catalysts

MDPI

Review

Recent Progress on the Production of Liquid Fuel 2,5-Dimethylfuran via Chemoselective Hydrogenolysis Biomass-Derived 5-Hydroxymethylfurfural

Jiadai He †, Jiayi Peng †, Renhui Ling and Jianjian Wang *

School of Chemistry and Chemical Engineering, State Key Laboratory of Coal Mine Disaster Dynamics and Control, Institute of Advanced Interdisciplinary Studies, Multi-Scale Porous Materials Center, Chongqing University, Chongqing 401331, China; hejiadaichongqing@163.com (J.H.); 15342832428@163.com (J.P.); 18897977059@163.com (R.L.)

* Correspondence: wangjianjian@cqu.edu.cn

† These authors contributed equally to this work.

Abstract: 5-Hydroxymethylfurfural (HMF) is regarded as an important representative of biomass-derived platform chemicals due to its multiple functional groups, including a hydroxyl group, aldehyde group, and furan ring within its molecular structure. Chemoselective hydrogenolysis of HMF to produce high-value-added liquid fuel 2,5-dimethylfuran (DMF) has emerged as a prominent area of research nowadays. The present review provides a comprehensive overview of the recent advancements in catalyst design for efficient DMF production from HMF, with a primary focus on elucidating the key factors influencing the hydrogenolysis reaction. This encompasses an extensive range of catalyst types and reaction conditions. Furthermore, the reaction mechanisms over the active sites of various catalysts are analyzed in depth. Drawing upon the comprehensive summary of existing research, this review discusses the future research prospects of the catalytic hydrogenolysis of HMF and provides valuable insights for the efficient conversion of biomass resources.

Keywords: biomass; 5-hydroxymethylfurfural; 2,5-dimethylfuran; hydrogenolysis; heterogeneous catalysis

check for updates

Academic Editor: Binlin Dou

Received: 16 December 2024

Revised: 27 December 2024

Accepted: 30 December 2024

Published: 31 December 2024

Citation: He, J.; Peng, J.; Ling, R.; Wang, J. Recent Progress on the Production of Liquid Fuel 2,5-Dimethylfuran via Chemoselective Hydrogenolysis Biomass-Derived 5-Hydroxymethylfurfural. *Catalysts* **2025**, *15*, 31. https://doi.org/10.3390/catal15010031

1. Introduction

With the rapid development of the social economy, the swift depletion of fossil resources and the associated environmental issues have garnered widespread attention [1–6]. As a result, the development and application of renewable and clean energy sources such as wind energy, nuclear energy, and biomass energy have become research hotspots [7–9]. Among these, biomass can be used as an alternative to replace limited fossil reserves to produce fuels and chemicals, thereby minimizing environmental problems [10–13]. Biomass, a plant-based material, is the only carbon-based resource in the world that can be continuously regenerated, setting it apart from other renewable energy sources such as hydropower, wind energy, solar energy, and ocean energy. Biomass offers several advantages, including abundant reserves, relatively low cost, wide applications, and broad distribution. Furthermore, the inadequate disposal of biomass can lead to significant environmental concerns. Biomass feedstocks can be converted into various platform compounds through biological or chemical methods, which can then be further catalytically upgraded into high-energy-density and high-value-added chemicals, promoting sustainable development [14–17]. Therefore, to meet the growing demand for fuels and chemicals, the upgrading and conversion of biomass platform chemicals have gradually become a research focus in recent years.

China produces nearly 400 million tons of agricultural and forestry waste annually, with the main components being cellulose (40–50%), hemicellulose (25–35%), and lignin (15–20%). Some organic oxygenated heterocyclic compounds obtained from cellulose and lignocellulosic biomass are considered platform molecules for producing various chemicals, which can be converted into bio-based fuels and chemicals [18–20]. HMF is a derivatives of hexose degradation, and is recognized as an important biomass-derived platform compound [21]. It is the significant furan-based platform molecule with tremendous synthetic potential and excellent reactivity, primarily due to its structural features, such as the aldehyde group, hydroxyl group, and furan ring. These functional groups provide diversity for metal-catalyzed hydrogenation/oxidation reactions, leading to the production of many high value-added chemicals. As shown in Figure 1, 1,2,6-hexanetriol (HTO), 2,5-dihydroxymethylfuran (DHMF), 1,6-hexanediol (HDO), 2,5-dimethyltetrahydrofuran (DMTHF), 2,5-furandicarboxylic acid (FDCA), 2,5-diformylfuran (DFF), levulinic acid (LA), and DMF can be obtained during the selective conversion of HMF [22–25]. Among them, DMF attracts a lot of attention nowadays due to its high energy density (30 MJ/L) and high boiling point (92–94 °C) compared to bio-ethanol. Additionally, DMF is nearly insoluble in water and is easy to store. All of these advantages make it an ideal and promising candidate for liquid fuel due to its properties being close to jet fuel [26,27]. Therefore, various catalytic systems have been designed to selectively produce DMF via HMF hydrogenolysis.

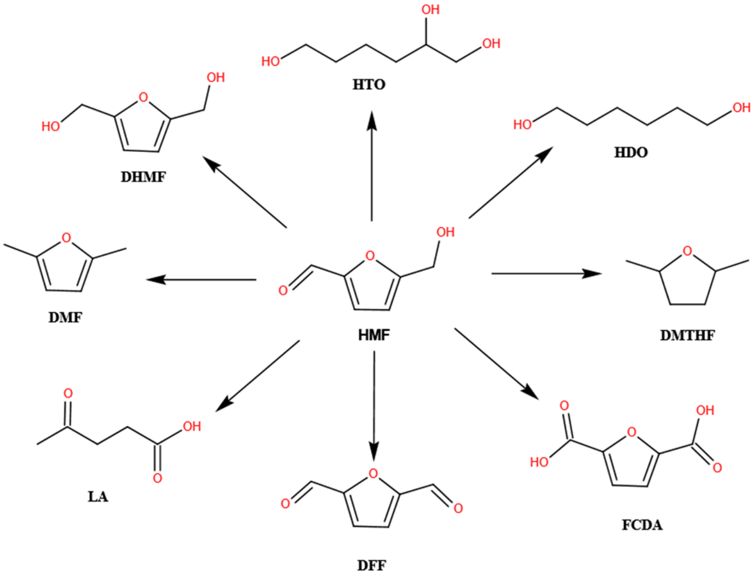

Figure 1. HMF as a platform compound for the synthesis of various chemicals.

As shown in Figure 2, there are two possible pathways for the production of DMF. In pathway 1, HMF is first converted into DHMF by the hydrogenation of the C=O bond, followed by the sequential hydrogenolysis of 5-methyl-furfuryl alcohol (MFA) to produce DMF. In pathway 2, before the hydrogenation of the C=O bond, HMF undergoes hydrogenolysis to form 5-methyl-furfural (5-MF), which is then hydrogenated to MFA, and further hydrogenolysis of the generated MFA produces DMF. During the HMF hydrogenolysis process, the ring hydrogenation or ring-opening reaction also occurs, and many by-products are simultaneously co-generated [28,29]. Therefore, to design a catalyst with active sites to chemoselectively activate special chemical bonds is important to efficiently produce DMF from HMF.

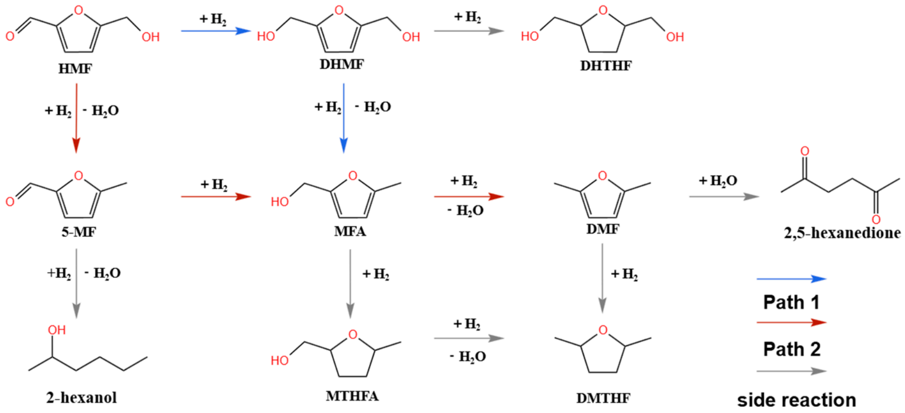

Figure 2. The reaction pathway during the conversion of HMF to produce desired DMF.

Recently, significant advancements have been made in the selective hydrogenolysis of HMF to produce DMF, and several studies also highlight the efficient synthesis of DMF under even milder reaction conditions. In this review, our objective is to summarize these recent developments reported in the literature and elucidate catalysis principles that can guide the design of the catalytic system for the effective conversion of HMF to DMF. Specifically, we will focus on the design of heterogeneous catalysts including both noble and non-noble-metal catalysts in recent years and subsequently explore the correlation between catalyst structure and reaction activity. Ultimately, we aim to provide valuable insights for readers to devise more efficient, selective, environmentally friendly, and mild catalytic systems in their future endeavors.

2. Production of DMF via Selective Hydrogenolysis of HMF over Noble Metal-Based Catalyst

Noble metal-catalysts, due to their high activity, have been widely applied in the hydrogenolysis of HMF under mild reaction conditions [30,31]. Tables 1 and 2 summarize the recently reported noble metal-based mono-metallic and bimetallic catalysts for the selective conversion of HMF to DMF, respectively.

Table 1. Comparison of various noble metal-based mono-metallic catalysts for catalytic conversion of HMF to DMF.

Catalyst	Solvent	HMF Concentration (mg/mL)	Reaction Conditions	Conversion (%)	DMF Yield (%)	References
Ru/C	IPA	10.0	190 °C/2.0 MPa H_2/6 h	97.0	81.0	[32]
Ru/CNTs	Dioxane	5.0	150 °C/0.2 MPa H_2/1 h	97.0	83.5	[33]
Pt/CNTs-ALD	1-Butanol	12.5	160 °C/1.0 MPa H_2/10 h	>99	47.0	[34]
Pt/C	1-Propanol	10.0	180 °C/3.3 MPa H_2	>99	68.5	[35]
Pt/rGO	1-Butanol	21.0	120 °C/3.0 MPa H_2/2 h	>99	73.2	[36]
Pt@HPS	1-Butanol	42.7	180 °C/0.1 MPa H_2/2 h	>99	98.0	[37]
Pd/C	Dioxane	12.6	118 °C/0.2 MPa H_2/15 h	>99	85.0	[38]
Pd/C	THF	64.0	80 °C/2.0 MPa H_2/24 h	>99	95.6	[39]
Pd/C	IPA	3.9	170 °C/2.0684 MPa H_2/4 h	>99	99.0	[40]
Pd/MOF-808	THF	18.9	100 °C/1.0 MPa H_2/3 h	>99	>99.0	[41]

2.1. *Noble Metal-Based Mono-Metallic Catalyst*

In recent years, significant efforts have been dedicated to the production of DMF. Ru-based catalysts are widely employed for the hydrogenolysis of HMF to DMF and exhibit substantial potential in biomass conversion to biofuels.

Jae et al. [32] and Priecel et al. [33] reported the selective hydrogenolysis of HMF over Ru/C (Ru supported on carbon) and Ru/CNTs (Ru supported on carbon nanotubes) catalysts prepared by the incipient wetness impregnation method. Under reaction conditions of 190 °C and 150 °C, the DMF yields reached 81.0% and 83.5%, respectively, with HMF conversions around 97.0%. Moreover, Jae et al. [42] investigated the reaction pathway of Ru-based catalysts by using a mixture of commercial Ru/C and RuO_2 as catalysts for the hydrogenolysis of HMF to DMF, studying the structure–performance relationship. It was found that the main component in the catalyst was RuO_2, and the synergistic effect between Ru and RuO_2 was crucial for DMF production. Consequently, Tzeng et al. [43] further explored the impact of carbon properties on the growth of Ru after thermal reduction and the electronic configuration of Ru on carbon supports. Using carbon materials with different surface textures, such as microporous, mesoporous, and non-porous carbon black, as catalyst supports, they found that the nature of carbon materials influenced the formation of Ru nanoparticles during thermal reduction and the interaction between Ru and the carbon surface. Thus, the catalytic pathway of HMF hydrogenolysis to DMF using carbon-supported Ru catalysts was highly related to the electronic structure of Ru nanoparticles. Additionally, the types of support and reaction conditions should be well controlled to obtain a higher yield of DMF over Ru-based catalysts.

Pt-based catalysts have attracted widespread attention due to their unique electrochemical properties. These properties are attributed to the large radial expansion of the d orbitals [44], which provides high selectivity for the hydrogenation of the C=O bond. However, because Pt is highly active, it is difficult to control the hydrogenation rate. This often leads to further hydrogenation reactions, resulting in by-products. Consequently, carbon materials are among the most commonly used supports for Pt-based catalysts to suppress by-products in this reaction, including graphite, carbon black, activated carbon, fullerenes, carbon nanotubes, and carbon nanofibers [45–47]. The π-electrons from the graphene layers of carbon-based materials transfer to the Pt nanoparticles (NPs), enhancing the selectivity towards the C=O bond [45,48]. Building upon previous research on noble metal Pt supported on carbon materials, Wang et al. [34] investigated a series of Pt catalysts supported on different carbon materials, including multi-walled CNTs (MWCNTs), reduced graphene oxide (rGO), graphitic carbon nitride (g-C_3N_4), and biochar (BC), to study the influence of carbon supports. They found that the interaction between Pt and carbon supports was the primary factor determining the main products in the selective hydrogenation of HMF. Due to the relatively strong interaction between Pt and multi-walled CNTs, the resultant catalyst was effective for the selective hydrogenolysis of HMF to DMF. The primary product of the Pt/CNTs-ALD catalyst was DMF, with a yield of 47.0%. As shown in Table 1, when Pt/C and Pt/rGO were used as catalysts, the DMF yields were only 68.5% and 73.2%, respectively [35,36]. In contrast, other metal oxide supports, such as SiO_2 and Al_2O_3, did not possess this unique property. Moreover, Wang et al. [49] studied Pt catalysts using alkaline metal oxide MgO as the support, which exhibited 99.0% selectivity for DHMF but could not convert it to DMF. Meanwhile, Pt catalysts using typical acidic metal oxide TiO_2 as the support showed 28.0% selectivity for DHMF and 10.0% selectivity for 5-MF, with the primary products being ring-opened compounds. Therefore, Pt catalysts supported on these metal oxides exhibited poor catalytic performance.

Catalysts with a core-shell structure offer several advantages, including high activity, high selectivity, enhanced stability, strong tunability, reduced metal loss, and improved mass transfer efficiency [50]. These features make core-shell structure catalysts particularly advantageous in hydrodeoxygenation (HDO) reactions. The shell material effectively protects the core material, preventing it from erosion and poisoning during the reaction while also providing more active sites and higher reaction selectivity. By adjusting the composition and structure of the core and shell materials, the catalytic performance can be further optimized, thereby improving hydrodeoxygenation efficiency. Wang et al. [37]

reported a simple method for preparing bimetallic PtCo nanoparticles with a diameter of 3.6 ± 0.7 nm inside hollow carbon spheres (HCS). As shown in Figure 3, platinum nanoparticles with a uniform particle size of 1.2 ± 0.3 nm were firstly encapsulated in hollow polymer spheres (Pt@HPS). Cobalt ions were then introduced via the ion exchange method to form Pt@HPS-Co^{2+}. In the final step, the polymer product Pt@HPS-Co^{2+} was calcined at 500 °C under a H_2/Ar (5%/95%) atmosphere, resulting in the formation of PtCo bimetallic nanoparticles encapsulated within HCS. Due to the carbon nanospheres maintaining an exceptionally small particle size and enabling uniform alloyed PtCo nanoparticles, the resultant PtCo@HCS catalyst achieved a DMF yield of up to 98.0% after a 2 h reaction at 180 °C under 0.1 MPa of H_2. The structure of this material is not only intriguing, but the synthesis method described in the report also offers a pathway for designing diverse core-shell structures by encapsulating bimetallic nanoparticles within hollow carbon structures.

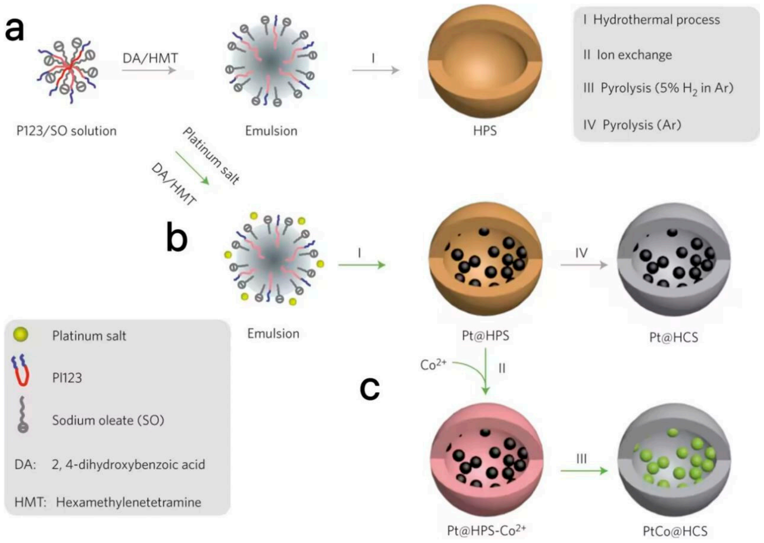

Figure 3. Synthetic process of (**a**) HPS, (**b**) Pt@HCS, and (**c**) PtCo@HCS [37]. Copyright © 2014, Springer Nature Limited.

Pd-based catalysts are another common type of noble metal catalysts used in the hydrogenation and deoxygenation of HMF, and they have shown some remarkable results. Pd-based catalysts can selectively promote the hydrogenation of the aldehyde group in HMF, and by modifying the support, adjusting the metal particle size, and introducing other metals, the hydrogenation activity of Pd-based catalysts towards the aldehyde group can be significantly improved. Besson et al. [51] have summarized the universality of catalysts with Pd nanoparticles supported on carbon carriers in the selective hydrogenation of HMF. In fact, Pd-based catalysts have been extensively studied to reduce the oxygen content in HMF under mild conditions (Table 1), but in most cases, the resulting products are mixtures, making separation costly. However, it is noteworthy that formic acid plays multiple roles in hydrogenation/hydrogenolysis and in suppressing decarbonylation. Therefore, Mitra et al. [38] explained the different pathways of hydrogenation/deoxygenation and the decarbonylation/hydrogenation of HMF on Pd/C catalysts. They also used formic acid as a hydrogenation promoter and achieved an 85% DMF yield after 15 h at 118 °C under an external hydrogen pressure of 0.2 MPa. However, despite the relatively mild reaction conditions, the corrosiveness of formic acid, the long reaction time, and the difficulty in separating it from the reaction mixture pose significant challenges and can lead to unwanted by-products. To address the need for a greener and more efficient process without adding any other reagents, Yang et al. [39] achieved over 95.6% DMF yield at 80 °C, using a Pd/C catalyst prepared in γ-valerolactone (GVL) for the conversion of HMF. Similarly, Solanki et al. [40] developed a Pd/C catalyst using an improved wet impregnation method without any additives. The uniformly dispersed Pd nanoparticles on the activated carbon provided adsorption sites to enhance the hydrogenation of HMF. The synergistic effect of Pd-PdO formed in the catalyst during the hydrogenation/deoxygenation mechanism also contributed to the improved catalytic activity, achieving a complete conversion of HMF with 99% yield to DMF within just 4 h. The high performance under mild conditions was attributed to the weak interaction between the metal and ester in the catalyst, which stabilized the metal particles. More importantly, the weak interaction prevented the oxidation of Pd^0 and altered the electronic state of Pd. Zhang et al. [41] also innovated with Pd-based catalysts, focusing on the support to create new approaches for low-temperature, high-activity Pd catalysts. They prepared a Pd/MOF-808 catalyst using a simple stepwise impregnation method, with Pd NPs supported on MOF-808. This catalyst efficiently converted HMF to DMF with a 99% yield within 3 h at 100 °C without any additives.

In summary, some noble metal (Pt- and Pd-based) catalysts have demonstrated excellent catalytic performance in the hydrogenolysis of HMF to DMF, achieving high DMF yields. These noble metal catalysts, such as Ru, Pt, and Pd, have become the focus of research for this reaction due to their efficient hydrogenation capability and selectivity. However, several challenges remain before the large-scale production of DMF can be realized, including high H_2 pressure and reaction temperature, the need for acid additives, catalyst stability, and the high usage of noble metals. Nonetheless, the high selectivity and activity of noble metal catalysts make them central to the research on HMF hydrogenolysis to DMF. Despite some challenges, their excellent catalytic performance lays a solid foundation for future industrial applications.

2.2. Noble Metal-Based Bimetallic Catalyst

Noble metal-based single-metal catalysts often suffer from poor stability, primarily due to the weak interaction between the support and metal nanoparticles. This weak interaction can lead to the leaching of metal nanoparticles during the catalytic process. To enhance the interaction between the support and metal nanoparticles, doping with another metal can be an effective strategy to improve catalyst stability [52]. To further enhance the performance of noble metal-based catalysts, it is crucial to introduce a suitable second metal element into Ru, Pt, Pd, and other noble metal-based catalysts. Due to geometric and electronic effects, bimetallic catalysts exhibit different properties from single-metal catalysts. Bimetallic systems offer additional degrees of freedom, allowing for the adjustment of catalytic performance by altering the composition and size of their geometric and electronic structures [53,54]. Therefore, compared to single-metal catalysts, bimetallic catalysts have a broader potential for performance regulation and higher catalytic efficiency.

As shown in Table 2, bimetallic catalysts (such as Ru-Co, Pt-Co, Pd-Au, and Fe-Pd) have been developed for the hydrogenolysis of HMF to DMF. In 2014, Zu et al. [55] synthesized a Ru/Co_3O_4 catalyst via a simple co-precipitation method. This catalyst exhibited excellent catalytic performance under relatively low reaction temperatures and H_2 pressures (130 °C, 0.7 MPa) in tetrahydrofuran (THF) solvent, achieving a DMF yield of 93.4%. During the reaction, Ru was responsible for hydrogenation, while CoO_x played a role in the absorption of hydrogenation products and the cleavage of C-O bonds. Gao et al. [56] prepared a RuCo bimetallic catalyst supported on microspheres using a simple one-pot embedding method. The strong interaction between Ru species and the support in the catalyst led to the uniform distribution of RuCo NPs and abundant surface defects (such as oxygen vacancies and Co^{2+} species) on the CoO_x support. This facilitated the dissociation of H_2 into active hydrogen and the adsorption/activation of the C=O bond in HMF, resulting in excellent catalytic performance for the hydrogenolysis of HMF to

DMF. The RuCo/CoO_x catalyst achieved a yield of 96.5% at 200 °C under 0.5 MPa of H_2 after 2 h. Similarly, Esen et al. [57] studied the synergy and selectivity of Ru and Co in hydrogenation/hydrogenolysis reactions. They prepared a novel sol-gel Ru-Co/SiO_2 catalyst and tested it for HMF hydrogenolysis to DMF. At 140 °C for 4 h under a hydrogen pressure of 0.2 MPa, the DMF yield exceeded 99%.

Table 2. Comparison of various noble metal-based bimetallic catalysts for catalytic conversion of HMF to DMF.

Catalyst	Solvent	HMF Concentration (mg/mL)	Reaction Conditions	Conversion (%)	DMF Yield (%)	References
Ru/Co_3O_4	THF	25.0	130 °C/0.7 MPa H_2/24 h	>99	93.4	[55]
RuCo/CoO_x	Dioxane	50.4	200 °C/0.5 MPa H_2/2 h	>99	96.5	[56]
Ru-Co/SiO_2	THF	5.0	140 °C/0.2 MPa H_2/4 h	>99	>99	[57]
Pt-Co/MWCNTs	1-Butanol	16.7	160 °C/0.1 MPa H_2/8 h	>99	92.3	[28]
Pt-Co/C	1-Propanol	10.0	160 °C/3.3 MPa H_2/	>99	98.0	[58]
Fe-Pd/C	THF	12.6	150 °C/2.0 MPa H_2/2 h	>99	88.0	[59]
PdAu/C	THF	12.6	60 °C/0.1 MPa/36 h	>99	96.0	[60]

Pt-based catalysts, similar to Ru-based ones, have high selectivity for hydrogenating the C=O bond and are widely used in selective hydrogenation/hydrogenolysis reactions. However, if the activity of Pt-based catalysts is too high, DMF may undergo over-hydrogenation, leading to a decrease in DMF yield. Therefore, it is important to introduce an appropriate second metal element or promoter into Pt-based catalysts. Wang et al. [28] prepared Pt/MWCNTs single-metal catalysts and Pt-Co/MWCNTs bimetallic catalysts (Figure 4a) via ALD. After the introduction of Co, the Pt-Co/MWCNTs catalyst achieved a DMF yield of 92.3% after 8 h at 160 °C with 0.1 MPa of H_2. The authors also revealed that a higher Co loading could create steric hindrance, affecting the activity of the Pt-Co bimetallic catalyst. Therefore, moderate Co loading can suppress by-product formation and improve DMF yield. Through control experiments and density functional theory (DFT) calculations, they demonstrated the synergistic effect between bimetallic Pt-Co NPs and the MWCNTs support, enhancing charge transfer between Pt NPs and Co NPs, as shown in Figure 4b–d. Luo et al. [58] synthesized a bimetallic Pt-Co/C catalyst via a solvothermal method, which was superior to the traditional wet impregnation method. Experimental results obtained in a continuous flow reactor with a 1-propanol solvent at 160 °C with 3.3 MPa of H_2 showed that the Pt_3Co_2/C catalyst achieved a DMF yield of 98.0%. Such a catalyst maintained its catalytic performance for a period of at least 14 h under a LHSV of 0.2 min^{-1} (LHSV = HMF mass/((catalyst mass) × (time))). Characterization results indicated that Pt_3Co_2 had a special structure, consisting of a Pt-rich core and a monolayer Co oxide surface (as shown in Figure 5). This structure can prevent side reactions, further inhibiting the over-hydrogenation and ring-opening of the furan ring, while providing active sites for the effective conversion of HMF to DMF, thereby enhancing selectivity for DMF.

Pd-based catalysts can catalyze the hydrogenolysis of HMF at temperatures below 100 °C in the presence of homogeneous acids. However, homogeneous acids are difficult to separate from the reaction mixture and can lead to unwanted by-products [38,61]. Therefore, the introduction of other metals can significantly enhance the aldehyde hydrogenation activity of Pd-based catalysts and increase the selectivity for DMF. Nishimura et al. [60] prepared PdAu/C catalysts with different Pd/Au molar ratios (x/y). Under atmospheric hydrogen pressure with the help of homogeneous HCl acid, they found that the $Pd_{50}Au_{50}$/C catalyst achieved a 99% HMF conversion and a 96.0% DMF yield after 36 h. As previously mentioned, the use of acid additives is not environmentally friendly.

Therefore, Talpade et al. [59] successfully developed a magnetically separable Fe-Pd/C bimetallic nanoparticle catalyst, which achieved a high conversion and selectivity without the use of liquid acids. This catalyst not only showed excellent selectivity for DMF but also helped reduce noble metal consumption, making the catalyst more cost-effective. Under conditions of 150 °C with 2 MPa of H_2, the HMF conversion reached 100% along with a maximum DMF yield of 88.0% within 2 h.

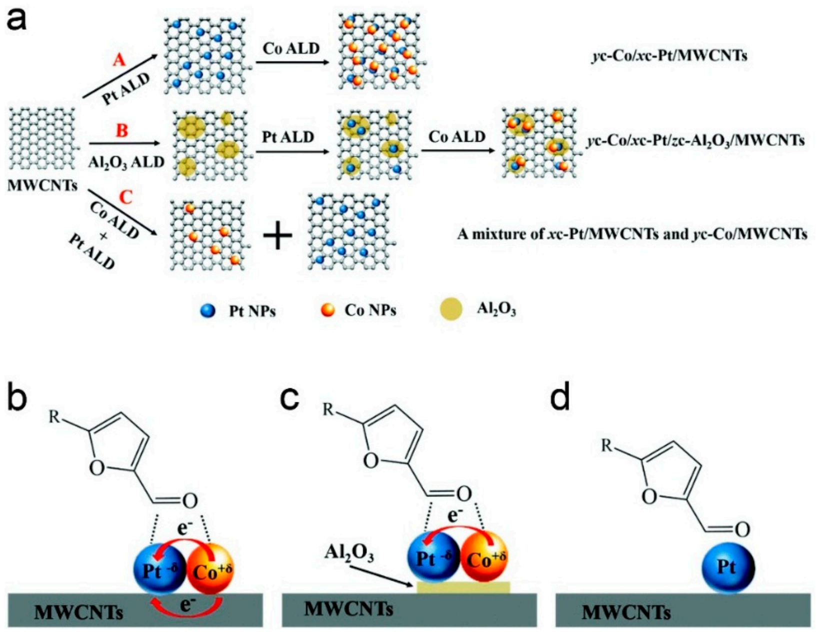

Figure 4. (**a**) Scheme for the synthesis of these three catalysts. Adsorption models of reactant on (**b**) *y*c-Co/*x*c-Pt/MWCNTs, (**c**) *y*c-Co/*x*c-Pt/zc-Al_2O_3/MWCNTs, and (**d**) a mixture of *x*c-Pt/MWCNTs and *y*c-Co/MWCNTs. Recombined from Reference [28]. Copyright © 2018, Royal Society of Chemistry.

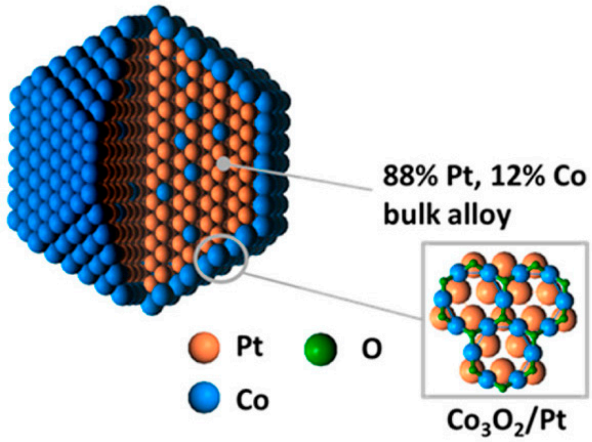

Figure 5. The special structure of Pt_3Co_2 [58]. Copyright © 2016, American Chemical Society.

Bimetallic catalysts typically exhibit higher catalytic activity and selectivity, enabling efficient HMF conversion under milder reaction conditions. Additionally, the design of bimetallic catalysts provides more tuning options, allowing the optimization of catalytic performance and enhancement of catalyst stability by adjusting the proportion and distribution of the two metals. However, noble metal-based bimetallic catalysts also have some drawbacks. First, the preparation process is more complex, requiring a precise control of metal proportions and distribution. Second, the involvement of two noble metals significantly increases material costs, which could become an economic barrier to large-scale applications. Nonetheless, the excellent performance and wide tuning potential of noble metal-based bimetallic catalysts make them promising candidates for reactions like HMF hydrogenolysis to DMF.

3. Production of DMF via Selective Hydrogenolysis of HMF over Non-Noble-Metal-Based Catalyst

As mentioned above, most catalysts used for converting HMF to DMF involve noble metals such as Ru, Pt, and Pd. While noble metal-based catalysts exhibit excellent performance in the hydrogenation of biomass-derived HMF, their high cost somewhat limits their large-scale industrial application. Therefore, from an economic perspective, it is crucial to develop a series of low-cost and highly efficient non-noble-metal catalysts (such as Ni, Co, Cu, etc.) as alternatives to noble metals for the hydrogenation systems of HMF [62–65]. The following sections will discuss these types of catalysts in detail, and the catalytic performances of these catalysts are summarized in Tables 3 and 4.

Table 3. Comparison of various non-noble metal-based mono-metallic catalysts for catalytic conversion of HMF to DMF.

Catalyst	Solvent	HMF Concentration (mg/mL)	Reaction Conditions	Conversion (%)	DMF Yield (%)	References
Ni/C	THF	18.0	180 °C/4.5 MPa H_2/2 h	>99	75.0	[66]
Ni/NDC	Ethanol	6.3	150 °C/8.0 MPa H_2	>99	80.0	[67]
Ni/TiO_2	Dioxane	33.3	220 °C/3.0 MPa H_2/2 h	>99	85.0	[68]
Raney Ni	Dioxane	42.9	180 °C/1.5 MPa H_2/15 h	>99	88.5	[69]
NiSi-PS	Dioxane	39.5	150 °C/1.5 MPa H_2/2 h	>99	90.2	[70]
Ni-Al_2O_3	Dioxane	42.9	180 °C/1.2 MPa H_2/4 h	>99	91.5	[71]
Co/Beta-DA	THF	10.5	150 °C/1.5 MPa H_2/3 h	>99	83.1	[72]
Co@CoO	THF	30.0	130 °C/1 MPa H_2/2h	>99	89.0	[73]
Co/Mix-ZrO_2	THF	10.0	130 °C/1.0 MPa H_2/2 h	>99	90.7	[74]
Co/rGO	Ethanol	25.0	200 °C/2.9 MPa H_2/1 h	>99	94.1	[75]
$CoNC_x$/NiFeO	THF	25.0	180 °C/1.0 MPa H_2/6 h	>99	94.3	[76]
Co@NGs	Ethanol	9.0	200 °C/2.0 MPa H_2/4 h	>99	94.7	[77]
Cu/Al_2O_3	Methanol	14.3	240 °C/6 MPa H_2/6 h	>99	73.9	[78]
Cu/SBA-15	THF	12.6	180 °C/2.0 MPa H_2/8 h	>99	90.0	[79]
Cu/ZnO	Dioxane	42.9	220 °C/1.5 MPa H_2/5 h	>99	91.8	[31]
Cu/Fe_2O_3-Al_2O_3	THF	12.6	148 °C/0.2 MPa H_2/10 h	>99	93.9	[80]

3.1. Non-Noble Metal-Based Mono-Metallic Catalyst

A Ni-based catalyst is often used for hydrogenation reactions due to its relatively high activity compared to other transition metal-based catalysts since it can facilitate the cleavage of C=O bonds in biomass-derived molecules. Therefore, some researchers have chosen Ni-based catalysts for the hydrogenolysis of HMF to DMF. Carbon materials are often used as carriers for Ni-based catalysts due to their large pore volume, high surface area, chemical inertness, mechanical stability, and thermal stability [81]. Gyngazova et al. [66] prepared a series of Ni/C catalysts with different Ni loadings using the wet impregnation method. The 10 wt% Ni/C catalyst, which exhibited the best performance, achieved 100% HMF conversion and a 75.0% DMF yield after 2 h at 180 °C (Table 3). Kinetic analysis showed that the rate-determining step of the reaction was the hydrogenation of HMF to DHMF. Additionally, most side reactions were kinetically hindered due to the high activation energy, leading to good selectivity for DMF over Ni/C. Similarly, Brandi et al. [67] used a Ni/NDC catalyst (35 wt% loading of Ni supported on nitrogen-doped carbon) in a continuous flow system to study the conversion of HMF under different hydrogen pressures, reaction temperatures, and space times. Under optimal conditions (150 °C, 8.0 MPa of H_2), the HMF conversion reached above 99.0%, and the DMF yield was as high as 80.0% with a LHSV of 0.05 S^{-1}. High H_2 pressure was found to be crucial for the efficient production of DMF from HMF. Kong et al. [69] prepared a Raney Ni catalyst for the hydrogenolysis of HMF.

At 180 °C, the conversion of HMF reached 100%, with a DMF yield of 88.5%. Following this work, they prepared Ni NPs embedded layered nickel silicate (NiSi-PS) catalyst by tuning the synergy between metal and acid sites [70], which showed excellent performance in HMF hydrogenolysis, especially under low-temperature conditions (130–150 °C). The NiSi-PS catalyst relied on the synergy between highly dispersed Ni NPs and acid sites formed by the coordination of unsaturated Ni(II) sites located in the layered nickel silicate structure, achieving efficient low-temperature hydrogenolysis. Compared to the traditional impregnated Ni/SiO_2 catalyst, NiSi-PS achieved a 90.2% DMF yield at 150 °C with 1.5 MPa of H_2 after 2 h. Although the activity of the Ni-contained catalyst is not as high as that of Pt or Pd, its moderate activity helps avoid a further hydrogenation of the products, and the main product of the reaction can be controlled by adjusting the reaction conditions.

In addition to carbon materials, metal oxides and molecular sieves are also commonly used as supports for Ni catalysts. Kong et al. [71] first proposed a Ni-Al_2O_3 catalyst derived from layered double hydroxides (LDHs), which could selectively catalyze the conversion of HMF to DMF, DMTHF, and others. By adapting co-precipitation method, they prepared a highly dispersed and structurally excellent LDH precursor that enabled a high dispersion of Ni species. Furthermore, the metal Ni and acid sites on the obtained catalyst could be finely tuned by annealing at different temperatures, adjusting their dispersibility, reducibility, and the interaction between Ni and Al_2O_3. Finally, by adjusting the surface active sites and reaction conditions, the selective conversion of HMF to the desired products could be customized. The material annealed at 850 °C achieved a DMF yield of 91.5% under the conditions of 180 °C with 1.2 MPa of H_2 for 4 h. Recently, Przydacz et al. [68] synthesized Ni/TiO_2 catalysts using different types of TiO_2 materials (with varying polymorphic properties and morphologies) as supports and studied their activities in HMF hydrogenolysis. The results showed that the morphology and crystal structure of TiO_2 significantly influenced the characteristics of the loaded Ni nanoparticles and their interaction strength with the support. The rutile-type TiO_2 stabilized larger Ni microcrystals, enhanced the Ni-Ti interaction, and increased hydrogen adsorption capacity, thus improving catalytic activity. Although DMF was the main product, the production of DMTHF was also promoted. In contrast, the anatase-type TiO_2-supported catalyst stabilized smaller Ni metal particles and, due to the higher acidity and larger surface area of the support, achieved a high DMF yield of 85.0% at 220 °C with 3 MPa of H_2, after 2 h. Therefore, by adjusting the characteristics of TiO_2, the reaction selectivity can be controlled to obtain the desired products.

Cobalt-based catalysts have also attracted increasing attention due to their low cost, abundance, and excellent catalytic activity in C=O bond hydrogenation reactions. As shown in Table 3, many studies have reported the application of cobalt catalysts in the hydrogenation of HMF to DMF. Chen et al. [72] synthesized a series of Co/Beta-DA (Co supported on dealuminated Beta zeolite) catalysts with varying calcination temperatures and Co contents, among which the 20 wt% Co/Beta-DA catalyst exhibited the best catalytic performance. A DMF yield of 83.1% was achieved at 150 °C with 1.5 MPa of H_2 after 3 h. The microenvironment and particle size of cobalt were closely related to the calcination temperature during catalyst preparation (Figure 6). After calcination at 450 °C, cobalt existed in the form of isolated active sites on the zeolite framework, while CoO_x was distributed on the surface and pores of the zeolite. After H_2 reduction, most of the Co was reduced to metallic cobalt. A series of characterizations revealed that compared to other topologies (FAU, MOR, and MFI), Beta-DA zeolite was the best support for HMF conversion. The catalyst support not only plays a crucial role in the hydrogenation reaction of HMF, significantly influencing the catalytic activity of the metal center, but also greatly affects its surface and electronic properties due to its crystal structure. Therefore, catalytic activity can be regulated by adjusting the crystal phase of the support. Xiao et al. [74] prepared a series of Co/ZrO_2 catalysts with monoclinic, tetragonal, and mixed phases of ZrO_2 as the supports, labeled as Co/m-ZrO_2, Co/t-ZrO_2, and Co/Mix-ZrO_2, respectively. These catalysts exhibited different activities in the conversion of HMF to DMF. Characterization analysis and catalytic performance showed that Co/t-ZrO_2 exhibited a stronger metal–support interaction, leading to electron transfer from cobalt to Zr(III), resulting in a higher concentration of partially reduced Zr(III) species and oxygen vacancies, which led to a higher carbonyl hydrogenation activity than Co/m-ZrO_2. However, the sequence of hydrogenolysis rates of the two catalysts was reversed, determined by the total acidity of the catalyst. The Co/Mix-ZrO_2 catalyst combined the advantages of both monoclinic and tetragonal phases, exhibiting high hydrogenation and hydrogenolysis activities. This could be attributed to the synergy between the hypoxic Zr^{3+}-V_O center in t-ZrO_2 and the abundant acid sites in m-ZrO_2, as well as the promotion from the high specific surface area. Under the conditions of 130 °C and 1 MPa of H_2, the Co/Mix-ZrO_2 catalyst achieved a DMF yield of 90.7%.

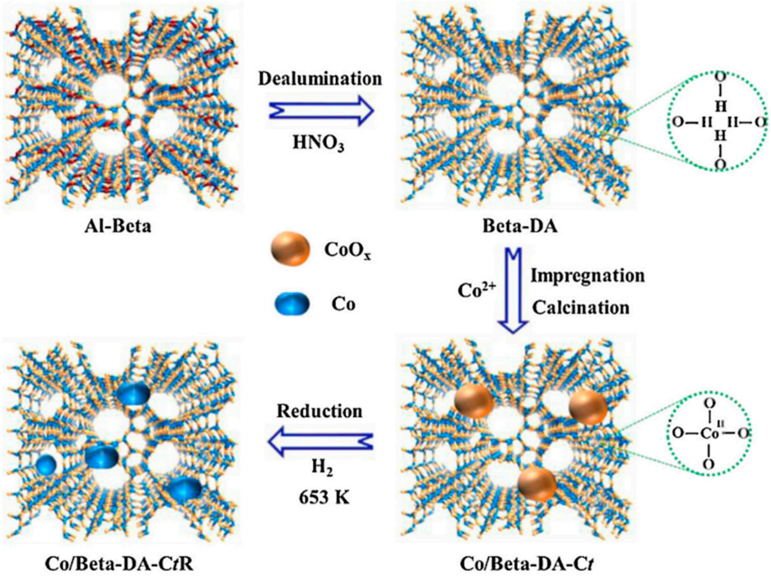

Figure 6. Illustration of the synthetic process of the Co/Beta-DA-C*t*R catalyst [72]. Copyright © 2020, Elsevier B.V.

Traditional non-noble-metal-supported catalysts often face challenges such as low selectivity and catalyst deactivation during HMF conversion. Many researchers are dedicated to developing novel catalysts, among which core-shell structured catalysts have gained significant attention due to their excellent stability and activity. Shuang et al. [73] prepared a Co@CoO core-shell catalyst. Firstly, the precursor was obtained by the co-precipitation method, and then calcined in air at 450 °C for 4 h to obtain Co_3O_4, which was further reduced to Co@CoO. This catalyst consisted of a metallic Co core and a CoO shell, forming a unique core-shell structure. The structure significantly enhanced the stability and selectivity of the catalyst, enabling efficient hydrogenolysis of HMF to DMF under mild conditions. The high activity of the Co@CoO catalyst arose from the unique CoO species with suitable oxygen vacancies, which strongly adsorbed HMF and catalyzed the heterolytic splitting of H_2, generating highly active $H^{\delta-}$ species. Moreover, the core-shell structure improved the electronic environment and surface activity of the metal center, enhancing catalytic performance while suppressing the formation of by-products. Among the catalysts studied, Co@CoO-250 exhibited the best performance, achieving an 89.0% DMF yield at 130 °C after 2 h, while maintaining excellent activity and stability after multiple recycling cycles.

Yang et al. [75] synthesized a Co/rGO catalyst via an impregnation–calcination method. In a batch reactor at 200 °C with 2 MPa of H_2, Co/rGO could afford 100% HMF conversion with 94.1% DMF yield within 1 h. The study showed that the new active sites formed by Co atoms, Co clusters, and graphene planes exhibited good hydrogenolysis activity. The synergy between Co/C and CoO_x with rGO enabled the Co/rGO catalyst to demonstrate excellent catalytic performance in several aspects, including high C=O/C-O bond cleavage specificity, excellent catalytic activity, and reusability. Xia et al. [76] prepared a $CoNC_x$/NiFeO catalyst by adsorbing cobalt(II) phthalocyanine (CoPc) onto ultrathin NiFe-LDHs, followed by pyrolysis at 550 °C under a nitrogen atmosphere for 5 h. The $CoNC_x$/NiFeO catalyst exhibited excellent catalytic performance under mild reaction conditions (180 °C, 1.0 MPa of H_2, and 6 h), achieving a 99.8% HMF conversion and 94.3% DMF yield. Wang et al. [77] prepared a Co@NGs catalyst with the carbonization method, where metallic Co was encapsulated by nitrogen-doped graphene (NGs) as shown in Figure 7. Experimental results showed that the Co@NGs catalyst exhibited nearly 100% HMF conversion and 94.7% DMF yield under the conditions of 200 °C with 2 MPa of H_2 after 4 h, significantly outperforming conventional nitrogen-doped carbon-supported Co catalysts. This excellent performance was attributed to the strong electronic interaction at the interface between metallic cobalt and doped nitrogen, and also to the fact that the graphene shell effectively inhibits the aggregation and leaching of Co nanoparticles, maintaining the catalytic activity and stability of metallic Co.

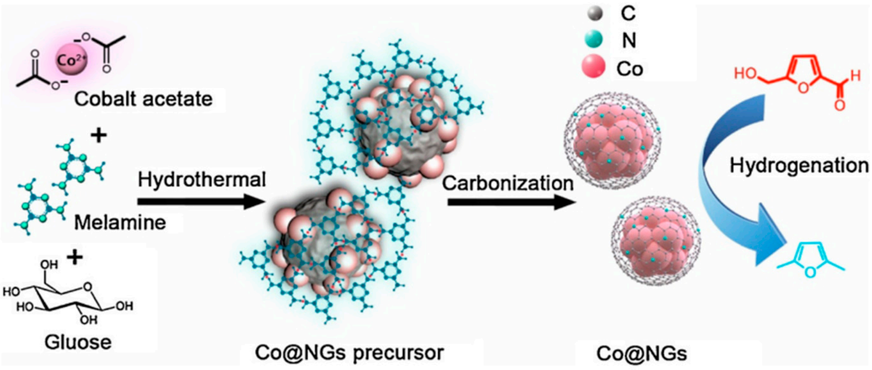

Figure 7. Scheme for the synthesis of Co@NGs catalyst [77]. Copyright © 2019, Elsevier B.V.

Compared to Ni-based or Co-based catalysts, Cu-based catalysts exhibit better selectivity for DMF because Cu can exert a strong repulsive effect on the carbonyl carbon atom, showing a higher affinity for C=O bonds than for C=C bonds. This means that Cu-based catalysts are superior for C=O hydrogenation and have a lesser impact on ring addition and decarbonylation. Zhang et al. [78] prepared a series of Cu-based catalysts supported on different oxides (Al_2O_3, ZnO, ZrO_2, and CeO_2) and studied their performance in the hydrogenolysis of HMF using methanol as a hydrogen donor. It was found that Cu/Al_2O_3 exhibited a relatively higher DMF yield compared to other catalysts, attributed to its smaller copper particles, stronger support acidity, and the ability to promote in situ conversion of methanol into more active hydrogen species. A DMF yield of 73.9% was achieved at 240 °C in methanol solvent after 6 h. Esteves et al. [80] studied the effect of different metal oxide-supported Cu catalysts on the selective hydrogenation of HMF to DMF, concluding that the properties of metal dispersion and acidic sites play a crucial role in catalytic activity. They found that Cu/Fe_2O_3-Al_2O_3 achieved an approximately 90% DMF yield at 148 °C within 10 h. In addition, Lakshmi et al. [79] studied the application of molecular sieves as Cu-based supports for the hydrogenolysis of HMF to DMF. They found that 15 wt% Cu/SBA-15 catalyst showed high activity for DMF production, affording a 90.0% DMF yield at 180 °C with 2 MPa of H_2 for 8 h. Additionally, Zhu et al. [31] developed a Cu/ZnO catalyst via a simple co-precipitation method, and a DMF yield of up to 91.8% can be achieved at 220 °C with 1.5 MPa of H_2 for 5 h, resulting from a high concentration of surface Cu, suitable support acidity, and favorable microstructure.

Overall, the low cost and abundant resources of non-noble-metal-based catalysts help reduce production costs and reliance on precious metals. However, non-noble-metal catalysts also encounter several challenges compared to their noble metal counterparts, including relatively lower activity and more stringent reaction conditions. These issues warrant further investigation and resolution in future research efforts.

3.2. Non-Noble Metal-Based Bimetallic Catalyst

Although single non-noble-metal catalysts have shown certain catalytic activity in the hydrogenolysis of HMF to DMF, they also present some challenges. For instance, these catalysts often require harsher reaction conditions to achieve optimal conversion, which increases energy consumption and can lead to the corrosion and wear of the equipment. Additionally, single non-noble-metal catalysts tend to lead to over-hydrogenation during the reaction, resulting in a significant amount of by-products that lower the yield of the desired DMF product. To address these issues, researchers have started exploring bimetallic catalysts using two non-noble-metals as the active sites that utilize the synergistic effect between two metal species to enhance catalytic activity and selectivity (Table 4). These bimetallic catalysts not only enhance reaction efficiency but also demonstrate better resistance to poisoning and sintering, extending the catalyst's lifespan [82,83]. Furthermore, by adjusting the metal ratio and the support, catalytic performance can be further optimized to meet different reaction conditions. These advantages make bimetallic catalysts promising candidates for HMF conversion to DMF.

Table 4. Comparison of various non-noble metal-based bimetallic catalysts for catalytic conversion of HMF to DMF.

Catalyst	Solvent	HMF Concentration (mg/mL)	Reaction Conditions	Conversion (%)	DMF Yield (%)	References
Ni-Cu/SBA-16	THF	10.0	210 °C/2.0 MPa H_2/4 h	>99	60.7	[63]
Cu-Co/Al_2O_3	THF	15.8	220 °C/3.0 MPa H_2/8 h	>99	78.0	[84]
Co_x-Cu@C	IPA	16.7	160 °C/2.5 MPa H_2/3 h	>99	85.0	[85]
Cu-Fe alloy	IPA	3.9	170 °C/2.0 MPa H_2/4 h	97.0	90.2	[86]
Cu-Ni alloy	THF	6.3	220 °C/4.0 MPa H_2/12 h	>99	93.5	[87]
Ni-W_2C/AC	THF	10.5	180 °C/4.0 MPa H_2/2.5 h	>99	96.0	[88]
4Ni-Cu/TS-1	THF	12.6	180 °C/0.5 MPa H_2/7 h	>99	97.3	[89]
$NiCu_3$/C	1-Propanol	10.0	180 °C/3.3 MPa H_2	>99	98.7	[90]
Cu-Co@C	Ethanol	25.0	180 °C/5.0 MPa H_2/8 h	>99	99.4	[91]

By introducing another metal with Lewis acid sites to modify Ni-based catalysts, deoxygenation capability can be imparted, forming bifunctional catalysts that satisfy both hydrogenation and deoxygenation requirements. Huang et al. [88] reported a highly efficient Ni-W_2C/AC catalyst for the selective hydrogenolysis of HMF to DMF, and a 96.0% DMF yield was achieved at 180 °C with 4 MPa of H_2 after 2.5 h. The reaction mechanism was elucidated by capturing reaction intermediates, highlighting the synergy between Ni and W_2C where Ni provided hydrogenation ability and W_2C contributed deoxygenation capability. The activity of Ni-based catalysts can be also improved by introducing copper, forming Ni-Cu bimetallic catalysts. For instance, Umasankar et al. [63] found that a 5Ni-12Cu/SBA-16 catalyst afforded a DMF yield of 60.7% at 210 °C with 2 MPa of H_2 for 4 h compared to about 40% over a 5Ni-8Cu/SBA-16 catalyst under the same reaction conditions. In another study, Guo et al. [89] prepared bimetallic Ni-Cu catalysts with different Ni/Cu ratios using solid-state grinding, loading them onto titanium silicate-1 (TS-1). The strong interaction in the Ni-Cu alloy structure prevented further reaction of the furan ring, resulting in minimal by-product formation. A 100% HMF conversion and 97.3% DMF yield can be obtained at 180 °C with 0.5 MPa of H_2 after 7 h. Luo et al. [90] synthesized a nanocrystalline $NiCu_3/C$ catalyst via the solvothermal method, and the DMF yield reached 98.7% at 180 °C with 3.3 MPa of H_2 with a LHSV of 0.4 min^{-1}, which outperformed the Ni/C and Cu/C monometallic catalysts. This improvement was attributed to the alloy nanoparticles produced by the solvothermal method, which eliminated catalyst heterogeneity and inhibited the over-hydrogenation reaction.

Cu-Co bimetallic catalysts are also widely used in the conversion of HMF to DMF, and Al_2O_3 is one of the most commonly used supports. Srivastava et al. [84] found that the Cu-Co/Al_2O_3 catalyst exhibited a DMF yield of 78.0% at 220 °C with 3 MPa of H_2 for 8 h. Zhang et al. [85] prepared bimetallic Co_x-Cu@C catalysts through the thermal decomposition of MOFs (as shown in Figure 8), achieving in situ loading of cobalt into copper catalysts. An 85.0% DMF yield was achieved at 160 °C with 2.5 MPa of H_2 for 3 h. Reaction mechanism studies showed that cobalt doping effectively enhanced the hydrogenation activity of copper-based catalysts toward C−O bonds at low temperatures. In addition to combining with Ni and Co, Cu can also be doped with Fe to form bimetallic catalysts. Solanki et al. [86] synthesized a Cu-Fe bimetallic catalyst using the co-precipitation method, and a 97.0% HMF conversion and a 90.2% DMF yield were achieved at 170 °C with 2 MPa of H_2 for 4 h. Detailed investigation revealed that the Lewis acidity and oxophilic nature of Fe in the catalyst were initially activated by attacking its electron rich oxygen of HMF, which was the C=O group, while the Brönsted acidity of Cu and Fe species jointly promoted deoxygenation of C-O bonds, thereby improving DMF yield.

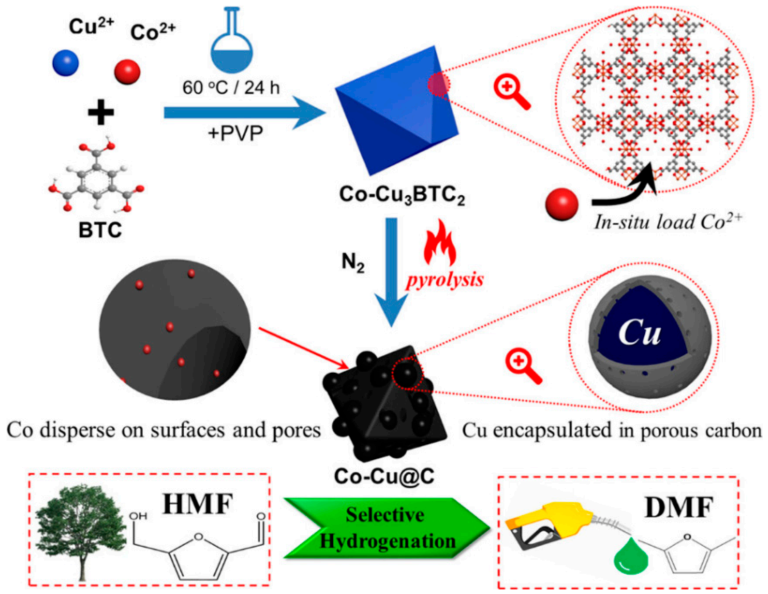

Figure 8. Synthetic process and catalytic application of Co_x-Cu@C catalyst [85]. Copyright © 2021, American Chemical Society.

4. Conclusions and Outlook

The hydrogenolysis of biomass-derived HMF to liquid fuel DMF is a key pathway for high-value biomass utilization, promoting green energy development. Despite progress in DMF production from HMF, challenges remain regarding diverse reaction products, harsh conditions, and catalyst selectivity and stability.

To enhance DMF production from HMF and address existing heterogeneous catalytic system bottlenecks, future research should focus on the following: (1) Designing efficient heterogeneous catalysts by optimizing active sites and pore structures to improve multi-step reaction coupling efficiency, inhibit side reactions, and increase DMF selectivity and yield. (2) Using theoretical calculations to understand the relationship between HMF bond cleavage and catalyst active sites, guiding catalyst design. (3) Optimizing reaction conditions and developing microkinetic models to understand surface reaction kinetics, aiding in process optimization. (4) Combining theoretical calculations, in situ characterization, and high-throughput experiments to establish practical microkinetic models that reveal key reaction steps and mechanisms for designing stable catalysts. (5) Exploring new energy methods like microwave heating and photoelectric coupling to improve efficiency and energy use. (6) Integrating heterogeneous and biocatalysis to create synergistic systems for efficient and economical HMF-to-DMF conversion.

Author Contributions: Conceptualization, J.H. and J.W.; validation, R.L. and J.W.; writing—original draft, J.H. and J.P.; writing—review and editing, J.W. All authors have read and agreed to the published version of the manuscript.

Funding: This work was financially supported by the Chongqing Human Resources and Social Security Bureau Project (cx2024049), the State Key Laboratory of Coal Mine Disaster Dynamics and Control (2011DA105287-MS202203), the Natural Science Foundation of Chongqing (CSTB2022NSCQ-MSX0458), and the Joint Fund for Innovation and Development of Chongqing (CSTB2022NSCQ-LZX0030).

Data Availability Statement: Not applicable.

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

Abbreviations

HMF	5-Hydroxymethylfurfural
DMF	2,5-Dimethylfuran
HTO	1,2,6-Hexanetriol
DHMF	2,5-Dihydroxymethylfuran
HDO	1,6-Hexanediol
DMTHF	2,5-Dimethyltetrahydrofuran
FDCA	2,5-Furandicarboxylic acids
DFF	2,5-Diformylfuran
LA	Levulinic acid
MFA	5-Methyl-furfuryl alcohol
5-MF	5-Methyl-furfural
C	Carbon
CNTs	Carbon nanotubes
MWCNTs	Multi-walled CNTs
Ru	Ruthenium
Pt	Platinum
Pd	Palladium
NPs	Nanoparticles
rGO	Reduced graphene oxide
g-C_3N_4	Graphitic carbon nitride
BC	Biochar
ALD	Atomic-layer deposition
HDO	Hydrodeoxygenation
Co	Cobalt
HCS	Hollow carbon spheres
HPS	Hollow polymer spheres
GVL	γ-Valerolactone

NDC	Nitrogen-doped carbon
NiSi-PS	Ni NPs embedded layered nickel silicate
LDHs	Layered double hydroxides
Beta-DA	Dealuminated Beta zeolite
NGs	Nitrogen-doped graphene
IPA	Isopropanol
THF	Tetrahydrofuran

References

1. Liu, H.Z.; Wang, H.; Nong, H.Z.; He, Y.T.; Chen, Y.L.; Wang, H.L.; Yu, M. Opportunities and implementation pathway for China's forestry development under the "Dual Carbon" strategy. *Carbon Res.* **2024**, *3*, 59. [CrossRef]
2. Wang, Y.T.; Zhao, D.Y.; Rodríguez-Padrón, D.; Len, C. Recent Advances in Catalytic Hydrogenation of Furfural. *Catalysts* **2019**, *9*, 796. [CrossRef]
3. Höök, M.; Tang, X. Depletion of fossil fuels and anthropogenic climate change—A review. *Energy Policy* **2013**, *52*, 797–809. [CrossRef]
4. Xu, B.J.; Zhong, R.Y.; Hochman, G.; Dong, K.Y. The environmental consequences of fossil fuels in China: National and regional perspectives. *Sustain. Dev.* **2019**, *27*, 826–837. [CrossRef]
5. Huo, J.; Peng, C. Depletion of natural resources and environmental quality: Prospects of energy use, energy imports, and economic growth hindrances. *Resour. Policy* **2023**, *86*, 104049. [CrossRef]
6. Wang, J.N.; Azam, W. Natural resource scarcity, fossil fuel energy consumption, and total greenhouse gas emissions in top emitting countries. *Geosci. Front.* **2024**, *15*, 101757. [CrossRef]
7. Gielen, D.; Boshell, F.; Saygin, D.; Bazilian, M.D.; Wagner, N.; Gorini, R. The role of renewable energy in the global energy transformation. *Energy Strategy Rev.* **2019**, *24*, 38–50. [CrossRef]
8. Jaiswal, K.K.; Chowdhury, C.R.; Yadav, D.; Verma, R.; Dutta, S.; Jaiswal, K.M.S.; Sangmesh, B.; Karuppasamy, K.S.K. Renewable and sustainable clean energy development and impact on social, economic, and environmental health. *Energy Nexus* **2022**, *7*, 100118. [CrossRef]
9. Hassan, Q.; Viktor, P.; Al-Musawi, T.J.; Ali, B.M.; Algburi, S.; Alzoubi, H.M.; Al-Jiboory, A.K.; Sameen, A.Z.; Salman, H.M.; Jaszczur, M. The renewable energy role in the global energy Transformations. *Renew. Energy Focus* **2024**, *48*, 100545. [CrossRef]
10. Arslanoglu, A.; Sert, M. Direct conversion of biomass to platform chemicals, catalyzed using a deep eutectic solvent of N,N diethyl ethanol ammonium chloride-oxalic acid in a microwave reactor. *Fuel* **2019**, *258*, 116142. [CrossRef]
11. Kuttin, K.W.; Yu, H.W.; Yang, M.M.; Ding, L.; Chen, X.L.; Yu, G.S.; Wang, F.C. Experimental and numerical modeling of carbonized biomass gasification: A critical review. *Green Carbon* **2024**, *2*, 176–196. [CrossRef]
12. Wang, H.; Zhang, X.H.; Li, X.H.; Li, Y.T.; Kong, D.B.; Zhen, Z.Y.; Geng, L.N.; Zhi, L.J.; Li, Z.T. Hierarchically Porous Biomass Carbon Derived from Orange Peel for Atomically Dispersed Co-N-C Sites Toward Advanced Oxygen Reduction Reaction. *Renewables* **2023**, *1*, 353–361. [CrossRef]
13. Zhu, Z.Y.; Men, Y.; Zhang, W.J.; Yang, W.H.; Wang, F.; Zhang, Y.J.; Zhang, Y.Y.; Zeng, X.Y.; Xiao, J.; Tang, C.; et al. Versatile carbon-based materials from biomass for advanced electrochemical energy storage systems. *eScience* **2024**, *4*, 100249. [CrossRef]
14. Gaudino, E.C.; Cravotto, G.; Manzoli, M.; Tabasso, S. From waste biomass to chemicals and energy via microwave-assisted processes. *Green Chem.* **2019**, *21*, 1202–1235. [CrossRef]
15. Khalid, M.; De, B.S.; Shahgaldi, S. Electrocatalytic lignin oxidation for hydrogen and fine chemical co-production using platinized nickel foam in a 3D printed reactor. *DeCarbon* **2024**, *6*, 100074. [CrossRef]
16. Luo, S.; Wang, J.J. Research progress on tungsten-based catalysts for selective conversion of biomass to diols. *Pet. Process. Petrochem.* **2024**, *55*, 52–63. Available online: http://www.sylzyhg.com/EN/Y2024/V55/I2/52 (accessed on 12 February 2024).
17. Tang, N.; Yang, Y.P.; Liu, K.; Li, P.; Wang, J.J. Research progress in construction of heterogeneous catalysts for efficient conversion of biomass and their derivatives to lactic acid. *Low-Carbon Chem. Chem. Eng.* **2024**, *49*, 50–62. Available online: https://www.dthxyhg.com/thesisDetails#10.12434/j.issn.2097-2547.20230408&lang=en (accessed on 25 November 2024).
18. Sivec, R.; Grilc, M.; Hus, M.; Likozar, B. Multiscale Modeling of (Hemi)cellulose Hydrolysis and Cascade Hydrotreatment of 5-Hydroxymethylfurfural, Furfural, and Levulinic Acid. *Ind. Eng. Chem. Res.* **2019**, *58*, 16018–16032. [CrossRef]
19. Wang, H.; Fu, F.B.; Huang, M.; Feng, Y.H.; Han, D.X.; Xi, Y.B.; Xiong, W.L.; Yang, D.J.; Niu, L. Lignin-based materials for electrochemical energy storage devices. *Nano Mater. Sci.* **2023**, *5*, 141–160. [CrossRef]
20. Zhao, P.P.; Zhang, Y.Y.; Wang, Y.; Cui, H.Y.; Song, F.; Sun, X.Y.; Zhang, L.P. Conversion of glucose into 5-hydroxymethylfurfural catalyzed by acid-base bifunctional heteropolyacid-based ionic hybrids. *Green Chem.* **2018**, *20*, 1551–1559. [CrossRef]
21. Hu, B.; Lu, Q.; Jiang, X.Y.; Dong, X.C.; Cui, M.S.; Dong, C.Q.; Yang, Y.P. Pyrolysis mechanism of glucose and mannose: The formation of 5-hydroxymethyl furfural and furfural. *J. Energy Chem.* **2018**, *27*, 486–501. [CrossRef]

22. Ashok, R.P.B.; Oinas, P.; Forssell, S. Techno-economic evaluation of a biorefinery to produce gama-valerolactone (GVL), 2-methyltetrahydrofuran (2-MTHF) and 5-hydroxymethylfurfural (5-HMF) from spruce. *Renew. Energy* **2022**, *190*, 396–407. [CrossRef]
23. Kim, J.; Bathula, H.B.; Yun, S.K.; Jo, Y.; Lee, S.; Baik, J.H.; Suh, Y.W. Hydrogenation of 5-hydroxymethylfurfural into 2,5-bis (hydroxymethyl)furan over mesoporous Cu-Al_2O_3 catalyst: From batch to continuous processing. *J. Ind. Eng. Chem.* **2021**, *102*, 186–194. [CrossRef]
24. Rao, K.T.V.; Hu, Y.L.; Yuan, Z.S.; Zhang, Y.S.; Xu, C.B.C. Green synthesis of heterogeneous copper-alumina catalyst for selective hydrogenation of pure and biomass-derived 5-hydroxymethylfurfural to 2,5-bis(hydroxymethyl)furan. *Appl. Catal. A Gen.* **2021**, *609*, 117892. [CrossRef]
25. Zhu, B.; Chen, C.L.; Huai, L.Y.; Zhou, Z.Q.; Wang, L.; Zhang, J. 2,5-Bis(hydroxymethyl)furan: A new alternative to HMF for simultaneously electrocatalytic production of FDCA and H_2 over CoOOH/Ni electrodes. *Appl. Catal. B Environ.* **2021**, *297*, 120396. [CrossRef]
26. Román-Leshkov, Y.; Barrett, C.J.; Liu, Z.Y.; Dumesic, J.A. Production of dimethylfuran for liquid fuels from biomass-derived carbohydrates. *Nature* **2007**, *447*, 982–985. [CrossRef] [PubMed]
27. Pires, A.P.P.; Han, Y.L.; Kramlich, J.; Garcia-Perez, M. Chemical Composition and Fuel Properties of Alternative Jet Fuels. *BioRes.* **2018**, *13*, 2632–2657. [CrossRef]
28. Wang, X.F.; Liu, Y.Z.; Liang, X.H. Hydrogenolysis of 5-hydroxymethylfurfural to 2,5-dimethylfuran over supported Pt-Co bimetallic catalysts under mild conditions. *Green Chem.* **2018**, *20*, 2894–2902. [CrossRef]
29. Zhao, C.X.; Liu, J.N.; Li, B.Q.; Ren, D.; Chen, X.; Yu, J.; Zhang, Q. Multiscale Construction of Bifunctional Electrocatalysts for Long-Lifespan Rechargeable Zinc-Air Batteries. *Adv. Funct. Mater.* **2020**, *30*, 2003619. [CrossRef]
30. Xu, C.; Paone, E.; Rodríguez-Padrón, D.; Luque, R.; Mauriello, F. Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural. *Chem. Soc. Rev.* **2020**, *49*, 4273–4306. [CrossRef] [PubMed]
31. Zhu, Y.F.; Kong, X.; Zheng, H.Y.; Ding, G.Q.; Zhu, Y.L.; Li, Y.W. Efficient synthesis of 2,5-dihydroxymethylfuran and 2,5-dimethylfuran from 5-hydroxymethylfurfural using mineral-derived Cu catalysts as versatile catalysts. *Catal. Sci. Technol.* **2015**, *5*, 4208–4217. [CrossRef]
32. Jae, J.; Zheng, W.Q.; Lobo, R.F.; Vlachos, D.G. Production of Dimethylfuran from Hydroxymethylfurfural through Catalytic Transfer Hydrogenation with Ruthenium Supported on Carbon. *ChemSusChem* **2013**, *6*, 1158–1162. [CrossRef]
33. Priecel, P.; Endot, N.A.; Carà, P.D.; Lopez-Sanchez, J.A. Fast Catalytic Hydrogenation of 2,5-Hydroxymethylfurfural to 2,5-Dimethylfuran with Ruthenium on Carbon Nanotubes. *Ind. Eng. Chem. Res.* **2018**, *57*, 1991–2002. [CrossRef]
34. Wang, X.F.; Zhang, C.C.; Jin, B.T.; Liang, X.H.; Wang, Q.F.; Zhao, Z.; Li, Q.B. Pt-Carbon interaction-determined reaction pathway and selectivity for hydrogenation of 5-hydroxymethylfurfural over carbon supported Pt catalysts. *Catal. Sci. Technol.* **2021**, *11*, 1298–1310. [CrossRef]
35. Luo, J.; Arroyo-Ramírez, L.; Gorte, R.J.; Tzoulaki, D.; Vlachos, D.G. Hydrodeoxygenation of HMF Over Pt/C in a Continuous Flow Reactor. *AIChE J.* **2015**, *61*, 590–597. [CrossRef]
36. Shi, J.J.; Wang, Y.Y.; Yu, X.N.; Du, W.C.; Hou, Z.Y. Production of 2,5-dimethylfuran from 5-hydroxymethylfurfural over reduced graphene oxides supported Pt catalyst under mild conditions. *Fuel* **2016**, *163*, 74–79. [CrossRef]
37. Wang, G.H.; Hilgert, J.; Richter, F.H.; Wang, F.; Bongard, H.J.; Spliethoff, B.; Weidenthaler, C.; Schüth, F. Platinum-cobalt bimetallic nanoparticles in hollow carbon nanospheres for hydrogenolysis of 5-hydroxymethylfurfural. *Nat. Mater.* **2014**, *13*, 294–301. [CrossRef] [PubMed]
38. Mitra, J.; Zhou, X.Y.; Rauchfuss, T. Pd/C-catalyzed reactions of HMF: Decarbonylation, hydrogenation, and hydrogenolysis. *Green Chem.* **2015**, *17*, 307–313. [CrossRef]
39. Yang, Y.D.; Liu, H.Y.; Li, S.P.; Chen, C.J.; Wu, T.B.; Mei, Q.Q.; Wang, Y.Y.; Chen, B.F.; Liu, H.Z.; Han, B.X. Hydrogenolysis of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran under Mild Conditions without Any Additive. *ACS Sustain. Chem. Eng.* **2019**, *7*, 5711–5716. [CrossRef]
40. Solanki, B.S.; Rode, C.V. Selective hydrogenolysis of 5-(hydroxymethyl) furfural over Pd/C catalyst to 2,5-dimethylfuran. *J. Saudi Chem. Soc.* **2019**, *23*, 439–451. [CrossRef]
41. Zhang, K.L.; Meng, Q.L.; Wu, H.H.; He, M.Y.; Han, B.X. Selective Hydrogenolysis of 5-Hydroxymethylfurfural into 2,5-Dimethylfuran under Mild Conditions Using Pd/MOF-808. *ACS Sustain. Chem. Eng.* **2022**, *10*, 10286–10293. [CrossRef]
42. Jae, J.; Zheng, W.Q.; Karim, A.M.; Guo, W.; Lobo, R.F.; Vlachos, D.G. The Role of Ru and RuO_2 in the Catalytic Transfer Hydrogenation of 5-Hydroxymethylfurfural for the Production of 2,5-Dimethylfuran. *ChemCatChem* **2014**, *6*, 848–856. [CrossRef]
43. Tzeng, T.W.; Lin, C.Y.; Pao, C.W.; Chen, J.L.; Nuguid, R.J.G.; Chung, P.W. Understanding catalytic hydrogenolysis of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) using carbon supported Ru catalysts. *Fuel Process. Technol.* **2020**, *199*, 106225. [CrossRef]
44. Bailón-García, E.; Maldonado-Hódar, F.J.; Pérez-Cadenas, A.F.; Carrasco-Marín, F. Catalysts Supported on Carbon Materials for the Selective Hydrogenation of Citral. *Catalysts* **2013**, *3*, 853–877. [CrossRef]

45. Toebes, M.L.; Prinsloo, F.F.; Bitter, J.H.; van Dillen, A.J.; de Jong, K.P. Influence of oxygen-containing surface groups on the activity and selectivity of carbon nanofiber-supported ruthenium catalysts in the hydrogenation of cinnamaldehyde. *J. Catal.* **2003**, *214*, 78–87. [CrossRef]
46. Breen, J.P.; Burch, R.; Gomez-Lopez, J.; Griffin, K.; Hayes, M. Steric effects in the selective hydrogenation of cinnamaldehyde to cinnamyl alcohol using an Ir/C catalyst. *Appl. Catal. A Gen.* **2004**, *268*, 267–274. [CrossRef]
47. Samant, P.V.; Pereira, M.F.R.; Figueiredo, J.L. Mesoporous carbon supported Pt and Pt-Sn catalysts for hydrogenation of cinnamaldehyde. *Catal. Today* **2005**, *102*, 183–188. [CrossRef]
48. Ma, H.X.; Wang, L.C.; Chen, L.Y.; Dong, C.; Yu, W.C.; Huang, T.; Qian, Y.T. Pt nanoparticles deposited over carbon nanotubes for selective hydrogenation of cinnamaldehyde. *Catal. Commun.* **2007**, *8*, 452–456. [CrossRef]
49. Wang, J.; Zhao, J.R.; Fu, J.H.; Miao, C.L.; Jia, S.Y.; Yan, P.F.; Huang, J.H. Highly selective hydrogenation of 5-hydroxymethylfurfural to 2,5-bis (hydroxymethyl)furan over metal-oxide supported Pt catalysts: The role of basic sites. *Appl. Catal. A Gen.* **2022**, *643*, 118762. [CrossRef]
50. Wang, S.D.; Cui, Y.H.; Zhao, C.X.; Liang, C.H.; Li, C. In Situ Fabrication of the Al_2O_3@NiMo Core-Shell Catalyst from LDH for Low-Pressure Hydrodeoxygenation of Fatty Acid Methyl Ester. *Ind. Eng. Chem. Res.* **2022**, *61*, 18232–18242. [CrossRef]
51. Besson, M.; Gallezot, P.; Pinel, C. Conversion of Biomass into Chemicals over Metal Catalysts. *Chem. Rev.* **2014**, *114*, 1827–1870. [CrossRef] [PubMed]
52. Goyal, R.; Sarkar, B.; Bag, A.; Siddiqui, N.; Dumbre, D.; Lucas, N.; Bhargava, S.K.; Bordoloi, A. Studies of synergy between metal-support interfaces and selective hydrogenation of HMF to DMF in water. *J. Catal.* **2016**, *340*, 248–260. [CrossRef]
53. Li, T.T.; Ji, N.; Jia, Z.C.; Diao, X.Y.; Wang, Z.J.; Liu, Q.L.; Song, C.F.; Lu, X.B. Effects of metal promoters in bimetallic catalysts in hydrogenolysis of lignin derivatives into value-added chemicals. *ChemCatChem* **2020**, *12*, 5288–5302. [CrossRef]
54. Zeng, Z.J.; Tang, Q.; Wen, B.; Luo, L.; Liu, X.X.; Xu, Q.; Zhong, W.Z. Zn-modified Co/N-C catalysts for adjustable conversion of 5-hydroxyme-thylfurfural to furan-based chemicals. *J. Environ. Chem. Eng.* **2024**, *12*, 112190. [CrossRef]
55. Zu, Y.H.; Yang, P.P.; Wang, J.J.; Liu, X.H.; Ren, J.W.; Lu, G.Z.; Wang, Y.Q. Efficient production of the liquid fuel 2,5-dimethylfuran from 5-hydroxymethylfurfural over Ru/Co_3O_4 catalyst. *Appl. Catal. B Environ.* **2014**, *146*, 244–248. [CrossRef]
56. Gao, Z.; Fan, G.L.; Liu, M.R.; Yang, L.; Li, F. Dandelion-like cobalt oxide microsphere-supported RuCo bimetallic catalyst for highly efficient hydrogenolysis of 5-hydroxymethylfurfural. *Appl. Catal. B Environ.* **2018**, *237*, 649–659. [CrossRef]
57. Esen, M.; Akmaz, S.; Koc, S.N.; Gürkaynak, M.A. The hydrogenation of 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) with sol-gel Ru-Co/SiO_2 catalyst. *J. Sol-Gel Sci. Technol.* **2019**, *91*, 664–672. [CrossRef]
58. Luo, J.; Yun, H.; Mironenko, A.V.; Goulas, K.; Lee, J.D.; Monai, M.; Wang, C.; Vorotnikov, V.; Murray, C.B.; Vlachos, D.G.; et al. Mechanisms for High Selectivity in the Hydrodeoxygenation of 5-Hydroxymethylfurfural over PtCo Nanocrystals. *ACS Catal.* **2016**, *6*, 4095–4104. [CrossRef]
59. Talpade, A.D.; Tiwari, M.S.; Yadav, G.D. Selective hydrogenation of bio-based 5-hydroxymethyl furfural to 2,5-dimethylfuran over magnetically separable Fe-Pd/C bimetallic nanocatalyst. *Mol. Catal.* **2019**, *465*, 1–15. [CrossRef]
60. Nishimura, S.; Ikeda, N.; Ebitani, K. Selective hydrogenation of biomass-derived 5-hydroxymethylfurfural (HMF) to 2,5-dimethylfuran (DMF) under atmospheric hydrogen pressure over carbon supported PdAu bimetallic catalyst. *Catal. Today* **2014**, *232*, 89–98. [CrossRef]
61. Thananatthanachon, T.; Rauchfuss, T.B. Efficient Production of the Liquid Fuel 2,5-Dimethylfuran from Fructose Using Formic Acid as a Reagent. *Angew. Chem. Int. Ed.* **2010**, *49*, 6616–6618. [CrossRef] [PubMed]
62. Iriondo, A.; Mendiguren, A.; Güemez, M.B.; Requies, J.; Cambra, J.F. 2,5-DMF production through hydrogenation of real and synthetic 5-HMF over transition metal catalysts supported on carriers with different nature. *Catal. Today* **2017**, *279*, 286–295. [CrossRef]
63. Umasankar, S.; Tamizhdurai, P.; Krishnan, P.S.; Narayanan, S.; Mangesh, V.L.; Shanthi, K. Effect of copper on NiCu bimetallic catalyst supported on SBA-16 for the catalytic hydrogenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran. *Biomass Bioenergy* **2020**, *143*, 105868. [CrossRef]
64. Shao, Y.W.; Wang, J.Z.; Sun, K.; Gao, G.M.; Li, C.; Zhang, L.J.; Zhang, S.; Xu, L.L.; Hu, G.Z.; Hu, X. Selective hydrogenation of furfural and its derivative over bimetallic NiFe-based catalysts: Understanding the synergy between Ni sites and Ni-Fe alloy. *Renew. Energy* **2021**, *170*, 1114–1128. [CrossRef]
65. Sunyol, C.; Owen, R.E.; González, M.G.; Salagre, P.; Cesteros, Y. Catalytic hydrogenation of furfural to tetrahydrofurfuryl alcohol using competitive nickel catalysts supported on mesoporous clays. *Appl. Catal. A Gen.* **2021**, *611*, 117903. [CrossRef]
66. Gyngazova, M.S.; Negahdar, L.; Blumenthal, L.C.; Palkovits, R. Experimental and kinetic analysis of the liquid phase hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran over carbon-supported nickel catalysts. *Chem. Eng. Sci.* **2017**, *173*, 455–464. [CrossRef]
67. Brandi, F.; Bäumel, M.; Shekova, I.; Molinari, V.; Al-Naji, M. 5-Hydroxymethylfurfural Hydrodeoxygenation to 2,5-Dimethylfuran in Continuous-Flow System over Ni on Nitrogen-Doped Carbon. *Sustain. Chem.* **2020**, *1*, 106–115. [CrossRef]

68. Przydacz, M.; Jedrzejczyk, M.; Brzezinska, M.; Rogowski, J.; Keller, N.; Ruppert, A.M. Solvothermal hydrodeoxygenation of hydroxymethylfurfural derived from biomass towards added value chemicals on Ni/TiO_2 catalysts. *J. Supercrit. Fluids* **2020**, *163*, 104827. [CrossRef]
69. Kong, X.; Zhu, Y.F.; Zheng, H.Y.; Dong, F.; Zhu, Y.L.; Li, Y.W. Switchable synthesis of 2,5-dimethylfuran and 2,5-dihydroxymethyltetrahydrofuran from 5-hydroxymethylfurfural over Raney Ni catalyst. *RSC Adv.* **2014**, *4*, 60467–60472. [CrossRef]
70. Kong, X.; Zhu, Y.F.; Zheng, H.Y.; Li, X.Q.; Zhu, Y.L.; Li, Y.W. Ni Nanoparticles Inlaid Nickel Phyllosilicate as a Metal-Acid Bifunctional Catalyst for Low-Temperature Hydrogenolysis Reactions. *ACS Catal.* **2015**, *5*, 5914–5920. [CrossRef]
71. Kong, X.; Zheng, R.X.; Zhu, Y.F.; Ding, G.Q.; Zhu, Y.L.; Li, Y.W. Rational design of Ni-based catalysts derived from hydrotalcite for selective hydrogenation of 5-hydroxymethylfurfural. *Green Chem.* **2015**, *17*, 2504–2514. [CrossRef]
72. Chen, N.M.; Zhu, Z.G.; Ma, H.K.; Liao, W.P.; Lü, H.Y. Catalytic upgrading of biomass-derived 5-hydroxymethylfurfural to biofuel 2,5-dimethylfuran over Beta zeolite supported non-noble Co catalyst. *Mol. Catal.* **2020**, *486*, 110882. [CrossRef]
73. Xiang, S.; Dong, L.; Wang, Z.Q.; Han, X.; Daemen, L.L.; Li, J.; Cheng, Y.Q.; Guo, Y.; Liu, X.H.; Hu, Y.F.; et al. A unique Co@CoO catalyst for hydrogenolysis of biomass-derived 5-hydroxymethylfurfural to 2,5-dimethylfuran. *Nat. Commun.* **2022**, *13*, 3657. [CrossRef] [PubMed]
74. Xiao, T.C.; Liu, X.H.; Xu, G.Y.; Zhang, Y. Phase tuning of ZrO_2 supported cobalt catalysts for hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran under mild conditions. *Appl. Catal. B Environ.* **2021**, *295*, 120270. [CrossRef]
75. Yang, F.; Mao, J.B.; Li, S.M.; Yin, J.M.; Zhou, J.X.; Liu, W. Cobalt-graphene nanomaterial as an efficient catalyst for selective hydrogenation of 5-hydroxymethylfurfural into 2,5-dimethylfuran. *Catal. Sci. Technol.* **2019**, *9*, 1329–1333. [CrossRef]
76. Xia, J.; Gao, D.; Han, F.; Li, Y.; Waterhouse, G.I.N. Efficient and Selective Hydrogenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran Over a Non-noble $CoNC_x$/NiFeO Catalyst. *Catal. Lett.* **2022**, *152*, 3400–3413. [CrossRef]
77. Wang, J.S.; Wei, Q.H.; Ma, Q.X.; Guo, Z.Y.; Qin, F.F.; Ismagilov, Z.R.; Shen, W.Z. Constructing Co@N-doped graphene shell catalyst via Mott-Schottky effect for selective hydrogenation of 5-hydroxylmethylfurfural. *Appl. Catal. B Environ.* **2020**, *263*, 118339. [CrossRef]
78. Zhang, Z.H.; Wang, C.X.; Gou, X.; Chen, H.; Chen, K.Q.; Lu, X.Y.; Ouyang, P.K.; Fu, J. Catalytic in-situ hydrogenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran over Cu-based catalysts with methanol as a hydrogen donor. *Appl. Catal. A Gen.* **2019**, *570*, 245–250. [CrossRef]
79. Lakshmi, D.D.; Rao, B.S.; Yogita; Lingaiah, N. Selective hydrodeoxygenation of 5-hydroxymethylfurfural to 2,5-dimethylfuran over mesoporous silica supported copper catalysts. *Mater. Sci. Energy Technol.* **2021**, *4*, 357–366. [CrossRef]
80. Esteves, L.M.; Brijaldo, M.H.; Oliveira, E.G.; Martinez, J.J.; Rojas, H.; Caytuero, A.; Passos, F.B. Effect of support on selective 5-hydroxymethylfurfural hydrogenation towards 2,5-dimethylfuran over copper catalysts. *Fuel* **2020**, *270*, 117524. [CrossRef]
81. Zhang, Z.N.; Liu, C.W.; Liu, D.; Shang, Y.N.; Yin, X.Q.; Zhang, P.; Mamba, B.B.; Kuvarega, A.T.; Gui, J.Z. Hydrothermal carbon-supported Ni catalysts for selective hydrogenation of 5-hydroxymethylfurfural toward tunable products. *J. Mater. Sci.* **2020**, *55*, 14179–14196. [CrossRef]
82. Srivastava, S.; Jadeja, G.C.; Parikh, J. A versatile bi-metallic copper-cobalt catalyst for liquid phase hydrogenation of furfural to 2-methylfuran. *RSC Adv.* **2016**, *6*, 1649–1658. [CrossRef]
83. Zhang, Z.H.; Pei, Z.H.; Chen, H.; Chen, K.Q.; Hou, Z.Y.; Lu, X.Y.; Ouyang, P.K.; Fu, J. Catalytic In-Situ Hydrogenation of Furfural over Bimetallic Cu-Ni Alloy Catalysts in Isopropanol. *Ind. Eng. Chem. Res.* **2018**, *57*, 4225–4230. [CrossRef]
84. Srivastava, S.; Jadeja, G.C.; Parikh, J. Influence of supports for selective production of 2,5-dimethylfuran via bimetallic copper-cobalt catalyzed 5-hydroxymethylfurfural hydrogenolysis. *Chin. J. Catal.* **2017**, *38*, 699–709. [CrossRef]
85. Zhang, Q.T.; Zuo, J.L.; Wang, L.; Peng, F.; Chen, S.Z.; Liu, Z.L. Non Noble-Metal Copper-Cobalt Bimetallic Catalyst for Efficient Catalysis of the Hydrogenolysis of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran under Mild Conditions. *ACS Omega* **2021**, *6*, 10910–10920. [CrossRef] [PubMed]
86. Solanki, B.S.; Rode, C.V. Selective hydrogenation of 5-HMF to 2,5-DMF over a magnetically recoverable non-noble metal catalyst. *Green Chem.* **2019**, *21*, 6390–6406. [CrossRef]
87. Zhu, C.H.; Wang, H.Y.; Li, H.; Cai, B.J.; Lv, W.; Cai, C.L.; Wang, C.G.; Yan, L.; Liu, Q.Y.; Ma, L.L. Selective Hydrodeoxygenation of 5-Hydroxymethylfurfural to 2,5-Dimethylfuran over Alloyed Cu-Ni Encapsulated in Biochar Catalysts. *ACS Sustain. Chem. Eng.* **2019**, *7*, 19556–19569. [CrossRef]
88. Huang, Y.B.; Chen, M.Y.; Yan, L.; Guo, Q.X.; Fu, Y. Nickel-Tungsten Carbide Catalysts for the Production of 2,5-Dimethylfuran from Biomass- Derived Molecules. *ChemSusChem* **2014**, *7*, 1068–1072. [CrossRef] [PubMed]
89. Guo, D.W.; Lai, J.H.; Cheng, F.; Zhao, W.G.; Chen, H.; Li, H.; Liu, X.X.; Yin, D.L.; Yu, N.Y. Titanium silicalite-1 supported bimetallic catalysts for selective hydrogenolysis of 5-hydroxymethylfurfural to biofuel 2, 5-dimethylfuran. *Chem. Eng. J. Adv.* **2021**, *5*, 100081. [CrossRef]

90. Luo, J.; Monai, M.; Wang, C.; Lee, J.D.; Duchon, T.; Dvorák, F.; Matolín, V.; Murray, C.B.; Fornasiero, P.; Gorte, R.J. Unraveling the surface state and composition of highly selective nanocrystalline Ni-Cu alloy catalysts for hydrodeoxygenation of HMF. *Catal. Sci. Technol.* **2017**, *7*, 1735–1743. [CrossRef]
91. Chen, B.F.; Li, F.B.; Huang, Z.J.; Yuan, G.Q. Carbon-coated Cu-Co bimetallic nanoparticles as selective and recyclable catalysts for production of biofuel 2,5-dimethylfuran. *Appl. Catal. B Environ.* **2017**, *200*, 192–199. [CrossRef]