

Review

Homogeneous Catalyzed Valorization of Furanics: A Sustainable Bridge to Fuels and Chemicals

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Abstract: The development of efficient biomass valorization is imperative for the future sustainable production of chemicals and fuels. Particularly, the last decade has witnessed the development of a plethora of effective and selective transformations of bio-based furanics using homogeneous organometallic catalysis under mild conditions. In this review, we describe some of the advances regarding the conversion of target furanics into value chemicals, monomers for high-performance polymers and materials, and pharmaceutical key intermediates using homogeneous catalysis. Finally, the incorporation of furanic skeletons into complex chemical architectures by multifunctionalization routes is also described.

Keywords: furanics; homogeneous catalysis; biomass upgrading



Citation: Padilla, R.; Koranchalil, S.; Nielsen, M. Homogeneous Catalyzed Valorization of Furanics: A Sustainable Bridge to Fuels and Chemicals. *Catalysts* **2021**, *11*, 1371. <https://doi.org/10.3390/catal11111371>

Academic Editors: Leonarda Francesca Liotta and Valeria La Parola

Received: 30 October 2021
Accepted: 11 November 2021
Published: 13 November 2021

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1. Introduction

The transition from a fossil-based economy to a bio-based society represents a fundamental goal to diminish environmental issues and reduce the strong dependency on petrochemicals [1]. The replacement of fossil-based fuels and materials with biofuels and bioproducts is of paramount importance for this transition. Catalysis is the core of modern chemical conversions and a key component of sustainable chemistry. The production processes for the vast majority of our fuels and chemicals use catalysts [2].

However, two of the main drawbacks of the catalytic valorization of lignocellulosic biomass are the relatively low stored potential chemical energy as well as the high oxygen content [3]. Hence, there is great interest in valorizing biomass to value-added compounds. Towards this end, new catalytic processes with higher efficiencies, greater tolerance to diverse biomass feedstock, and longer catalyst lifetimes require significant development across disciplines [4,5].

In particular, homogeneous catalysis is a unifying technology, pursuing the yield of valuable feedstock from biomass with more efficient, selective, environmentally benign, and cost-effective catalytic systems [6,7]. A major new development in homogeneous catalysis is the application of organometallic complexes as catalysts [8–11]. Using new catalysts and atom-economical methodologies leads to potential benefit for both the organic synthesis and biomass valorization communities [12].

These new strategies promote the adoption of renewable chemicals produced from biomass as part of the establishment of biorefineries. In addition to converting biomass into alternative fuels and chemicals, this feedstock can be brought into play to render many other processes sustainable. Moreover, life cycle assessment models have shown that bio-based chemicals can have 60–95% lower carbon footprints compared with petroleum derived chemicals [13].

Biomass transformation involves multiple processing steps in which it gets depolymerized and converted to furfurals. The catalytic upgrading of furfurals is one of the most important steps to produce biofuels and renewable chemicals. Among many biomass-derived products, furanics have been extensively studied using biocatalysis [14], homoge-

neous [8–11] and heterogeneous catalysis [15], and electrocatalysis [16] in different reaction media. Furanics can be produced from non-edible biomass and provide opportunities for sustainable new products often with unique properties that can be used, for example, in the polymer, solvent, and surfactant industries [17,18].

In this context, cellulose- and hemicellulose-derived furans, namely, furfural (FAL), methyl furfural (MF), 5-hydroxymethylfurfural (HMF), 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), 2,5-bis(hydroxymethyl)furan (DHMF), furfuryl alcohol (FA), 5-methyl furfuryl alcohol (MFA), and 2,5-dimethylfuran (DMF) already represent an important class of bio-based substrates for modern biorefineries (Figure 1) [19,20]. In fact, in the biorefinery strategy, HMF stands out as a sustainable alternative towards fuels, chemicals, and materials, and could eventually replace petroleum-derived products [21].

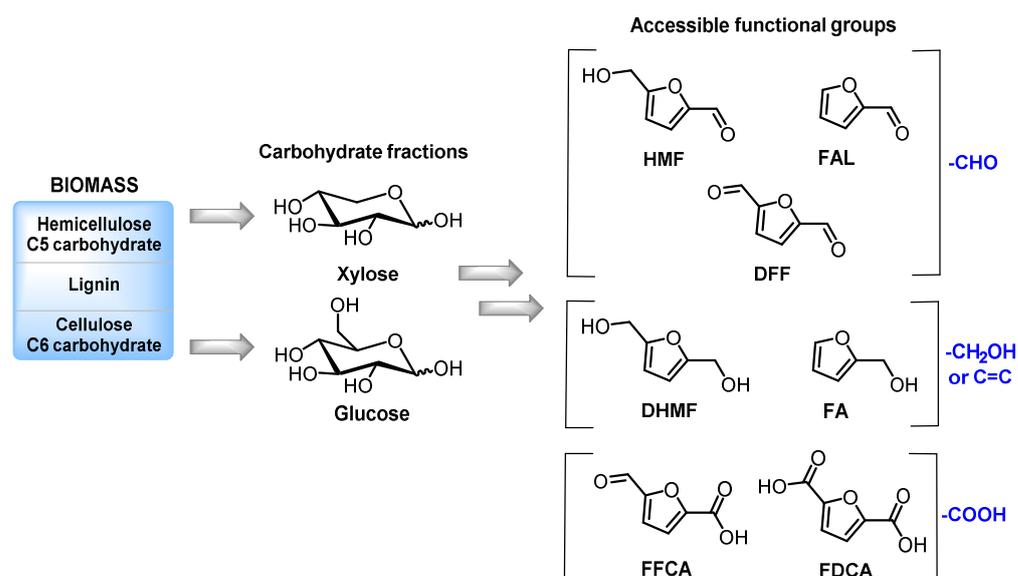


Figure 1. Examples of furanic substrates and target functionalities.

For instance, hydrodeoxygenation (HDO) and deoxygenation (DO) of furans (including HMF) produce value-added chemicals and liquid fuels [22–24]. In the HDO process, hydrocarbon components are generated from biomass derivatives with lower oxygen content via a catalytic reaction in the presence of H₂ [25]. In the DO procedure, the modification of the hydrocarbon skeleton is carried out by the removal of oxygen through hydrogenation, decarboxylation, decarbonylation, and dehydration without hydrogen gas [26,27].

Furthermore, these furan derivatives are used as valuable C5/C6 resources for the synthesis of chemicals and biofuel components, such as levulinic acid (LA), succinic acid, 1,6-hexanediol, cyclopentanone, adipic acid, furoic acid, etc. [28]. Moreover, C5/C9 alkanes can also be produced by the hydrolytic ring opening and complete hydrogenation of furans and their aldol products [29].

This review highlights recent advances in which homogeneous catalyzed reactions transform biomass-derived furanics into renewable and more valuable platform chemicals. In particular, furanic-based derivatives produced by homogeneously catalyzed processes, such as hydrogenation, oxidation, amination, condensation, halogenation, esterification, decarbonylation, and ring opening, are described. We will illustrate the recent development of well-defined and selective catalysts whose performance and stability are positioning homogeneous catalysis as key technologies for biomass transformation.

2. Homogeneous Catalysts as a Toolbox for Biorefining

Nature has been refining catalysts for life-sustaining reactions for billions of years [30]. The design of robust non-biological catalysts enable fast and selective chemical transformations under conditions that are currently not possible.

Hence, there is an enormous opportunity for developing homogeneously catalyzed processes, to re- and defunctionalize biogenic substrates and deliver the production of high-value chemicals [31]. The use of catalysts has potential advantages, including using oxygenated functionalities present in biomass, avoiding the use of harmful reagents, and, in some cases, offering a high yield route [32]. This technology offers the opportunity to fulfill green chemistry requirements, particularly reduced energy consumption, the manufacture of bulk chemicals (which ensures high atom economies [3] or E factors), and the production of biodegradable substances [33].

Homogeneous catalysis often works at much lower temperatures than heterogeneous catalysis, which is highly advantageous when it comes to avoiding side reactions, such as condensation. In fact, noble-metal complexes are well established as catalysts for the catalytic conversions of key intermediates derived from biomass.

The significance of homogeneous catalysis is growing rapidly particularly in the area of the pharmaceutical and polymer industry. For instance, William. S. Knowles, Ryoji Noyori and K. Barry Sharpless received the Nobel Prize in 2001 for their achievements in the field of asymmetric homogeneous catalysis. Their discoveries contributed to the development of industrial syntheses of pharmaceutical products and other biologically active substances [34].

For example, the successful industrial synthesis of the amino acid L-DOPA was developed by Knowles at Monsanto. This chiral drug for treating Parkinson's disease was synthesized using the $[\text{Rh}((R,R)\text{-DiPAMP})\text{COD}]\text{BF}_4$ complex in quantitative yield with 95% of enantiomeric excess (*ee*) [35–37].

The Takasago process catalyzed the asymmetric isomerization of an allylic amine to an enamine with the (*S*)-BINAP-Rh complex and furnished the industrial syntheses of the chiral aroma substance menthol [38,39] with approximately 1000 tons of the annual world production [40]. Another well-known example is the enantioselective hydrogenation or transfer hydrogenation of aldehydes and ketones. This method allows the industrial-scale production of optically active compounds, including medicines, agrochemicals, and perfumes.

Among them, Noyori type catalysts have shown high productivity (turnover number, TON up to 10^6), high turnover frequency (TOF) under mild conditions, and excellent enantioselectivity (95% *ee*) similar to enzymes [41]. This process constitutes one of the most efficient artificial catalytic reactions developed to date. A broader applications of Noyori's catalyst includes Rh(I) and Ru(II) species, where BINAP-Ru is used as a catalyst in the industrial production of the anti-inflammatory naproxen (Figure 2) [42,43].

Considering these examples, the conversion of bio-based feedstocks represents a huge challenge for catalysis. The design of a catalyst for biomass transformations requires the development of water tolerant catalysts that are highly resistant to acidic and chelating media and to the impurities present in the fermentation broth [44]. Furthermore, catalysts with strong hydrogenation and finite deoxygenation abilities are necessary for the upgrading of biomass [45].

The catalytic deoxygenation of biomass is very important to produce highly functional intermediates, such as furanics with aldehyde and alcohol moieties [46]. Those chemicals can be produced via different processes. For example, the typical reactions that the furanic aldehyde functionality can undergo are reduction to alcohols by H_2 or by hydrogen transfer (Meerwein–Ponndorf–Verley reduction) [47], decarbonylation [48], reductive amination to amines [49], oxidation to carboxylic acid [50], acetalization [51], aldol and Knoevenagel condensations [52], acylation, and Grignard reactions [53]. The second reactive functionality is the hydroxyl group that can undergo hydrogenolysis of the C–O bond, oxidation to an aldehyde or acid, etherification, acetalization, esterification, and halogenation reactions [54].

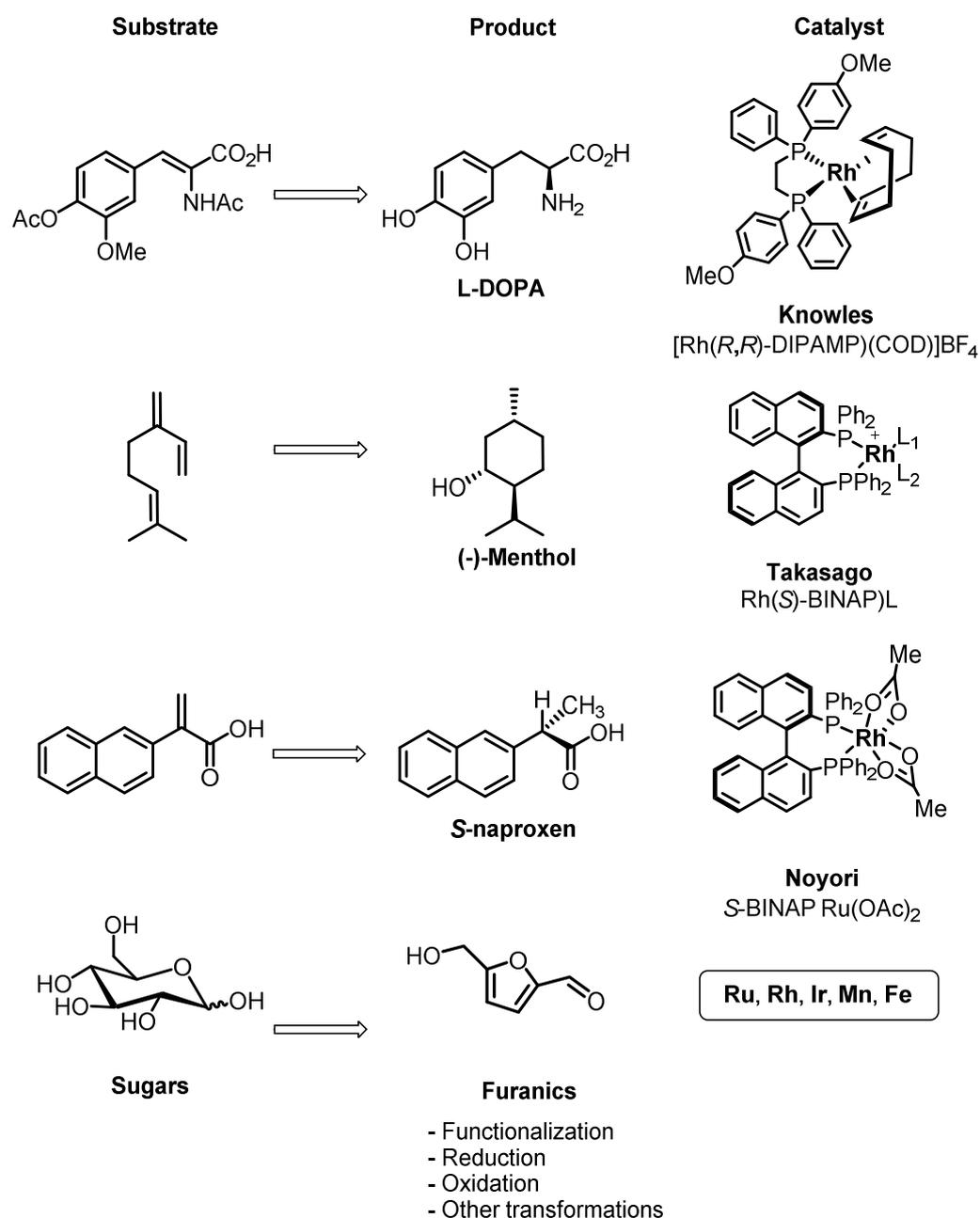


Figure 2. Examples of homogeneous catalyzed processes in industry.

Finally, the furan ring can be transformed by hydrogenation, ring-opening, alkylation, oxidation, halogenation, and nitration reactions [55–57]. In general, these reactions lead to liquid alkanes, solvents, fuel additives, plasticizers, and resin precursors. These transformations involve at least one step of an addition of hydrogen to reduce an unsaturated double bond or simply promote the cleavage of a single bond.

3. Homogeneous Catalysts for the Production of FAL and HMF

Furanic energy platform chemicals, such as FAL and HMF, can be produced by hydrothermal conversion of biomass [58]. Both chemicals are extremely relevant for biofuel and bio-based chemical industries.

The development of process technologies and implementation of industrial-scale HMF production has been reported [59–61]. Compared to FAL, HMF is an important building block widely recognized for the production of liquid fuels, resins, solvents, pharmaceu-

ticals, and fine chemicals [4,62,63]. The current commercial production of HMF mostly relies on the syrups extracted from energy crops [64,65]. However, the use of different biomass resources or food wastes as an alternative feedstock could enable more sustainable manufacturing practices.

For instance, AVA Biochem produces HMF from lignocellulose at various levels of purity (up to $\geq 99.9\%$) [66]. In this case, the hydrothermal carbonization of lignocellulose towards hydrochar is combined with the production of HMF. Thus, the lignocellulosic biomass is decomposed under high temperature (200–300 °C) and pressure to glucose and fructose in the presence of water. Further dehydration of fructose leads to a HMF-containing water mixture that is subjected to extraction and separation from the reaction mixture [58,67].

Likewise, FAL is an important renewable, non-petroleum based chemical feedstock. The industrial production of FAL is based on biomass hydrolysis and subsequent dehydration of the obtained pentoses using a homogeneous Brønsted acid catalyst in aqueous media [68]. The furanic platform chemicals are one of the most notable examples of the biorefinery process [69]. The worldwide production of FAL was estimated at nearly 500 kT per year [70]. However, the present yield of FAL in industrial processes is relatively low (approximately 50%) [58]. The condensation and degradation products as well as the formation of humins decrease the efficiency of the process. Many attempts to increase the yield have suggested the addition of ionic liquids, biphasic systems, and heterogeneous and homogeneous catalysts.

Diverse catalysts and methodologies are employed for the synthesis of HMF and FAL (Figure 3). In general, the dehydration of fructose produces HMF under acidic conditions at elevated temperatures in water. It is well known that fructose is the most convenient starting material for the preparation of HMF, while glucose is less reactive and undergoes isomerization to yield fructose before the dehydration [71]. Likewise, the subsequent rehydration of HMF may occur, and its rearrangement leads to the formation of LA and formic acid [72].

This pathway can influence the overall efficiency of the process leading to the formation of humin-like furanic polymers due to the low stability of HMF [73,74]. To prevent this, Ishida reported the reaction in DMSO, affording high yields of HMF in the presence of Lewis acids, such as LaCl_3 at 140 °C [72,75]. Another strategy for the direct production of HMF from various carbohydrates is the use of ionic liquids (ILs) in the presence of a series of relatively eco-friendly metal chlorides.

For instance, Zhao described a pioneering work of the use of [EMIM]Cl with various metal chlorides, such as CrCl_2 , FeCl_2 , FeCl_3 , VCl_3 , MoCl_3 , PdCl_2 , PtCl_4 , RuCl_3 , and RhCl_3 achieving high catalytic activities for the dehydration of fructose to HMF with yields ranging from 60–83% at 80 °C [76]. Interestingly, CrCl_2 showed better activity for the conversion of glucose to HMF with a 70% yield in 3 h at 100 °C. In fact, CrCl_2 reacts with the IL to form active species [EMIM]CrCl₂, which facilitates sugar isomerization and dehydration [77].

Other metal chlorides, including SnCl_4 [78], CuCl_4 [79], RuCl_3 [80], IrCl_3 [81], ZrCl_4 [82], ZrOCl_2 [83], HfCl_4 [84], NbCl_5 [85], and YCl_3 [86], have been reported as catalysts for the transformation of carbohydrates into HMF in different solvents. This methodology represents an important advance in the use of lignocellulose for the production of primary furanics via a green process without volatile organic solvents [74,87].

The transition metal chlorides with Lewis acidity promote the aldose–ketose isomerization during the sugar conversion and yield furan platform chemicals (HMF and FAL) with relatively low catalyst loading [53]. The use of ionic liquids as a solvent/additive has been proposed as alternative to promote the hydrothermal conversion of biomass in an indirect recycling of the reaction phase.

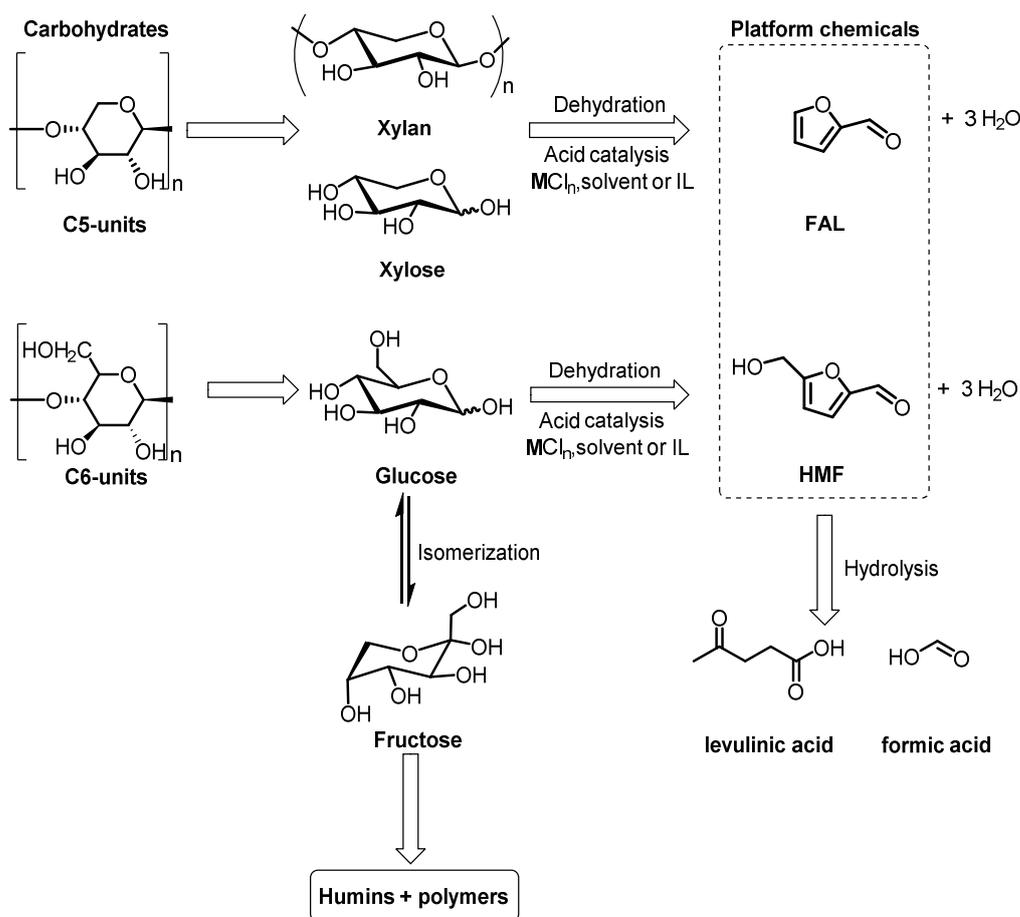


Figure 3. Upgrading of lignocellulosic polysaccharides to the primary furanics FAL and HMF.

Wrigstedt explored the use of $CrCl_3$ in the presence of mineral acids and alkali metal salts for the dehydration of glucose and fructose in a water–THF mixture [88]. The addition of acid prevents the formation of a chromium–glucose chelate complex hampering the isomerization of glucose and leading to similar yields of HMF and FAL (53% and 59%, respectively).

Lin explored the use of a relatively low-toxic, recyclable, and inexpensive catalytic system with chromium(III) chloride ($CrCl_3 \cdot 6H_2O$) and tetraethylammonium chloride (TEAC) ionic liquid. The efficient conversion of glucose into HMF was achieved in 71% at $130\text{ }^\circ\text{C}$ in 10 min [73].

Yadav and coworkers reported the transformation of glucose into HMF promoted by cobalt-based metallophthalocyanines [89]. The results demonstrated high catalytic activity of the cobalt phthalocyanine (Co-PC) with an electron-withdrawing nitro group. Subsequent studies with this catalytic system suggested that stronger Lewis acidity in combination with ionic liquids ([EMIM]Cl or [BMIM]Cl) could improve the conversion of glucose into HMF in high yields (>88%) at $100\text{ }^\circ\text{C}$ after 3 h.

Among these examples, metal triflates constitute a viable alternative for the production of HMF with much lower corrosion and environmental pollution. In particular, Wang and coworkers investigated the catalytic activity of various triflate salts from which $Sc(OTf)_3$ and $Yb(OTf)_3$ showed an 80% yield in DMSO at $120\text{ }^\circ\text{C}$ and 2 h [90]. Likewise, Li investigated the production of HMF from glucose when using $Hf(OTf)_4$ in *sec*-butyl phenol at $165\text{ }^\circ\text{C}$ and 25 min. The higher valence state of the metal cations involves stronger Lewis acidities facilitating the isomerization of glucose and the dehydration of fructose while improving the yield of HMF.

Other substrates, like xylose, can be subjected to similar reactions with HCl/CrCl₃ catalytic mixture in aqueous media producing FAL in 39% yield [91]. Marcotullio [92,93] and Liu [94] found that the use of FeCl₃ increased the rate of conversion of xylose or xylotriose in water or water-CPME (cyclopentyl methyl ester) mixtures at 180 °C. The conversion rate was improved under these reaction conditions, reaching a 65–74% yield for xylose and 78% for xylotriose. Overall, furans produced from carbohydrates have high potential for the synthesis of useful monomers based on renewable sources. In the next sections, we will discuss the most relevant transformation of bio-based furanics, such as FAL and HMF compounds, by homogeneous catalysts.

4. Catalytic Reduction of Furanics

The currently forecasted transition to a hydrogen economy allows the use of renewable hydrogen as clean energy source for many applications [95]. For example, green and sustainable organo synthesis can use renewable hydrogen to achieve the chemical reduction of carbohydrate-based feedstocks and convert the highly unsaturated biomass to value-added chemicals. Thus, the efficient hydrogenation of carbonylic functionalities in biomass derived substrates, such as HMF, FAL, and MF, represent a good strategy in organic synthesis for the sustainable production of fuels or building block chemicals [96].

In fact, the selective hydrogenation of HMF into DHMF is very similar to the reduction of α,β -unsaturated aldehydes or ketones to the corresponding unsaturated alcohols [97]. This reductive process has been achieved by different hydrogenation methodologies, including electrocatalytic hydrogenation [98] or in the presence of heterogeneous catalysts at high temperatures and pressures [99].

However, most of the catalysts compromise the activity to attain high selectivity by modifying the active metal with second components or introducing additives or oxide supports. In particular, Tomishige reported a heterogeneous multicomponent-based Ir-Re catalyst supported on SiO₂ for the selective hydrogenation of HMF to DHMF in high yield (99%) under 8 bar H₂ at 30 °C [96,100].

Moreover, DHMF is an important starting molecule for the polymerization or etherification processes (biodiesel, polyester, and polyurethane foams) [98]. Other bulk chemicals are derived from FAL, such as FA, methyl-tetrahydrofuran (MTHF), THF, and maleic acid (MA) [26].

Conventionally, furfuryl alcohol is produced over copper-chromite catalysts, which are highly toxic and cause serious environmental issues [101]. Therefore, the exploration of non-chromium catalysts for the green catalysis of FAL hydrogenation to FA is ongoing. For example, heteropolyacid catalysts have shown potential for this hydrogenation process, which is of great interest as a building block for resins [102]. An alternative to these solid Lewis acid catalysts is the addition of mineral acids (H₂SO₄, HCl, and H₃PO₄) and salts with transition metals (CrCl₃ and SnCl₄) in aqueous media [103].

Even though these catalytic advances in the production of biomass-derived furanic alcohols provide green alternatives to stoichiometric reducing agents, homogeneous catalysis that, in principle, might improve selectivity under mild reaction conditions, have been scarcely investigated. A gradual evolution of the catalytic hydrogenation of HMF to DHMF by homogeneous catalysts has been described using high-pressure H₂ gas or other hydrogen sources and an inorganic/organic base (Figure 4).

For example, Elsevier studied the catalytic hydrogenation of HMF with a half-sandwich Ru-NHC complex (0.5 mol%) in the presence of KO^{*t*}Bu and THF under 50 bar H₂ at 70 °C [104]. This catalytic system showed a 99% conversion after 2 h and was successfully extended to other key biomass-derived substrates, such as cinnamaldehyde or dimethyl oxalate. Furthermore, Hashmi investigated the same reductive process using Ru(methylallyl)₂COD (4.5 mol%) combined with an NHC-based ligand at 10 bar H₂ and 120 °C [105]. The reaction afforded 92% yield of DHMF and 12% of the side product THFDM after 16 h.

Mazzoni reported the use of the dimeric Shvo's catalyst (0.1 mol%) to produce DHMF in toluene/H₂O under 10 bar H₂ at 90 °C in 99% yield [106]. Recently, Nielsen reported the highly effective and selective hydrogenation of the bio-based furanic aldehydes, such as HMF and MF under mild reaction conditions to the corresponding alcohols catalyzed by Ru-PNP and Ir-PNP complexes under 30 bar H₂ at 25 °C and 60 °C, respectively [107]. This methodology allowed a high conversion rate up to TOF >1900 min⁻¹ and the quantitative isolated yield of DHMF and MFA.

This work showed solvent-free catalytic reactions in large scale, which is important to reduce costs and the environmental impact as well as to improve the efficiency [108]. In another attempt, Beller demonstrated the use of a base-metal PNP-Mn complex (1 mol%) for the production of DHMF in toluene under 30 bar H₂ at 100 °C, affording 90% conversion after 24 h [109]. Unfortunately, efforts to isolate the product remained cumbersome during the purification yielding 64% of the product due to decomposition.

There is also an important need for the development of environmentally benign technologies to improve the catalytic efficiency of FA production. Currently, FA is the most important monomer in furfural-based polymers [110]. Some technologies propose the production of bifunctionalized monomers from FA and its derivatives as precursors for polymer synthesis. In fact, biorenewable C5 alcohols are considered important commodity chemicals for the production of polyesters, polyurethanes, polyethers, and fuel additives [68].

In this sense, there are several promising alternatives for the production of FA. For example, Li [111], Bhanage [112], and Rothenberg [113,114] used a Ru-catalyst for the reduction of FAL to FA at a low temperature in the presence of different solvents. Mika also reported Ru(acac)₃ pre-catalyst in the presence of a bidentate ligand DPPB (1,4-bis(diphenylphosphino)butane) at 160 °C in EtOAc for 0.6 h with a maximum TOF = 6273 h⁻¹ and 99% conversion [115]. Ladipo explored the activity of cis-[Ru(6,6'-Cl₂(bpy)₂(OH₂)₂](CF₃SO₃)₂ (1 mol%) for the production of FA at 100 °C, 51 bar H₂ in EtOH [116]. The results displayed good selectivity (99%) and conversion (99%) after 2 h.

Deng and Fu reported high turnover numbers, up to 13,877 h⁻¹ and 50% yield for the transformation of FAL to FA using iridium half-sandwich catalyst (0.0083 mol%) in the presence of a phosphate buffer solution at 120 °C, 10 bar H₂ and 4 h [117]. The side products LA (41%) and gamma-valerolactone (GVL, 9%) were also observed. Choudhury accomplished the catalytic reduction of FAL using a neutral iridium half-sandwich system at 30 °C, 1 bar H₂ in EtOH/H₂O mixture, producing a 94% yield after 2 h [118].

Additionally, an efficient catalytic hydrogenation of FAL using Triphos-Ru(CO)H₂ has been reported by Grainger and coworkers. A catalyst loading of 0.05 mol% gave full conversion after 16 h at 120 °C and 30 bar H₂ [119]. The combination of relatively low catalyst loading of Ru-PNP (0.05–0.1 mol%) promoted the effective catalytic conversion of FAL to FA in 99% after 30 min employing mild conditions and green solvents [107].

Among these examples, Makhubela reported the selective production of bio-based alcohols, including FA using a Pt(II) complex (0.2 mol%) containing a Schiff base ligand. The catalyst displayed complete conversion of the substrate at 140 °C, 20 bar H₂ with good selectivity towards FA in EtOH and 88% yield after 10 h [120]. The pre-catalyst showed enhanced activity and selectivity in the presence of HCOOH affording a highest TOF of 1060 h⁻¹. Recently, Aguirre studied the activity of Ru-NPN pincer complex with 0.033 mol%, producing FA in high yield (99%) at 120 °C under 20 bar H₂ in *i*PrOH [121].

Within this context, the replacement of precious metal catalysts by earth-abundant metals results in a beneficial practice in terms of green chemistry [122]. For instance, Beller reported the first example of a base-metal catalyzed hydrogenation of furanic aldehydes. The Fe(II) tetraphos system [FeFP(PhPPh₂)₃][BF₄] (0.8 mol%) exhibited full chemoselectivity for the reduction of FAL to FA in *i*PrOH/TFA (trifluoroacetic acid) mixture at 120 °C, 20 bar H₂ and 2 h.

The desired alcohol was obtained with a 99% yield [123]. Kirchner studied the same reductive process with Fe-PNP (0.05 mol%) and DBU (1 mol%) at 40 °C, 30 bar H₂, and 16 h.

The combination of this catalyst with a supported ionic liquid phase (SILP) promoted the hydrogenation of aldehydes. Kirchner, Hoffmann, and Bica reported the catalytic activity of this system for the reduction of FAL to FA in a mixture of IL/*n*-heptane in 87–98% yield under 10–50 bar H₂ at 25 °C in 1 h [124–126].

In the case of manganese catalysts, the hydrogenation of carbonyl compounds proceed at relatively high catalyst loading at elevated temperatures in the presence of strong bases [127]. Filonenko and Pidko reported manganese-based hydrogenation catalysis for the conversion of carbonyl derivatives including biomass aldehydes, such as FAL [128]. The Mn(I)-CNP precatalyst (50 ppm) is activated in the presence of a hydride donor promoter KHBET₃ (1 mol%) and 25 bar H₂, 24 h at 80 °C in *i*PrOH. The desired alcohol (FA) was isolated in 54% yield (Figure 5). Kirchner improved the yield up to 77% by using a monohydride Mn-PNP complex (0.1 mol%) and H₂ pressure of 50 bar at 25 °C and 18 h [129].

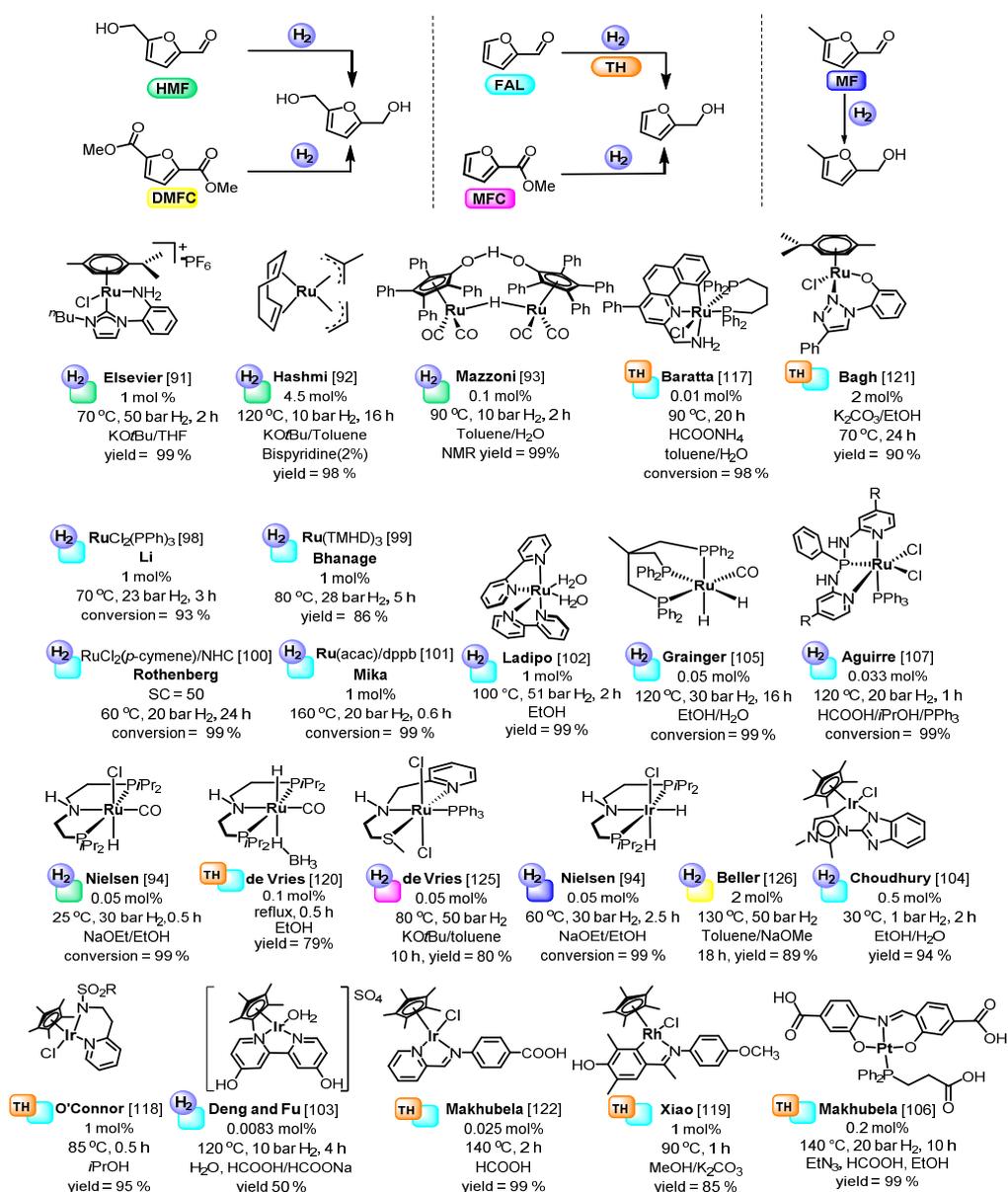


Figure 4. Well-defined precious-metal complexes for the selective hydrogenation/transfer hydrogenation of furanic aldehydes and esters to alcohols.

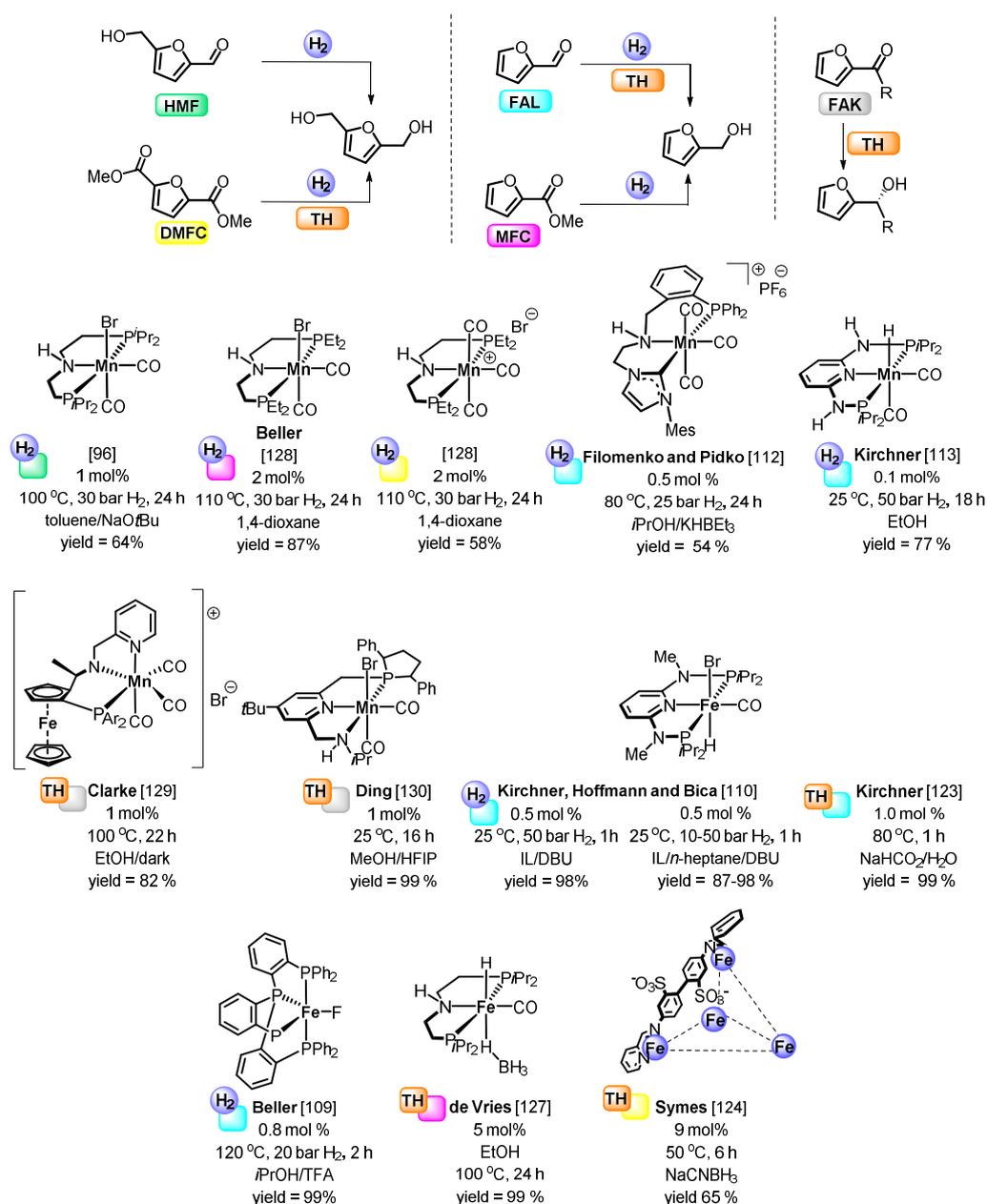


Figure 5. Base-metal complexes for the selective hydrogenation/transfer hydrogenation of furanic ketones as well as aldehydes and esters to alcohols.

To avoid the use of high-pressure reactors and harsh reaction conditions for classical hydrogenation, catalytic transfer hydrogenation is considered an attractive alternative. This process involves the transfer of a proton and a hydride from the donor molecule to the unsaturated substrate. There are examples of sacrificial hydrogen donors, such as formic acid, *i*PrOH, EtOH, and MeOH. In fact, the replacement of molecular dihydrogen as a reducing agent by a sacrificial hydrogen donor/solvent, such as EtOH, is an ecofriendly and safe option.

The first example of transfer hydrogenation of carbonyl compounds is the well-known Meerwein–Ponndorf–Verley reduction, which involved the use of aluminum alkoxide as a promoter for the reduction of a ketone in the presence of a secondary alcohol as a sacrificial hydrogen source [130]. Although this process has been widely utilized in both academic and industrial processes, the major drawbacks of this protocol are the requirement of a large amount of aluminum alkoxide reagent, unwanted side reactions,

and the moisture sensitivity of aluminum alkoxides [131]. The catalytic TH is a relatively new process in biomass value addition with outstanding results for the production of biofuels. Furthermore, this synthetic procedure decreases the risk of overpressure in the system and simplifies the reactor design.

Several iridium and ruthenium-based catalysts have been reported for the selective transfer hydrogenation of aldehydes using water as solvent and formates as hydrogen source. On the other hand, secondary alcohols have a higher tendency to release hydrogen than primary alcohols [132,133]. Often the combination of a hydrogen donor and H₂ gas is necessary to avoid the oxidized product of the raw material or aldehydes and ketones from the alcoholic hydrogen donor.

The chemoselective reduction of FAL to the corresponding alcohol was achieved by Baratta and coworkers using benzo[h]quinoline RuCl₂(CNN^{Ph})(PP) pincer complex (0.01 mol%) and HCOONH₄ as a hydrogen donor. The heteroaromatic aldehyde was selectively reduced to FA with a conversion of 98% at 90 °C in toluene/water after 20 h [134].

O'Connor established a proof of concept for TH of HMF under base-free conditions employing *i*PrOH as a source of hydrogen. The complete reduction of the aldehyde functionality was carried out with a Cp*Ir(pyridinesulfonamide)Cl complex (1 mol%) at 85 °C in 30 min. Both HMF and FAL were reduced with 99% and 95% yields, respectively. This represents one of the few examples for the selective hydrogenation of furanic aldehydes without base or formation of side products [135]. In contrast, Xiao explored the TH of HMF using a rhodacycle (1 mol%) with MeOH and Cs₂CO₃ as base. The productivity of this complex along with its high stability provided 82% yield at 90 °C in 1 h [136].

Similarly, de Vries reported using Ru-MACHO-BH (0.1 mol%) complex for the TH of FAL using *i*PrOH or EtOH as a hydrogen source [137]. The desired product was isolated in 79% yield after 16 h under reflux. A contrasting system was developed by Bagh and coworkers for the TH of FAL using a phosphine-free air-stable ruthenium(II)-triazole complex (2 mol%) in the presence of EtOH and K₂CO₃ at 70 °C. The reaction provided a 90% yield of FA [138].

Makhubela tested the efficiency of pyridyl-imine iridium(III) for the production of FA with HCOOH as the source of hydrogen using a catalyst loading as low as 0.025 mol% and Et₃N as a base [139]. The catalyst showed good selectivity with TOF of 1481 h⁻¹ and 74% conversion at 140 °C.

The expansion of catalytic reduction of aldehydes can also use base-metal catalytic systems. For example, Kirchner used Fe-PNP hydride complex for the TH of FAL employing NaHCO₂/H₂O at 80 °C producing a 99% yield of FA after 1 h [140]. Symes reported the combination of the reducing agent NaCNBH₃ as hydride source and Nitschke's Fe₄L₆ cage as an enzyme-like catalyst. The encapsulation of furfural inside a supramolecular cage prevents the oligomerization of reactive intermediates and selective production of FA and 2-methylfuran [141].

Other outcomes for the hydrogenation of aldehydes enabled the reduction of carbonylic moieties, such as esters. In particular, de Vries demonstrated the effective ester hydrogenation of methyl furan 1-carboxylate (MFC) to FA with 0.05 mol% of Ru-NNS complex. Presumably, the use of toluene maximizes the conversion and yield of FAL to 80% at 80 °C, 50 bar H₂, and 10 h [142].

Similarly, Beller described the use of a PNP-Ir complex for the reduction of MFC to the corresponding alcohol. The reaction was carried out with 2 mol% catalyst loading in the presence of NaOMe under 50 bar H₂ and 130 °C. The product was isolated in 89% yield after 18 h [143].

Parallel to these works, de Vries explored the hydrogenation of esters catalyzed by PNP-pincer base metal complexes. In this regard, Fe-MACHO-BH (5 mol%) promoted the reduction of MFC to FA (99% yield) in EtOH at 100 °C and 24 h [144]. Interestingly, high yields of FA (87%) were also observed with the PNP-Mn catalyst (2 mol%) in 1,4-dioxane at 110 °C and 30 bar H₂ [128]. In addition, the hydrogenation of dimethyl furan-2,5-

dicarboxylate (DMFC) towards BHMF was afforded with a 58% yield by using the cationic Mn-PNP tricarbonyl complex (2 mol%) under similar reaction conditions [109,145].

Clarke used a Mn-PNN complex for the TH of MFC at 100 °C in the presence of KOtBu and EtOH. A catalyst loading of 1 mol% achieved an 82% yield after 22 h [146]. Likewise, the enantioselective ketone hydrogenation has been demonstrated in recent years. For instance, Ding reported a lutidine-based chiral Mn-PNN complex for the asymmetric hydrogenation of 2-acetylfuran employing 1 mol% of the catalyst under milder reaction condition [147]. The heteroaromatic ketone was reduced to the corresponding chiral alcohol in 99% yield and 85% *ee*.

Among these examples, other processes and catalytic systems have been developed for the transformation of furanic aldehydes into hydrogenation/ring opening products such as ketoacids and diketones. For instance, 1-hydroxyhexane-2,5-dione (HHD) is one of the ketone derivatives obtained from HMF (Figure 6). It is considered an important intermediate generated in-situ for the formation of cyclopentanone-based chemicals through aldol-condensation [148].

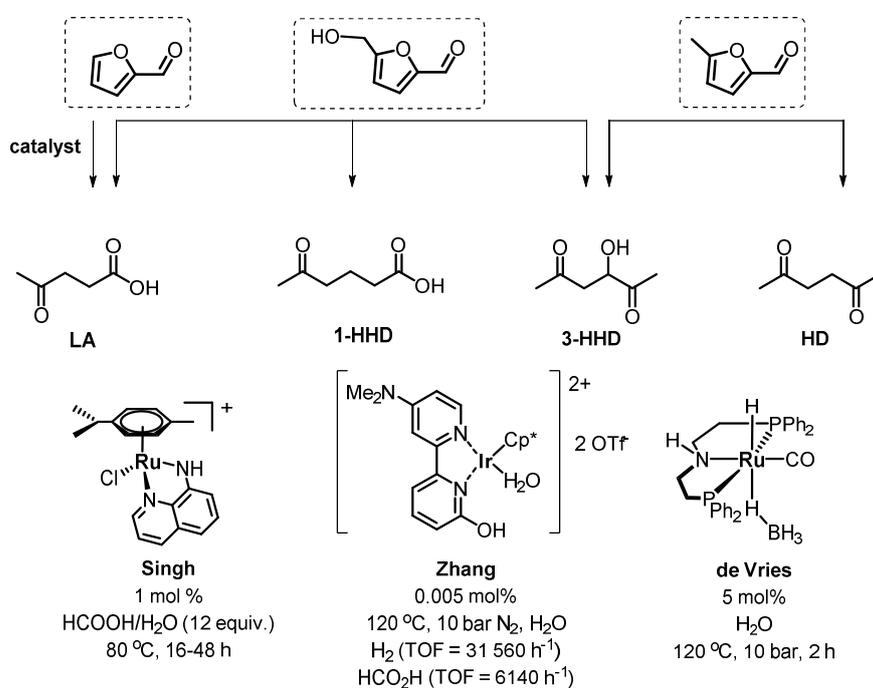


Figure 6. Ring opening reduction of furanic aldehydes with transition metal catalysts.

The transformation of furans (HMF, FAL, and MF) to ketoacids and diketones was studied by Singh and coworkers employing the water soluble 8-aminoquinoline arene-ruthenium (II) complex [149]. This one pot catalytic transformation allows the production of levulinic acid, 1-hydroxy-hexane-2,5-dione (1-HHD), 3-hydroxyhexane-2,5-dione (3-HHD) and hexane-2,5-dione (HD) in the presence of 1 mol% catalyst and an excess of HCOOH at 80–100 °C. This H-donor source is non-toxic organic acid and in combination with water as solvent, facilitate the hydrolytic ring opening of furans.

Zhang investigated the catalytic hydrogenation of HMF using a family of bipyridine Cp*Ir(III) complexes [150]. Thus, the hydrogenation and hydrolytic ring opening of HMF with the half-sandwich complex (0.26 mol%) in H₂O under 20 bar H₂ at 110 °C for 1 h, produced 86% of HHD. Further studies with analogous Cp*Ir(III) precatalyst containing a functionalized bipyridine and lower catalyst loading (0.00083 mol%) afforded a TOF = 31,560 h⁻¹ and 67% yield at 120 °C, 35 bar H₂ for 6 h under acidic conditions. The HHD formation was also possible in the presence of HCO₂H as hydrogen donor with TOF = 6140 h⁻¹ and 64% yield [151].

Within this context, de Vries presented a protocol for the one-pot synthesis of 2-hydroxy-3-methylcyclopent-2-enone (MCP) via ring opening of HMF to HHD in the presence of half-sandwich $\text{Cp}^*\text{Ir}(\text{dpa})\text{Cl}$ (dpa=dipyridylamine) in $\text{H}_2\text{O}/\text{KOH}$ at $120\text{ }^\circ\text{C}$, 10 bar H_2 and 2 h. The MCP was isolated in 55% yield. Interestingly, the presence of base promoted aldol condensation leading to MCP instead of the expected 3-(hydroxymethyl)cyclopent-2-en-1-one (HCPEN) [152]. The subsequent hydrogenation of MCP towards 3-methyl-1,2-cyclopentanediol was also tested with Ru-MACHO-BH (0.5 mol%) in THF at $100\text{ }^\circ\text{C}$, 20 bar H_2 affording 96% yield. Noteworthy, the use of this Ru-PNP catalyst for the direct ring opening of HMF diminished the yield of HHD to 5% under similar reaction conditions (Figure 6).

Hydrodeoxygenation of Furanics

Biodiesel and ethanol have been promoted over the past decade as a sustainable substitute for fossil fuels [153]. As result, there is a growing incentive to identify new strategies for converting non-edible biomass to biofuels. Among those examples, furanic derived fuels (or drop-in fuel compounds) also constitute a sustainable alternative to fossil-based products [154].

The upgrading of biomass-derived furanics to furanic biofuels is carried out by catalytic hydrogenation and hydrodeoxygenation (HDO) [155]. In this regards, the catalytic HDO of HMF or other chemical modifications allow the synthesis of more suitable liquid biofuels. In both types of reactions, the hydrogen atoms are added to the molecule to decrease the degree of unsaturation or cleave C–O bonds.

In fact, FAL and 5-HMF, which are generated by the corresponding dehydration of C5 and C6 sugars in the acid hydrolysis of lignocellulose, produce 2-methylfuran (2-MF), and 2,5-dimethylfuran (DMF), as hydrodeoxygenation (HDO) products. The other drop-in fuels compounds include 2,5-dimethyltetrahydrofuran (DMTHF), 5-ethoxymethylfurfural (EMF), ethyl levulinate (EL), GVL, distillate range hydrocarbons and aromatic aviation fuel additive [156].

Thus, the selective HDO of HMF is a general approach to produce the liquid biofuel DMF, which has combustion properties comparable to those of gasoline, [157] representing an alternative fuel with many desirable characteristics that overcome the drawbacks of low-carbon alcohols such as ethanol and *n*-butanol [158]. For example, DMF has the highest research octane numbers (RON = 119) of the mono-oxygenated C6 compounds, while preserving a high energy density (30 kJ cm^{-3}) and ideal boiling point ($92\text{--}95\text{ }^\circ\text{C}$) [159]. In general, ethers can be blended into petroleum-derived diesel up to 17% with no adverse effects on engine performance and decreasing particulate emissions [160].

One of the most promising transportation biofuel is 5-ethoxymethylfurfural (EMF) with energy density of (30.3 MJ/L), which is similar to gasoline (31.3 MJ/L) and diesel (33.6 MJ/L) [161]. This chemical is usually synthesized from biomass sugars (glucose, fructose, or inulin) over an acid catalyst in ethanol. In comparison with the traditional hydrolysis, the use of the ethanolic system minimize the waste-water treatment and discharge [162]. The reported homogeneous catalysts for the synthesis of EMF include inorganic acids and soluble metal salts.

For instance, Liu reported the use of $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, FeCl_3 , and $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ for the production of EMF with yield up to 33% [163]. Zhang and Deng reported the one-pot conversion of fructose into EMF using FeCl_3 in the presence of ethanol-[BMIM] Cl as solvent. This methodology improved the production of EMF in 91% yield after 4 h at $100\text{ }^\circ\text{C}$. Presumably, the ionic liquid stabilize HMF and improve the selectivity of the reaction [164]. HMF is often used as a precursor for liquid hydrocarbon fuels via the production of linear alkene aldol condensation and HDO producing hydrocarbons in the approximate molecular weight range for diesel and jet fuel [165].

HDO of sugars and furans have been reported with heterogeneous hydrogenation and hydrogenolysis catalytic systems. However, the homogeneous catalyst systems based on transition metal complexes is scarcely studied. The atom economy for the hydrogenation

and HDO processes is extremely high, and only water is formed as byproduct [155]. However, the activation energies of the hydrogenation and HDO steps can lead to a mixture of partially hydrogenated products and intractable mixtures limiting its use [166]. The HDO of highly polar and reactive sugar-derived furans forces the use of a polar liquid reaction medium, such as H₂O. The high temperatures used for this process (>150 °C) are required to trigger any dehydration or hydrolysis steps [167].

It is known that the selective hydrogenolysis of the hydroxymethyl moiety of HMF forms 5-methylfurfural (5-MF), which has potential applications as a fuel oxygenate and a chemical intermediate. Further reduction of 5-MF leads to 2,5-dimethylfuran (DMF) via 2-(hydroxymethyl)-5-methylfuran (HMMF). As a promising biofuel, DMF has similar physicochemical properties to gasoline and also a green solvent. It has also been demonstrated as a crucial chemical intermediate to produce *p*-xylene for terephthalate polymers [168].

Hydrogenation of the furan ring in DMF produces 2,5-dimethyltetrahydrofuran (DMTHF), which is a promising fuel oxygenate and a renewable substitute for tetrahydrofuran (Figure 7). Schlaf reported the use of the [(4'-Ph-terpy)Ru(H₂O)₃](OTf) catalyst and its iridium analogue (4'-Ph-terpy)Ir(OTf)₃ for the conversion of DMF to hydrodeoxygenated products DMTHF and 2,5-hexanediol (2,5-HD), 2,5-hexanedione (2,5-HDO) and hexane in aqueous acidic medium at high temperature (175–225 °C) and 55 bar H₂ [169]. However, the aqueous acidic medium and high temperatures eventually can decompose the catalysts. Depending on reaction conditions, the ruthenium system with 0.1 mol% loading, leads to 2,5-HD (69% at 175 °C) or DMTHF (80% at 200–225 °C) with the concomitant generation of small amounts of 2-hexanone and hexane.

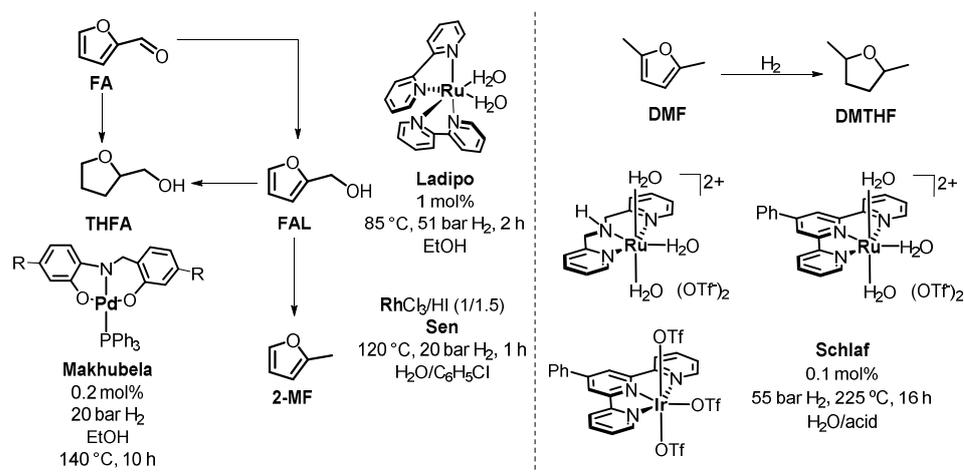


Figure 7. Catalytic HDO of HMF and catalyzed by transition metal complexes.

Both catalyst were deactivated by formation of unreactive bis-chelate complexes $[M(4'\text{-Ph-terpy})_2]n^+$ ($M = \text{Ru, Ir}$; $n = 2$ or 3) diminishing the catalytic activity under HDO harsh reaction conditions. The same author evaluated the catalyst $[\text{Ru}(2,2'\text{-dipicolylamine})(\text{OH}_2)_3](\text{OTf})_2$ yielding 55% of 2,5-dimethyltetrahydrofuran in the presence of acid co-catalyst (H₃PO₄) at $150\text{ }^{\circ}\text{C}$.

Most of the intermediates and HDO products observed with homogeneous systems are limited to furfural. For instance, Sen and coworkers used RhCl₃/HI (1/1.5) system to the direct conversion of xylose in a biphasic water/chlorobenzene mixture at $140\text{ }^{\circ}\text{C}$ and 20 bar H₂, producing 80% yield of 2-MF accompanied with the production of I₂ [170].

In other attempt, Ladipo showed a cascade hydrodeoxygenation reaction of FAL employing an active Ru(II)-bis(diimine) complex. The catalyst $[\text{Ru}(6,6'\text{-Cl}_2\text{bpy})_2(\text{OH}_2)_2](\text{BARF})_2$ (1 mol%) displayed good selectivity leading from FAL into FA (93%) at $85\text{ }^{\circ}\text{C}$, 51 bar H₂ and 2 h. Further transformation of FA at $130\text{ }^{\circ}\text{C}$, led to a very useful chemical precursor THFA (99%) via hydrogenation. The subsequent hydrogenolysis yielded 2-MF under similar reaction conditions [116].

Makhubela reported a Pd(II)-Schiff base complex for the conversion of FAL towards FA (88%) and THFA as a second product (12%). The reaction was carried out using 0.2 mol% catalyst loading with 20 bar H₂ at 140 °C and 10 h [120].

Under catalytic conditions, the ring opening of furfuryl alcohol can happen in two sides of the furanic ring. The reductive ring opening next to the hydroxyl group leads to 1,5-pentanediol formation, whereas the opposite side ring opening gives 1,2-pentanediol. [53] There is not such a catalytic process to control the selectivity of this reaction, because the chemical environments of the two furanic C–O bonds are similar. The opposite is true for the hydrogenation tetrahydrofurfuryl alcohol, where the formation of 1,5-pentanediol is favored.

5. Oxidative Transformations

Oxidative transformation of HMF lead to 2,5-diformylfuran (DFF), and/or 2,5-furandi carboxylic acid (FDCA). In this regard, the selective oxidation of HMF to the industrial precursor 2,5-diformylfuran (DFF) is relevant for the synthesis of pharmaceuticals, fungicides, and functional polymers [171]. In fact, selective oxidation reactions of HMF are currently viewed as attractive routes to 2,5-furandicarboxylic acid (FDCA) and/or 2,5-diformylfuran (DFF) and 5-formyl-2-furancarboxylic acid (FFCA), monomers for furan-containing polymers and materials with special properties [172].

While a variety of oxidants have been used for oxidation of HMF to FDCA and DFF, only few reports describe catalytic oxidations of HMF with oxygen or air, the most economical oxidants [173]. Recently, much progress has been made in the development of homogeneous catalytic systems for this transformation (Figure 8). For example, Corma reported the use of immobilized vanadyl–pyridine complexes affording 82% conversion and high selectivity ($\geq 99\%$) at 130 °C [37,174].

In general, the efficient and selective formation of DFF can be achieved by using vanadium-catalyzed systems. Xu reported a homogeneous catalytic mixture of Cu(NO₃)₂/VOSO₄ (2 mol%, 1:1 ratio) for the selective oxidation of HMF to DFF under mild reaction conditions (25–80 °C, 1.5 h, 10 bar O₂) in CH₃CN [175,176]. The inorganic catalyst is easily removed from the reaction mixture. Nevertheless, the instability and high cost of HMF limit the production of DFF [177]. A sustainable option is the catalytic conversion of carbohydrates to DFF without further purification of HMF.

The commercialization of FDCA produced from fructose-derived HMF is one example of the successful use of biomass [178]. In this industrial process, fructose is dehydrated in methanol solvent to the HMF analogue methoxymethylfurfural (MMF). Then, MMF is oxidized to FDCA using the homogeneous oxidation catalyst [179].

Moreover, FDCA has significantly wide attention particularly as a substitute of petrochemical-derived terephthalic acid in the synthesis of useful polymers [180]. In fact, FDCA can undergo coupling with mono-ethylene glycol to produce polyethylene furanoate (PEF), a green replacement for polyethylene terephthalate (PET) [181]. Even though, several methods for the synthesis of FDCA have been reported such as electrochemical oxidation and biocatalytic oxidation, synthesis of FDCA is mainly carried out via catalytic methods using heterogeneous or homogeneous catalysts.

Thus, HMF has been oxidized with O₂ to FDCA in the presence of heterogeneous Pt catalysts with stoichiometric amounts of alkali [182,183] and to DFF with TEMPO radicals [183] or supported vanadium catalysts [157]. On the other hand, homogeneous catalytic system for the synthesis of FDCA has been scarcely reported when compared to heterogeneous catalysts.

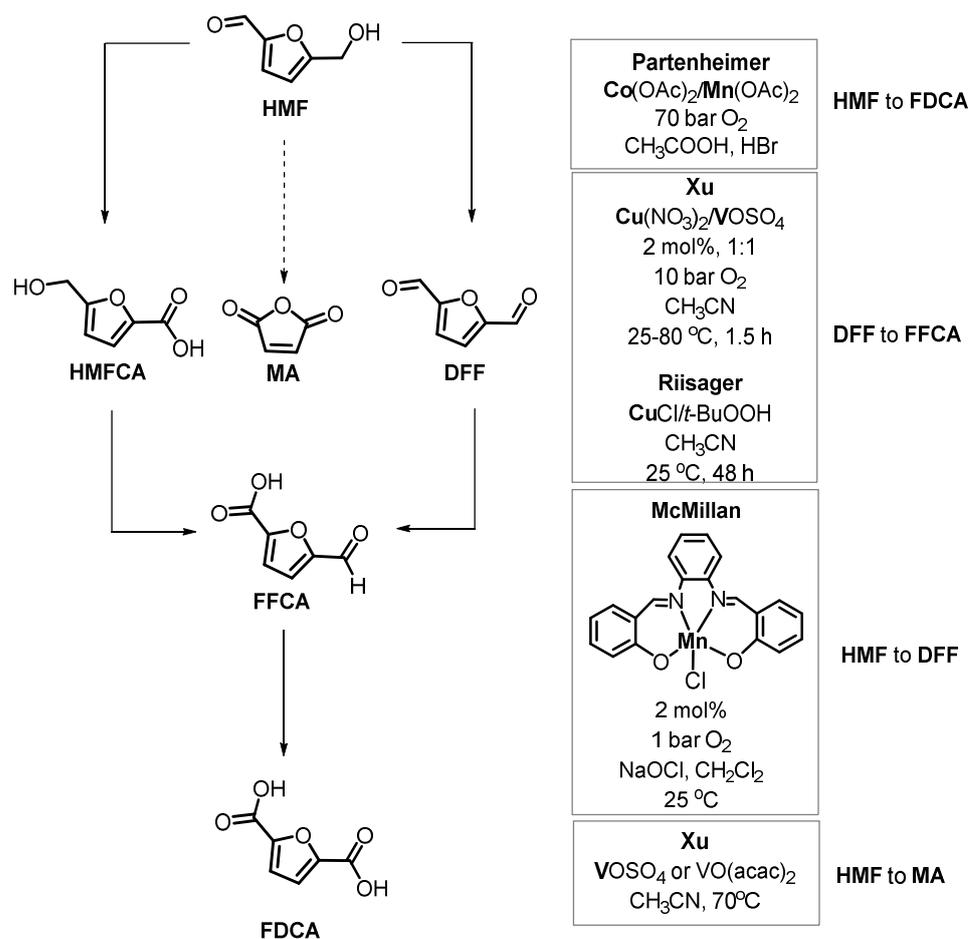


Figure 8. Methods of oxidation of furanics.

Partenheimer described the first examples of aerobic HMF oxidation reactions, catalyzed with homogeneous metal/bromide systems. The aerobic oxidation of HMF to FDCA was achieved at 125 °C under 70 bar air pressure in acetic acid solvent using $\text{Co}(\text{OAc})_2$, $\text{Mn}(\text{OAc})_2$, and HBr as the catalysts, commonly known as the Amoco Mid-Century (MC) catalyst [184]. They observed that HMF can be oxidized to DFF or 2,5-furandicarboxylic acid with high selectivity by tuning the reaction conditions. The oxidation of HMF with the MC catalyst proceeded via the formation of peroxy radical in the chain propagation step.

The peroxy radicals were formed through the abstraction of H-atom of HMF by the bromide radical, generated in the catalytic cycle by the oxidation of HBr with Co(III) or Mn(III), followed by reaction of aryl alkyl radical with O_2 . Although both hydroxymethyl and aldehyde groups of HMF could be simultaneously oxidized, the authors proposed that the OH group of HMF is selectively oxidized by dioxygen and metal/bromide catalysts to obtain 2,5-diformylfuran (DFF) in 57% isolated yield. HMF can be also oxidized via a network of identified intermediates to 2,5-furandicarboxylic acid (FDCA) in 60% yield. For comparison, benzyl alcohol gives benzaldehyde in 80% using the same catalytic system.

Similarly, Abu-Omar reported the use of $\text{Co}(\text{OAc})_2/\text{Zn}(\text{OAc})_2/\text{NaBr}$ mixture for the aerobic oxidation of HMF into FDCA [185]. DFF was observed as the only oxidation product without an acid additive, but FDCA was obtained in a yield of 60% with trifluoroacetic acid as an additive. McMillan proposed an efficient methodology for the efficient oxidation of HMF to DFF using a Mn(III)-salen (2 mol%) complex in the presence of NaOCl as oxidant under 1 bar O_2 in CH_2Cl_2 at 25 °C. The yield of the expected product was improved up to 89% [186].

The use of other oxidant such as *tert*-butyl hydroperoxide (*t*-BuOOH) was also studied for the transformation of HMF into FDCA. Riisager reported the oxidation of HMF into

FDCA in CH_3CN with *t*-BuOOH as the oxidant and copper salts as catalyst [187]. The use of CuCl together with LiBr as the additive yielded 43% of FDCA after 48 h at room temperature, whereas using CuCl_2 as the catalyst afforded 45% without additive.

Another important chemical intermediate derived from HMF is maleic anhydride (MA), which is mainly used for the synthesis of unsaturated polyester resins [188]. In fact, FA is the starting material for the production of maleic anhydride or maleic acid, via oxidation. Xu and co-workers reported the selective oxidation of HMF to MA using vanadyl complexes such as $\text{VO}(\text{SO}_4)$ and $\text{VO}(\text{acac})_2$ without proceeding through any oxidized furan intermediates [189]. The reaction was performed at 70 °C in CH_3CN affording 52% yield of MA. To the best of our knowledge, the heteropolyacid catalyst $\text{H}_3\text{PMO}_{12}\text{O}_{40}$ modified with $\text{VO}(\text{acac})_2$ have shown the best catalytic performance towards the formation of MA in 56% yield [190,191].

Interestingly, $\text{Pd}(\text{OAc})_2$ catalyst showed a 16% yield to furoic acid, while only traces of this compound were observed over other metal catalysts. However, the major competitive process for the selective oxidation is the polymerization of furfural to generate resins under the oxidative conditions. The by-product of furfural oxidation in gas phase is furan. In fact, furan is the first intermediate in the mechanism of the furfural oxidation and an important intermediate in chemical industry. Hence, even though it cannot be produced directly from biomass, it is produced from FA [192].

6. Other Chemical Transformation of Furanics

6.1. Catalytic Carbonyl Coupling of Furanics with Nucleophilic Nitrogen Sources

The introduction of nitrogen-containing functionalities in biomass-derived compounds, add value and expand their industry applicability [193]. In fact, reductive amination of HMF constitutes an important basic route for the sustainable production of nitrogen-containing compounds from biorenewables [194]. HMF can be converted into valuable N-containing furanyl compounds through the reductive amination of aldehyde groups (Figure 9).

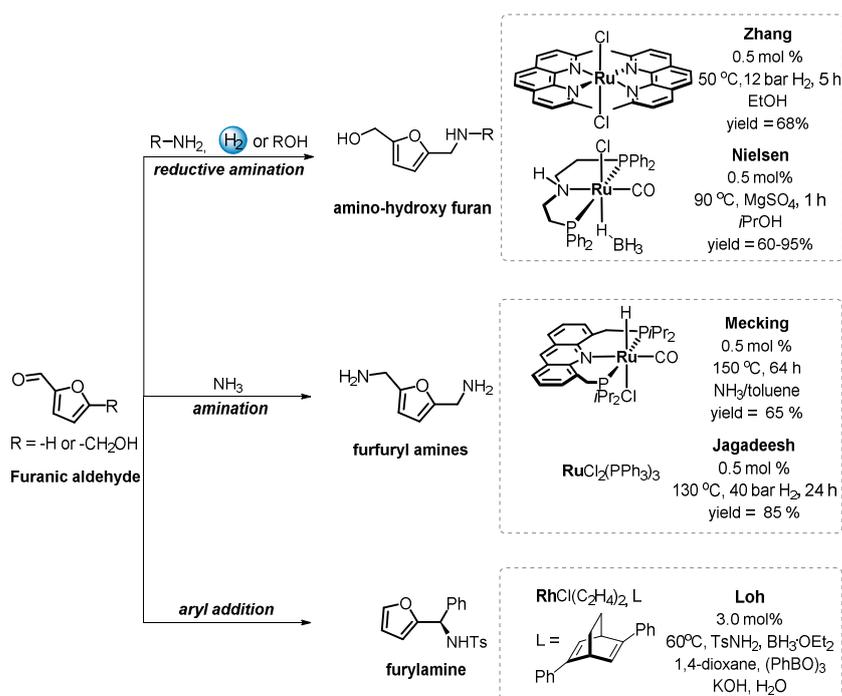


Figure 9. Synthesis of N-containing building blocks via reductive amination of furanics.

N-Substituted 5-(hydroxymethyl)-2-furfuryl amines have a wide application in pharmaceutical industry, e.g., for the production of calcium antagonists, muscarinic agonists, cholinergic agents, and carcinogenesis inhibitors [195]. These structures are conventionally

prepared by a Mannich-type reaction starting from FAL or FA with primary amines under harsh reaction conditions [196]. However, the C2 aldehyde group makes the C5 position of furan ring difficult for addition because of the deactivating effect [197].

The use of a metal catalysts is a prerequisite for efficient reductive amination via two reaction routes, including initial reduction to alcohols followed by amination or first the amination to form coupled imines and subsequent hydrogenation [198]. Zhang reported an optimal Ru-based catalyst Ru(DMP)₂Cl₂, (DMP) dichlorobis(2,9-dimethyl-1,10-phenanthroline)ruthenium(II) for the reductive amination of HMF with aniline. N-phenyl-5-(hydroxymethyl)-2-furfuryl amine was obtained in 68% yield at 50 °C with 12 bar H₂ in 5 h.

H₂ is employed as the reducing agent, which improves the atom economy of the reaction in the presence of bio-based EtOH as solvent making the process more sustainable [199]. Particularly, the catalytic performance of Ru(DMP)₂Cl₂ was more effective at 60 °C with a sharp increase in the yield (up to 98%). Hence, this catalytic system was efficient for synthesizing a number of new aminomethyl-hydroxymethylfurans with primary and secondary amines.

Homogeneous catalysis can promote the direct amination and reductive amination of furanic aldehydes and its derived alcohols into polymers. Mecking described the reductive amination of HMF with ammonia in the presence of the Milstein Ru-acridine diphosphine complex (Figure 9) to furfuryl diamines. This reaction led to the desired product 2,5-bis(aminomethyl)furan in 65% yield at 150 °C after 4 h with 2.5 bar of H₂ [200]. The monoamine derivative 2,5-bis(aminomethyl)furan is also an important monomer for the manufacture of long-chain polyamides. Bis(hydroxymethylfurfuryl)amine is a key furan-based monomer for the synthesis of functional biopolymers, which can be synthesized from the reductive amination of HMF.

Thus, the reductive amination of HMF with *n*-heptylamine was achieved with the already described Ru(DMP)₂Cl₂ catalyst. The bis(hydroxymethylfurfuryl)amine was obtained in 90% yield at 110 °C with 0.2 bar of H₂ and 12 h [201]. The condensation of HMF with the alkylamine followed by hydrogenation forms the amine, which yielded bis(hydroxymethylfurfuryl)amine after subsequent addition reaction, dehydration and hydrogenation. The authors claimed through comparison experiments and X-ray photoelectron spectroscopy analysis that the synergistic effect of Ru (II) and DMP ligand was accountable for the remarkable catalytic performance of the Ru-based catalyst.

Furfurylamines derived from the selective reductive amination of furfurals exhibits diverse applications in the industry, including the preparation of pharmaceutical, such as antiseptic agents, antihypertensives, and diuretics as well as agrochemicals, pesticides, and synthetic resins and polymers [202]. The synthesis of furfurylamines from furfurals by reductive amination has been investigated using various reducing agents and catalysts. Reducing agents such as hydrogen gas, silanes, borohydrides, and formic acid have been reported in the literature.

Jagadeesh described the use of RuCl₂(PPh₃)₃ for the reductive amination of furfural with ammonia, providing 85% yield of furfurylamine in 24 h and 130 °C under 40 bar of H₂ [203]. Noteworthy, the Ru-hydride species RuH₂(PPh₃)₃ or RuHCl(PPh₃)₃, formed in the reaction served as active catalytic species reacting with formed furfuryl imine. Recently, Nielsen reported an efficient, chemoselective, and base free transfer hydrogenation of furfural to furfuryl amines employing Ru-MACHO-BH as catalyst and *i*PrOH as H-donor. A relatively low catalyst loading (0.5 mol%) in the presence of MgSO₄ as drying agent resulted in full conversion of furfural to furfuryl amines at 90 °C after 1 h [204]. The general applicability of this method was tested with various amines affording moderate to excellent yield.

Loh described the asymmetric arylation of FAL in the presence of a rhodium-catalyst [RuCl(C₂H₄)₂]₂L (L = (1*R*,4*R*)-2,5-Diphenylbicyclo[2.2.2]octa-2,5-diene) to produce furylamine with 97% yield and 99% *ee* [205]. This methodology provides highly functionalized amines, which can be converted to piperidone-based pharmaceuticals.

6.2. Functionalization of Furanics and C–C Bond Formation

Furan-derived compounds are accessible intermediates for many other transformations in organic synthesis and constitute structural motifs in natural products or biologically drug molecules [206,207]. For example, Sheldon reported the palladium-catalyzed carbonylation of HMF with PdCl₂/TPPTS system in water at 70 °C and 5 bar CO (Figure 10) [208]. In addition to 4-formyl-2-furancarboxylic acid, they observed MF as byproduct from the reduction of HMF.

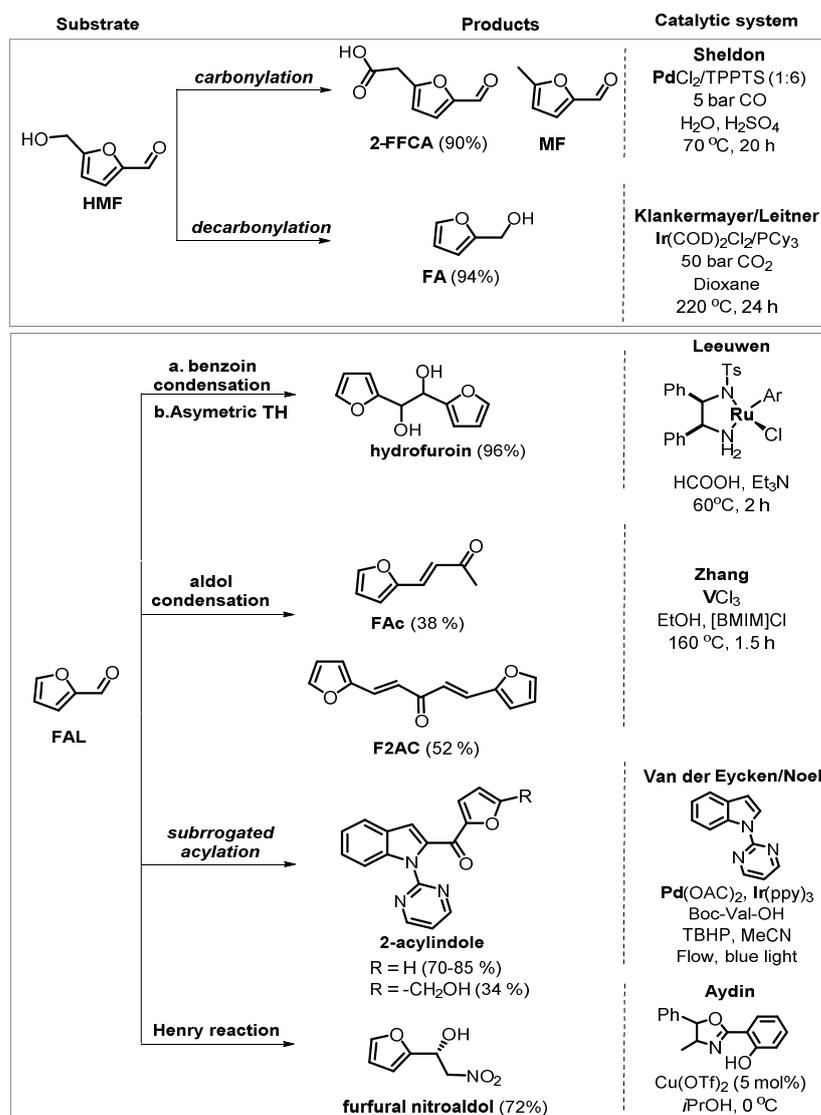


Figure 10. Biomass derived furanic-based intermediate for drugs syntheses.

The decarbonylation/reduction of HMF was explored by Klankermayer and Leitner [209]. The reaction was carried out with a catalytic system IrCl(cod)₂ (cod=1,5-cyclooctadiene) as the metal precursor in the presence of a phosphine ligand (PCy₃) in boiling 1,4-dioxane resulting in 41% conversion with 97% selectivity towards DHMF after 48 h. Interestingly, the addition of CO₂ increased the conversion up to 99%, suppressing the formation of humins. The substitution of solvent with THFA converted all the mixture into a single product stream of THFA.

The elongating of carbon chains of biomass-derived furanic compounds to produce fuel precursors or furan-based platform molecules can be achieved using several strategies, including aldol condensation [210,211], hydroxyalkylation/alkylation [212,213], Knoevenagel condensation [214], benzoin condensation [215], and Diels–Alder reaction [216].

The benzoin condensation of furfural is a well-known process for the synthesis of furoin. This class of compound is relevant for the preparation of alkane fuels via the HDO process. Leeuwen described the asymmetric reduction of the carbonyl group of furoin with a chiral catalyst $\text{RuCl}(p\text{-cymene})((S,S)\text{-TsDPEN})$ (0.5 mol%) to produce hydrofuroin with a 96% yield [217].

In general, aldol condensation reactions involve the enolization of a carbonyl group containing an $\alpha\text{-C-H}$ followed by C–C coupling with another carbonyl and subsequent dehydration. Some homogeneous catalysts have been successfully applied in the synthesis of diesel-fuel-range multi-carbon precursors via aldol condensation. For instance, Zhang reported various metal chlorides catalysts, such as NiCl_2 , CoCl_2 , CrCl_3 , VCl_3 , and FeCl_3 , for the aldol condensation of furfural with acetone in $[\text{BMIM}]\text{Cl}$ (1-butyl-3-methylimidazolium chloride) at 140 °C and 1.5 h [218]. The enhanced catalytic activity was observed with VCl_3 in the presence of ethanol, giving a 38% yield of furfurylideneacetone (FAC) and a 52% yield of (2-furanyl)-1,4-pentadien-3-one (F2Ac) at 160 °C and 1.5 h. Apparently, the acetal reaction of furfural with ethanol reduced the formation of side reactions of furfural.

Van der Eycken and Noël used HMF as acyl surrogates for the direct C-2 acylation of indoles at ambient temperature via dual photoredox/transition-metal catalysis in both batch and flow conditions [219]. The reaction was carried out in the presence of $\text{Pd}(\text{OAc})_2$ (10 mol%), *fac*- $[\text{Ir}(\text{ppy})_3]$, (2 mol%), *N*-(*tert*-butoxycarbonyl)-L-valine (Boc-Val-OH, 20 mol%) in CH_3CN (0.1 M) under argon, and exposed to light source for 24 h at 25 °C. Thus, the heteroatomic aldehydes, such as FAL and 2-thenaldehyde (TA), led to the corresponding 2-acylindole with a relatively moderate yield (68–85%). Interestingly, HMF showed low reactivity and a lower yield (34%). Presumably, this detrimental effect is due to the poor compatibility of the hydroxymethyl group with an oxidative single electron transfer pathway.

Finally, Aydin described the asymmetric Henry reaction of FAL with nitromethane catalyzed by $\text{Cu}(\text{OTf})_2$ (5 mol%) in the presence of an excess of a chiral oxazoline base ligand and *i*PrOH at 0 °C. The product furfural nitroaldol was isolated with a 72% yield and 80% *ee*. This β -nitro alcohol can be converted into other key building block molecules of natural products or pharmaceuticals [220].

6.3. Undirected C–H Activation

The catalytic activation of aromatic C–H bonds leading to the formation of a C–C bond is extremely relevant for chemical and pharmaceutical industries. In this regard, furans constitute key substrates for the synthesis of functionalized synthons. For example, Reiser and coworkers explored the transformation of furfuryl ester to cyclopropane in 36% yield and 91% *ee* employing a chiral CuBox catalyst $\text{Cu}(\text{OTf})_2\text{iPr-Box}$ (Figure 11). In general, cyclopropanes are valuable synthetic building blocks in organic synthesis for the construction of natural products and drugs [221].

Fujiwara reported Pd-catalyzed intermolecular dehydrogenative Heck reactions of furans with activated olefins in the presence of $\text{Pd}(\text{OAc})_2$ giving styrene-type products with a 75% yield with catalyst loadings as low as 0.5 mol% in AcOH-dioxane [222]. Since then, other systems have been reported to increase the TON with various oxidants, additives and solvents.

Hartwig reported the Ir-catalyzed oxidative coupling of furans with unactivated olefins to produce branched vinylfurans in the presence of a second alkene as the hydrogen acceptor [223]. The catalytic system $\text{Ir}(\text{coe})_2\text{Cl}_2$ complex (2 mol%) and the air-stable bisphosphine ligand (\pm)-TMS-SEGPHOS (4 mol%) were combined to carry out the reaction at 50 °C for 24 h in *tert*-butylethylene (TBE) as a sacrificial hydrogen acceptor. Higher yields (up to 99%) and selectivities were reported with furans containing electron-donating groups at C-2 on the furan.

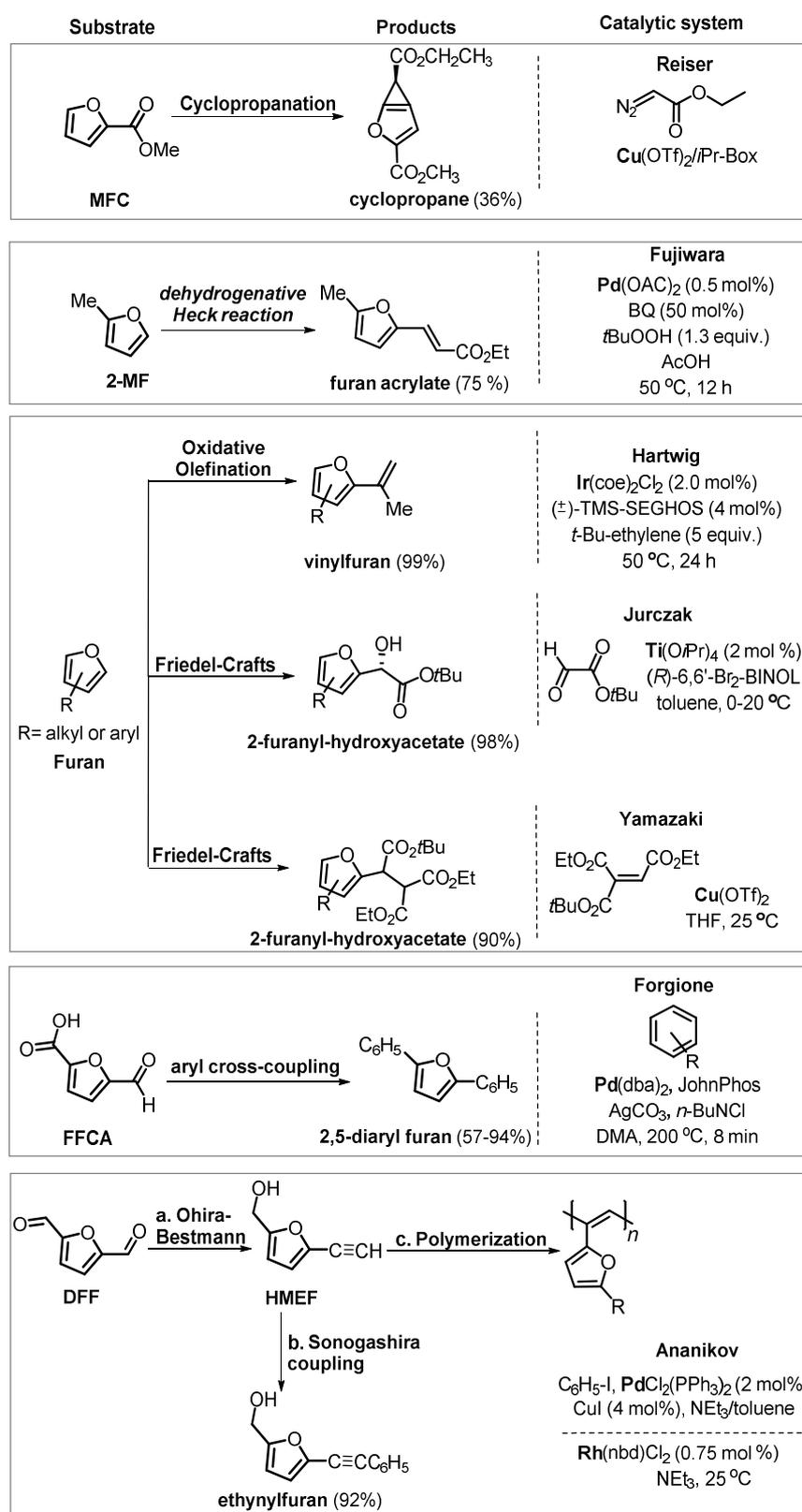


Figure 11. Catalytic functionalization of furanics in the presence of homogeneous catalytic systems.

Other synthetic methodologies for the production of bio-based synthons, such as 2-furanyl-hydroxyacetates, have been reported. For example, Jurczak published examples of efficient Friedel–Crafts reactions of a series of furans with alkyl glyoxylates promoted

by a 6,6'-dibromo-BINOL/Ti(IV) complex (2–5 mol%) in toluene at 20 °C affording up to 98% yields of 2-furanyl-hydroxyacetates with high enantioselectivity (90–97% *ee*) [224]. Yamazaki also described the Friedel-Crafts process using Cu(OTf)₂ (10 mol%) in THF at 25 °C [225]. The reaction gave yields of up to 90% with 60% *ee* for the substituted furan.

Forgione described the modification of biomass-derived 2,5-furandicarboxylic acid to produce 2,5-diaryl furans through the highly regioselective decarboxylative cross-coupling reaction with Pd(dba)₂ with high catalyst loadings (15 mol%) in dimethylformamide (DMF) [226]. The addition of silver-containing base, Ag₂CO₃ (1.5 equiv) and (2-biphenyl)di-*tert*-butylphosphine (JonhPhos) increased the yield to 80% at 200 °C. The same approach was applied for the synthesis of the muscle relaxant dantrolene from HMF [227].

Terminal alkynes are important precursors of substituted polyacetylenes, which exhibit unique optical, mechanical, magnetic, and electrical properties [228]. The conventional alkynylation of aldehydes requires harsh basic conditions, making the process unsuitable for HMF. Ananikov established that an alternative to, e.g., the Corey–Fuchs or the Seyferth–Gilbert reactions, is the Sonogashira coupling of 2-hydroxymethyl-5-ethynylfuran (HMEF) with iodobenzene in the presence of PdCl₂(PPh₃) (2 mol%) at 60 °C overnight. The corresponding alkyne was produced at a 92% yield [229]. The polymerization of terminal alkynes is feasible in the presence of Rh-based catalytic systems. Thus, ethynyl derivatives derived from HMF were subjected to the polymerization reaction catalyzed by Rh(nbd)Cl₂ (nbd=norbornadiene) (0.75 mol%) in triethylamine at 25 °C.

7. Conclusions

Biomass is the most accessible and low-cost economical solution for the production of sustainable transportation fuels as well as the only non-petroleum route to organic molecules for the manufacture of bulk and fine chemicals. However, designing a sustainable and cost-effective biorefinery remains a great challenge. The upgrading of biomass feedstock involves chemical transformations, such as hydrolysis, dehydration, isomerization, oxidation, hydrogenation, deoxygenation, and hydrodeoxygenation.

Effective catalysts are critical for developing efficient and clean chemical processes in industry. Thus, the design of catalysts for such transformations require new classes of homogeneous catalyst that are compatible with the highly oxygenated nature of biomass. In addition, low-temperatures (<200 °C), the aqueous-phase processing of sugars, the development of effective homogeneous catalysts with earth-abundant metals, and reductions in the use of harmful reagents are desired.

The use of furanic molecules (HMF, FAL, BHMF, DFF, and FDCA) as starting materials for synthetic applications is highly attractive for the scientific community and for industrial applications. Over the past years, significant advances have been reported for the production of biofuels with new catalysts. The highlighted examples in this review demonstrated the range of potential chemical transformations that can occur for biomass-derived platform molecules employing homogeneous catalysis. With the widespread application of these synthetic methodologies, further progress is expected in this field.

Author Contributions: Conceptualization, R.P.; writing—original draft preparation, R.P. and S.K.; writing—review and editing, R.P., S.K. and M.N.; visualization, R.P., S.K. and M.N.; project administration, M.N.; funding acquisition, M.N. All authors have read and agreed to the published version of the manuscript.

Funding: The authors thank VILLUM FONDEN (19049) and Novo Nordisk Foundation (NNF20OC0064560) for funding this research.

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

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