

Review

Energy Densification of Biomass-Derived Furfurals to Furanic Biofuels by Catalytic Hydrogenation and Hydrodeoxygenation Reactions

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Abstract: The concomitant hydrolysis and dehydration of biomass-derived cellulose and hemicellulose to furfural (FUR) and 5-(hydroxymethyl)furfural (HMF) under acid catalysis allows a dramatic reduction in the oxygen content of the parent sugar molecules with a 100% carbon economy. However, most applications of FUR or HMF necessitate synthetic modifications. Catalytic hydrogenation and hydrogenolysis have been recognized as efficient strategies for the selective deoxygenation and energy densification of biomass-derived furfurals generating water as the sole byproduct. Efficient and eco-friendly catalysts have been developed for the selective hydrogenation of furfurals affording renewable furanic compounds such as 2-methylfuran, 2,5-dimethylfuran and 2-methyltetrahydrofuran with potential applications as biofuel, solvent and chemical feedstock. Hydrogen gas or hydrogen donor molecules, required for the above processes, can also be renewably obtained from biomass using catalytic processes, enabling a circular economy. In this review, the recent developments in the energy densification of furfurals to furanic compounds of commercial significance are elaborated, emphasizing the role of catalyst and the reaction parameters employed. Critical discussion on sourcing hydrogen gas required for the processes, using hydrogen donor solvents, catalyst design and the potential markets of furanic intermediates have been made. Critical evaluations of the accomplishments and challenges in this field are also provided.

Keywords: catalysis; deoxygenation; furanic biofuels; hydrogenation; lignocellulose; renewable chemistry



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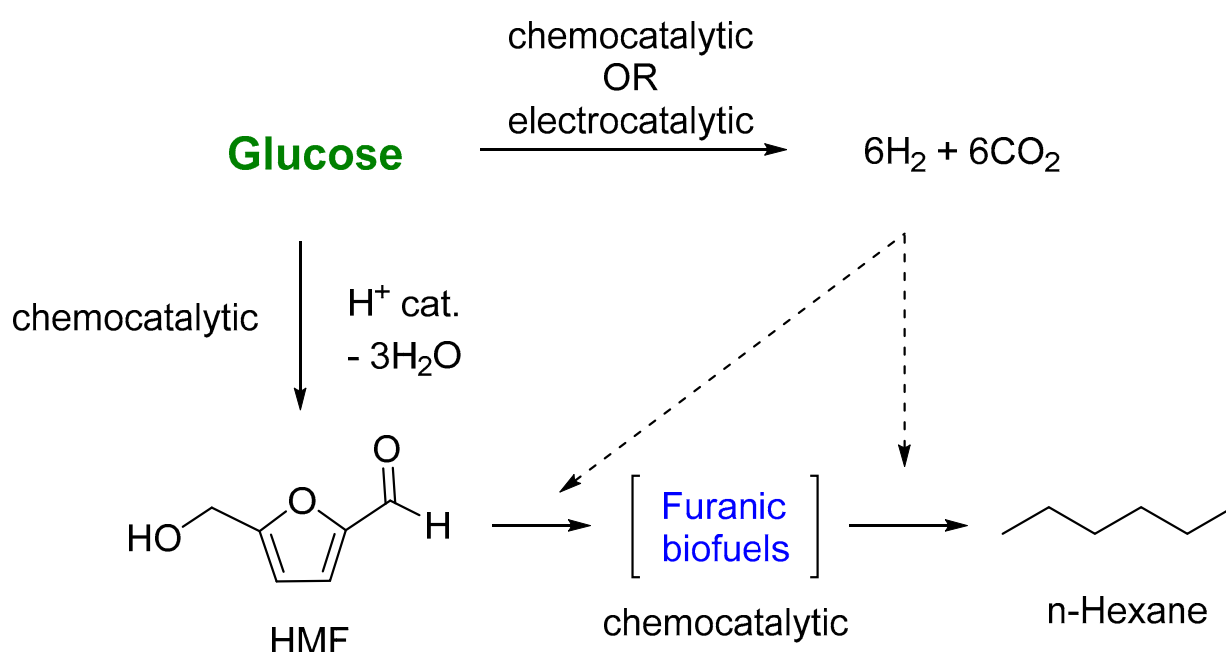


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1. Introduction

Adopting biomass-derived fuels and chemicals would help relieve the economic and environmental distresses triggered by the excessive use of petrofuels and petrochemicals [1]. Furthermore, the suitable integration of renewable, carbon-neutral biomass in the chemical industry would be an indispensable step toward their long-anticipated sustainability [2,3]. However, selecting the biomass feedstock is critical to not compete with the animal and human food supply chain [4]. In this regard, cellulosic biomass has been considered as a suitable feedstock to produce fuels and chemicals [5]. Only a fraction of around 180 billion tons of lignocellulosic biomass produced annually in the world is utilized [6]. The major challenge in the value addition of biomass is to selectively depolymerize, defunctionalize and deoxygenate the biopolymers into simple molecules with desired structural features and physicochemical properties [7,8]. In this regard, the catalytic value addition of biomass is advantageous since the processes are fast, selective, biomass independent and the chemical industries are well-versed with the catalytic processes [9,10]. The acid-catalyzed hydrolysis of cellulose and lignocellulose fractions into sugars followed by dehydration of the latter into furanics such as furfural (FUR) and 5-(hydroxymethyl)furfural (HMF) are well-documented in the literature [11]. The sequential elimination of three molecules of water from a molecule of glucose forms HMF under acid catalysis [12]. The elegant

process decreases the oxygen content of glucose by 50 mol% without cleaving C-C bonds or producing toxic byproducts. Similarly, the acid-catalyzed dehydration of xylose, a major constituent sugar in the pentosans, produces FUR [13]. Both FUR and HMF can access various synthetic value addition pathways with several established and emerging commercial markets for their derivatives [11]. The removal of all the oxygen atoms from a mole of glucose by combining catalytic hydrogenation and hydrogenolysis reactions requires seven moles of hydrogen and leads to n-hexane (Scheme 1) [14]. The process can be contemplated as a renewable production of naphtha-range hydrocarbons. On the other hand, the combination of acid-catalyzed dehydration and catalytic hydrogenation of glucose can lead to more valuable furanic chemicals via the FUR and HMF intermediates [15,16]. The value addition of cellulosic biomasses via the furanic platform allows to preserve some of the crucial functionalities in the sugar moiety and exploit them for synthetic upgrading.



Scheme 1. Hydrodeoxygenation of glucose to n-hexane using renewably-produced molecular hydrogen.

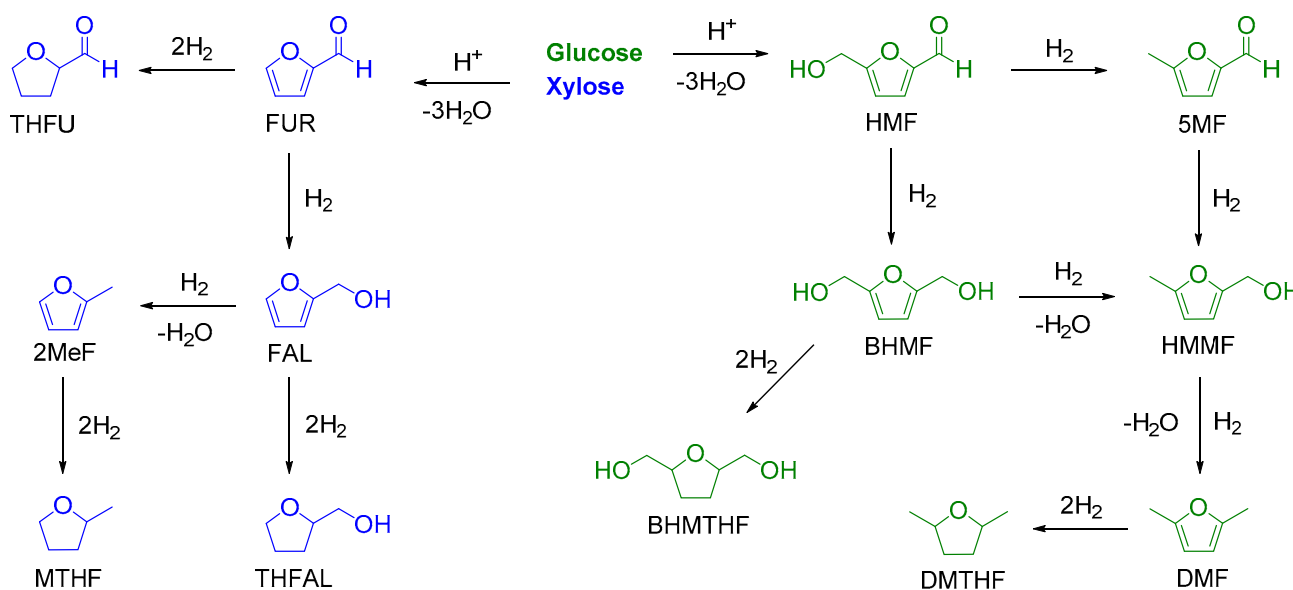
The preparations of both FUR and HMF (Scheme 2) were reported more than a century ago, but the molecules received renewed attention only in the 1990s [17]. A wide range of products of commercial significance, including fuels and fuel additives, solvents, surfactants, plasticizers, polymers, agrochemicals and pharmaceuticals, have been produced using HMF and FUR as renewable molecular scaffolds [18–20]. Both FUR and HMF were shortlisted as sugar-derived chemicals of huge commercial potentials by the United States Department of Energy (US-DOE) in 2004. The biomass to HMF transformation is typically carried out in the aqueous or a polar medium (e.g., ionic liquid) in the presence of an acid catalyst of some sort. Even though mineral acid catalysts have been studied extensively, the current focus is on developing inexpensive, selective, recyclable and eco-friendly heterogeneous acid catalysts to prepare HMF directly from lignocellulosic biomass. In general, satisfactory yields of HMF are obtained from simple sugars such as fructose under relatively mild conditions. However, the high-yielding preparation of HMF from untreated cellulosic biomass often requires special reaction conditions that undermine the economic feasibility and environmental acceptability of the process. In addition, the hydrophilicity and instability of HMF in aqueous acid make its isolation and purification from the reaction media laborious. Hence, even after decades of research, the commercial-scale preparation of HMF from real biomass feedstock remains elusive. The hydrophobic analogs of HMF

have better hydrolytic stability and somewhat solved the isolation issue from the aqueous medium. The production of FUR from biomass, however, has been commercialized, and many of its derivatives have established markets. In contrast with HMF, FUR has better stability (thermal, storage) and higher solubility in organic solvents, making it simpler to isolate from an aqueous reaction medium. Two different classes of products are targeted from biomass feedstock. The first category of biomass-derived products is the renewable, drop-in equivalent of petroleum-derived products. These products enjoy the advantage of having an established market and supply chain with no additional regulatory hurdle. The second category of products is renewable chemical equivalents of the existing ones. These products are presumably better than the products currently in use with superior performance, designed biodegradability and lesser environmental footprint. However, these novel products often encounter strict regulatory guidelines and struggle to set a foothold into new markets. The diesel- and gasoline-range hydrocarbon fuels from biomass qualify for the first kind, whereas the oxygenated furanics and levulinates fall in second category. Catalytic hydrogenation and hydrodeoxygenation (HDO) processes are routinely used for making various deoxygenated derivatives from HMF and its hydrophobic analogs. In both types of reactions, the hydrogen atoms are added to the molecule to decrease the degree of unsaturation or cleave C–O bonds. The atom economy of hydrogenation and HDO processes is high, and only water is formed as an innocuous byproduct. A major target in the process is to develop inexpensive but efficient catalysts in terms of their stability, selectivity and recyclability. Product selectivity is a decisive factor since the narrow differences in the activation energies of the hydrogenation and HDO steps can lead to an intricate mixture of partially hydrogenated products. Even though the individual products are of high value in their pure form, their intractable mixture is of limited use. Selective hydrogenolysis of the hydroxymethyl arm of HMF forms 5-methylfurfural (5MF), which has potential applications as a fuel oxygenate and a chemical intermediate. Further reduction of 5MF 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 [21]. Hydrogenation of the furan ring in DMF produces 2,5-dimethyltetrahydrofuran (DMTHF), which is a promising fuel oxygenate and a renewable substitute for tetrahydrofuran. Selective hydrogenation of the aldehyde group of HMF forms 2,5-bis(hydroxymethyl)furan (BHMF). Hydrogenation of the furan ring in BHMF forms 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF). On the other hand, catalytic hydrogenation of the aldehyde group in FUR leads to furfuryl alcohol (FAL). Ring hydrogenation of FAL leads to tetrahydrofurfuryl alcohol (THFAL). Hydrogenolysis of the hydroxymethyl group in FAL forms 2-methylfuran (2MeF). Ring hydrogenation of 2MeF forms 2-methyltetrahydrofuran (MTHF). The ring hydrogenation of FUR without reducing the aldehyde group forms tetrahydrofuraldehyde (THFU).

The source of molecular hydrogen for the catalytic reduction of furfurals is of utmost importance. At present, hydrogen is commercially produced by the steam reforming of natural gas [22]. Petroleum and coal are the other two major sources of hydrogen production [23]. In recent years, hydrogen production via the electrolysis of water is gaining more interest and is expected to increase its market share at an accelerated pace [24].

Hydrogen gas produced by polluting technologies is termed ‘grey hydrogen’ and does not have appreciable environmental benefits in their applications [25]. Hydrogen produced from renewable resources such as the electrolysis of water by producing electricity from a combination of renewable energy sources (e.g., solar, hydro) is termed ‘green hydrogen’ and is preferred for its environmental incentives [26]. Other color codes of hydrogen gas include ‘yellow hydrogen’ where solar energy is used alone for electricity generation, and ‘pink hydrogen’ using nuclear energy. There is also ‘blue hydrogen’, where it is produced by the steam reforming of natural gas, but the CO₂ is captured, stored permanently and not allowed to release into the environment. Biomass can be converted into hydrogen by using thermal routes, such as gasification and steam-reforming

of biomass feedstock, and enzymatic routes such as fermentative hydrogen production and biocatalyzed electrolysis [27–29]. The chemocatalytic conversion of biomass to hydrogen is an emerging field [30]. Sourcing molecular hydrogen and furfurals for downstream energy densification could prove a self-reliant and sustainable chemical technology and circular economy. Converting sugars such as glucose into molecular hydrogen by electrocatalysis has received significant interests in recent years. Biomass-derived hydrogen can be made cleaner than ‘grey hydrogen’ depending on the feedstock chosen, technology adopted and utilization of the byproduct, i.e., CO₂. Finally, it may be said that until the production of hydrogen by electrolysis of water using renewable energy sources reaches technical maturity, a combination of the above technologies is the near future to satisfy the increasing demand of hydrogen.



Scheme 2. Catalytic hydrogenation of biomass-derived FUR and HMF into furanic intermediates.

Catalytic transfer hydrogenation (CTH) is increasingly being used for biomass value addition pathways [31]. The CTH processes use a liquid hydrogen donor molecule (alone or diluted in an inert solvent) in the presence of a suitable metal-based catalyst. 2-Propanol, 2-butanol, ethanol and methanol are commonly used alcoholic hydrogen donor molecule that produces molecular hydrogen in the presence of a metal catalyst (e.g., Pd, Ru) and become oxidized into their corresponding aldehydes or ketones. Formic acid, formate salts and cyclohexene are frequently used hydrogen donor molecules. The CTH processes have the advantage of not using overpressure of gaseous hydrogen, thereby working under milder reaction conditions and simplified reactor design. The process uses renewable ‘green hydrogen’ to work. However, the aldehydes or ketones produced must be separated from the product and recycled. In addition, the reaction often requires elevated temperatures for faster dehydrogenation reaction of the hydrogen donor and also basic additives. Often a combination of a hydrogen donor molecule and H₂ gas is used in combination to avoid forming the oxidized product of the former. Even though CTH process is relatively new in biomass value addition, it has produced some remarkable results in producing furanic biofuels (discussed in the later sections). However, the obligation of using a large excess of the hydrogen donor molecules and their energy-intensive separation from the product must be resolved. Further studies on developing robust, inexpensive, efficient and recycle catalysts that allow both the dehydrogenation and hydrogenation reaction to take place on their surface are required.

The recent developments in the energy densification and upgrading of biomass-derived furfurals to furanic biofuels by catalytic hydrogenation and hydrodeoxygenation

processes are discussed in this review. The selective preparation and application of various value-added furanic compounds are elaborated, emphasizing the catalyst design, the reaction parameters employed and the process economy. The review attempts to summarize the research accomplishments to date, recognize the challenges and proposes research directions to decipher them.

2. Catalytic Reduction of Furfurals to Furanic Compounds

Selective hydrogenation and HDO of biomass-derived furfurals produce several furanic compounds of significant commercial interest. In the following section, the targeted syntheses of such furanic compounds are elaborated.

2.1. Catalytic Reduction of FUR to Furanic Biofuels

2.1.1. FUR to FAL and Biofuels Thereof

Selective reduction of the aldehyde group in FUR leads to FAL. The acid-catalyzed polycondensation of FAL forms cross-linked furanic resins [32]. These thermoset polymers are used in the polymer matrix, concrete, coatings, adhesives and various composite materials [33–36]. A host of compounds, such as THFAL, furfuryl ethers, LA and levulinic esters, are prepared from FAL [37–40]. 5-(Dimethylaminomethyl)-2-furfuryl alcohol, a key intermediate for synthesizing the anti-ulcer drug Ranitidine is also sourced from FAL [41]. Both liquid and vapor-phase hydrogenation of FUR in a batch and continuous setting have been studied. The commercial process uses a copper chromite catalyst in the vapor-phase reduction of FUR to FAL [42]. The process economy is dependent on the production of FUR from biomass, and inexpensive waste biomass feedstock is preferred for the process. The catalysts employed for the transformation include noble metal-based as well as transition metal-based catalysts. Current research in this area is focusing on the one-pot preparation of FAL from biomass, crude FUR as feedstock, and developing eco-friendly catalysts for this transformation [43]. There are dedicated reviews available on FAL; therefore, the readers are referred to those for comprehensive information [44,45].

2.1.2. FUR to 2MeF

Reduction of the aldehyde group in FUR to a methyl group leads to 2MeF, a potential biofuel and chemical intermediate for further value addition. Ahmed et al. patented the vapor-phase hydrogenation of FUR to yield 2MeF and MTHF using commercially available catalysts [46]. Zhu et al. reported a coproduction of 2MeF and γ -butyrolactone (GBL) involving the hydrogenation of FUR and dehydrogenation of 1,4-butanediol in the presence of a Cu-Zn bimetallic catalyst. Hydrogen molecules released during the dehydrogenation reaction served as the hydrogen source for 2MeF without requiring an external hydrogen source [47]. Zheng et al. also reported the coproduction of 2MeF and GBL using a copper chromite catalyst [48]. Yang et al. studied the effect of calcination temperatures on the catalytic performance of the Cu-Zn-Al catalyst toward the synthesis of 2MeF and GBL starting from FUR and 1,4-butanediol, respectively [49]. The CTH of FUR to 2MeF was investigated using a Ru/C catalyst in 2-propanol. 2-Propanol served as a solvent as well as a hydrogen donor solvent (Entry 28, Table 1) [50]. The same group also studied the effect of different alcohols on the yield of 2MeF using Ru/RuO₂/C catalyst. A decline in yield was observed with increasing alcohol polarity due to etherification of FAL. Mechanistic study revealed that the Lewis acid-mediated hydride transfer was responsible for the hydrogenation of carbonyl group in FUR [51]. Niu et al. carried out a liquid-phase CTH of furfural over a series of Cu-Zn-Al catalysts with varying Cu/Zn molar ratios. With the Cu/Zn molar ratio fixed at 2.5, 2MeF was isolated in a 72% yield. The catalytic activity remained nearly unchanged for six consecutive cycles [52]. Scholz et al. synthesized Cu, Ni and Pd catalysts supported on Fe₂O₃ via the coprecipitation method and applied them for the hydrogenolysis of FUR to 2MeF using 2-propanol as the hydrogen donor solvent. Among the three catalysts, Pd/Fe₂O₃ exhibited remarkable activity toward hydrogenolysis,

which was attributed to the morphology of Pd particles and their strong interaction with the supporting material [53].

Dong et al. studied the influence of preparatory methods of the Cu/SiO₂ catalyst to convert FUR into 2MeF. The Cu/SiO₂ catalyst synthesized via the ammonia evaporation method afforded 2MeF in a 95% yield, noticeably higher than the catalyst prepared by the conventional method. The cooperative effect between surface Cu⁰, Cu⁺ species and acid sites helped to improve the selectivity of 2MeF [54]. Using the Cu/SiO₂ catalyst prepared by hydrothermal method and methanol as a hydrogen donor solvent, 2MeF was obtained in a 90% yield starting from FUR [55]. Xylose was converted to FAL and then to 2MeF in a continuous fixed bed reactor using a combination of H β zeolite and CuO/ZnO/Al₂O₃ catalyst. GBL/water system served as the biphasic solvent system, and the yield of 2MeF increased up to 86.8% due to the combined effect between H β zeolite and GBL [56]. Yang et al. synthesized two mineral-derived Cu/ZnO catalysts consisting of aurichalcite and zincian malachite for the hydrogenation of FUR to FAL and 2MeF. The catalyst composed of aurichalcite showed excellent selectivity (ca. 94.5%) toward 2MeF due to high surface area and high dispersion of Cu species on the catalyst surface [57]. Up to 95% selectivity toward 2MeF was obtained using a 5% Ir/C catalyst under optimized reaction conditions. The catalyst was recovered up to four consecutive cycles without any significant loss of activity [58]. Jaatinen et al. studied the liquid-phase hydrogenation of FUR to 2MeF using monometallic and bimetallic catalysts consisting of Cu, Fe and Ni. With varying metal loading of the prepared catalysts, 10% Ni/C was found to provide the maximum yield of 2MeF [59]. Spinel ferrite supported Ru catalyst prepared via sol-gel method attained 97% conversion of FUR under mild reaction conditions. The catalyst was easily recoverable, and the activity remained unaltered even after five consecutive cycles [60]. A series of Cu-based catalysts were synthesized by complexing copper (II) ions with dodecylamine for the vapor-phase hydrogenation of FUR. Among the synthesized catalysts, 10% Cu catalysts showed better selectivity toward 2MeF at a hydrogen flow rate of 10 mL/min. The use of mesoporous silica as the support provided weak acidic sites for the hydrogenolysis of C–O bond in FAL [61]. Interestingly, a self-supported nanoporous Cu–Al–Co ternary alloy catalyst developed by Hutchings et al. exhibited better catalytic activity and stability toward the HDO of FUR [62]. A Cu catalyst supported on activated carbon efficiently converted FUR to 2MeF via the FAL intermediate. The catalyst calcinated at 400 °C for 2 h afforded a quantitative yield of 2MeF [63]. Wang et al. studied the effect of acidity on the catalytic performance of Ni₂P in liquid-phase HDO of FUR to 2MeF. The synergistic effect between Brønsted and Lewis acidic sites present in the catalyst increased the catalytic efficiency resulting in the quantitative conversion of FUR [64]. A Cu–Cu₂O/N-RGO catalyst, prepared via microwave-assisted reduction and ammonia evaporation, also possessed high catalytic activity [65]. A bifunctional, mesoporous Cu–Al₂O₃ catalyst exhibited enhanced reactivity toward HDO of FUR due to its high dispersion and small particle size. The Lewis acid sites present on the oxide support are highly electrophilic and interact with the formyl group in FUR [66]. In the two catalysts mentioned above, the catalytic activity is attributed to the synergistic effects of surface Cu⁰ and Cu⁺ species in the catalyst. Vapor-phase HDO of FUR using molybdenum carbide catalyst at low temperature and pressure exhibited selectivity toward 2MeF and furan [67]. The density functional theory (DFT) calculations, surface science experiments and flow-reactor evaluation revealed that molybdenum carbide is a promising catalyst for the HDO of FUR [68]. Methanol acted as the hydrogen donor for the CTH of FUR to 2MeF in the presence of a FeVO₄ catalyst. DMF and 2-vinylfuran were identified as the byproducts during the reaction [69]. The Pt and Ru-based noble-metal catalysts afforded quantitative conversion of FUR even at relatively low metal loading (ca. 3 wt.%). The superior activity of the catalysts was attributed to high metal dispersions on the supporting material. In comparison, the Ni-based catalysts had lesser activity toward the hydrogenation reaction. The particle size of Pt was estimated in the range of 5–10 nm, whereas the particle size was below 5 nm in Ru catalysts [70]. Dong et al. studied the effect of catalyst supports (SiO₂, Al₂O₃ and ZnO) on the synthesis of 2MeF using chromium-

free Cu catalysts. The Cu/SiO₂ catalyst exhibited the best activity, which accredits to the adsorption and desorption behavior of the catalyst and the presence of weak acidic sites on its surface. Cu/Al₂O₃ and Cu/ZnO catalysts exhibited low selectivity toward 2MeF but high selectivity for FAL, respectively [71]. Dehydration of xylose into FUR was carried out in a plug-flow reactor under mild reaction conditions in a biphasic solvent system, then hydrogenated to 2MeF using a Cu/Fe catalyst. A noticeable decrease in catalytic activity was observed after 20 h of reaction time [72]. Electrochemical hydrogenation of FUR to 2MeF resulted in 60% faradaic efficiency using phosphorus-doped carbon-supported single atom Cu catalyst. The catalyst was synthesized by pyrolyzing chitosan and coordinating it with Cu²⁺ ions [73].

Table 1. Synthesis of 2MeF from FUR.

| S/N | Reaction Conditions | Catalyst | Yield (%) | Ref. |
|-----|---|--|-----------|------|
| 1 | 170 °C, 4 h, 3 MPa H ₂ , 2-propanol | 17.16 wt.% Cu/AC-400/2 | 100 | [63] |
| 2 | 252 °C, 3 min (residence time), water-toluene | 50Cu/50Fe-SiO ₂ | 98 | [72] |
| 3 | 210 °C, 4.7 s (residence time), BDO | 1.3Cu-Zn | 96.5 | [47] |
| 4 | 240 °C, 4 h, 1.5 MPa H ₂ , 1,4-dioxane | 15 wt.% Cu-Cu ₂ O/N-RGO | 95.5 | [65] |
| 5 | 210 °C, 5 h, H ₂ flow rate 10 mL/min, CPME | 10Cu-MS | 95 | [61] |
| 6 | 200 °C, 9.5 h, 0.1 MPa H ₂ | 39.3 wt.% AC-CZ | 94.5 | [57] |
| 7 | 220 °C, 5 h, 0.69 MPa H ₂ , 2-propanol | 5% Ir/C | 94 | [58] |
| 8 | 220 °C, 4 h, 2-propanol | 5Cu-3Re/Al ₂ O ₃ | 94 | [81] |
| 9 | 225 °C, LHSV 0.7 h ^{−1} , BDO | Cu-Zn-Al | ~93 | [49] |
| 10 | 210 °C, 4 h, formic acid, 2-propanol | 10%Ni-10%Cu/Al ₂ O ₃ | 92 | [75] |
| 11 | 260 °C, 3 h, 1.5 MPa H ₂ , 2-propanol | 17.2 wt.% Ni ₂ P | 91.2 | [64] |
| 12 | 200 °C, LHSV 0.2 h ^{−1} , 0.1 MPa H ₂ , BDO | Cu ₂ Cr ₂ O ₅ | 91.1 | [48] |
| 13 | 200 °C, 8 h, formic acid, 2-propanol | 10 wt.% Ni-Cu/C | 91 | [79] |
| 14 | 220 °C, 2 h, methanol | 10 wt.% Cu/SiO ₂ -HT | 90 | [55] |
| 15 | 220 °C, WHSV 0.5 h ^{−1} , 0.1 MPa H ₂ | Cu/SiO ₂ | 89.5 | [71] |
| 16 | 190 °C, WHSV 0.02 h ^{−1} , 0.1 MPa H ₂ , GBL/water | Hβ/CuO/ZnO/Al ₂ O ₃ | 86.8 | [56] |
| 17 | 200 °C, 0.1 MPa H ₂ , WHSV 2.0 h ^{−1} | 24 wt.% AE-Cu/SiO ₂ | 84.5 | [54] |
| 18 | 180 °C, 4 h, 2.1 MPa N ₂ , 2-propanol | 8 wt.% Ru/NiFe ₂ O ₄ | 83 | [60] |
| 19 | 320 °C, 1 h, 0.1 MPa N ₂ , methanol | FeVO ₄ | 80 | [69] |
| 20 | 220 °C, 4 h, 3 MPa H ₂ , DMTHF | 23Cu-12Co/γ-Al ₂ O ₃ | 80 | [78] |
| 21 | 220 °C, 4 h, 4 MPa H ₂ , 2-propanol | 10 wt.% Cu-Co/γ-Al ₂ O ₃ | 78 | [74] |
| 22 | 180 °C, 10 h, 2.04 MPa N ₂ , 2-butanol/2-pentanol | 41 wt.% Ru/RuO ₂ /C | 76 | [51] |
| 23 | 250 °C, WHSV 0.4 h ^{−1} , H ₂ flow rate 80 mL/min, CPME | 21.3 wt.% Cu/Al ₂ O ₃ | ~75.9 | [66] |
| 24 | 180 °C, 4 h, 0.1 MPa N ₂ , 2-propanol | 25 wt.% Cu _{2.5} Zn-Al-600 | 72 | [52] |
| 25 | 240 °C, 7 h, H ₂ flow rate 60 mL/min | Cu ₉₅ -Al-Co ₅ | 64.8 | [62] |
| 26 | 230 °C, 4 h, 2-propanol | 25 wt.% CuNi ₂ Al | 64.8 | [80] |
| 27 | 220 °C, 4 h, 2-propanol | 10Cu-3Pd/ZrO ₂ | 61.9 | [77] |
| 28 | 180 °C, 10 h, 2.04 MPa N ₂ , 2-propanol | 5% Ru/C | 61 | [50] |
| 29 | 180 °C, 7.5 h, 2.5 MPa N ₂ , 2-propanol | 2% Pd/Fe ₂ O ₃ | 60 | [53] |
| 30 | 180 °C, 8 h, 0.5 MPa H ₂ , 2-propanol | 22 wt.% Pt-Co/C | 59 | [76] |
| 31 | 240 °C, 2 h, 4 MPa H ₂ , 2-propanol | 3Pt/AC-S | 50 | [70] |
| 32 | 230 °C, 2 h, 4 MPa H ₂ , 2-propanol | 10 wt.% Ni/C | 48.9 | [59] |

Abbreviations: BDO, 1,4-Butanediol; HT, Hydrotalcite; AC-CZ, Aurichalcite Cu/ZnO catalyst; CPME, Cyclopentyl methyl ether; MS, Mesoporous silica; AE, Ammonia evaporation method; AC-400/2, Activated carbon calcinated at 400 °C for 2 h; RGO, Reduced graphene oxide; AC-S, Spruce-based activated carbon; GBL, γ-Butyrolactone; DMTHF, 2,5-Dimethyltetrahydrofuran; WHSV, Weight hourly space velocity; LHSV, Liquid hourly space velocity.

Several bimetallic catalysts were used for the hydrogenation of FUR, which furnished 2MeF in good yields. Different supporting materials were synthesized for the Cu-Co bimetallic catalysts (e.g., Cu-Co/SiO₂, Cu-Co/γ-Al₂O₃ and Cu-Co/H-ZSM-5) with varying Cu/Co molar ratios for the liquid-phase hydrogenation of FUR to 2MeF. The catalyst supported on acidic carriers (H-ZSM-5 and γ-Al₂O₃) were found to be successful toward the hydrogenation reaction due to the formation of spinel CuCo₂O₄ oxides. Out of the three catalysts, the Cu-Co/γ-Al₂O₃ (Cu/Co = 1) catalyst exhibited the best catalytic performance due to the presence of additional Cu-CoO_x species [74]. Formic acid was used as

the hydrogen donor to synthesize 2MeF in a 92% yield over the 10% Ni-Cu/ Al_2O_3 catalyst. At high Ni loadings, a gradual decrease in the acidity of catalyst was observed due to less availability of support surface [75]. Dohade et al. reported a 59% yield of 2MeF using a Pt-Co/C catalyst under mild reaction conditions. The catalyst was recycled and reused for four consecutive cycles without any significant loss of activity [76]. A combined yield of 83.9% (2MeF and MTHF) was achieved using the Cu-Pd/ ZrO_2 catalyst [77]. Gandarias et al. reported an innovative approach for the production of 2MeF from corncob, which involved the production of FUR and its selective conversion to 2MeF over the Cu-Co/ $\gamma\text{-Al}_2\text{O}_3$ [78]. Carbon-supported Ni-Cu catalyst formed 2MeF in a 91% yield at a reaction temperature of 200 °C. Formic acid as a hydrogen source increased the conversion of FUR to 2MeF in 2-propanol [79]. Similarly, alumina-supported Cu-Ni catalyst synthesized by coprecipitation method effectively catalyzed the conversion of FUR to 2MeF and MTHF. A combined yield of 85% for 2MeF and MTHF was obtained under the optimized reaction conditions in the presence of 2-propanol [80]. The Cu-Re/ Al_2O_3 catalyst attained complete conversion of FUR at 220 °C and 4 h in 2-propanol. The high stability of the catalyst is attributed to the synergism between the support and metal nanoparticles (NPs). The Cu and Ru species enhanced the hydrogenation and hydrogenolysis of FUR and FAL, respectively [81].

In general, noble metal catalysts afforded better yields of 2MeF compared to non-noble metal catalysts. Using 2-propanol as a hydrogen donor solvent improved the conversion of FUR and increased the selectivity toward 2MeF. Around 5–10 wt.% metal loading on the support was efficient for the hydrogenation reaction. However, more research is required to analyze catalyst poisoning, recyclability and leaching.

Ruthenium and copper have been the most frequently employed noble metal and non-noble metal, respectively, for the catalytic transformation of FUR to 2MeF. Ruthenium catalysts generally worked under lower reaction temperatures compared to copper-based catalysts. The alcoholic solvents such as 2-propanol were used as the reaction medium as well as the hydrogen donor. A combination of molecular hydrogen and hydrogen donor solvent was also examined. Regardless of the catalyst employed, a relatively high reaction temperature (ca. 170–220 °C) was required for the hydrogenolysis process. Bimetallic catalysts showed superior catalytic activity than their constituent metal catalysts. The reaction was studied under batch as well as continuous process conditions. The surface area of the catalyst, distribution of metallic sites on the catalyst surface and the acid sites on the supporting material determine the catalyst selectivity.

A major concern about the catalytic hydrogenation processes is the recovery and recyclability of the metal catalyst used. Very low mol% of active metal should be used, especially for catalysts involving the noble metals. Ideally, the catalyst should be reusable for multiple cycles without requiring extensive reactivation steps (e.g., calcination). Common deactivation mechanisms of the catalyst candidates include physical blockage of the active sites by coke formation. In addition, chemisorption of various side products on the catalyst surface also deactivates the catalyst. The metal NPs often agglomerate under the reaction conditions forming larger particles with lower surface area available for catalysis. The metal NPs often leach from the catalytic support and enter into the reaction medium. This process not only leads to catalytic deactivation but also product contamination. Even though transition metals are preferably for their low cost and lower environmental footprint, emphasis must be given on the energy requirement of the process since in many cases, the transition metal-based catalysts require more demanding reaction conditions than the noble metal catalysts.

2.1.3. FUR to THFAL

The targeted preparation of THFAL by the catalytic hydrogenation reaction of FUR is tabulated in Table 2. In 1989, Merat et al. reported the complete conversion of FUR to THFAL over a mixture of commercially-available supported Ni and Cu catalysts [40]. Liu et al. investigated the hydrogenation of FUR to THFAL using monometallic Ni and bimetallic Ni-Cu supported on multi-walled CNTs. A 10 wt.% Ni/CNT and Cu-Ni/CNT

(Cu/Ni = 1:1, molar ratio) provided 84.3% and 90.3% yields of THFAL, respectively [82]. Similarly, the bimetallic Ni-Co catalyst supported on SBA-15 synthesized by incipient-wetness impregnation method afforded quantitative conversion of FUR [83]. The introduction of metal-organic frameworks (MOFs) as support to Pd NPs increased the selectivity of THFAL. The Pd NPs were uniformly dispersed on the support due to the presence of amino groups [84]. The hydrogenation of FUR was catalyzed by Pd nanoclusters supported on various supports (MgO, TiO₂, ZrO₂, Al₂O₃, CeO₂, SiO₂ and HAP) under mild reaction conditions. A noticeable increase in yield was observed when Pd-HAP was employed for the hydrogenation reaction. The quasi-coordination effect between the metal and support is responsible for the high stability of the catalyst and better activation of hydrogen [85]. The direct conversion of FUR to THFAL was achieved with FAL as an intermediate using a combination of Pd/Al₂O₃ and Ru/ZrO₂ catalysts [86]. The reduction of silica-supported nickel nitrate resulted in the formation of Ni/SiO₂ (particle size of <4 nm), which was active toward the gas-phase hydrogenation of FUR [87]. Pd/UiO-66 with an average Pd particle size of 2–3 nm prepared by the impregnation method achieved 100% THFAL selectivity under mild reaction conditions compared with Pd/SiO₂ and Pd/ γ -Al₂O₃ catalysts. The conversion of FUR to THFAL proceeded faster when the intermediate was FAL and not THFU [88].

Table 2. The catalytic preparation of THFAL from FUR.

| S/N | Reaction Conditions | Catalyst | Yield (%) | Ref. |
|-----|---|---|--------------|-------|
| 1 | 40 °C, 3 h, 1 MPa H ₂ , 2-propanol | 1% Pd-HAP | 100 | [85] |
| 2 | 30 °C, 3 h, 0.5 MPa H ₂ , water | 1.1Pd/Al ₂ O ₃ and 1.7Ru/ZrO ₂ | 100 | [86] |
| 3 | 60 °C, 4 h, 1 MPa H ₂ , water | 1.2 wt.% Pd/UiO-66 | 100 | [88] |
| 4 | 120 °C, 2 h, 1 MPa H ₂ , 2-propanol | 100 wt.% Ni/C | 100 | [94] |
| 5 | 30 °C, 14 h, 1 MPa H ₂ , water | Ru_OS- β -CD | 100 | [100] |
| 6 | 40 °C, 4 h, 2 MPa H ₂ , water | 5.4 wt.% Pd@MIL-101(Cr)-NH ₂ | 99.5 | [84] |
| 7 | 110 °C, 3 h, 3 MPa H ₂ , 2-propanol | 17.2 wt.% Ni/MMO-CO ₃ | 99 | [99] |
| 8 | 140 °C, 4 h, 4 MPa H ₂ , water | 40 wt.% Ni/Ba-Al ₂ O ₃ | 98 | [95] |
| 9 | 130 °C, 3 h, 4 MPa H ₂ , methanol | Ni+Cu | 97 | [40] |
| 10 | 150 °C, 6 h, 2 MPa H ₂ , 2-propanol | 70 wt.% PdCo ₃ O ₄ @NC | 95 | [93] |
| 11 | 150 °C, 6 h, 2.5 MPa H ₂ , 2-propanol | 0.5 wt.% PdMPAV ₂ /Al ₂ O ₃ | 95 | [92] |
| 12 | 30 °C, 2 h, 0.3 MPa H ₂ , 2-propanol | 0.97% Pd-Pt/TiO ₂ | 95 | [91] |
| 13 | 210 °C, 6 h, 7 MPa H ₂ , 2-propanol | 10Ni-10Co/MS | 94.6 | [97] |
| 14 | 140 °C, 0.5 h, H ₂ flow rate 30 mL/min | 10 wt.% Ni/SiO ₂ | 94 | [87] |
| 15 | 2 °C, 1 h, 8 MPa H ₂ , water | 2 wt.% Pd-Ir/SiO ₂ | 94 | [101] |
| 16 | 35 °C, 12 h, 2 MPa H ₂ , water | 50 wt.% PtNi/C | 93 | [96] |
| 17 | 30 °C, 12 h, 1 MPa H ₂ , water | 5 wt.% Rh/C | 92 | [89] |
| 18 | 90 °C, 2 h, 5 MPa H ₂ , ethanol | 13.8 wt.% Ni-Co/SBA-15 | 92.1 | [83] |
| 19 | 130 °C, 10 h, 4 MPa H ₂ , ethanol | 10 wt.% Ni/CNT Cu-Ni/CNT | 84.3 90.3 | [82] |
| 20 | 140 °C, 4 h, 4 MPa H ₂ , water | Ni(40)/MgO(30)-M | 81 | [90] |
| 21 | 100 °C, 1 h, 2 MPa H ₂ , water | 40 wt.% Ru-MoO _x /CN | 43 | [98] |

Abbreviations: CNT, Carbon nanotube; MIL-101(Cr)-NH₂, Amine-functionalized MOF; HAP, Hydroxyapatite; UiO-66, Zr-MOF with benzenedicarboxylic acid as linker; M, Montmorillonite MK10 mesoporous clay; PdMPAV₂, Palladium exchanged vanadium incorporated molybdophosphoric acid; MS, Mesoporous silica; CN, N doped carbon; MMO-CO₃, Mixed metal oxide with carbonate as the interlayer anion; OS- β -CD, Oleic succinyl β -cyclodextrin.

One-pot selective hydrogenation of FUR over rhodium-loaded carbon exhibited 93% selectivity toward THFAL in the aqueous media. Changing the solvent to *N,N*-dimethylacetamide increased the yield of THFAL up to 95%. The uniform distribution of Rh NPs (4.8 nm, average size) over the carbon support also played a vital role in improving the yield [89]. Sunyol et al. employed mesoporous clays with different acid properties as support for Ni catalyst. The acidity of the support caused catalyst deactivation, which got neutralized with the addition of magnesium oxide. The group concluded that the hydrogenation of furfural relied more on the acidity rather than the amount of metallic

nickel [90]. Among various supports, palladium supported on titania displayed better catalytic activity with 1.19 wt.% Pd loading. The addition of a small amount of Pt enhanced the performance of Pd and increased the selectivity up to 95% [91]. Koley et al. introduced a heteropoly acid framework for the selective hydrogenation of FUR. The group studied the effect of various reaction parameters and investigated different supports for the liquid phase hydrogenation reaction. Palladium-exchanged vanadium incorporated molybdophosphoric acid supported on alumina achieved quantitative conversion of FUR under mild reaction conditions. The formation of MTHF was observed in small quantities during the dehydration of THFAL [92]. The use of PdCo_3O_4 NPs encapsulated in a graphitic N-doped carbon matrix achieved a 95% yield of THFAL, whereas the PdFe_3O_4 catalyst provided only 70% of THFAL. The enhanced Lewis acidic nature of Co_3O_4 is attributed to the synergistic effect between Co_3O_4 and Pd(II). The catalysts were prepared via depositing Pd NPs over ZIFs metal-organic framework, followed by pyrolysis in the presence of molecular hydrogen [93]. Direct pyrolysis of Ni MOFs resulted in the formation of Ni/C nanocatalyst with a uniform dispersion of Ni in the carbon matrix. A quantitative yield of THFAL was obtained when the catalyst was calcinated at 500 °C [94]. Alkaline-earth metal-modified Ni/ Al_2O_3 improved the selectivity toward THFAL under optimized reaction conditions. The addition of 10 mol% barium to the catalyst increased the yield up to 89% [95].

Bimetallic Pt-Ni alloy was prepared by co-impregnation method and deposited on activated carbon, and then reduced by hydrogen at 400 °C. Small particle size and uniform distribution of Pt-Ni on the support increased the selectivity toward THFAL [96]. Likewise, Ni-Co catalysts with different supports and metal loadings were investigated for the hydrogenation reaction. The mesoporous silica-supported Ni-Co catalyst with 1:1 (Ni:Co molar ratio) loading displayed 90.4% selectivity of THFAL at 200 °C and a hydrogen pressure of 7 MPa. The nickel catalyst was becoming deactivated during the reaction [97]. One-pot pyrolysis of biowaste (chitin) and metal salts resulted in a bimetallic catalyst with nitrogen-doped carbon as support ($\text{Ru-MoO}_x/\text{CN}$). The catalyst was stable for up to five consecutive cycles without any significant loss of activity. The ruthenium NPs facilitated the activation and dissociation of hydrogen, whereas MoO_x species were responsible for adsorption and carbonyl group activation [98]. Nickel catalysts supported on mixed metal oxide were synthesized from LDHs precursors with carbonate or nitrate as the interlayer anions. By tuning the surface microstructure, the nitrate and carbonate anion displayed high selectivity toward FAL (97%) and THFAL (99%), respectively [99]. An improvement in the catalytic activity of ruthenium NPs for FUR hydrogenation was observed using oleic succinyl β -cyclodextrin as the stabilizer [100]. Low conversion of FUR to THFAL was observed in the presence of Pd/ SiO_2 . Pd-Ir/ SiO_2 (ca. ≤ 4 nm) exhibited complete conversion of FUR with 94% selectivity toward THFAL, accrediting to high TOF of Pd-Ir than monometallic Pd [101].

Hydrogen pressure of 1–3 MPa was adequate for the reaction. Carbon-based supports were efficient and cost-effective. Due to the deactivation of the catalyst, harsh reaction conditions are employed for Ni-based catalysts. It is difficult to generalize the effect of solvent polarity due to changes in catalyst loadings and reaction conditions. Designing supporting materials for heterogeneous catalysts with suitable porous structures and acid-base properties also remains a challenge.

Palladium and nickel metal-based catalysts favored the hydrogenation of the furan ring. The process typically required a high overpressure of H_2 gas. Water or alcoholic solvents were routinely employed as the reaction medium.

2.1.4. FUR to THFU

Hydroformylation of dihydrofurans using rhodium-containing catalysts such as $\text{HRh}(\text{CO})(\text{PPh}_3)_3$, $\text{RhCl}(\text{CO})(\text{PPh}_3)_2$ and $\text{Rh}(\text{acac})\text{CO}_2$ primarily lead to the formation of THFU [102–104]. In 2020, Yang et al. reported the synthesis of THFU from FUR using layered double hydroxide as support for palladium. The use of water as a solvent prevented

the hydrogenation of the carbonyl group by inhibiting the adsorption of the carbonyl group on the metal surface. The synergism between water and the support (LDH-MgAl-NO₃) improved the selectivity of the product [105]. Polar solvents favored the hydrogenation of the furan ring rather than the carbonyl group of FUR [106].

2.1.5. FUR to MTHF

The one-step conversion of FUR to MTHF was reported over a dual solid catalyst consisting of Cu₂Si₂O₅(OH)₂ and Pd/SiO₂ in a fixed-bed reactor. The Cu-based catalysts are well known for their hydrogenation-deoxygenation of CH=O bonds, whereas Pd-based catalysts for the hydrogenation of C=C bonds. Firstly, Cu₂Si₂O₅(OH)₂ catalyst packed in the upper part of the reactor converted FUR to 2MeF, then converted to MTHF using Pd/SiO₂ catalyst at the bottom part of the reactor. The selectivity of MTHF increased with the number of active hydrogen atoms on the surface of the catalyst [107]. Similarly, a two-stage conversion of FUR to MTHF was performed using Co/SiO₂ and Ni/SiO₂ catalysts, with 2MeF as the intermediate. Deposition of carbonaceous substances on the active sites during hydrogenation of FUR eventually decreased the catalytic activity. The authors concluded that the direct conversion of FUR to MTHF via THFAL is disfavored [108]. The selective transformation of FUR to MTHF was achieved by combining several non-noble metals with Ir/C catalyst. Ir-Ni/C catalyst provided a good yield (ca. 73.3%) of MTHF due to uniform dispersion of the nanosized (2–5 nm) metal particles over the support. Different preparatory methods adopted for catalyst making changed the surface concentration of the metal, which affected the selectivity of the product. Low temperature and low metal loading favored the selectivity of FAL and 2MeF [109].

2.2. Catalytic Reduction of HMF to Furanics

2.2.1. HMF to BHMF

BHMF, prepared by the selective hydrogenation of the aldehyde group in HMF, has received significant attention as a diol-based renewable monomer for polymeric applications. Furthermore, BHMF is a chemical intermediate for further value addition and often forms as a side product during the preparation of other hydrogenated furanic derivatives starting from HMF. However, in this section, the targeted production of BHMF is reported. Both molecular hydrogen and hydrogen donor molecules have been employed as reducing agents in the presence of suitable catalysts. Thananattathanachon et al. hydrogenated HMF to BHMF using a homogeneous iridium-based catalyst with a diamine-based ligand. The reaction was performed under transfer hydrogenation conditions using a base additive (e.g., Et₃N) and formic acid as the hydrogen donor molecule. The reaction was performed in THF solvent at a slightly elevated temperature (ca. 40 °C). Using only 0.5 mol% of the Cp*Ir(TsDPEN) catalyst and Et₃N as a base additive, a nearly quantitative yield of BHMF was obtained directly from fructose without prior isolation of the HMF (Entry 4, Table 3) [110]. In 2012, Balakrishnan et al. reported the selective hydrogenation of HMF to BHMF using only 0.25 mol% of a Pt/Al₂O₃ catalyst in ethanol. BHMF was obtained in good yield (ca. 85%) under mild reaction conditions (23 °C, 18 h, 1.4 MPa H₂). The reaction time was drastically reduced to 5 h without compromising the yield of BHMF by using a Pt₁Sn₁/Al₂O₃ bimetallic catalyst at a slightly elevated (ca. 60 °C) reaction temperature [111]. Ohyama et al. reported an excellent yield (>96%) of BHMF by the catalytic hydrogenation of HMF using sub-nano Au clusters supported on γ-Al₂O₃ as the catalyst. The reaction was completed within 2 h at 120 °C under a 5.8 MPa of H₂ pressure. Metal oxides possessing basic properties showed high selectivity toward BHMF when used as supports over Au. Other metal-oxide-based supports (e.g., TiO₂, ZrO₂) led to low yields of BHMF due to ring-opening reactions. The turnover frequency (TOF) of the catalyst was dependent on the size of Au NPs. A TOF of nearly 800 h^{−1} was achieved when the diameter of Au NPs was lowered to 1 nm [112]. Immobilized ruthenium clusters (50 Ru atoms) in nanosized mesoporous zirconium silica (MSN-Zr) were synthesized by using an impregnation method for the preparation of BHMF from HMF. The reaction was performed

for 4 h at RT in an aqueous medium under 0.5 MPa of H₂ pressure. The Ru/MSN-Zr catalyst afforded 92.1% selectivity of BHMF at 98.1% conversion of HMF [113]. Ir-ReO_x-SiO₂ was used as an active and selective catalyst for the hydrogenation of HMF to BHMF. The reaction worked under very mild conditions (30 °C, 0.8 MPa H₂), and a nearly quantitative yield of BHMF was ensured. The high activity of the catalyst was attributed to the synergy between Ir metal sites and ReO_x [114]. A series of earth-abundant Cu-ZnO catalysts were prepared from minerals such as aurichalcite and used to hydrogenate HMF into BHMF and DMF. Under optimized reaction parameters (100 °C, 1 h, 1.5 MPa H₂, 30 wt.% Cu-ZnO catalyst with the Cu/Zn molar ratio of 2), BHMF was obtained in 99.1% selectivity with an 83.5% conversion of HMF. The presence of microstructures, high Cu concentration on the surface, and suitable acidity were responsible for the catalyst's high reactivity [115]. A Pt/MCM-41 catalyst was employed for the selective hydrogenation of an aqueous solution of HMF to BHMF. Low selectivity toward BHMF was observed when the reaction was performed in both acidic and basic media, and the results suggested that a neutral aqueous medium was apt for the above-mentioned conversion. A 98.9% yield of BHMF was obtained when the reaction was conducted for 2 h at 35 °C under 0.8 MPa of H₂ and 20 wt.% loading of the Pt/MCM-41 catalyst [116]. Inexpensive and active ZrO(OH)₂ was used as a catalyst for the MPV reduction of HMF to BHMF under transfer hydrogenation conditions. Ethanol was used as a solvent as well as a hydrogen donor. The reaction was performed at 150 °C for 2.5 h under N₂ atmosphere, a 94.1% conversion of HMF to BHMF with an 88.9% selectivity was achieved. The addition of a small amount of benzoic acid resulted in catalyst deactivation, which suggested that the catalytic activity was dependent on the basic sites present on the catalyst surface [117]. Magnetic zirconium hydroxides (MZHs) with a moderate Zr/Fe molar ratio (ca. 2) displayed the highest catalytic activity, resulting in an 89.6% yield of BHMF under optimized conditions (150 °C, 5 h). The reaction was conducted under transfer hydrogenation conditions using 2-butanol as the solvent and hydrogen donor. Combining basic hydroxyl groups with the acidic zirconium metal centers was crucial for the key step of hydride transfer to the aldehyde group in HMF [118]. Xiang et al. demonstrated a one-pot preparation of BHMF and DMF from fructose using a combination of HY zeolite and an inexpensive hydrotalcite (HT) catalyst HT-Cu/ZnO/Al₂O₃ catalyst in a fixed bed reactor. HY zeolite as the acid catalyst and γ -butyrolactone (GBL) as a renewable solvent afforded quantitative conversion of fructose. The HT-Cu/ZnO/Al₂O₃ catalyst then hydrogenated HMF to BHMF and DMF. Interestingly, the selectivity was conveniently altered by simply changing the reaction temperature. At 140 °C, a 48.1% yield of BHMF was obtained, whereas DMF formed in a 40.6% yield by raising the reaction temperature to 240 °C [119]. Upare et al. reported a two-step process of converting fructose to BHMF in high isolated yield. In the first step, fructose was dehydrated to HMF in >97% yield in 1-butanol using Amberlyst-15 (A-15) as the acid catalyst. In the second step, the crude HMF was hydrogenated to BHMF using a Cu(50)-SiO₂ nanocomposite. A 93% yield of BHMF was attained under optimized conditions (100 °C, 1.5 MPa H₂, 4 h) using BuOH as the solvent. The catalyst was highly stable, and no leaching of Cu centers from the SiO₂ support was encountered [120]. The MPV reduction of HMF under CTH condition over a magnetic zirconium-cyanuric acid coordination polymer (MZCCP) acting as the catalyst also provided BHMF. The transformation was conducted using 2-butanol as the hydrogen donor solvent, and an excellent yield of BHMF (ca. 93.4%) was achieved under moderate reaction conditions (140 °C, 5 h). The catalyst was conveniently separated from the reaction mixture by using an external magnet and successfully recycled for five consecutive cycles without any noticeable loss of activity [121]. Similarly, the selectivity toward BHMF reached up to 92.2% when SBA-15 supported bimetallic Zr-Ba and 2-propanol were used as the catalyst and hydrogen donor, respectively. The addition of BaO decreased the number of acidic sites present in the catalyst, thereby suppressing the etherification of HMF. After five consecutive cycles, a marginal drop in yield of BHMF from 87% to 81.6% was observed [122]. A 20 mol% Cu-Al₂O₃ catalyst was prepared by solid-state grinding method and used for the hydrogenation of HMF to BHMF. The effects

of various reaction parameters were studied on the yield of BHMF. A 93% yield of BHMF was ensured in a methanolic medium after 1 h reaction at 130 °C under 3.0 MPa of H₂ pressure. The presence of both metallic copper and electrophilic copper centers (Cu⁺/Cu²⁺) on the catalyst was attributed to its high activity. A series of potassium-doped Cu/Al₂O₃ catalysts with varying potassium content were synthesized by Hu et al. and examined for the hydrogenation reaction. Among the catalysts examined, 1.5K-Cu/Al₂O₃ was found to be less acidic with well-dispersed Cu particles. Increasing the potassium content decreased the formation of byproducts such as 5MF and improved the selectivity toward BHMF [123]. Interestingly, KF was used as the catalyst and polymethylhydrosiloxane as the hydrogen source to convert HMF to BHMF in DMSO. The authors proposed that a combination of KF and A-15 can catalyze the direct synthesis of BHMF from hexose sugars [124]. A kinetic study on the hydrogenation of HMF to BHMF was explored by Jain et al. using a 5% Ru/C catalyst in the aqueous phase. The reaction was conducted for 1 h at 55 °C under 0.69 MPa of H₂ pressure. Increasing the reacting temperature to 100 °C leads to over-reduced products, including DMF and BHMTHF. The bimetallic Cu-Ru/C catalyst favored the formation of DMF at elevated temperatures [125]. Methanol was employed as an unconventional hydrogen transfer agent under mild reaction conditions. A quantitative yield of BHMF was obtained using MgO as the catalyst in methanol [126]. Liu et al. studied the effect of water on the hydrogenation of HMF in THF over a Cu/γ-Al₂O₃ catalyst. Several hydrogenolysis and ring-opened products were unidentified when the reaction was conducted in the absence of water. The addition of 5 wt.% of water (95:5 *w/w*, THF: water) resulted in the formation of BHMF and 5MF as the primary products with relatively low concentrations of DMF and MHMF (2-methyl-5-hydroxymethylfuran) [127]. The hydrogenation of HMF on Pt/CeO₂-ZrO₂ with 1% Pt loading could achieve a 95% yield when the reaction was performed at RT and atmospheric pressure. The influence of various parameters, including metal loading, solvent, duration of the experiment, has been studied. The use of 0.25% Pt/CeO₂-ZrO₂ catalyst at 0.5 MPa hydrogen pressure for 6 h attained an 87% yield of BHMF. The high hydrogenation ability of the catalyst accounts for the formation of hydrogen species on the Pt centers [128]. Zirconium-containing organic-inorganic nanohybrid catalyst, prepared via a simple assembly of metal ions and ligands, was successful for the CTH of HMF to BHMF. The catalyst exhibited excellent catalytic activity in the presence of 2-propanol, which served both as a source of H₂ gas and as a solvent [129]. Different carbon-based supports (multi-walled carbon nanotubes, reduced graphene oxide, graphitic carbon nitride and biochar) were synthesized via impregnation (IM) or atomic layer deposition (ALD) method to examine the effects of carbon material on the catalytic performance of Pt catalysts. The average particle size of Pt was in the range of 1.6–1.9 nm for catalysts prepared by IM method and ~1.4 nm for catalysts prepared via ALD method. The presence of abundant functional groups on the surface of biochar (BC) increased the catalytic efficiency of Pt/BC-IM catalyst [130]. Copper-alumina catalyst furnished the best yields of BHMF (ca. 93%), which is attributed to the uniform distribution of Cu NPs [131]. Activated carbon (AC) combined with cup-stacked carbon nanotubes (CSCNTs) served as a support for Pd NPs and was used as the catalyst for the hydrogenation of HMF to BHMF. The hybrid (hydrophilic and hydrophobic) design of the supporting material, along with an increase in H₂ pressure from 3.4 to 4.8 MPa, led to the nearly quantitative conversion of HMF [132]. A mesoporous Cu-Al₂O₃ catalyst exhibited excellent catalytic performance toward the synthesis of BHMF in a continuous fixed-bed reactor. Presence of water in the reaction medium decreased the catalytic performance due to adsorption on the catalyst's surface, which in turn decreased the surface coverage of HMF [133].

The electrochemical reduction of HMF to BHMF was carried out using a photoelectrochemical cell composed of n-type BiVO₄ semiconductor anode and catalytic Ag cathode. The selectivity toward BHMF and the Faradaic efficiency approached 100%. The Ag electrode showed a wide potential region where hydrogenation of HMF happened without inducing H₂ evolution from water [134]. Kwon et al. conducted the electrochemical

hydrogenation of HMF in the presence and absence of glucose on solid monometallic electrodes in a neutral solution. Glucose enhanced the hydrogenation of HMF and suppressed the hydrogenolysis in the presence of an Ag electrode with >85% selectivity toward BHMF [135]. The overpotential for HMF hydrogenation lowered in acidic media (0.5 M H₂SO₄) compared to neutral media, but a further reduction of BHMF to BHMTHF was observed [136].

Table 3. Selective preparation of BHMF from HMF.

| S/N | Reaction Conditions | Catalyst | Yield (%) | Ref. |
|-----|---|---|-----------|-------|
| 1 | 160 °C, 3 h, methanol | MgO | 100 | [126] |
| 2 | 0 °C, 1 h, [EMIm]TFSI | NaOH | 100 | [138] |
| 3 | 100 °C, 1 h, 1.5 MPa H ₂ , 1,4-dioxane | 33 wt.% Cu-ZnO | 99.1 | [115] |
| 4 | 40 °C, 2 h, formic acid, THF, NaOH/NEt ₃ | Cp*Ir(TsDPEN) | 99 | [110] |
| 5 | 35 °C, 2 h, 0.8 MPa H ₂ , water | 20 wt.% Pt/MCM-41 | 98.9 | [116] |
| 6 | 130 °C, 1 h, 3 MPa H ₂ , methanol | Cu/Al ₂ O ₃ | 93 | [123] |
| 7 | 120 °C, WHSV 1 h ^{−1} , 2 MPa H ₂ , ethanol | 1.5K-Cu/Al ₂ O ₃ | 98.9 | |
| 8 | 30 °C, 6 h, 0.8 MPa H ₂ , water | Ir-ReO _x /SiO ₂ | 98 | [114] |
| 9 | 100 °C, 4 h, 1.5 MPa H ₂ , 1-butanol | Cu(50)SiO ₂ | >97 | [120] |
| 10 | 140 °C, 2 h, 3.8 MPa H ₂ , water | Au/Al ₂ O ₃ | >96 | [112] |
| 11 | 25 °C, 6 h, PMHS, DMSO | KF | 95 | [124] |
| 12 | 20 °C, 2 h, 0.1 MPa H ₂ , ethanol | 1% Pt/CeO ₂ -ZrO ₂ | 95 | [128] |
| 13 | 140 °C, 5 h, 2-butanol, N ₂ atmosphere | MZCCP | 93.4 | [121] |
| 14 | 130 °C, 1 h, 3 MPa H ₂ , methanol | 20 mol% Cu/Al ₂ O ₃ | 93 | [131] |
| 15 | 100 °C, 5 MPa H ₂ , WHSV 0.2 h ^{−1} , ethanol | Cu-Al ₂ O ₃ | >90 | [133] |
| 16 | 150 °C, 2.5 h, 2-propanol | 20 wt.% ZrBa/SBA | 90.6 | [122] |
| 17 | 25 °C, 4 h, 0.5 MPa H ₂ , water | 5 wt.% Ru/MSN-Zr | ~90.4 | [113] |
| 18 | 160 °C, 10 h, 1 MPa H ₂ , 1-butanol | 10 wt.% Pt/BC-IM | 90.1 | [130] |
| 19 | 150 °C, 5 h, 2-butanol | MZH | 89.6 | [118] |
| 20 | 23 °C, 18 h, 1.37 MPa H ₂ , ethanol | Pt/Al ₂ O ₃ | 85 | [111] |
| 21 | 150 °C, 2.5 h, ethanol | 100 wt.% ZrO(OH) ₂ | 83.6 | [117] |
| 22 | 140 °C, 4 h, 2-propanol | 40 wt.% Zr-DTPA | 80 | [129] |
| 23 | RT, 18 h, water | NaOH | 80 | [137] |
| 24 | 110 °C, 2 h, 4.8 MPa H ₂ , water | 2% Pd/CSCNT-AC | ~75 | [132] |
| 25 | 175 °C, 0.5 h, 2.06 MPa H ₂ , THF/water | Cu/γ-Al ₂ O ₃ | ~68 | [127] |
| 26 | 140 °C, 10 h, 0.1 MPa H ₂ , GBL/water | HT-Cu/ZnO/Al ₂ O ₃ | 48.2 | [119] |
| | 55 °C, 1 h, 0.69 MPa H ₂ , water | 5% Ru/C | 43 | [125] |

Abbreviations: TsDPEN, N-tosyl-1,2-diphenylethylenediamine; MSN-Zr, Nanosized mesoporous zirconium silica; MZH, Magnetic zirconium hydroxide; MZCCP, Magnetic zirconium-cyanuric acid coordination polymer; PMHS, Polymethylhydrosiloxane; DTPA, Diethylenetriaminepentaacetic acid; BC-IM, Biochar prepared by impregnation method; CSCNT-AC, Activated carbon combined with cup-stacked carbon nanotubes; RT, Room temperature; [EMIm]TFSI, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide; DMSO, Dimethylsulfoxide.

Subbiah et al. reported the synthesis of BHMF from HMF in 87% yield via the Cannizzaro reaction. Among various alkali hydroxides, NaOH exhibited good performance even with only 1.1 equivalence [137]. Kang et al. used the ionic liquid as a reusable solvent for water-free Cannizzaro reaction of HMF into BHMF. Among various alkali- and alkaline-earth metal hydroxides examined, NaOH was found most suitable providing 100% (of theoretical) yield of BHMF under mild conditions. Among various ionic liquids employed, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIm]TFSI) provided the best results [138].

Copper-based heterogeneous catalysts are efficient for the selective hydrogenation of the carbonyl group without affecting the furan ring. Nickel-based catalysts are not effective, as the hydrogenation can lead to the formation of DMF and BHMTHF. Polar solvents increased the selectivity due to high solubility of H₂ gas in those medium. It can be summarized that highly dispersed metal catalysts are efficient for maximizing the yield of BHMF. Noble metal catalysts worked under markedly milder reaction conditions than the transition metal catalysts. For example, Ru and Pt-based catalysts worked under ambient temperature and a few atm. of H₂ pressure, whereas the Cu catalysts required

>100 °C and significantly higher pressure of H₂. Mostly alcoholic solvents were used as the medium, though ethers and aqueous medium were also explored. 2-Propanol was successfully used as the hydrogen donor solvent for the CTH of HMF to BHMTHF.

2.2.2. HMF to BHMTHF

Selective hydrogenation of HMF to BHMTHF can be carried out by reducing the aldehyde group followed by the furan ring or vice versa [139]. Chen et al. developed a palladium NPs immobilized on amine-functionalized MOF catalyst for the selective preparation of BHMTHF from HMF that went through BHMF as the intermediate. Nitrogen-containing supports can modify the catalytic performance by fine-tuning the acidity, basicity and surface area of the catalyst. The presence of free amine moieties in the MOF played a key role in forming uniform and well-dispersed palladium NPs. Up to 96% yield of BHMTHF was obtained by conducting the reaction in an aqueous medium for 12 h at 30 °C under 1.0 MPa H₂ pressure [140]. Raney-type catalysts using Co, Ni and Cu metals were employed for the reduction of HMF to DMF and BHMTHF. Raney-Ni catalyst favored the hydrogenation reaction over the deoxygenation reaction and provided BHMTHF in 96% yield at 100 °C under 1.5 MPa H₂ pressure. When the reaction temperature was increased to 180 °C, the selectivity changed to deoxygenation, and DMF was favored with yield reaching as high as 88.5% after 15 h reaction in the 1,4-dioxane medium. The acid sites present on the catalyst surface promoted both hydrogenation and hydrogenolysis of the furan ring and hydroxymethyl group, respectively [141]. A two-stage synthesis of BHMTHF was performed using Raney-Cu and Raney-Ni catalysts, which converted HMF to BHMF and then to BHMTHF. The selectivity of BHMTHF reached 98% at 90 °C and 9 MPa H₂ pressure. It was observed that an increase in substrate concentration had little effect on product selectivity [142]. The earth-abundant Ni/Al₂O₃ catalyst was prepared from the hydrotalcite precursor and applied for the hydrogenation/hydrogenolysis of HMF to BHMTHF, DMF and BHMF. The product selectivity was modulated by fine control over the surface metal-acid bifunctional sites and reaction conditions. The high activity of the Ni/Al₂O₃ catalyst was attributed to the fine dispersion of Ni and Al₂O₃ particles and their molecular-level synergy. Here the acid promoted the dehydration of hydroxymethyl group, whereas Ni promoted the hydrogenation of intermediates formed [143]. The Ni/Al₂O₃ catalyst was synthesized from Ni-Al layered double hydroxides and used for the selective liquid-phase hydrogenation of HMF to BHMTHF in the aqueous medium. The quantitative yield of BHMTHF was achieved within 6 h at 80 °C under a hydrogen pressure of 2 MPa [144]. Fructose was directly converted to BHMTHF via HMF using a combination of A-15 as the acid catalyst and Ru/SiO₂ as the hydrogenation catalyst within a water-cyclohexane biphasic medium. The as-synthesized hydrophobic Ru/SiO₂-TM catalyst provided 61% selectivity toward BHMTHF at 56% conversion of fructose under optimized conditions (130 °C, 4 h, 4 MPa H₂). Interestingly, the selectivity toward BHMTHF was dependent on the acid catalyst used and the concentration of HMF in the reaction mixture at any instant [145]. HMF was hydrogenated over supported Ru, Pd and Pt catalysts in monophasic and biphasic reactor systems. High yields (ca. 88–91%) to BHMTHF were reported using Ru supported on materials with high isoelectric points, such as ceria, magnesia–zirconia and γ -alumina. A THF-water biphasic medium was found most suitable for the selective preparation of BHMTHF. The yield of BHMTHF decreased with the addition of acids such as H₂SO₄ (due to ring-opening to polyols) but improved when solid supports such as MgO and Al₂O₃ were used. The Pd and Pt catalysts showed lesser activity and lower selectivity toward BHMTHF [146]. Graphene-supported Ru-Pd catalyst synthesized via solvothermal method catalyzed the hydrogenation of HMF at RT. Compared to their monometallic constituents, the bimetallic catalyst (Ru:Pd = 1:1, molar ratio) afforded a significantly better yield of BHMTHF under similar reaction conditions [147]. Ethanol was found to be the best solvent for the catalytic hydrogenation of HMF to BHMTHF [106]. Ru containing di-phosphorus ligands furnished a stereoisomeric mixture of BHMTHF under a reaction temperature of 120 °C for 16 h at 1 MPa H₂ pressure [148].

Conclusively, by adjusting the reaction temperature and hydrogen pressure, the non-precious metal-based heterogeneous catalysts can afford BHMTHF in good yields.

2.2.3. HMF to 5MF

Typically, 5MF is synthesized from 2MeF, *N,N*-dimethylformamide and phosgene [149]. In 1982, Hamada et al. patented the production of 5MF from 5-(chloromethyl)furfural (CMF) using palladium catalyst in the presence of H₂ gas [150]. Homogeneous ruthenium(II)bis(diimine) complexes were employed for the chemoselective hydrogenation of FUR to FAL, in which 5MF formed with modest selectivity [151]. Peng et al. developed a novel one-pot metal-free strategy to synthesize 5MF from starch using HCl and NaI in the presence of H₂. The method described above gave an 80.8% yield of 5MF starting from HMF in a biphasic system [152]. The utilization of polyvinylpyrrolidone as a capping agent for Pd NPs increased the 5MF selectivity up to 90%. Formic acid acted both as a H₂ source and as a reactant to form esterified intermediate (5-formylfuran-2-yl)methyl formate (FFMF) [153]. The direct conversion of biomass-derived carbohydrates into 5MF (ca. 68%) in a biphasic system concluded that both homogeneous RuCl₃ and heterogeneous Pd/C displayed similar reactivities [154]. From L-rhamnose, 5MF was obtained in good yields using 20 wt.% NaCl solution and AlCl₃ [155]. Single metal atoms supported on oxygen defective Nb₂O₅ could efficiently catalyze the hydrogenation reaction in the presence of H₂. Among various metal atoms employed, a complete conversion of HMF was achieved using platinum metal. It was concluded that the selectivity of 5MF is independent of H₂ pressure and reaction temperature [156].

2.2.4. HMF to DMF

A combination of catalytic hydrogenation and hydrogenolysis of HMF leads to DMF. DMF is particularly attractive because of its physicochemical properties similar to gasoline. It has a nearly ideal boiling point (92–94 °C), high energy density (30 kJ cm^{−3}) and high research octane number (RON = 119). It is immiscible with water and is easier to blend with gasoline than ethanol. With stricter guidelines for incorporating aromatic compounds such as toluene in gasoline, DMF can be used as a high octane (RON = 119), cleaner-burning fuel additive to gasoline or other biofuels. It has also been proposed as a key intermediate for the renewable synthesis of *p*-xylene to access the terephthalate polymers market. The vapor-phase hydrogenation of HMF in the presence of a suitable metal-based catalyst produces DMF. In the following section, an overview of the types of catalysts employed for the transformation and the reactions applied is elaborated. DMF has also been synthesized from the hydrophobic analogs of HMF, such as CMF. The one-pot preparation of DMF directly from carbohydrates has also been attempted. The reaction has been conducted under conventional heating and microwave conditions using a host of organic solvents as the diluent and reagent at times (e.g., hydrogen donor solvent for the transfer hydrogenation process). Both molecular hydrogen and hydrogen donor solvents (e.g., 2-propanol) have been employed for the hydrogenation process. Hundreds of publications appeared in the literature over the past decade on preparing DMF from HMF and other feedstock. An excellent yield of DMF was ensured using a selective catalyst and optimized reaction conditions in many cases. However, most processes presently use purified HMF as the starting material to avoid catalyst poisoning triggered by the impurities present in crude HMF. Robust catalysts that are immune to the impurities present in HMF could make the process simpler, more energy-efficient and commercially more attractive. The current research in this area primarily focuses on (1) direct conversion of inexpensive carbohydrates to DMF in satisfactory yields, (2) design of efficient, recyclable and eco-friendly catalysts, and (3) use of energy-efficient conditions for the preparation and purification of DMF. There are reviews available on the synthesis of DMF, which elaborated the synthetic routes, catalysts and reaction conditions [157–160].

Table 4 lists some representative publications on the preparation of DMF starting from HMF. Li and co-workers synthesized a series of layered double hydroxides (LDHs)

using Co, Ni and Fe, and their corresponding layered double oxide (LDO) supported Ru catalysts for the hydrogenation of HMF. Out of the synthesized catalysts, Ru/CoFe-LDO gave up to a 98.2% yield of DMF under mild reaction conditions of 180 °C and 6 h [161]. Among various heterogeneous catalysts employed for the synthesis of DMF, 3% Pd/C exhibited the best catalytic activity with a selectivity of 99% toward DMF. The catalyst was recycled and reused for four consecutive cycles without significant loss of activity [162]. The organic matrix deposition method was found to be successful for the nanodispersion of Ni on mesoporous nitrogen-rich carbon material. The synthesized Ni-OMD₃ catalyst with 3 wt.% metal loading could achieve >99% conversion of HMF. The synergy between the nitrogen atom of the support and metal was strong when the size of Ni NPs was less than 5 nm [163]. Feng et al. examined various supports (ZSM-5, Y-zeolite, β -zeolite, COK-12, mordenite and ZrO₂) on Ru, of which Ru/ZSM-5 showed excellent results for the hydrogenation of HMF to DMF [164]. Recently, a Pd/C catalyst prepared in γ -valerolactone (Pd-GVL/C) attained an excellent yield of DMF without using any additive. The preparation of catalysts in GVL furnished Pd particles with a narrow size distribution, increasing catalytic efficiency [165]. The same group designed another Co-N-C/NiAl-MMO catalyst, which displayed outstanding selectivity of DMF [166]. Nitrogen-doped carbon decorated copper-based catalyst with cyclohexanol as a hydrogen source produced DMF in 96.1% yield. Strong interaction between the Cu NPs and the support prevented aggregation of NPs, leading to better catalytic stability [167]. In 2013, Nishimura et al. reported the catalytic hydrogenation of HMF to DMF in an atmosphere of H₂ gas using a Pd-Au/C catalyst. The catalytic efficiency was examined by varying the molar ratio of Pd and Au [168]. Wang and co-workers designed Pt-Co NPs supported on hollow carbon spheres for the hydrogenolysis of HMF. A complete conversion of HMF was attained within 10 min of reaction time [169]. Esen et al. analyzed various SiO₂ supported catalysts prepared by the sol-gel method and observed that bimetallic Ru-Co/SiO₂ afforded an excellent yield of DMF [170]. Gao et al. fabricated Ru-Co bimetallic NPs inside dandelion-like CoO_x microsphere structures and used them for the hydrogenolysis of HMF to DMF. The catalyst achieved an excellent yield (96.5%) of DMF in a short reaction time. Strong interaction between Ru species and the support enabled complete absorption and activation of C=O bond in HMF, with accounts for the complete conversion [171]. Yang and co-workers described that Ni-Co/C could exhibit exceptional stability and activity for the hydrogenation reaction. A series of catalysts with different metal loadings and supporting materials were investigated, 2%Ni-20% Co/C furnished the maximum yield of DMF in both batch and fixed bed reactors [172]. Li and co-workers developed an innovative vapor-phase coupling process between the dehydrogenation of cyclohexanol and hydrogenation of HMF to produce phenol and DMF, simultaneously [173]. The Cu-Pd bimetallic catalyst supported on reduced graphene oxide showed an excellent yield of DMF using 2-propanol as the H₂ source [174]. MOF-derived Cu-Pd bimetallic NPs encapsulated with carbonaceous porous matrix (Cu-Pd@C) yielded 96.5% of DMF under 120 °C and 1.5 MPa H₂ [175]. A Cu-Co/C catalyst with the Cu: Co molar ratio of 1:3 gave a near quantitative (ca. 99.4%) yield of DMF under the optimized reaction conditions. The inexpensive catalyst showed excellent recyclability over six catalytic cycles [176]. Mesoporous alumina-supported Ni-Mo catalyst synthesized by evaporation-induced self-assembly method achieved a 95% yield of DMF [177]. Quantitative conversion of HMF with the yield of DMF reaching as high as 96% was reported with a nickel-tungsten carbide catalyst on activated carbon (Ni-W₂C/AC). 5MF was found to be a key intermediate of the reaction. The efficiency of the catalyst was attributed to the synergism between Ni particles and tungsten carbide [178]. Titania-supported Ni-Fe catalyst was found to be efficient toward the hydrodeoxygenation of HMF. The high surface area and low acidity of the catalyst support (i.e., TiO₂) suppressed the formation of side products [179]. Activated charcoal-supported Ru-Ir alloy NPs (2.2 nm) were effective for converting HMF to DMF (ca. 99%). The formation of electron-rich Ir(0) species and electron-deficient Ru(0) species on the surface of the catalyst helped enhance the hydrogenation reaction [180]. Al-Zr mixed oxide catalyst (AZMO) prepared by the

coprecipitation method possessed high surface area and acidity. The use of mixed oxide as a support for bimetallic Pt-Co increased the selectivity of DMF, and the active sites of the catalysts were intact even after reuse. A nominal decrease in activity was observed after the fourth catalytic cycle [181].

Table 4. Selected publications on the high-yielding preparation of DMF from HMF.

| S/N | Reaction Conditions | Catalyst | Yield (%) | Ref. |
|-----|---|--|-----------|-------|
| 1 | 120 °C, 8 h, 1.5 MPa H ₂ , THF | 40 wt.% Ru-Co/SiO ₂ | >99.9 | [170] |
| 2 | 170 °C, 6 h, 1.5 MPa H ₂ , THF | 40 wt.% Co-N-C/NiAl-MMO | 99.9 | [166] |
| 3 | 180 °C, 8 h, 5 MPa H ₂ , ethanol | 8 wt.% Cu-Co/C | 99.4 | [176] |
| 4 | 120 °C, 1 h, 1 MPa H ₂ , THF | 36 wt.% Ru-Ir/C | 99 | [180] |
| 5 | 200 °C, 6 h, 3 MPa H ₂ , water | 2.5 wt.% Ni-OMD ₃ | 98.7 | [163] |
| 6 | 170 °C, 4 h, 2 MPa H ₂ , 2-propanol | 3%Pd/C | 98.5 | [162] |
| 7 | 180 °C, 6 h, 1 MPa H ₂ , THF | 40 wt.% Ru/CoFe-LDO | 98.2 | [161] |
| 8 | 180 °C, 2 h, 1 MPa H ₂ , butanol | 20 wt.% Pt-Co/HCS | 98 | [169] |
| 9 | 240 °C, 4 h, 0.1 MPa H ₂ , 1,4-dioxane | Ni ₂ -Cu ₁ | >97 | [173] |
| 10 | 220 °C, 3 h, 3 MPa H ₂ , 1,4-dioxane | 15 wt.% NiFe/PC500 | 97 | [179] |
| 11 | 100 °C, 2 h, 1 MPa H ₂ , THF | 2%Pd-5%Co/AZMOCP | 97 | [181] |
| 12 | 120 °C, 7 h, 1.5 MPa H ₂ , THF | 47 wt.% Cu-28 wt.% Pd@C | 96.5 | [175] |
| 13 | 200 °C, 2 h, 0.5 MPa H ₂ , 1,4-dioxane | 20 wt.% RuCo/CoO _x | 96.5 | [171] |
| 14 | 220 °C, 0.5 h, cyclohexanol | 20 wt.% NC-Cu/MgAlO | 96.1 | [167] |
| 15 | 60 °C, 12 h, 0.1 MPa H ₂ , THF | Pd ₅₀ Au ₅₀ /C | 96 | [168] |
| 16 | 180 °C, 3 h, 4 MPa H ₂ , THF | 10 wt.% Ni-47 wt.% W ₂ C/AC | 96 | [178] |
| 17 | 80 °C, 24 h, 2 MPa H ₂ , THF | 8 wt.% Pd-GVL/C | 95.6 | [165] |
| 18 | 180 °C, 3 h, 1.7 MPa H ₂ , ethanol | 50 wt.% Ru/ZSM-5 | 95 | [164] |
| 19 | 130 °C, 24 h, 1 MPa H ₂ , THF | 2%Ni-20%Co/C | 95 | [172] |
| 20 | 180 °C, 2 h, 0.3 MPa H ₂ , 2-propanol | 10Cu-1Pd/RGO | 95 | [174] |
| 21 | 130 °C, 7 h, 1 MPa H ₂ , 2-propanol | 5Ni-7MoS ₂ /mAl ₂ O ₃ | 95 | [177] |

Abbreviations: LDO, Layered double oxide; OMD, Organic matrix deposition method; GVL, γ -Valerolactone; MMO, Mixed metal oxide; NC, Nitrogen-doped carbon; HCS, Hollow carbon nanospheres; RGO, Reduced graphene oxide; AC, Active carbon; PC500, Ultrafine TiO₂ powder; AZMOCP, Al-Zr mixed oxide synthesized via coprecipitation method.

Even though satisfactory results were obtained in some studies, more study is needed in fine-tuning the features of catalysts to improve the selectivity toward DMF. Bimetallic catalysts proved to be efficient for the above conversion, but their stability and recyclability must be considered. The reaction temperature in the range of 180–200 °C and 0.5–3 MPa H₂ pressure were optimal for the synthesis of DMF. High metal dispersion and moderate acidity are the two crucial factors determining the conversion of HMF to DMF.

2.2.5. HMF to DMTHF

Grochowski et al. developed a dual catalytic system comprising of aqueous HI and Rh salts for the synthesis of DMTHF directly from fructose. Hydroiodic acid served as the acid catalyst for the dehydration of fructose to HMF and as a reducing agent for the conversion of HMF to 5MF. In the process, HI was oxidized to molecular iodine, which was reduced back to HI by hydrogenation using the Rh-based catalyst. A series of intermediates such as 5MF and DMF were involved in the one-step conversion of fructose to DMTHF [182]. Jackson et al. introduced a sulfur-poisoned Pt/C catalyst to synthesize DMTHF in ethanol medium at 175 °C and 10.3 MPa of H₂ pressure. 2,5-Hexanedione was the only isolated intermediate formed during the reaction. The catalyst recovery was difficult due to the loss of sulfur during the reaction [183]. Zhou et al. studied the cooperative effect between Pt/C and a solid acid resin in converting 2,5-hexanedione to DMTHF. Under mild reaction conditions (90 °C, 3 MPa H₂, 3 h), a 99% yield of DMTHF was achieved [184]. Ni/SBA-15 could achieve a complete conversion of HMF to DMTHF through 5MF as an intermediate using 1,4-dioxane [185]. The use of a Cu-Zn nanoalloy catalyst afforded a 97% combined yield of DMF and DMTHF (5:1) by the selective HDO of HMF [186].

The efficiency of various catalytic systems can be compared by the turnover frequency (TOF) of the catalyst. An increase in TOF values with decrease in particle size shows the effect of particle size on hydrogenation reactions. The use of CNTs as a support decreased the TOF values due to their inert surface area, which substantiates that the support also plays an important role in the catalytic performance. In addition, the TOF values of bimetallic catalysts were found to be higher than their monometallic counterparts, in general. The result can be justified by the synergism between the particles of dissimilar metals. For a given metal, the TOF values are higher when the reaction is carried out in gas-phase rather than in liquid-phase. The values are reproducible and provides understanding about the working of catalytic cycles. Unfortunately, many works in this area do not report TOF values for the catalyst used and therefore, it is challenging to compare the catalytic systems.

3. Effect of Process Parameters on The Selectivity of Furanics

Catalytic hydrogenation of the aldehyde group and the furan ring did not require high reaction temperatures. Therefore, the catalytic transformation of FUR and HMF to THFAL and BHMF could be achieved at reaction temperatures around 100 °C. On the other hand, hydrogenolysis of the C–O bond is promoted at a higher temperature. The preparation of 2MeF and DMF typically requires a reaction temperature range of 100–200 °C. Synthesis of 2MeF and DMF above 200 °C was also reported in the literature (Figure 1A). Both noble and non-noble catalysts were found effective for the hydrogenation and hydrogenolysis steps. Among the noble metal catalysts, palladium and platinum are the most commonly used, whereas copper and nickel are the most popular non-noble-metal catalysts for the catalytic hydrogenation of furanic compounds (Figure 1B). The copper-based catalysts were found effective for the hydrogenation of aldehyde and the hydrogenolysis of C–O bond and used extensively to prepare 2MeF from FUR. Palladium catalysts were also effective for the hydrogenolysis reaction and used for making DMF from HMF. Palladium and nickel-based catalysts were effective for the hydrogenation of furan rings and favored the formation of THFAL from FUR. The ruthenium-based catalysts were also effective for reducing the carbonyl group and used to prepare DMF from HMF. The solvent used in the hydrogenation reactions greatly influences selectivity toward a specific furanic product. Solvent influences the hydrogen bonding of substrate and solubility of H₂ gas. Alcohols are routinely used as a green solvent for catalytic hydrogenation reactions. In some cases, the alcohol solvent also acts as the hydrogen donor. 2-Propanol is the most frequently employed hydrogen-donor alcohol for CTH due to its bulk availability, inexpensiveness, recyclability and low toxicity. Water is also a frequently used solvent for catalytic hydrogenation reactions. The insolubility of many hydrogenated furanic compounds in water allows isolating the products by simple phase separation without employing an organic extractant. Ethers such as 1,4-dioxane have also found use in the hydrogenation reaction (Figure 1C). The H₂ pressure in the range of 1–2 MPa was proved as optimal for the hydrogenation of FUR and HMF (Figure 1D). The requirement of H₂ pressure is very much dependent on the type of metal catalyst employed. Noble-metal catalysts typically require lesser hydrogen pressure compared to non-noble metal catalysts. In general, the hydrogenation of aldehyde to a hydroxymethyl can be carried out using 1 MPa or less.

However, hydrogenolysis of the hydroxymethyl group to a methyl group or ring-hydrogenation requires higher pressure (1–2 MPa).

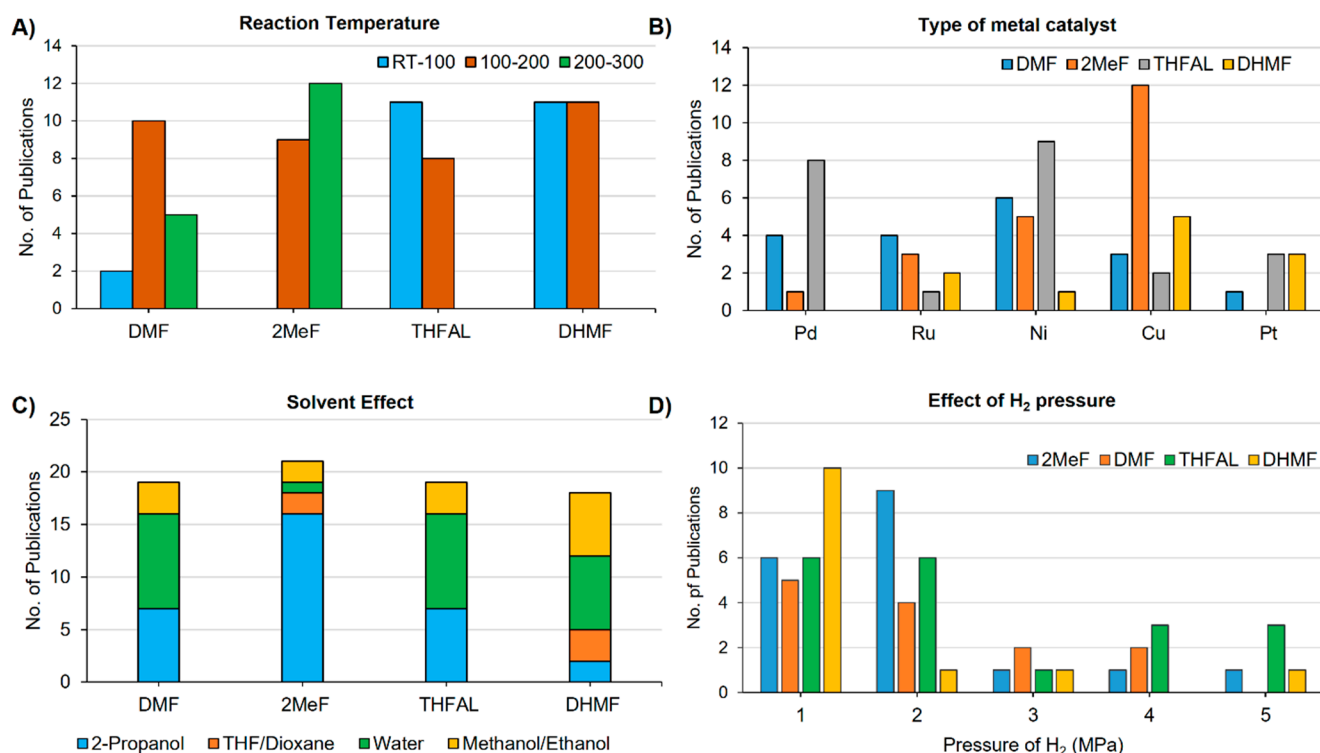


Figure 1. Graphical plots of the number of journal publications on DMF, 2MeF, THFAL, and DHMF against varied (A) reaction temperature, (B) type of metal catalyst, (C) solvent, and (D) hydrogen pressure. (Data taken from Tables 1–4).

Many of the properties of furanic biofuels closely resemble petrofuels such as gasoline. Table 5 lists the physicochemical and thermal properties of selected furanic biofuels. Among the four compounds, DMF shows superior properties for fuel applications. For example, DMF has the highest calorific value and research octane number, whereas it has least solubility in water.

Table 5. Physicochemical and thermal properties of selected furanic biofuels.

| Properties | DMF | DMTHF | 2MeF | MTHF |
|-------------------------------------|---------------------------------------|---|---------------------------------------|--|
| Molecular formula/Molar mass | C ₆ H ₈ O/96.13 | C ₆ H ₁₂ O/100.16 | C ₅ H ₆ O/82.10 | C ₅ H ₁₀ O/86.13 |
| Density (g/cc) | 0.89 | 0.83 | 0.91 | 0.85 |
| Flash point (°C) | −1 | −26.6 | −22 | −10 |
| Lower calorific value (LCV) (MJ/kg) | 33.8 | 32.8 | 31.2 | 32.8 |
| Research octane number | 119 | 92 | 103 | 86 |
| Solubility in water (g/L) | 1.47 | 6.70 | 3 | 150 |
| (C + H)/O (weight ratio) [a] | 5.00 | 5.25 | 4.12 | 4.37 |

[a] Calculated from the molecular formula.

4. Conclusions

In this review, the energy densification of biomass-derived FUR and HMF into furanic biofuels by catalytic hydrogenation and hydrodeoxygenation has been discussed. Recent literature on the preparation of each of these derivatives has been tabulated and summarized. The achievements and challenges associated with the furanic derivatives have been highlighted. Detailed discussion on the effect of catalyst and the reaction parameters on the selectivity and yield of these derivatives have been elaborated. It can be concluded that the economic feasibility of the large-scale production and applications of the furanic biofuels and value-added chemicals heavily relies on the process scalability and cost of producing the furfurals from biomass. In this regard, even though FUR is commercially

produced, the same for HMF is yet to be realized. The catalyst plays a crucial role in determining the selectivity of a particular product. For a specific catalyst, the reaction conditions can be tweaked to alter the chemical selectivity from one product to another. In most of the reported processes, a heterogeneous metal-based catalyst was employed due to the better recoverability and recyclability of the heterogeneous catalysts compared to their homogeneous counterpart. The noble metal-based catalysts provided excellent catalytic activity even under low catalytic loading and showed good recoverability. However, developing transition-metal-based catalysts have received the most focus in recent years since they are abundant and inexpensive. However, in most cases, these catalysts require more demanding reacting conditions when compared to noble-metal catalysts. In many cases, the catalysts were successfully recovered and recycled for multiple cycles without significant loss of activity. However, the catalyst becomes deactivated by leaching active sites from the catalyst support and blocking the active sites by coke formation. The catalytic centers in the multi-component catalysts show cooperative activity at the molecular level and often show superior catalytic activity compared to the individual components. The furanic compounds have potential applications as a fuel oxygenate, green solvent and chemical feedstock.

5. Future Perspectives

The use of abundant, non-food, inexpensive and preferably waste biomass for the production of FUR and HMF is preferred from both the economic as well as environmental perspectives. The problems associated with the isolation of HMF from the reaction media must be sorted out by employing energy-efficient and eco-friendly processes. The hydrophobic analogs of HMF, such as CMF, have shown promise in this regard. However, detailed research is required for toxicological study and life cycle analysis of the biomass-derived furanic compounds to better understand the potential environmental impact in their large-scale use. Newer applications and markets for the furanic compounds must be explored for the preparation to be economically more advantageous. Even though hydrogen can be produced from greener routes such as electrolysis of water and from biomass, the processes yet to reach maturity and commercialization. An inexpensive and sustainable source of hydrogen to synthesize partially-hydrogenated furanic compounds must be ensured for the processes to be considered truly green. The international and national policies regarding the use of biofuels and biorenewable chemicals will continue to play pivotal roles in the commercial adoption of these molecules.

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Abbreviations

FUR, Furfural; HMF, 5-(hydroxymethyl)furfural; FAL, Furfuryl alcohol; THFAL, Tetrahydrofurfuryl alcohol; 2MeF, 2-Methylfuran; MTHF, 2-Methyltetrahydrofuran; THFU, Tetrahydrofuraldehyde; 5MF, 5-Methylfurfural; DMF, 2,5-Dimethylfuran; DMTHF, 2,5-dimethyltetrahydrofuran; BHMF, 2,5-Bis(hydroxymethyl)furan; BHMTHF, 2,5-Bis(hydroxymethyl)tetrahydrofuran; HMMF, 2-(Hydroxymethyl)-5-methylfuran; HDO, Hydrodeoxygenation; CTH, Catalytic transfer hydrogenation; MOF, Metal organic framework.

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