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Review on Hydrogenation of Biomass Derived 5-Hydroxymethylfurfural to 2,5-Dimethylfuran

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ABSTRACT

Biofuels play a crucial role as potential substitutes for fossil fuels in the transition towards sustainable energy systems. Among these bioenergy carriers, 2,5-dimethylfuran (2,5-DMF) has emerged as a promising alternative fuel due to its favorable physicochemical properties. Biomass resources such as cellulose and hemicellulose the two principal structural components of lignocellulosic biomass can be converted via hydrolysis and pyrolysis into a range of biomass-derived fuels. This conversion pathway is of particular significance for the sustainable utilization of renewable resources in support of green and circular economies. Recent advances in the catalytic transformation of 5-hydroxymethylfurfural (5-HMF) from biomass into 2,5-DMF via selective dehydration are reviewed, with a focus on reaction mechanisms, single-metal catalysts (Ru-, Pt-, Cu-, and Ni-based), bimetallic catalysts, and various solvent systems, including tetrahydrofuran, alcohols, acids, water, and biphasic systems. Notably, 2,5-DMF derived from biomass exhibits a high energy density, elevated octane number, immiscibility with water yet high miscibility with gasoline, along with advantages such as high productivity, low initial capital cost, and the capacity to valorize agricultural by-products.

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1. Introduction

Energy is the material foundation of economic development and social progress, and a strategic resource for nations worldwide. Currently, coal, petroleum, and natural gas dominate the global energy mix; however, their non-renewable nature and excessive consumption cause severe environmental pollution, threatening sustainable development. Developing renewable, environmentally friendly energy sources is therefore essential. Among these, biomass particularly cellulose is abundant, widely distributed, and convertible into diverse green fuels, making it one of the most promising emerging energy resources [1].

Among cellulose-derived biofuels, 2,5-dimethylfuran (2,5-DMF) has emerged as a promising candidate, offering a high energy density (31.5 MJ/L), exceeding that of ethanol and comparable to gasoline. Its relatively high boiling point (~92–94 °C) and low volatility minimize evaporation losses, while low water solubility, stability in air, and resistance to moisture absorption enhance storage and handling. Moreover, 2,5-DMF can be synthesized from cellulose-based biomass, reducing dependence on fossil resources and food-based feedstocks, lowering costs, and mitigating environmental impacts [2], [3].

Owing to these favorable physicochemical properties, 2,5-DMF is regarded as a promising next-generation green biofuel. Its synthesis can be achieved via a two-step catalytic conversion of biomass. As illustrated in Figure 1, the first step involves the dehydration (or hydrolysis followed by dehydration) of biomass-derived carbohydrates, such as fructose, glucose, or cellulose, to yield the intermediate 5-hydroxymethylfurfural (5-HMF). The second step entails the catalytic hydrogenolysis of 5-HMF to produce the target compound, 2,5-DMF [4]–[6].

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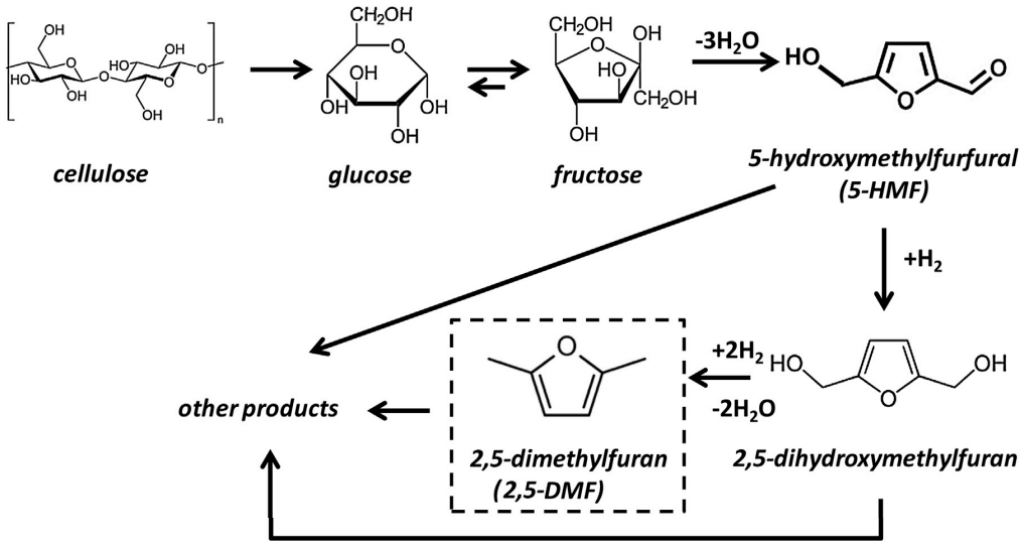

Figure 1. *The reaction process of cellulose into 2,5-DMF*

2. Reaction mechanism

5-HMF contains two reactive functional groups: an aldehyde group (–CHO) and a hydroxymethyl group (–CH_2OH) attached to the furan ring. Under hydrodeoxygenation and hydrogenolysis conditions, in the presence of a catalyst and a hydrogen donor (molecular H_2, formic acid, or electrochemical hydrogenation), two main competitive pathways for functional group activation exist:

Pathway A (C=O hydrogenation first): the aldehyde group of 5-HMF is first hydrogenated to form 2,5-dihydroxymethylfuran (2,5-DHMF). Subsequently, the hydroxymethyl group undergoes hydrogenolysis to yield the key intermediate 5-methylfurfuryl alcohol (5-MFA). Finally, hydrogenolysis of the –OH group in 5-MFA produces 2,5-DMF. Side reactions, such as excessive hydrogenation of the furan ring or ring-opening cracking, may also occur, generating by-products including 2,5-dimethyltetrahydrofuran (2,5-DMTHF), 2,5-dihydroxymethyltetrahydrofuran (2,5-DHMTHF), and 2,5-hexanedione (2,5-HD).

Pathway B (C–O hydrogenolysis first): the hydroxymethyl group in 5-HMF is first hydrogenolyzed to form 5-methylfurfural (5-MF). The aldehyde group in 5-MF is then hydrogenated to yield 5-MFA, followed by further hydrogenolysis to produce 2,5-DMF. This route is often observed when 2,5-DHMF is not detected as an intermediate, as illustrated in Figure 2 [7].

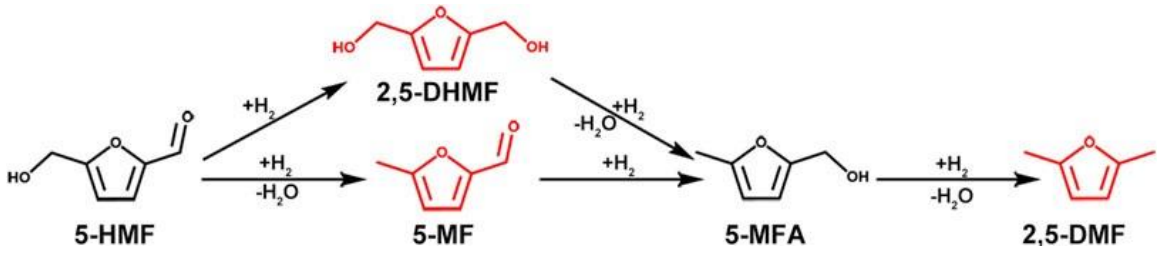

Figure 2. *Reaction pathways for the hydrogenolysis of 5-HMF to 2,5-DMF.*

Hydrogenation of the carbonyl (C=O) group in 5-HMF produces 2,5-bis(hydroxymethyl)furan (2,5-BHMF), a versatile intermediate used as a monomer for polyurethane foams and polyesters. In contrast, hydrogenolysis of both the aldehyde (C=O) and hydroxymethyl (C–OH) groups yields 2,5-DMF (Figure 3). Generally, hydrogenolysis involving deoxygenation is kinetically more demanding than simple aldehyde hydrogenation. In electrochemical reduction, once 5-HMF's C=O is hydrogenated to 2,5-BHMF, subsequent C–OH hydrogenolysis proceeds inefficiently, making 2,5-BHMF a terminal product. This suggests that aldehyde hydrogenation competes with, rather than precedes, aldehyde hydrogenolysis. Similar mechanistic patterns have been observed in furfural and related compounds [8].

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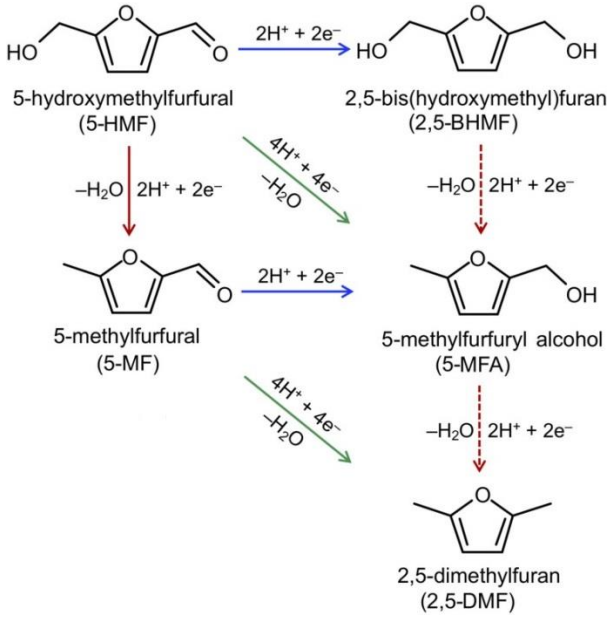

Figure 3. *Possible electrochemical reduction pathways of 5-HMF retaining the furan ring structure.*

3. Catalyst system

Hydrogen activation is central to the catalytic conversion of 5-HMF to 2,5-DMF. On metal catalysts, molecular hydrogen adsorbs and dissociates into surface-bound atomic hydrogen, the active reducing species. This hydrogen selectively targets polar functional groups, particularly the C=O and C–OH moieties of 5-HMF, driving hydrogenation and hydrogenolysis, while the conjugated furan ring (C=C) remains largely unaffected under mild conditions. Consequently, most catalysts favor reduction of aldehyde and alcohol groups, avoiding unwanted ring hydrogenation or ring-opening reactions [9]. Noble metals exhibit high catalytic activity, thermal stability, and corrosion resistance, leading to their widespread early use in 2,5-DMF synthesis; however, their high cost has spurred interest in developing more affordable alternatives. Current catalytic systems encompass both noble metals (Ru, Pd, Pt) and non-noble metals (Cu, Ni, Co), often supported on activated carbon to provide high surface area, stability, and favorable metal dispersion [10]–[12]. Table 1 summarizes recent research on catalysts for 5-HMF conversion to 2,5-DMF.

Table 1. *Catalysts studied in 5-HMF conversion into 2,5-DMF*

Catalysts	Solvent	T/°C	P/MPa	t/h	5-HMF con./% (mol)	2,5-DMF yield/% (mol)	Ref.
Ru-Co/AC	THF	200	1	1.5	98.7	97.9	[13]
Ni-C_3N_4/HC	THF	190	1.5	4	100	94.2	[12]
CuCoNiAl-MMO	THF	180	1	6	99.8	95.3	[7]
Pt-FeO_x/AC	n-butanol	180	1.5	6	86.4	91.1	[14]
$Ni_2Mo_3N/Ni_6Mo_6C_{1.06}$	2-propanol	160	2	5	100	99	[15]
Ru-ZrO_2-MCM-41	THF	160	1.5	1	99	90	[16]
25c-Co/3cPt/MWCNT	1-butanol	160	1	8	100	92.3	[17]
2CuCo-IG	2-butanol	140	2	2	100	93.7	[18]
Cu2ZnAl-600-300	IPA	180	1	4	99.9	91.7	[19]
Br-Pd/Al_2O_3	THF	30	0.5	6	100	96.1	[20]

Pd/NMC	FA	160	0.5	3	99.9	97	[21]
Pd-GVL/C	THF	80	2	24	99	95.6	[22]
Cu-Fe	IPA	170	2	4	97	93	[23]
Co_{20}-Cu@C	IPA	160	2.5	3	100	85	[24]
Cu/SiO_2-HT-8.5	THF	200	0.6	8	99.9	57.1	[25]
CuNi/ZrO_2-SBA-15	IPA	180	2	3	100	100	[26]
Ni/SBA-15	DIO	180	3	0.5	93	71	[27]
Ni^0NiO/ATZ3$_{WI}$	FA	210	2	24	99	46	[28]
CoNC$_x$/NiFeO	THF	180	6	1	99.8	94.3	[29]
Cu-Co@C	Ethanol	180	8	5	100	99.4	[30]
Ru/CNT	DIO	150	2	1	100	83.5	[31]
Cu/ZrO_2	n-Butanol	200	1.5	2	99	60.6	[32]
$PdAu_4$/GC800	THF	150	1	4	86.8	94.4	[33]
Ni-Cu_3/C	1-Propanol	180	3.3	-	100	98.7	[34]
Ni-Co/C	THF	210	-	24	99	90	[35]
Cu-Co/Al_2O_3	THF	220	3	8	99.9	78	[36]
Ru-MoO$_x$/C	n-Butanol	180	1.5	1	100	79.8	[37]

3.1. Single metal catalyst

Among supported single-metal catalysts, Ru/C and Pd/C are widely used due to their exceptional catalytic efficiency, stability, and well-established hydrogenation performance. To reduce costs, non-precious metals such as Ni and Cu have gained attention, with Ni notably effective at cleaving C–O bonds under mild conditions. Fe-based catalysts have also demonstrated appreciable activity in selective 5-HMF hydrogenation, broadening the scope of viable catalysts [23], [38]. Enhancing catalytic performance often involves incorporating a secondary transition metal into noble-metal frameworks to harness synergistic effects that boost hydrogenation efficiency and selectivity. Beyond catalyst design, operational parameters including solvent, hydrogen source, temperature, reaction time, and hydrogen pressure play critical roles in determining 5-HMF conversion and 2,5-DMF yield.

3.1.1. Noble Metal-Based Catalyst

Ru-based catalysts are widely employed for 5-HMF hydrogenation due to their relative affordability among precious metals and excellent catalytic activity, especially under acidic hydrothermal conditions. The Ru/ZSM-5 catalyst achieved a 98% 5-HMF conversion with 97% selectivity to 2,5-DMF at 180 °C using ethanol solvent and 250 psi H_2 for 3 h [39]. Ru/C catalysts, pre-reduced at 200°C and operated at 70 bar H_2 in 1,4-dioxane for 6 h, showed moderate activity with 27% conversion and 16% 2,5-DMF yield [40]. As reported in [13], bifunctional 5%Ru–1%Co/AC catalysts prepared via a two-step reduction ($NaBH_4$ reduction of Ru followed by Co impregnation and H_2 reduction) achieved 98.7% conversion and 97.9% 2,5-DMF yield within 1.5 h. A Ru–Ir/C alloy catalyst (~2.2 nm nanoparticles) dispersed on activated carbon achieved complete 5-HMF conversion with 99% 2,5-DMF selectivity at 120 °C under H_2 atmosphere, demonstrating excellent reusability [41]. Reference [16] demonstrated that 2 wt% Ru–ZrO_2–MCM-41 catalyzed 99% conversion and 90% 2,5-DMF yield at 160 °C in 1 h, highlighting the enhanced hydrogenation activity of Ru supported on activated carbon. These findings underscore the superior catalytic performance and potential of Ru-based catalysts for efficient 5-HMF conversion to 2,5-DMF.

Pt is well known for its high selectivity toward C–O bond hydrogenation, but its intrinsic high catalytic activity complicates rate control, limiting the use of Pt monometallic catalysts in 5-HMF

hydrodeoxygenation (HDO). Efficient conversion of 5-HMF to 2,5-DMF was achieved over 0.4 wt% Pt/Co_2AlO_4, which delivered >99% conversion and 99% selectivity at 180 °C, 2 MPa H_2, in isopropanol for 3 h. This performance is attributed to the synergy between highly dispersed Pt and the acid–base properties of the Co_2AlO_4 support, facilitating effective hydrogenolysis under mild conditions [42]. The study in [17] reported that Pt–Co bimetallic catalysts were synthesized via atomic layer deposition on multi-walled carbon nanotubes (MWCNTs). The 25c-Co/3cPt/MWCNTs catalyst achieved 100% conversion and 92.3% selectivity at 160 °C, 10 bar H_2, for 8 h, benefiting from synergistic Pt–Co and MWCNT interactions. However, excessive Co loading caused steric hindrance and reduced activity. According to [14], a 0.5%Pt–2%FeO_x/AC catalyst achieved 86.4% conversion and 91.1% 2,5-DMF yield at 180 °C, 1.5 MPa H_2, over 6 h. Sequential Fe and Pt loading produced well-dispersed Pt nanoparticles (~2.8 nm), with FeO_x enhancing Pt dispersion and introducing Lewis acid sites that synergistically promote C–O bond activation during hydrogenolysis.

Pd catalysts are recognized for their activity and recyclability in deoxygenation reactions. It was reported in [22] that Pd/C prepared in γ-valerolactone (Pd-GVL/C) achieved a 95.6% 2,5-DMF yield from 5-HMF at 80 °C without additives. The GVL–Pd interaction enhanced catalyst performance by improving particle dispersion and stability, while ester adsorption on Pd surfaces suppressed oxidation, sustaining activity under 2 MPa H_2 for 24 h. In [43], it was reported that a Pd catalyst supported on Zr-based MOF-808 delivered 99% 2,5-DMF yield at 100 °C in 3 h with excellent reusability over five cycles. The reaction proceeds via parallel hydrogenolysis of the hydroxymethyl group and hydrogenation of the aldehyde. Reference [44] reported that 3% Pd/C achieved near-complete 5-HMF conversion (99%) within 4 h, with maintained activity after four reuses. As reported in [20], a bifunctional Pd–Br catalyst featuring co-localized metal and acid sites was developed, reaching 96% 2,5-DMF yield at ambient temperature.

3.1.2. Non-Noble Metal-Based Catalysts

Co-based catalysts have garnered increasing attention due to their low cost, abundance, and notable activity in C=O hydrogenation. In [45], Pd catalysts supported on Co–CoO_x@NC were synthesized via pyrolysis of ZIF-67 for efficient 5-HMF hydrogenolysis. Strong Pd–support interactions, including Pd–N coordination, enhanced Pd dispersion and stability. The Co–CoO_x@NC support, with high surface area and abundant defects, promoted 5-HMF adsorption and activation. Metallic Pd and Co facilitated H_2 dissociation, while Pd–CoO_x interactions and oxygen vacancies enabled hydrogen spillover and carbonyl activation, resulting in a 97.8% 2,5-DMF yield and a proposed synergistic mechanism. A $CoNC_x$/NiFeO catalyst, prepared by adsorbing cobalt(II) phthalocyanine onto ultrathin NiFe-LDH nanosheets followed by pyrolysis at 550 °C under N_2, achieved 99.8% conversion and 94.3% selectivity in THF at 180 °C, 1.0 MPa H_2, over 6 h [29]. The bimetallic Co_x–Cu@C catalyst, synthesized via MOF pyrolysis, delivered 85% 2,5-DMF yield at 160 °C after 3 h [24]. The core–shell Co@CoO catalyst (Co_3O_4-250), featuring oxygen vacancies, achieved 89% yield at 130 °C over 2 h and maintained excellent stability for over 100 h at a WHSV of 26.6 h^{-1}, attributed to CoO species enhancing 5-HMF adsorption and H_2 activation [46]. The study in [47] reported that a Co@NGs catalyst exhibiting a strong Mott–Schottky effect was developed, where electron transfer from Co to N decreasing Co's electron density and enhanced selective hydrogenation. The nitrogen content modulated catalytic activity by increasing work function and improving interfacial rectification. Under 200 °C, 2 MPa H_2, and 4 h, the optimized catalyst achieved nearly 100% conversion and 94.7% 2,5-DMF selectivity, outperforming conventional N-doped carbon-supported Co catalysts.

Cu-based catalysts exhibit superior selectivity for 2,5-DMF due to strong repulsion toward the carbonyl carbon, favoring C=O bond hydrogenation while minimizing side reactions such as ring hydrogenation and decarbonylation [3]. It was reported in [18] that a nitrogen-doped carbon-confined CuCo bimetallic catalyst with a popcorn-like structure was developed, achieving 100% 5-HMF conversion and 93.7% 2,5-DMF selectivity under optimized conditions, along with excellent stability. The authors in [19] studied catalytic transfer hydrogenation of 5-HMF using isopropanol over a ternary Cu_xZnAl catalyst, obtaining 91.7% 2,5-DMF yield at 180 °C after 4 h. The high activity was attributed to a synergistic effect between Cu^0 and Cu^+ species, with the 2,5-DMF yield positively correlating with electrophilic Cu^+ content. As presented in [48], Cu-supported molecular sieves were evaluated, and it

was found that 15 wt% Cu/SBA-15 delivered a 90% 2,5-DMF yield at 180 °C, 2 MPa H_2, after 8 h. Copper catalysts on alumina and niobia–alumina supports (Cu/Al_2O_3, $Cu/Nb_2O_5–Al_2O_3–623$, $Cu/Nb_2O_5–Al_2O_3–773$, $Cu/Fe_2O_3–Al_2O_3$) achieved approximately 90% yield with complete conversion after 10 h, following a 2,5-BHMF-mediated pathway. In contrast, Cu/Fe_2O_3 and Cu/Nb_2O_5 catalysts, which exhibited low acidity and poor metal dispersion, showed negligible 2,5-DMF production. These findings highlight the potential of alumina and niobia–alumina supports for sustainable and cost-effective 5-HMF conversion [49].

Ni-based catalysts are widely utilized in hydrogenation due to their strong ability to cleave C=O bonds in biomass-derived compounds. Among transition metals, Ni exhibits notable hydrogenation activity, which can be further enhanced by promoter metals to improve catalytic performance and selectivity. Reference [12] developed a $Ni–C_3N_4$ catalyst supported on H_2-activated carbon via coordination impregnation pyrolysis, achieving complete 5-HMF conversion and 94.2% 2,5-DMF yield at 190 °C, 1.5 MPa H_2, within 4 h, outperforming many Ni-, Co-, and Cu-based catalysts. Reference [15] reported that the Ni_2Mo_3N phase provides strong hydrogenation activity, while $Ni_6Mo_6C_{1.06}$ facilitates C–O bond hydrogenolysis. An optimized $NiMoN_x$ catalyst (Ni:Mo = 1:2) used 2-propanol as solvent to promote ether formation and hydrogenolysis, yielding 99% 2,5-DMF at 160 °C, 2 MPa H_2, over 5 h. As demonstrated in [50], the morphology of TiO_2 strongly affects Ni particle size and metal–support interactions in Ni/TiO_2 catalysts. The rutile phase stabilized larger Ni particles, enhancing H_2 adsorption and promoting the formation of both 2,5-DMF and 2,5-DMTHF. In contrast, the anatase phase, characterized by higher acidity and surface area, stabilized smaller Ni particles and achieved an 85.0% 2,5-DMF yield at 220 °C and 3 MPa H_2 in 2 h. Results in [51] showed that 5% Ni/HC catalysts yielded 100% conversion and 85.1% 2,5-DMF selectivity at 220 °C, 1.5 MPa H_2 after 25 h. This performance was attributed to the synergistic effects among metallic Ni, NiO (Lewis acid sites), and hydrothermal carbon, which enhanced chemisorption. Additional catalysts such as $Ni_2In/MgO–Al_2O_3$ [52] and ternary $Ni–Al/CoO_x$-1 [53] achieved high yields of 2,5-DMF with excellent stability under mild conditions. Multifunctional NiCoTi-x metal oxides derived from layered double hydroxide precursors were also effective; the NiCoTi-8 catalyst (Ni:Co:Ti = 4:4:1) reached 90.7% conversion and 95.8% selectivity at 200 °C, 1.5 MPa H_2 [54].

Fe-based catalysts have garnered growing interest due to their low cost and promising catalytic efficiency. A magnetically separable bimetallic Cu–Fe (1:2) catalyst with hybrid nanomorphology demonstrated excellent selective hydrogenation of 5-HMF to 2,5-DMF, achieving 97% conversion and 93% selectivity at 443 K and 300 psi H_2 for 4 h [23]. This high performance stems from the synergistic effect of Cu, which strongly activates C–O bonds, and the oxophilic Fe that facilitates efficient deoxygenation. The catalyst's magnetic properties enable easy separation from the reaction mixture, and its stability was confirmed through multiple reuse cycles. Evidence in [55] confirmed that the $Fe_{0.8}Co_{3.0}Ni_{1.9}$/h-BN catalyst achieved 100% 5-HMF conversion and a 94.0% 2,5-DMF yield at 180 °C and 2.0 MPa H_2 over 4.5 h, exhibiting excellent activity and recyclability, demonstrating strong potential for sustainable biomass valorization.

3.2. Bimetallic catalyst

Noble-metal catalysts with a single active metal often suffer from limited stability due to weak metal–support interactions, leading to nanoparticle leaching during reactions. Incorporating a secondary metal enhances interfacial bonding, stability, and catalytic performance. In Ru-, Pt-, and Pd-based systems, the addition of a second metal exploits combined geometric and electronic effects, producing catalytic behaviors distinct from monometallic counterparts. The tunability of composition, particle size, and electronic structure in bimetallic catalysts offers improved control over activity and selectivity, enabling greater efficiency and versatility [56]–[58]. In [33], $PdAu_x$/GC800 catalysts (x = 1–4) were developed for the hydrogenation of 5-HMF to 2,5-DMF under neutral conditions without additives. The $PdAu_4$/GC800 catalyst demonstrated superior activity and stability, achieving 86.8% conversion and 94.4% selectivity at 150 °C in 4 h, with negligible deactivation after five cycles. The superior activity resulted from strong Pd–Au interactions facilitating charge transfer from Au to Pd, increasing active Pd^0 species, improving metal dispersion, and reducing particle size. $Ru–MoO_x/C$ catalysts prepared by wetness impregnation achieved 79.8% 2,5-DMF selectivity, where $Ru–MoO_x$ synergy promoted

sequential C=O hydrogenation and –CH_2OH hydrogenolysis; catalyst deactivation was linked to carbon support agglomeration and surface area loss. MoO_x/C alone favored –CH_2OH hydrogenolysis to 5-MF [37]. Bimetallic nanoparticles such as Fe–Pd/C, Cu–Pd/C, and Cu–Fe/C were synthesized, with Fe–Pd/C offering magnetic separability and excellent stability. High 5-HMF conversions (>95%) and 2,5-DMF selectivity (>85%) were achieved without acidic additives, supporting a green process. Kinetic studies based on the Langmuir–Hinshelwood–Hougen–Watson (LHHW) model yielded an activation energy of 11.6 kcal/mol, indicating a kinetically controlled hydrogenation reaction [59].

Monometallic non-noble catalysts for 5-HMF hydrogenolysis typically require harsh conditions and often suffer from over-hydrogenation, leading to diminished 2,5-DMF yields. Bimetallic non-noble catalysts harness synergistic effects to enhance activity, selectivity, and stability. Further optimization of metal ratios and supports allows tailored catalytic performance, making these systems promising for efficient 5-HMF conversion. For example, a CuCoNiAl-MMO catalyst synthesized by calcining a CuCoNiAl-LDH precursor at 500 °C for 5 h under N_2 exhibited excellent activity and selectivity under mild conditions (THF solvent, 180 °C, 6 h, 1.0 MPa H_2), achieving 99.8% 5-HMF conversion and 95.3% 2,5-DMF selectivity [7]. Cu–Co bimetallic nanoparticles coated with carbon layers were synthesized via direct heating of oxide precursors deposited with polyethylene glycol. The Cu–Co@C catalyst with a Cu:Co ratio of 1:3 achieved outstanding chemoselective hydrogenolysis of 5-HMF to 2,5-DMF, reaching a 99.4% yield [30]. Similar results were observed in [60], where 5 wt% Ni-loaded Cu(x) catalysts (x = 8–14%) supported on SBA-16 were prepared and evaluated for their hydrogenation performance. The 5Ni–12Cu/SBA-16 catalyst exhibited complete 5-HMF conversion and a 60.7% 2,5-DMF yield at 210 °C, 20 bar H_2, and 4 h, attributed to strong Cu–Ni synergy, good metal dispersion, and favorable surface acidity. Reference [36] reported that the Cu–Co/Al_2O_3 catalyst afforded a 78.0% 2,5-DMF yield at 220 °C and 3 MPa H_2 after 8 h. According to [61], the authors synthesized non-noble Ni–Cu catalysts with varied Ni/Cu ratios supported on TS-1 by solid-phase grinding. The 40%Ni–5%Cu/TS-1 catalyst achieved complete 5-HMF conversion and 97.3% 2,5-DMF selectivity under optimized conditions.

3.3. Solvent system

3.3.1. Tetrahydrofuran

Solvent selection critically impacts the catalytic conversion of 5-HMF to 2,5-DMF by influencing reaction efficiency and selectivity. Tetrahydrofuran (THF) is widely studied for its ability to facilitate hydrogenolysis, thereby enhancing catalytic performance and stability. As reported in [25], a Cu/SiO_2-HT-8.5 catalyst synthesized via hydrothermal methods achieved a total liquid fuel yield of 91.6%, comprising 57.1% 2,5-DMF and 34.5% 2,5-DMTHF, under optimal conditions (200 °C, 8 h, 5 mL THF). It was reported in [35] that a 2% Ni–20% Co/C catalyst achieved 99% 5-HMF conversion and 90% 2,5-DMF yield at 210 °C in 10 mL THF. The study in [62] utilized a Ni–Co/C catalyst with formic acid as a co-reagent, achieving a maximum 2,5-DMF yield of 96.5% at 210 °C, 1.5 MPa H_2, after 8 h in THF.

3.3.2. Formic acid

Formic acid (FA), serving as both an acidic solvent and an in situ hydrogen donor, is widely employed in the hydrogenolysis of 5-HMF to 2,5-DMF. Its capacity to decompose into H_2 under mild conditions simplifies the reaction by obviating the need for external hydrogen. The study in [63] achieved 99% 5-HMF conversion and 98% 2,5-DMF yield using a 1% $AuPd_{0.2}$/t-ZrO_2 catalyst (0.25 mol% metal) with 2 mmol 5-HMF and 20 mmol FA at 140 °C for 1.5 h under 0.1 MPa N_2. As presented in [21], a Pd/NMC catalyst achieved >99.9% conversion and >97.0% selectivity at 160 °C and 5 bar H_2 with FA as an additive. Additionally, a Ni^0–NiO/ATZ3WI catalyst demonstrated strong synergistic effects, achieving efficient hydrogenation using FA under 20 bar Ar at 210 °C for 24 h [28].

3.3.3. Alcohols

Low-order alcohols such as methanol, ethanol, and isopropanol (IPA) are attractive hydrogen donors due to their low cost, availability, and ease of storage and handling. Besides serving as hydrogen sources, they also act as solvents that facilitate catalytic transfer hydrogenation, enhancing the conversion of 5-

HMF to 2,5-DMF. The authors in [64] demonstrated that a Cu/PBSAC catalyst achieved 91.9% 5-HMF conversion and 71.7% 2,5-DMF selectivity at 190 °C after 6 h, which increased to over 96% yield after 10 h. The improved performance was attributed to smaller Cu particle size and larger support surface area, with metallic Cu^0 catalyzing IPA dehydrogenation and 5-HMF hydrodeoxygenation via hydrogenolysis to 5-MF, then to 2,5-DMF. The study in [65] demonstrated complete conversion and 99% 2,5-DMF yield over a ternary CuZnCo-3 catalyst at 210 °C for 5 h using ethanol as the hydrogen donor. The CoO_x phase promoted in situ H_2 generation, ZnO enhanced aldehyde hydrogenation, and Cu–Co alloy formation facilitated 5-HMF hydrogenation. Consistent with the findings in [66], the study reported transfer hydrogenation of 5-HMF to 2,5-DMF over a Cu_3Al-A catalyst using methanol under 1 MPa N_2 at 513 K for 1.5 h, achieving >99% conversion and 96.7 mol% yield, with a product formation rate of 215.4 μmol DMF g^{-1} Cu min^{-1}.

3.3.4. Other solvents

The authors in [67] developed a novel hydrodeoxygenation (HDO) process for converting 5-HMF to 2,5-DMF, coupled with the water-gas shift reaction (WGSR), using a single Au/ZrO_2 catalyst. This method leverages in situ generated H_2 from WGSR, eliminating the need for external hydrogen and reducing water consumption. The process achieved a 2,5-DMF yield of 78.5% with a hydrogen utilization efficiency of 88.2%. As reported in [27], Ni/SBA-15 catalysts were investigated for 5-HMF conversion under 30 bar H_2, 180 °C, and 0.5 h, using 12.5 mL DIO as the solvent and 0.261 g catalyst, achieving 93% 5-HMF conversion and 71% 2,5-DMF yield. The study in [68] investigated 5-HMF synthesis from D-galactose in a biphasic water/methyl isobutyl ketone (MIBK) system catalyzed by $HCl/AlCl_3$. Batch reactions at 112–153 °C with varying catalyst and substrate concentrations yielded up to 49 mol% 5-HMF after 1.5 h at 135 °C. As reviewed in [69], deep eutectic solvents (DES) act as green media for acid-catalyzed conversion of lignocellulosic biomass to 5-HMF and its subsequent transformation to 2,5-DMF, owing to their multifunctional roles as solvents, catalysts, and extractants.

4. Conclusions

2,5-Dimethylfuran (2,5-DMF) has emerged as a promising next-generation biofuel, addressing energy shortages and environmental pollution. Its production from 5-HMF a key biomass-derived platform chemical from lignocellulosic sources has garnered significant global and domestic attention. Numerous studies highlight the efficacy of mono- and bimetallic catalysts, especially those based on non-noble metals such as Ni, Co, and Cu, in enhancing selectivity and conversion under mild conditions. However, developing cost-effective, sustainable, and highly efficient catalysts remains a major challenge for industrial-scale processes. Optimizing multifunctional catalyst design alongside reaction parameters including solvent, hydrogen donor, temperature, pressure, and time is critical to improving 2,5-DMF yields. Integration of theoretical modeling with experimental work further advances mechanistic understanding, accelerating catalyst and process development. In Vietnam, where clean energy demand and biomass industries are rapidly growing, 2,5-DMF holds strong potential as an eco-friendly fuel to support sustainable development and mitigate climate impacts. Thus, intensified research and application of 2,5-DMF production from local biomass are essential to establish an economically and environmentally viable energy source.

Conflict of Interest

The author declares no conflict of interest in this article.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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