phenyl ether (BPE), a lignin-derived phenolic dimer which contains an α -O-4 linkage. The

methodology produced high carbon number saturated hydrocarbons in the presence of a multiple catalytic system. In the first step, BPE ether linkages were isomerized to alcohols using solid acid catalysts of silica (SA), alumina (AA) and silica-alumina aerogels (SAAs) (Yoon et al., 2013).⁷¹ In the second step, benzylphenols were subsequently hydrodeoxygenated to saturated cyclic hydrocarbons using silica-alumina-supported Ru catalysts. The extent of isomerization in phenylethers depends on Al/Si ratios in SAAs catalyst. Results showed that, SAA-38 and SAA-57 containing Al/(Si + Al) contents of 0.38 and 0.57, respectively, exhibited high catalytic activity among the prepared aerogel catalysts. BPE conversion on SAA-38 reached quantitative yields at a temperature range of 100-150 °C. Brønsted acid sites appeared to be catalytically active species responsible of the isomerization of phenyl ether to phenols as opposed to ether decomposition. As a result, deoxygenated C₁₃₋₁₉ hydrocarbons were predominantly obtained as opposed to cracked C₆₋₇ hydrocarbons.

Abu-Omar's et al. investigated the effect of bimetallic Pd/C and Zn catalytic system in the selective hydrodeoxygenation of monomeric lignin surrogates (Parsell et al., 2013).⁷² This system was also able to successfully cleave β-O-4 linkages found in dimeric lignin model complexes and synthetic lignin polymers with near quantitative conversions and high yields (80–90%) at relatively mild temperatures (150 °C) and pressures (20 bar H₂) using methanol as solvent. Results showed that 4-(hydroxymethyl)-2-methoxyphenol could be selectively deoxygenated in good yields without hydrogenation of the phenyl ring under the combined Pd/C and Zn²⁺ system. Controlled experiments suggested that the single use of Pd/C or Zn²⁺ was unable to promote HDO. These results demonstrate a synergy between Pd/C and Zn²⁺ in HDO as represented in a mechanistic approach (Figure S3). X-ray absorption spectroscopy (EXAFS) confirmed the absence of any bimetallic Pd–Zn alloy material in the proposed system.

Using the knowledge of HDO to effectively deoxygenate monomeric lignin compounds, efforts have been devoted towards HDO of lignin-derived oligomeric phenolic compounds. These components represent a large portion of lignin deconstruction intermediates in a biorefinery process. The production of low molecular weight products from oligomeric lignin with subsequent conversion to hydrocarbons has been reported (Yan et al., 2008).⁷³ The direct conversion of lignin into alkanes and methanol was carried out in a two-step process (hydrogenolysis and hydrogenation). White birch wood sawdust was treated with H₂ in dioxane/water/phosphoric acid using Rh/C as catalyst to obtain lignin monomers and dimers.

The resulting monomers and dimers obtained via selective C–O hydrogenolysis were then hydrogenated in near-critical water using Pd/C as the catalyst. Ben and Ragauskas also reported the production of renewable gasoline via two step catalytic hydrogenation of water insoluble heavy oils produced from pyrolysis of pine wood ethanol organosolv lignin (Ben et al., 2013).⁷⁴ In their report, they employed acidic zeolite catalysts for a single step thermal conversion of oligomeric lignin to gasoline-range liquid products. Results indicated that zeolites can significantly improve dehydration reactions, which facilitate the deoxygenation of pyrolysis oil. The authors provided the basis for the hydrolytic cleavage of C–O–C ether bonds and methoxy groups of lignin under tested hydrogenation and thermal conditions. The exact mechanism for the HDO activities of oligomeric lignin compounds still remain largely unknown, as the efficacy of HDO processes applied to oligomeric lignin to hydrocarbons conversion mainly depends on a selective inter-unit C–O–C bond cleavage. The development of catalytic processes that can both selectively depolymerize the lignin polymeric framework and remove oxygen via HDO reactions for the production of hydrocarbon fuels from oligomeric lignin intermediates still remains a significant challenge for future research.

Among non-noble metal catalysts, Ni-based catalysts can be highly active and selective in the conversion of crude lignin to monomeric phenol units (Song et al., 2013).⁷⁵ Two phenolic compounds (propenylguaiacol and propenylsyringol) can be obtained as main products with a selectivity >90% from ca. 50% conversion of birch wood lignin. Alcohols, such as methanol, ethanol and ethylene glycol could serve as nucleophilic reagents for C-O-C cleavage via alcoholysis as well as function as the source of active hydrogen when they come in contact with active Ni surfaces. Only trace amounts of propenyl syringol and propenyl guaiacol were observed when the reaction was conducted in dioxane (not a hydrogen donating solvent), hence confirming the proposed role of alcohols as in-situ hydrogen donating agents.

6. Future prospects and perspectives

The proposed contribution has been aimed to provide an overview on key steps in the design of HDO catalysts as well as process development for the production of high octane valued liquid fuels from biomass. Existing HDO methods currently suffer from serious drawbacks including a high cost in catalyst development (i.e. generally noble-metal catalysts), the requirement of extreme reaction conditions (high temperatures and pressures), the utilisation of molecular hydrogen as hydrogenating agent or even more expensive hydrogen-donating solvents for industrial applications (e.g. formic acid), a production in low scale, etc. More research is needed on the design of advanced HDO catalytic systems as well as reactor engineering to turn HDO processes into economically feasible and compatible with current infrastructure.

The major complexity in oxygenated biomass-derived platform molecules relates to the comparable strength in C-O and C-C bonds, resulting in a remarkable challenge to

achieve selective HDO without any hydrogenation of aromatic rings. In this regard, bifunctional catalysts have been certainly stepping up as optimum option in terms of chemo-selectivity. Understanding the nature of the active sites in bifunctional catalysts as well as reaction pathways of C–O bond scission are of primary importance as highlighted in this contribution illustrated with several examples (Parsell et al., 2013)⁷⁴.

In order to address the issue of production costs, Ni-based bimetallic catalysts containing a small quantities of noble metal additives (e.g., Ru, Pd or Au) may be a potentially effective replacement, where electron-rich Ni atoms preferentially occupy the catalyst surface to enhance molecular H₂ activation.

Together with the active metallic part, the catalyst support also plays a key role in HDO processes. A selection of proper catalyst supports is consequently essential. Acidic supports (e.g. alumina) can offer high HDO activity but with the associated disadvantage of deactivation due to coke formation originated in strong acidic sites. Related oxide-containing catalysts can suffer from a low stability in aqueous media at high temperatures (water generated in HDO processes can also deactivate the catalysts).

On the basis of already established findings, activated carbon can be a most promising catalyst support which can potentially provide an increasing selectivity for direct oxygen removal at low hydrogen consumption and minimum coke formation. In addition, the hydrophobic nature of carbon support can resist the deactivation of metal catalysts from water produced in the HDO reaction. Despite extensive research work aimed to develop efficient strategies for the production of hydrocarbon fuels from biomass-derived feedstocks, understanding the exact role of HDO catalysts from fundamental aspects for selective C–O bond hydrogenolysis is yet to be sufficiently developed to advance in the design of cost-effective multifunctional catalytic systems for biorefinery applications.

7. Conclusions

Biofuels can play an important role in our energy future to reduce our dependence from petroleum-derived resources as well as sustaining expected increased energy demands in years to come. Lignocellulosic biomass is an abundant and most promising renewable feedstock which holds a significant potential to be converted into useful end products including chemicals, materials and fuels. However, lignocellulosics conversion into fuels is rather challenging and requires of effective catalytic systems and technologies to achieve this aim. Hydrodeoxygenation processes can be the key to unlock the lignocellulosic biorefinery concept as promising synthetic tool to derive liquid hydrocarbon fuels from lignocellulosic biomass.

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Table 1

HDO catalyst	H ₂ source	Solvent	<i>T</i> (°C)	DMF yield (%)	References
Cu-Ru/C	H ₂ (6.8 bar)	1-BuOH	220	71	Roman-Leshkov et al. (2007)
Cu-Ru/C	H ₂ (6.8 bar)	1-BuOH	220	49	Binder and Raines (2009) ^a
Pd/C	H ₂ (62 bar)	[EMIM]Cl	120	15	Chidambaram and Bell (2010)
Pd/C	H ₂ (10 bar)	sc CO ₂ -H ₂ O	80	100	Chatterjee et al. (2014)
PtCo@HCS	H ₂ (10 bar)	1-BuOH	180	98	Wang et al. (2014)
Ni-W ₂ C/AC	H ₂ (40 bar)	THF	180	96	Huang et al. (2014)
Pd-Au/C	H ₂ (1 bar)	THF	60	~100	Nishimura et al. (2014)
Pd/C	Formic acid	THF	150/70	95	Thananattathanachon and Rauchfuss (2010)
Ru/C	Formic acid	THF	150/75	37	De et al. (2012)
Cu-PMO	MeOH	MeOH	260	48	Hansen et al. (2012)
Ru/C	<i>i</i> -PrOH	<i>i</i> -PrOH	190	81	Jae et al. (2013)
Pd/Fe ₂ O ₃	<i>i</i> -PrOH	<i>i</i> -PrOH	180	72	Scholz et al. (2014)
Cu electrode	H ₂ O	H ₂ SO ₄ solution	RT	36	Nilges and Schroder (2013)

^aCrude HMF produced from corn stover was used as starting material.

Table 2

HDO catalyst	H ₂ source	Solvent	<i>T</i> (°C)	2-MF yield (%)	References
Cu chromite/AC	H ₂	Vapor reaction	230	95	Burnett et al. (1948)
Cu/Zn/Al/Ca/Na (59:33:6:1:1)	H ₂	Vapor reaction	250	87	Zheng et al. (2006)
Ni-Fe/SiO ₂	H ₂	Vapor reaction	250	39	Sitthisa et al. (2011)
Mo ₂ C	H ₂	Vapor reaction	150	4.5	Lee et al. (2014)

Table 3

HDO catalyst	H ₂ source	Solvent	<i>T</i> (°C)	GVL yield (%)	References
Ru/C	H ₂ (34 bar)	MeOH	130	86 ^a	Hengne et al. (2012)
Ru/SiO ₂	H ₂ (100 bar)	sc CO ₂ -H ₂ O	200	99	Bourne et al. (2007)
RuCl ₃ /PPh ₃ / pyridine	Formic acid	Neat	150	93	Deng et al. (2009)
Ru-P/SiO ₂	H ₂ (40 bar)	H ₂ O	150	96	Deng et al. (2010)
ZrO ₂	2-BuOH	2-BuOH	150	92	Chia and Dumesic (2011)
Zr-Beta	2-BuOH	2-BuOH	120	97	Bui et al. (2013)
Pb-electrode	H ₂ O	H ₂ O/Buffer (pH 7.5)	RT	4.5	Xin et al. (2013)

^a Methyl levulinate was used as starting material.

Supporting Information

Hydrodeoxygenation processes: advances on catalytic transformations of biomass-derived platform chemicals into hydrocarbon fuels

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