

REVIEW

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# Recent advances in catalytic synthesis of 2,5-furandimethanol from 5-hydroxymethylfurfural and carbohydrates

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## Abstract

5-Hydroxymethylfurfural (HMF) is a versatile platform chemical derived from the dehydration of renewable carbohydrates (typically glucose/fructose-based monosaccharides, oligosaccharides, and polysaccharides). Some useful compounds, such as 2,5-furandimethanol (FDM), 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF), have been synthesized by reduction of HMF. Among these, FDM is a promising diol and can be further converted towards fine chemicals, liquid fuels and polymer materials. In this review, some typical catalytic systems for the synthesis of FDM from both HMF and carbohydrates were summarized. The discussion focused on controlling the reaction networks for the reduction of HMF. The reaction mechanisms and the stability of the catalysts were introduced briefly. Last but not least, the prospects of effective production of FDM were discussed as well.

**Keywords** Biomass, Carbohydrate, 2,5-Furandimethanol, Hydrogenation, HMF

## Introduction

Over the last century, the rapid economic development relied on the excessive consumption of non-renewable oil, coal and other fossil resources, resulting in serious resource and environment issues. To seek and utilize green and clean resources has become an urgent need. Biomass is the sole renewable and abundant resource containing organic carbon, thereby being regarded as the best replacement of fossil resources to supply chemicals and fuels for human beings sustainably. The utilization of some typical biomass resources, such as cellulose, hemicellulose, lignin, and chitin, has attracted increasing attention (Torres et al. 2020; Chen et al. 2021;

Takkellapati et al. 2018; Dai et al. 2020). Among these, cellulose is the most abundant biopolymer consisting numerous glucose monosaccharide units. Glucose can be further isomerized to fructose. The catalytic conversion of cellulose, glucose and fructose to 5-hydroxymethylfurfural (HMF) has been extensively investigated. HMF contains active furan ring, aldehyde group and hydroxymethyl group. As an important platform compound derived from biomass, HMF can be further converted into a number of useful chemicals via hydrogenation, oxidation, and amination, etc. (Hou et al. 2021). The investigation on the synthesis and conversion of HMF is still a hot research topic.

The selective reduction of HMF provides several valuable products. For example, 2,5-furandimethanol (FDM), 5-methylfurfural (MF), 5-methylfurfuryl alcohol (MFA) and 2,5-dimethylfuran (DMF) can be obtained by selective reduction of aldehyde and hydroxymethyl groups with retention of furan ring. Under some conditions, the furan ring of HMF also can be hydrogenated, offering useful products, such as 2,5-bis(hydroxymethyl)tetrahydrofuran

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(BHMTFH), 5-methyltetrahydrofurfuryl alcohol (MTHFA), and 2,5-dimethyltetrahydrofuran (DMTHF). The ring opening and hydrogenation reactions of HMF yield linear products, such as 1,6-hexanediol and 1-hydroxyhexane-2,5-dione. Some typical reduction products of HMF have been shown in Scheme 1. (He et al. 2022, 2018; Yu 2021; Turkin et al. 2022; Wozniak et al. 2018).

Among these hydrogenated products, FDM is a furan-derivative with two symmetrical hydroxymethyl groups, which has attracted much attention as an important intermediate. The etherification of FDM generates 2,5-bis(alkoxymethyl)furan, a potential bio-diesel additive with high energy density and advantageous fuel blending properties (Jae et al. 2014; Lewis et al. 2014; Cao et al. 2014). As a diol, FDM can be used to produce various polyesters (Lillie et al. 2017; Zhang et al. 2017; Jiang et al. 2014). For example, Zhang et al. (Zhang et al. 2017) reported the synthesis of polyesters with high molecular weight using FDM and other bio-based building blocks. The double bonds in FDM unit enhanced the stability of the polyesters. In addition, FDM is a promising synthon for the preparation of biologically active compounds (Gelmini et al. 2016). Previously, there have been some good reviews that summarized the production of FDM from biomass especially HMF (Arico 2021; He et al. 2022; Hu et al. 2018; Tang et al. 2017). However, many novel approaches and exciting achievements for the synthesis of FDM were reported recently. Therefore, a real-time review of this area is still necessary. In this review, we reviewed the recent progress in the synthesis of FDM

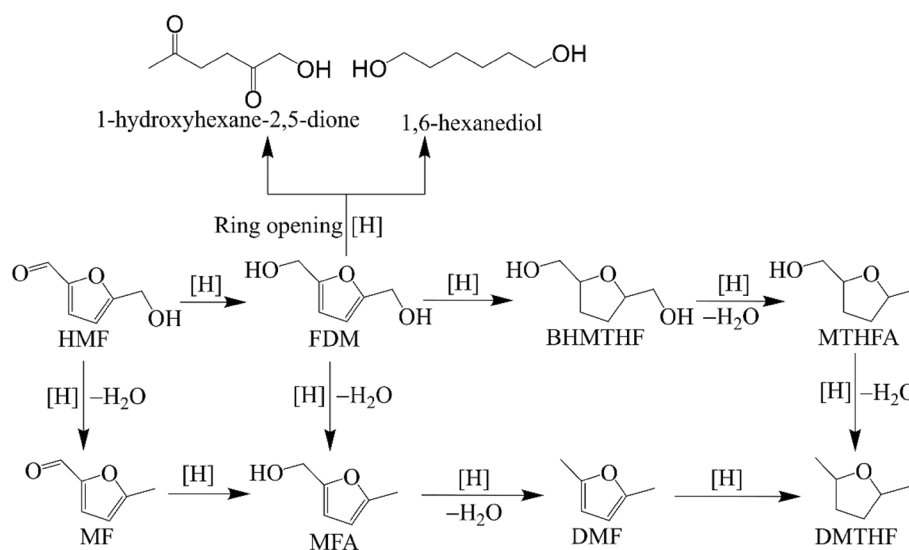
from biomass-based HMF and carbohydrates and discussed the catalytic paths and catalyst stability.

### The basic properties of FDM

FDM exists as light yellow solid with a density of 1.283 g/cm<sup>3</sup> at ambient temperature. The melting point, boiling point and flash point of FDM are 74–77 °C, 275 °C and 120 °C, respectively. FDM can be slightly dissolved in acetonitrile and DMSO. Some chemical and physical properties of FDM are listed in Table 1.

**Table 1** Some chemical and physical properties of FDM

Item	Content
CAS	1883-75-6
EINECS	217-544-1
chemical name	2,5-Furandimethanol
chemical formula	C <sub>6</sub> H <sub>8</sub> O <sub>3</sub>
molecular weight	128.13
InChI	InChI = 1/C <sub>6</sub> H <sub>8</sub> O <sub>3</sub> /c7-3-5-1-2-6(4-8)9-5/h1-2,7-8H,3-4H <sub>2</sub>
density	1.283 g/cm <sup>3</sup>
melting point	74–77 °C
boiling point	275 °C
flash point	120 °C
refractive index	1.542
vapor pressure	0.00248 mmHg at 25 °C
solubility	acetonitrile (slightly), DMSO (slightly)
appearance	light yellow solid



**Scheme 1.** Several reduction products of HMF

### Synthesis of FDM from HMF

The selective hydrogenation of aldehyde group on HMF towards hydroxymethyl group yields FDM. However, there are several hydrogenation reactions that may occur under true reaction conditions. For example, the aldehyde group, hydroxymethyl group, and furan ring might be hydrogenated, resulting in a mixture of cyclic compounds. In addition, the ring-opening reaction of HMF gives linear molecules. Therefore, it remains a challenge to control the selectivity of hydrogenated products of HMF. Till now, different methods including thermo-catalysis, photo-catalysis, and electro-catalysis have been employed for FDM synthesis from HMF, which will be discussed in this section.

#### Synthesis of FDM from HMF by thermo-catalysis

There are two types of hydrogen donors that have been widely used for the conversion of HMF to FDM. First,  $H_2$  is a typical hydrogen donor with good hydrogenation capacity. Both two hydrogen atoms of the  $H_2$  molecule can act as hydrogen donors, which meets the requirements of "Green Chemistry". Moreover, the separation of  $H_2$  from reaction mixtures can be simply achieved by release of excess  $H_2$  after hydrogenation reactions. Therefore,  $H_2$  has been selected as hydrogen donor in biomass conversion in many cases. Nevertheless, some potential safety hazards of flammable and explosive  $H_2$  drive the development of novel hydrogen resources. Typically, formic acid and some alcohols have replaced  $H_2$  in some hydrogenation examples, and good yield and selectivity have been obtained. Some of these hydrogen donors (i.e., formic acid, ethanol, etc.) can be produced from renewable biomass-based feedstock, which is attractive. However, the decomposition of these hydrogen donors generates some side-products, resulting in lower atom utilization and difficulties in product separation. Overall, different hydrogen donors have different advantages and disadvantages. The synthesis of FDM from HMF using various hydrogen donors will be discussed next.

#### $H_2$ as reduction reagent

The conversion of HMF over Ir-, Pd-, Au-, Pt-based catalysts have been reported. Chimentão et al. (Chimentao et al. 2019) studied the selective hydrogenation of HMF over Cl-free Ir/SiO<sub>2</sub> catalysts at 60 °C for 5 h in tetrahydrofuran (THF) under 10 bar  $H_2$  pressure, affording 100% selectivity with 60% conversion by inhibiting hydrogenation of the C=C bond. It is notable that chlorine species on Ir/SiO<sub>2</sub>(Cl) catalyst acted as the acid sites to activate the C–O bond, significantly facilitating the hydrogenation to form FDM and enhancing HMF conversion to 97%. The addition of H<sub>2</sub>SO<sub>4</sub> as a co-catalyst could promote the further conversion of FDM to DMF even

DMTHF. The same group (Chimentao et al. 2021) further studied the effect of second metal on Ir/SiO<sub>2</sub>, and the kinetic constants were in the order of Ir–Ni/SiO<sub>2</sub> > Ir–Co/SiO<sub>2</sub> > Ir–Ru/SiO<sub>2</sub> > Ir/SiO<sub>2</sub>, suggesting that the bimetallic catalysts showed higher catalytic activity compared to the monometallic Ir/SiO<sub>2</sub>. The oxophilic nature of the secondary metal might contribute to the higher activity.

The hydrogenation of HMF over Pd-based catalysts also has been demonstrated. There are several important variables that can affect product distribution, such as solvent, co-catalyst, reaction time, and the nature of Pd catalysts. Luijckx et al. (Luijckx et al. 2009) found that the etherification occurred between HMF and alcohols in alcoholic solvents employing 10% Pd/C, and the etherification products acted as intermediates to form DMF. When 1,4-dioxane was used, hydrogenolysis proceeded slowly, and 88.8% selectivity of FDM with 90% conversion was obtained at 60 °C for 740 min. Silva et al. (Silva et al. 2021) used hydrophobic cup-stacked carbon nanotubes (CSCNTs) and hydrophilic micrometric active carbon (AC) to fabricate a hybrid support, and the supported Pd catalysts on this carbonaceous substrate could catalyze the conversion of HMF to FDM with selectivity of > 85%. The electron-donating nature of the support lowered the electron density of Pd element and made reactant adsorption through the C=C double bonds more difficult, thereby increasing the selectivity for hydrogenation of the C=O double bond. In addition, the product selectivity was sensitive to hydrogen pressure, and low hydrogen pressure was required to prevent the over-hydrogenation to obtain high selectivity of FDM.

Pt-based catalysts are efficient for catalytic hydrogenation of HMF to FDM under mild conditions. Chatterjee et al. (Chatterjee et al. 2014) reported the hydrogenation of HMF without any additive over Pt/MCM-41, affording complete conversion with a selectivity of 98.9% in water. The highest selectivity of FDM was obtained under mild conditions (35 °C, 2 h, 8 bar  $H_2$ ). The catalyst could be reused at least 7 times without any obvious loss of catalytic activity. The catalytic activity is strongly influenced by the properties of reaction solvents. Among the studied solvents, water is the best choice for the formation of FDM, followed by typical polar protic solvents including methanol, ethanol, butanol and propanol. These polar protic solvents have negative  $\delta$  values, where the  $\delta$  value represents the difference between donor number and acceptor number. It was notable that the conversion of HMF decreased with increasing  $\delta$  value, which might be attributed to the Lewis acidity of these organic solvents. Vikanova et al. (Vikanova et al. 2021) demonstrated that 0.1% Pt/CeO<sub>2</sub>–ZrO<sub>2</sub> allowed the production of FDM from HMF in 97% yield with 100% selectivity. Ce<sup>3+</sup> ions seem to be adsorption centers of the carbonyl group,

which contributed to high selectivity of FDM. The addition of zirconium species yields defects at the interface, which provides additional sites for the activation of the carbonyl group of HMF. In fact, the acidic and basic sites of the supports played an important role on the hydrogenation of HMF. Wang et al. (Wang et al. 2022a) investigated the effect of different metal oxide supports on FDM synthesis. Interestingly, compared to the typical acidic metal oxide-like  $\text{TiO}_2$ , the use of basic metal oxide  $\text{MgO}$  afforded higher selectivity of FDM (99% vs. 28%), which can be explained by the different types of preferential chemisorption. In brief, the basic sites of metal oxide favored the adsorption of  $\text{C}=\text{O}$  on HMF, which enhanced the selectivity of FDM. Meanwhile, the acidic sites of metal oxide favored the adsorption of  $\text{C}=\text{C}$  group, resulting in poor FDM selectivity. The Pt atoms were responsible for the activation of  $\text{H}_2$ . The synergistic effect of basic sites and Pt boosted the formation of FDM. Unfortunately, the used Pt/ $\text{MgO}$  catalyst showed the decreasing catalytic activity, despite the excellent selectivity of FDM was obtained. The excellent FDM selectivity also could be obtained by confinement effect. For example, Chen et al. (Chen et al. 2020) prepared Pt nanoparticles (NPs) encapsulated into zeolite Y (Pt@Y) as heterogeneous catalysts for the conversion of HMF to FDM, giving nearly 100% yield in water at 80 °C. Good reusability and stability were also obtained. Due to the confinement effect of zeolite Y, the gap in the activation energies between hydrogenation of aldehyde groups and hydrogenolysis of hydroxyl groups was enlarged, and the hindrance effect prevented the adsorption of the furan ring on catalyst surface, resulting in the enhancement of FDM selectivity.

Ohyama et al. (Ohyama et al. 2013) studied the synthesis of FDM from HMF over gold sub-nano-cluster supported on various metal oxides. The acidic sites of metal

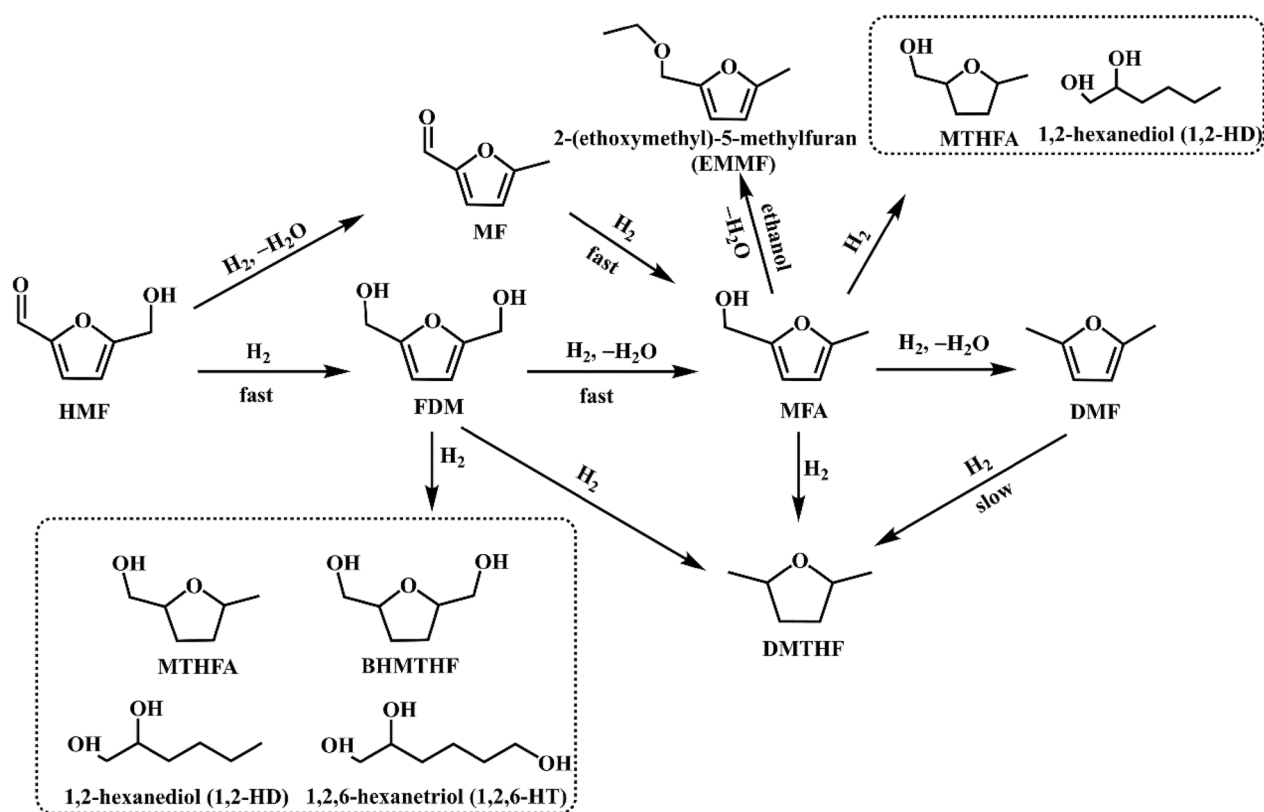
oxide supports promoted opening furan ring of HMF, leading to the decrease of FDM selectivity. Basic  $\text{Al}_2\text{O}_3$  was found to be favorable for the selective production of FDM. In addition to the acid–base property of supports, Au size is also important. Au sub-nano-clusters were more active than single gold atoms. Over 96% yield of FDM was obtained under 65 bar  $\text{H}_2$  at 120 °C for 2 h.

Some typical examples of selective synthesis of FDM from HMF over noble metal catalysts using  $\text{H}_2$  as donor are summarized in Table 2.

Some noble metal catalysts have exhibited good catalytic performance for the synthesis of FDM from HMF, but the rareness and high cost of noble metals limit the practical application. Therefore, to develop catalysts using non-noble metal elements is always attractive. Some Co-, Cu-, Ni-, Zr- and Hf-based catalysts have been reported for the reduction of HMF. Arias et al. (Arias et al. 2020) investigated the catalytic performance of monodisperse metallic Co NPs coated with thin carbon shell (Co@C). A 99% selectivity with 97% conversion was obtained in methanol under optimized conditions. The presence of the thin carbon layer suppressed the deep oxidation of Co NPs in air and facilitated their reduction at lower temperature. Compared to polar aprotic solvents, protic solvents (i.e., methanol) favored the polarization of the  $\text{C}=\text{O}$  group, which enhanced the selectivity of FDM. Chandrashekar et al. (Chandrashekar et al. 2022) prepared Co–NPs-based catalysts by the immobilization and pyrolysis of Co–terephthalic acid–piperazine metal–organic frameworks on  $\text{SiO}_2$ , and the dominant Co element in catalysts existed in metallic form. The as-prepared Co-catalysts were tested for the hydrogenation of HMF to FDM, providing a 95% yield in methanol at 70 °C for 16 h in the presence of 15 bar  $\text{H}_2$ . The products could be switched by changing reaction conditions. For

**Table 2** Some examples of catalytic hydrogenation of HMF to FDM over noble metal catalysts in the presence of  $\text{H}_2$

Catalyst	$\text{H}_2$ pressure (bar)	Solvent	T (°C)	t (h)	Conversion of HMF (%)	FDM yield (mol%)	Refs.
1%Ir/ $\text{SiO}_2$	10	THF	60	5	60	60	(Chimentao et al. 2019)
1%Ir/ $\text{SiO}_2(\text{Cl})$	10	THF	60	5	97	97	(Chimentao et al. 2019)
10%Pd/C	ca.1	1,4-Dioxane	60	12.3	90	79.9	(Luijckx et al. 2009)
2.0%Pd/CSCNT-AC	34	Water	110	2	75	63.8	(Silva et al. 2021)
Pt/MCM-41	8	Water	35	2	100	98.9	(Chatterjee et al. 2014)
0.1% Pt/ $\text{CeO}_2$ – $\text{ZrO}_2$	10	Ethanol	170	2	70	70	(Vikanova et al. 2021)
0.1% Pt/ $\text{CeO}_2$ – $\text{ZrO}_2$	10	Ethanol	170	8	97	97	(Vikanova et al. 2021)
Pt/ $\text{MgO}$	20	Isopropanol	120	1	84	83	(Wang et al. 2022a)
Pt/ $\text{TiO}_2$	20	Isopropanol	120	1	28	7.8	(Wang et al. 2022a)
Pt/ $\text{MgO}$	20	Isopropanol	150	1	99	98	(Wang et al. 2022a)
Pt@Y	20	Water	80	4	100	100	(Chen et al. 2020)
Au/ $\text{Al}_2\text{O}_3$	65	Water	120	2	–	> 96	(Ohyama et al. 2013)

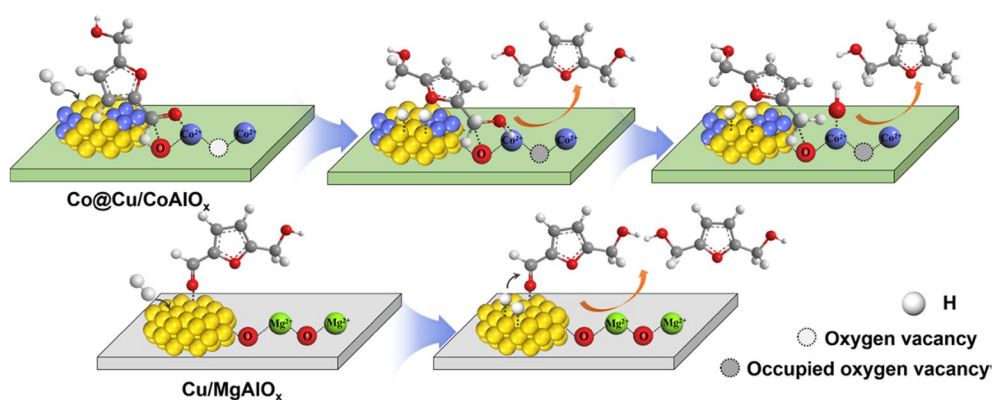


**Scheme 2.** Possible reaction pathways for the hydrogenation of HMF in ethanol over copper doped porous metal oxide catalysts. Reproduced with permission from Ref. (Kumalapatni et al. 2014), copyright Wiley

example, an 89% yield of MFA was obtained after increasing the temperature and H<sub>2</sub> pressure to 100 °C and 30 bar, respectively. Wang et al. (Wang et al. 2022c) reported the solvent-free synthesis of FDM from HMF over cobaltic nitrogen-doped carbon (Co-NC) catalysts, and a desirable FDM yield of 91.5% was afforded at 90 °C in the presence of 50 bar H<sub>2</sub>. The doped graphitic N might facilitate the polarization of H<sub>2</sub> to form H<sup>+</sup> and H<sup>-</sup>, which promoted the hydrogenation of HMF. This solvent-free system avoids the removal of solvent after reaction. Similar to HMF, furfural also could undergo hydrogenation to form furfuryl alcohol in satisfactory yield employing Co-NC catalysts.

Compared to cobalt, copper is more abundant on earth. Copper catalysts have been extensively studied. Kumalapatni et al. (Kumalapatni et al. 2014) investigated the tunable and selective hydrogenation of HMF to different products over Cu-based catalysts. The introduction of Cu<sup>2+</sup> during the preparation of hydrotalcite gave Cu-containing hydrotalcite, and the further calcination produced Cu-doped porous metal oxides. At 100 °C and 50 bar H<sub>2</sub>, a 99% selectivity of FDM and full conversion of HMF were obtained over Cu<sub>0.59</sub>Mg<sub>2.34</sub>Al<sub>1.00</sub> in ethanol. The increase of temperature to 140 °C led

to the decrease of FDM selectivity because of over-hydrogenation and other side-reactions. The addition of ruthenium dopant into the catalysts boosted the hydrogenation activity, which increased the total yield of DMF and DMTHF to 81%. Based on the identified reaction intermediates by GC-MS analysis and authentic standards, the authors proposed the reaction pathways for the conversion of HMF in ethanol in the presence of H<sub>2</sub>, as shown in Scheme 2. In addition to the hydrogenation of aldehyde group, hydroxyl group, and furan ring, etherification and ring-opening reactions also occurred. The reaction pathway and selectivity for HMF reduction over Cu-doped metal oxides could be tuned by adjusting interfacial structure, which was reported by Wang et al. (Wang et al. 2020). They prepared a series of catalysts with multiple interfaces by reduction of Cu-containing layered double hydroxides (LDHs). For example, Cu/MgAlO<sub>x</sub> was derived from CuMg<sub>5</sub>Al<sub>2</sub>-LDHs. The Cu particles of Cu/MgAlO<sub>x</sub> catalysts were partially encapsulated by the MgAlO<sub>x</sub> support, resulting in the formation of highly intimate Cu-MgAlO<sub>x</sub> interfaces. The specific Cu-MgAlO<sub>x</sub> interfaces selectively activated C=O bond to produce FDM, affording a 92.7% yield. In contrast to the Cu/MgAlO<sub>x</sub> catalyst, the Co@Cu/CoAlO<sub>x</sub> catalyst



**Scheme 3.** Possible Mechanism of HMF Hydrogenation over Cu/MgAlO<sub>x</sub> and Co@Cu/CoAlO<sub>x</sub> Catalysts. Reproduced with permission from Ref. (Wang et al. 2020). Copyright (2020) American Chemical Society

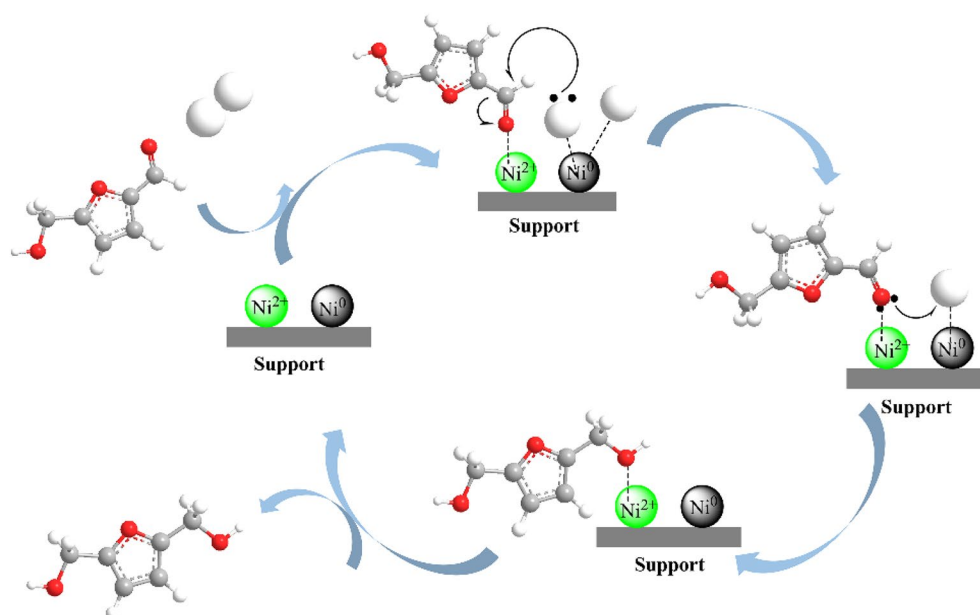
with both Cu–MgAlO<sub>x</sub> interfaces and metallic Co–Cu interfaces was prepared from CuCo<sub>x</sub>Al<sub>2</sub>–LDHs. By tuning the ratio of Co/Cu, the metallic Co–Cu interfaces could activate C–OH and even furan ring, offering 98.5% DMF and 83.6% DMTHF under optimized conditions. As shown in Scheme 3, the Cu particles of Cu/MgAlO<sub>x</sub> adsorbed the carbonyl oxygen atom of HMF to form an on-top (O)–Cu linkage, which produces FDM as the sole product. The unsaturated O–Co–V<sub>O</sub> (V<sub>O</sub> represents an oxygen vacancy) sites of Co@Cu/CoAlO<sub>x</sub> could interact with C=O or C–OH to form (C)–O–Co–(O) linkage, affording DMF as the product.

Some simple Cu-containing alloys also exhibited good catalytic performance. Bottari et al. (Bottari et al. 2015) found the commercial copper–zinc alloy nanoparticles with small size of < 150 nm could catalyze the selective hydrogenation of HMF to FDM in 95% yield in ethanol employing 70 bar H<sub>2</sub>. The direct use of commercial catalysts boosted the reproducibility of results regarding batch to batch variations. Almost at the same time, Zhu et al. (Zhu et al. 2015) reported the catalytic hydrogenation of HMF over homemade mineral-derived Cu–ZnO catalysts, affording 99.1% and 91.8% yields of FDM and DMF at 100 and 220 °C, respectively. At high temperature, such as 220 °C, the deposition of organic compounds on the catalysts led to the deactivation, and the removal of undesirable deposited carbonaceous species could be achieved by calcination and reduction.

Cu species exhibited good catalytic performance for the reduction of HMF. In addition, some useful methods have been used for the preparation of Cu-based catalysts. Here, we introduced several typical examples. Rao et al. (Rao et al. 2021) developed a solvent-free solid-state grinding method to prepare copper–alumina catalysts for the selective hydrogenation of HMF, which avoids the tedious preparation procedure and the use of any

solvents. The synergistic effect of Cu<sup>0</sup> and Cu<sup>2+</sup> as well as uniform distribution of copper NPs contributed to good catalytic performance, providing a 93% yield of FDM at 130 °C for 1 h in the presence of 30 bar H<sub>2</sub>. Another strategy for the preparation of Cu-based catalysts is to use metal organic frameworks (MOFs) as one of precursors. MOFs have some important natures, such as regular porosity, tunable pore size, the ability to stabilize metal/metal oxide NPs and prevent the agglomeration/growth of NPs (Falcaro et al. 2016), thereby becoming good alternatives as templates and/or precursors to fabricate heterogeneous catalysts. Feng et al. (Feng et al. 2019) reported ZIF-8 encapsulated Cu NP (CuNP@ZIF-8) catalysts for the reduction of HMF to FDM, affording a 99% yield in ethanol. Inductively coupled plasma optic emission spectrometer analysis and recyclability test suggested the good stability of highly dispersed Cu NPs which were immobilized by the frameworks of ZIF-8. Unlike the other studies (Rao et al. 2021), Feng et al. (Feng et al. 2019) demonstrated Cu<sup>1</sup> and Cu<sup>0</sup> species were responsible for the activation of aldehyde group and H<sub>2</sub>, respectively. The ligand is essential to the preparation of MOFs, and a large number of ligands are derived from non-renewable fossil resources. Bao et al. (Bao et al. 2022) employed renewable HMF-derived 2,5-furandicarboxylic acid as ligand to synthesize a novel Cu-based MOFs, and Cu NPs supported on carbon nanosheets were fabricated by post-treatment of the MOFs. The as-prepared Cu catalysts exhibited good catalytic activity and stability for the hydrogenation of HMF to FDM, providing a 99.4% yield.

In addition to catalysts, the reaction medium also influences product selectivity. Water is not only a cheap and green solvent, but also an important solvent additive to tune the product distribution. Liu et al. (Liu et al. 2015) studied the effects of water on the hydrogenation of



**Scheme 4.** Possible mechanism of HMF hydrogenation over Ni/CNTs catalysts (Huang et al. 2022)

HMF in THF in the presence of H<sub>2</sub> by reaction kinetics, in which Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was used as catalyst. High yield of DMF could be obtained in pure THF. Notably, the addition of small amount of water in THF (THF/water, *w/w*, 95/5) led to water coverage on active sites, which remarkably inhibited the further hydrogenolysis of FDM to other products (i.e., DMF) and enhanced the selectivity of FDM. The negative effect of water on the reduction rate of HMF provides an approach to adjust the selectivity of different products. Nevertheless, when the production of DMF was carried out on large scale, the water formation changed the solvent components and influenced the catalytic performance.

Ni-based catalysts have shown good catalytic performance in hydrogenation reaction. For the hydrogenation of HMF to FDM, several effective catalysts have been developed. Zhang et al. (Zhang et al. 2020) synthesized activated carbon (HC) employing sucrose as precursor by hydrothermal method, and the further loading of Ni component gave heterogeneous Ni/HC. The large surface area and a lot of oxygen-containing functional groups of the sucrose-derived carbon facilitated the dispersion and anchoring of Ni species. The metallic Ni species and big Ni NPs favored the selective hydrogenation of aldehyde group to yield FDM, and an 88% yield was obtained in 1,4-dioxane over reduced 10%-Ni/HC catalyst with big Ni particle size at 160 °C in the presence of 15 bar H<sub>2</sub>. The yield of FDM was acceptable, but the long reaction time of 24 h made it an energy-intensive process. Besides, the catalytic activity of the reused Ni/HC catalysts has

not been reported, in spite of good thermal stability of the catalysts at reaction temperature. The use of carbon nanotubes (CNTs) as support of Ni afforded a 95% selectivity with 99.8% conversion in ethanol under milder conditions (5 bar H<sub>2</sub>, 120 °C, 3 h), which was reported by Liu's group (Huang et al. 2022). In consistent with previous conclusion (Zhang et al. 2020), Ni<sup>0</sup> could activate H<sub>2</sub> and Ni<sup>2+</sup> as Lewis acid could adsorb oxygen-containing groups, which synergistically catalyzed the formation of FDM, as shown in Scheme 4. However, the excessive Ni<sup>2+</sup> species boosted deep reduction of HMF, decreasing the selectivity of FDM. The activity of spent Ni/CNTs catalysts decreased slightly due to the adsorbed organic compounds, and the re-calcination in 20% H<sub>2</sub>/Ar could partly recover the catalytic activity.

The impurities in substrate (i.e., HMF) might profoundly affect the catalytic performance. For example, DMSO has been widely used for the synthesis of HMF from carbohydrates because of its dissolving capacity and dehydration activity. Ojagh et al. (Ojagh et al. 2021) developed Ni/SiO<sub>2</sub> catalysts with high Ni dispersion for the synthesis of FDM from HMF in excellent yield. The addition of DMSO led to remarkable decrease of both HMF conversion and FDM yield. The poisoning effect of DMSO could be explained by that the sulfur and carbon deposition covered the active Ni species. Owing to the great influence of DMSO, the choice of reaction medium for one-pot conversion of carbohydrates to downstream products of HMF should be considered seriously. Both the positive effect of DMSO for HMF synthesis and

possible negative effect for HMF conversion should be taken into account.

Compared to monometallic catalysts, bimetallic catalysts have some potential advantages, such as tunable dispersion of NPs, adjustable hydrogenation activity, and facile isolation of catalysts. Several typical cases will be introduced as follow. Fe is a cheap metal and has been widely used to fabricate magnetic catalysis materials. Yu et al. (Yu et al. 2015) reported the hydrogenation of HMF over home-made bimetallic Ni–Fe/CNT catalysts. The introducing Fe species enhanced the dispersion of Ni component. In comparison with Ni/CNTs catalyst, an appropriate Ni/Fe ratio of 2.0 profoundly increased the selectivity of FDM from 76.4% to 96.1% at 110 °C for 18 h in 30 bar H<sub>2</sub>. The magnetic nature of Ni–Fe/CNT catalysts facilitated the separation of catalysts from reaction mixture for next catalytic run. Arias et al. (Arias et al. 2021) developed bimetallic CuFe NPs covered by thin carbon layers (denoted as CuFe@C) for the hydrogenation of HMF. Compared to monometallic Cu@C catalyst, the CuFe@C with an appropriate Cu/Fe ratio exhibited higher catalytic activity, which might be attributed to more active centers derived from the intimate contact between Cu and Fe.

Some typical examples of selective synthesis of FDM from HMF over non-noble metal catalysts using H<sub>2</sub> as donor are summarized in Table 3.

#### **Alcohols or carboxylic acids as reduction reagent**

Catalytic transfer hydrogenation (CTH) reaction has been regarded as a promising method for upgrading

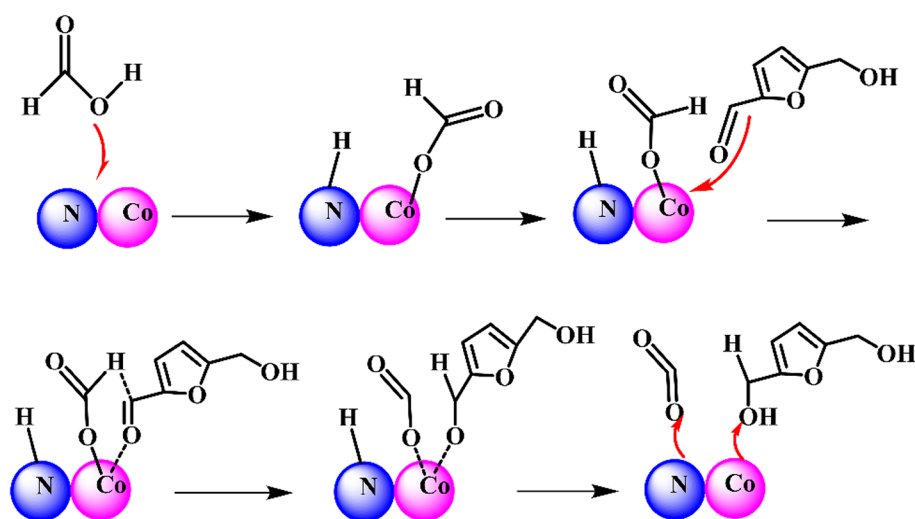
biomass-based carbonyl compounds, typically furfural and HMF, to their corresponding alcohols. Alcohols (i.e., methanol, ethanol, isopropanol) and carboxylic acids (typically formic acid) are used as hydrogen donors. Some recent advances in CTH of HMF have been summarized in this section.

Co-based catalysts are effective for CTH of HMF, in which either formic acid or isopropanol could act as hydrogen source. Xu et al. (Xu et al. 2021) developed N-doped carbon confined Co–N<sub>x</sub> (Co–NC) catalysts employing SBA-15 as a mesopore template. A 92.3% selectivity of FDM with 88.2% HMF conversion was obtained in the presence of 7.5 equiv. formic acid at 160 °C for 5 h, while the conversion of formic acid reached to 89.5%. It is notable that highly dispersed N-confined Co species (Co–N<sub>x</sub>) instead of bare Co NPs acted as main active centers, as shown in Scheme 5. The CTH reaction starts from the dissociation of C–H in formic acid to form N–H\* and Co–formate (Co–HCOO\*) species, which is the rate-determining step. Then, the carbonyl oxygen of HMF is adsorbed by Co and interacts with the Co–HCOO\* species. As a result, the transfer of hydrogen from formate to the carbonyl group proceeds via an intermolecular hydride transfer. Finally, the formation and desorption of FDM accompanies with the release of CO<sub>2</sub>. Wang et al. (Wang et al. 2022b) reported that Co<sub>1.6</sub>/UiO-66-NH<sub>2</sub> catalyzed the effective CTH of HMF into FDM in isopropanol, affording a 95.9% FDM selectivity with 92.6% HMF conversion under milder reaction conditions (100 °C, 4 h). Among the investigated isopropanol, methanol, ethanol, n-butanol and 2-butanol,

**Table 3** Some examples of catalytic hydrogenation of HMF to FDM over non-noble metal catalysts in the presence of H<sub>2</sub>

Catalyst	H <sub>2</sub> (bar)	Solvent	T (°C)	t (h)	Conversion of HMF (%)	FDM yield (mol %)	Refs.
Co@C	10	Methanol	110	2	97	96	(Arias et al. 2020)
Co–NPs@SiO <sub>2</sub>	15	Methanol	70	16	–	95	(Chandrashekar et al. 2022)
Co–NC	50	Solvent-free	90	3	99.3	91.5	(Wang et al. 2022c)
Cu <sub>0.59</sub> Mg <sub>2.34</sub> Al <sub>1.00</sub>	50	Ethanol	100	3	100	99	(Kumalapatni et al. 2014)
Cu/MgAlOx	10	1,4-Dioxane	180	5	97.3	92.7	(Wang et al. 2020)
CuZn	70	Ethanol	120	3	>99	95	(Bottari et al. 2015)
Cu–ZnO	15	1,4-Dioxane	100	2	100	99.1	(Zhu et al. 2015)
20 mol% Cu–Al <sub>2</sub> O <sub>3</sub>	30	Methanol	130	1	>99	93	(Rao et al. 2021)
CuNPs@ZIF-8	20	Ethanol	140	3	>99	99	(Feng et al. 2019)
CFP-300	20	Ethanol	120	4	100	99.4	(Bao et al. 2022)
10%–Ni/HC	15	1,4-Dioxane	160	24	93.6	88	(Zhang et al. 2020)
15 wt % Ni/CNTs	5	THF	120	3	99.8	94.8	(Huang et al. 2022)
10Ni/SiO <sub>2</sub>	40	n-Butanol	180	6	100	99	(Ojagh et al. 2021)
Ni <sub>2</sub> –Fe <sub>1</sub> /CNTs	30	n-Butanol	110	18	100	96.1	(Yu et al. 2015)
Cu <sub>0.24</sub> –Fe <sub>0.76</sub> @C	10	Methanol	110	4	94	93	(Arias et al. 2021)





**Scheme 5.** Proposed mechanism of CTH of HMF over Co-NC. Reproduced from Ref. (Xu et al. 2021), copyright Royal Society of Chemistry

isopropanol provided the highest HMF conversion and FDM selectivity. The alcohols with low reduction potentials favored the CTH of HMF. Another important finding is that both acidic and basic sites of Co/UiO-66-NH<sub>2</sub> catalysts have profound effect on catalytic activity, but the intrinsic mechanism is still unclear.

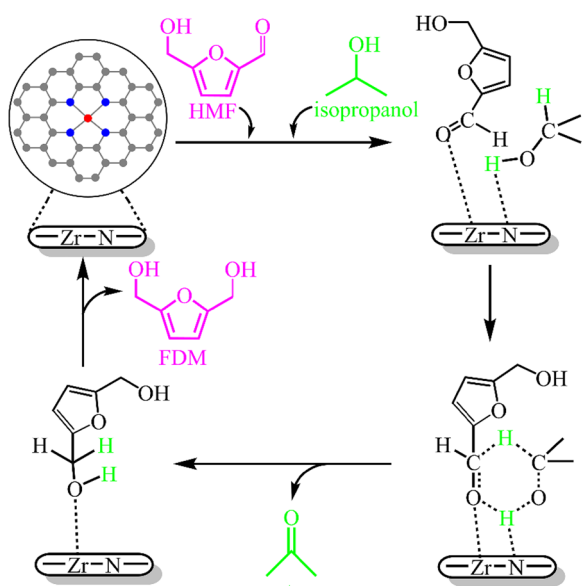
Hf-based catalysts have been reported for the CTH of HMF. Hu et al. (Hu et al. 2019) reported a new Hf-based metal-organic coordination polymer (Hf-DTMP) for the CTH of HMF to FDM in 2-butanol, providing a 96.8% yield at 130 °C for 4 h. The authors held a view that a large number of Lewis acid sites (Hf<sup>4+</sup>) and Lewis base sites (O<sup>2-</sup>) with synergistic effect contributed to the high catalytic activity. The results of control experiments revealed that Lewis base sites played more important roles.

Huang et al. (Huang et al. 2023) reported an example using CuO/boehmite for the CTH of HMF into FDM, in which ethanol was employed as both solvent and hydrogen donor. Boehmite contains both acid and base sites, which has a significant effect on catalytic performance. For instance, 2-hydroxymethyl-5-ethoxyfuran (HEMF) might be produced as a by-product from FDM and ethanol catalyzed by the hydroxyl group Brønsted acid (H<sup>+</sup>) on boehmite surface. When boehmite was used as a sole catalyst at 160 °C, the selectivities of FDM and HEMF were 59.7% and 25.1%, respectively. The addition of CuO hindered the Brønsted acid sites of boehmite and introduced Lewis acid sites (Cu<sup>2+</sup>) on the catalyst surface. The increase of the Lewis acid/Brønsted acid ratio inhibited the etherification of alcohols and boosted the selectivity of FDM. As a result, a 96.9% selectivity of FDM with 75.9% conversion was obtained over 40 wt% CuO/boehmite under the same conditions. In combination with

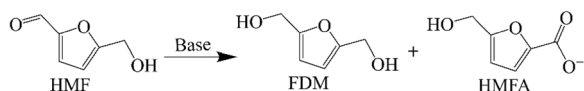
other findings (Wang et al. 2022b; Hu et al. 2019), more efforts should be devoted to tuning acid-base properties of catalysts for the enhancement of FDM formation. The reduction of CuO/boehmite by ethanol led to the decrease of catalytic activity, and the re-calcination in air recovered its activity.

The use of single atom catalysts for biomass valorization has attracted attention (Mondelli et al. 2020). For instance, Hu et al. (Hu et al. 2022) prepared Zr-based single-atom catalyst (Zr/NC) with low Zr content of 0.58 wt% by pyrolysis of Zr-doped ZIF-8. The Zr/NC catalyst could catalyze the CTH of HMF to FDM, offering an approaching 100% selectivity with full conversion at 130 °C for 2.5 h in isopropanol. The use of ethanol or n-butanol also afforded satisfactory yields of FDM up to 95%. The atomically dispersed Zr-N<sub>4</sub> species were confirmed to be the active sites, as shown in Scheme 6. Both the electron transfer from the pyridinic-N to Zr in the Zr-N<sub>4</sub> active sites and high Lewis acid-base strengths of Zr/NC contributed to the good catalytic activity. The Zr-N<sub>4</sub> structures were stable under investigated conditions, but the deposition of carbon on the spent Zr/NC led to gradual decrease of FDM yield.

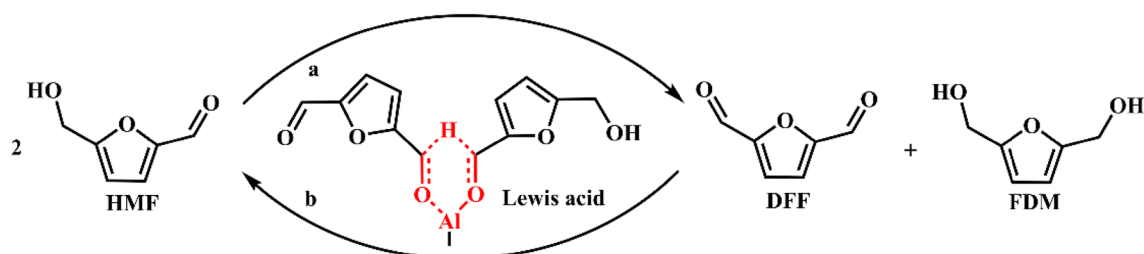
As discussed earlier, alcohols can act as a hydrogen donor for the reduction of HMF to FDM. A special example is Cannizzaro reaction. HMF contains an aldehyde group without a hydrogen atom at an  $\alpha$ -position. The base-induced Cannizzaro reaction of HMF generates FDM and 5-hydroxymethylfurfanoic acid (HMFA), as illustrated in Scheme 7. Some typical strong bases, such as NaOH, KOH, Ca(OH)<sub>2</sub>, have been used and provided good yields (Subbiah et al. 2013; Kang et al. 2012). For example, Subbiah et al. (Subbiah et al. 2013) investigated



**Scheme 6.** Reaction mechanism for the CTH of HMF to FDM in isopropanol over Zr/NC. Reprinted from Ref. (Hu et al. 2022), copyright Royal Society of Chemistry



**Scheme 7.** Synthesis of FDM from HMF by Cannizzaro reaction



**Scheme 8.** Lewis acid-catalyzed MPVO reaction of HMF to DFF and FDM. Reproduced with permission from Ref. (Li et al. 2017), copyright Wiley

the conversion of HMF in water in the presence of 1.1 equiv. NaOH at room temperature, and an 86% yield of FDM as well as 87% HMFA was obtained after 18 h. The generated FDM and HMFA could be isolated by selective crystallization. Similar to Cannizzaro reaction, the selective conversion of HMF to 2,5-diformylfuran (DFF) and FDM is another strategy. Li et al. (Li et al. 2017) investigated a special Meerwein–Ponndorf–Verley–Oppenauer (MPVO) reaction to produce DFF and FDM catalyzed by Al-based Lewis acid, where HMF acted as both oxidant and reductant. In such a process, a reversible equilibrium exists between HMF and DFF/DHMF, as illustrated in Scheme 8, resulting in low conversion. Owing to the lower solubility of FDM compared to DFF in acetonitrile, the use of acetonitrile as reaction medium facilitated the crude separation of FDM products from DFF products, thereby pushing the equilibrium shift towards HMF conversion. Under optimized reaction conditions, a 44.7% conversion of HMF with DFF/FDM molar ratio as 1.0 could be obtained. The use of HMF as hydrogen donor avoids external reductant, but the co-existence of oxidized product and FDM makes it more difficult to purify the products.

Some examples of CTH of HMF to FDM are summarized in Table 4.

#### Silane as reduction reagent

The silanes are water- and air-stable hydrogen sources and could be stimulated by metal-containing catalysts under mild conditions. Long et al. (Long et al. 2018)

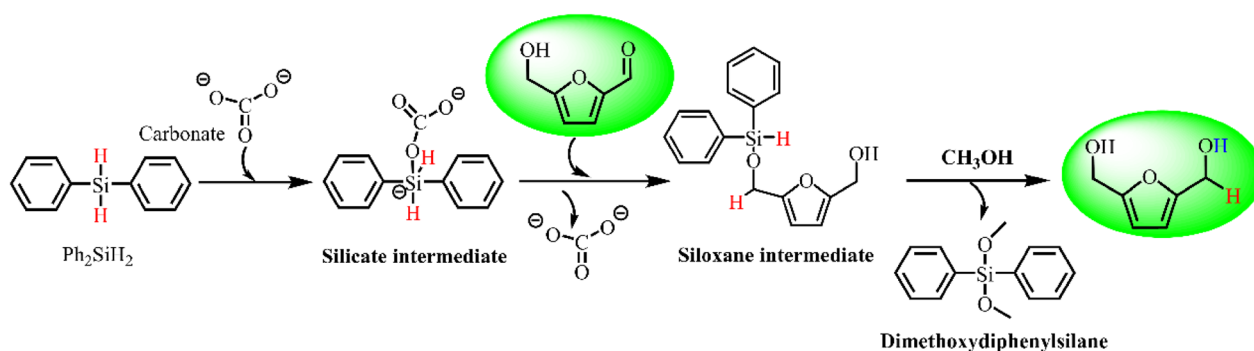
**Table 4** Some examples of CTH of HMF to FDM

Catalyst	H source	Solvent	T (°C)	t (h)	Conversion of HMF (%)	FDM yield (mol%)	Refs.
Co-NC	Formic acid	1,4-Dioxane	160	5	88.2	81.4	(Xu et al. 2021)
Co-NC	Formic acid	1,4-Dioxane	160	10	100	86	(Xu et al. 2021)
Co <sub>1.6</sub> /UiO-66-NH <sub>2</sub>	Isopropanol	Isopropanol	100	4	92.6	88.8	(Wang et al. 2022b)
Hf-DTMP	2-Butanol	2-Butanol	130	4	99.1	96.8	(Hu et al. 2019)
40 wt% CuO/Bhm	Ethanol	Ethanol	160	3	75.9	73.5	(Huang et al. 2023)
Zr/NC	Isopropanol	Isopropanol	130	2.5	100	99.6	(Hu et al. 2022)

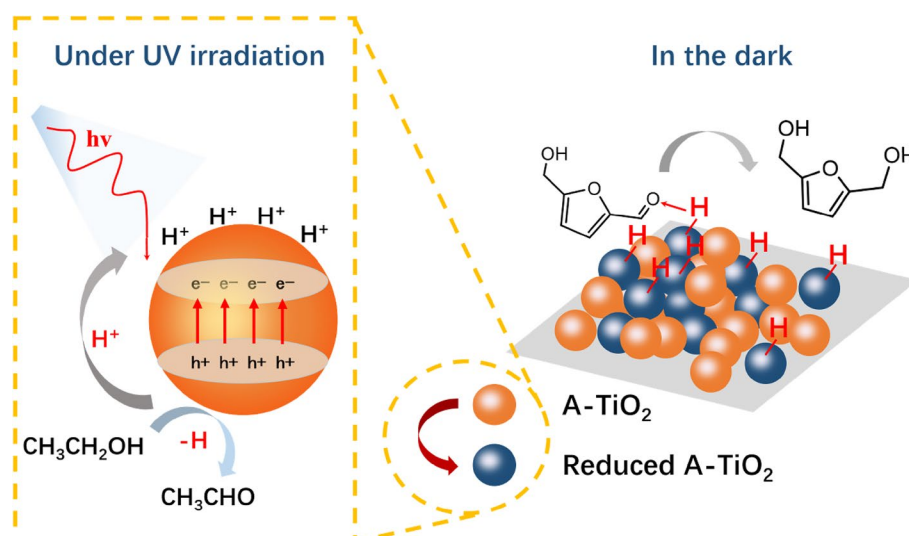
studied the selective reduction of HMF to FDM over alkali metal salts and alkaline earth metal salts using diphenylsilane as hydrogen source at room temperature. Among screened catalysts,  $K_2CO_3$  offered the full conversion of HMF with a 70.1% yield of FDM after 2 h. The relatively low yield of FDM could be attributed to the formation of stable siloxane intermediate. The addition of methanol facilitated the breakage of the siloxane bond to form FDM, boosting the yield of FDM to 94.2%. A possible reaction pathway has been shown in Scheme 9. The reduction reaction starts from the interaction of  $CO_3^{2-}$  and diphenylsilane to form a silicate intermediate with nucleophilicity. Then, the silicate intermediate activates the aldehyde group of HMF through hydride transfer to afford the siloxane intermediate, and the further hydrolysis generates FDM.

### Synthesis of FDM from HMF by photo-catalysis

Photo-catalysis provides a green and sustainable approach for the production of a variety of valuable compounds from biomass. Some cases about photo-catalytic reduction of HMF have been reported. Guo et al. (Guo and Chen 2016) reported the photo-induced reduction of HMF over a  $Pt/g-C_3N_4$  catalyst under visible light irradiation. Under optimized conditions, only a 6.5% yield of FDM was obtained. This is an early example employing photo-catalysis for the synthesis of FDM, and the catalytic efficiency was still unsatisfactory. Photo-induced holes and/or reactive oxygen species are sensitive to reaction conditions, which might induce undesirable side reactions. Qiao et al. (Qiao et al. 2019) proposed a two-step strategy for the synthesis of FDM from HMF on amorphous  $TiO_2$  using ethanol as hydrogen donor,



**Scheme 9.** Plausible reaction pathway for the HMF–FDM conversion. Reprinted from Ref. (Long et al. 2018), copyright MDPI



**Scheme 10.** Possible mechanism of HMF hydrogenation to FDM over amorphous  $TiO_2$ . Reprinted from Ref. (Qiao et al. 2019), copyright Royal Society of Chemistry

as shown in Scheme 10. The first step was carried out to store  $H^+/e^-$  species on the surface of  $TiO_2$  under UV irradiation, and acetaldehyde was formed by dehydrogenation of ethanol. Then, the second step was triggered in the dark after the addition of HMF. The oriented adsorption of the HMF aldehyde group and the enhanced desorption of FDM by acetaldehyde inhibited undesirable deep reduction, which increased the selectivity of FDM. A 99% conversion of HMF with a 99% selectivity of FDM was obtained under  $N_2$  atmosphere at 25 °C. Jaryal et al. (Jaryal et al. 2022) reported the photo-catalytic reduction of HMF over  $TiO_2$  in acetonitrile at room temperature using p-methoxybenzyl alcohol as hydrogen donor, and a 30% yield of FDM was achieved simultaneously with the formation of 4-anisaldehyde after 24 h.

#### Synthesis of FDM from HMF by electro-catalysis

If the cheap electricity is obtained from green and sustainable resources, such as solar and wind, electro-catalysis will be a potential future green methodology for biomass utilization. Especially when water acts as a proton source, electro-catalysis is regarded as a promising hydrogenation strategy. Some solid mono-metal electrodes have been used as catalysts. Koper's group (Kwon et al. 2013) investigated the hydrogenation of HMF over solid metal electrodes in neutral media. Among the studied metals, Ag electrode favored the selective production of FDM with selectivity up to 85% at all potentials. The highest concentration of FDM on Ag reached 13.1 mM  $cm^{-2}$  at  $-0.81$  V. Apart from electrodes, the applied potential also affected the product selectivity. The more negative potentials boosted the evolution of more hydrogen, thereby decreasing the selectivity of FDM. The pH value played an important role in terms of onset potential and final product. The same group (Kwon et al. 2015) demonstrated the electro-catalytic hydrogenation of HMF in 0.5 M  $H_2SO_4$  aqueous solution, and the further hydrogenation of furan ring was remarkably promoted because of lower activation energy under acidic conditions compared to neutral conditions.

The combination of Ag and an additional metal or metal oxide was used to enhance the hydrogenation of HMF (de Luna et al. 2020, 2021; Zhong et al. 2022; Zhao et al. 2022). For example, Zhong et al. (Zhong et al. 2022) developed Ag-decorated Cu nanowire arrays as electro-catalysts. A 97.1% FDM selectivity with 99.5% HMF conversion and 96.5% faradaic efficiency was achieved. The synergic role of Cu and Ag active sites promoted the rapid ion diffusion, which enhanced the electro-catalytic activity for selective synthesis of FDM. Zhao et al. (Zhao et al. 2022) reported dispersed Ag nanoparticles immobilized on one-dimensional  $TiO_2$  nanotubes for the electro-reduction of HMF, affording an 89.8% selectivity of FDM

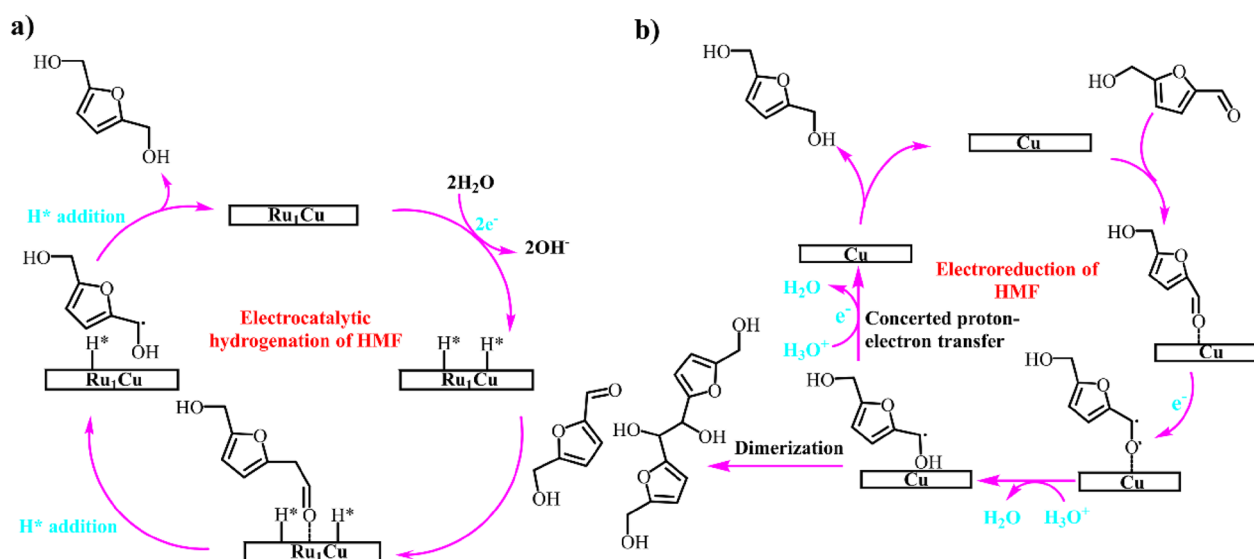
as well as a productivity value of 0.1 mmol  $cm^{-2} h^{-1}$ . The heterojunction-induced interactions between Ag and  $TiO_2$  disfavored the hydrogen evolution reaction and facilitated electron transfer across the interface. Moreover, the use of  $TiO_2$  as a support increased the utilization efficiency of Ag. These beneficial factors enhanced the catalytic performance.

The effective activation of water to form active H species and the inhibition of hydrogen evolution are of significance for selective synthesis of FDM. Ji et al. (Ji et al. 2022) reported that  $Ru_1Cu$  single-atom alloy catalyst showcased better performance for the reduction of HMF to FDM with boosting productivity (0.47 vs. 0.08 mmol  $cm^{-2} h^{-1}$ ) and faradic efficiency (85.6 vs. 71.3%) compared to Cu counterpart. It is notable that a high faradic efficiency of 87.5% could be obtained at high HMF concentration (100 mM). As shown in Scheme 11, the additional dispersed Ru switches the reaction pathways. The single-atom Ru enhanced the activation of water to generate  $H^*$  species that rapidly react with HMF to form FDM. In contrast, the carbonyl of HMF accepted an electron to form a radical intermediate that could be further converted into FDM or dimer.

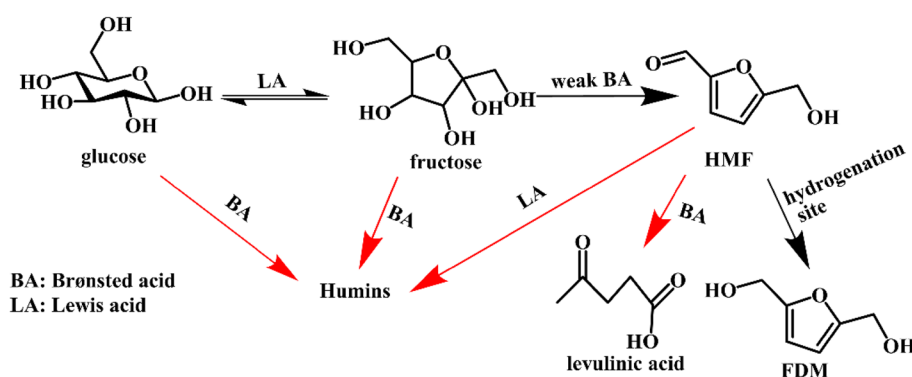
#### Synthesis of FDM from hexose

The selective hydrogenation of HMF has been widely studied, and high yields of FDM have been obtained in some cases. However, HMF is still not an accessible bulk chemical because of difficult purification process and the unstable nature. The direct conversion of carbohydrates to FDM without separation of HMF intermediate is an alternative method, but it faces challenges. It is well-known that HMF is usually produced by acid-catalyzed dehydration of hexose (typically fructose and glucose). Many undesirable side-reactions occur in the presence of acids, resulting in the formation of by-products, such as levulinic acid, formic acid, lactic acid, and humins, as shown in Scheme 12. Moreover, the direct hydrogenation of carbohydrates to corresponding sugar alcohols is also a possible side-reaction. Limited works on this topic have been reported. In addition, some typical examples will be introduced next.

Fructose is a widely used sugar for the synthesis of HMF. Some efforts have been devoted to the production of FDM from fructose. Owing to different requirements of fructose dehydration to HMF and HMF hydrogenation to FDM, in some examples, these two steps are carried out under different conditions, respectively. The biomass-derived formic acid can act as an acid catalyst for fructose dehydration and a hydrogen donor for hydrogenation. In 2010, Thananattathanachon et al. (Thananattathanachon and Raufuss 2010) reported a two-step method for the synthesis of FDM from fructose. Formic acid catalyzed the



**Scheme 11.** Proposed mechanisms of HMF hydrogenation to FDM over a)  $\text{Ru}_1\text{Cu}$  and b)  $\text{Cu}$ . Reproduced with permission from Ref. (Ji et al. 2022), copyright Wiley

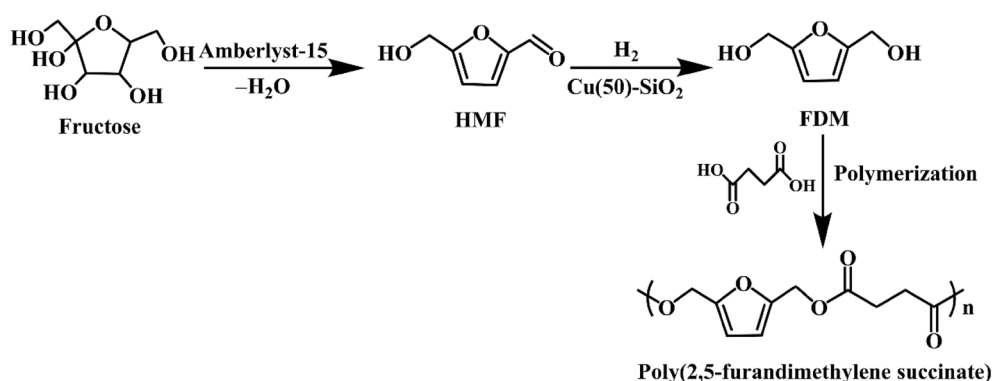


**Scheme 12.** Possible reaction network of FDM synthesis from hexose

dehydration of fructose to HMF in DMSO at 150 °C for 5 h. Then, the hydrogenation of as-formed HMF was carried out at 40 °C after adding excess formic acid (in THF), triethylamine, and Ir catalysts, providing an isolated 71% yield of FDM. Cai et al. (Cai et al. 2014) demonstrated one-pot tandem reactions in ionic liquid/water system. The dehydration of fructose was carried out in 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) at 130 °C for 20 min, providing a 75% yield of HMF. Then, the hydrogenation of resulting HMF was performed after adding water and supported metal catalysts. The selectivity of products was strongly dependent on the metal species. Under 60 bar  $\text{H}_2$  at 50 °C for 3 h, the use of 5% Ir/C and 5% Pd/C afforded 70% and 84% selectivities of FDM (based on HMF) and BHMTHE, respectively. Upare et al. (Upare et al. 2018) reported an integrated protocol for the synthesis of FDM-based polymer from fructose. FDM

was produced from fructose by sequential dehydration and hydrogenation in n-butanol, in which heterogeneous Amberlyst-15 and  $\text{Cu-SiO}_2$  were used, respectively. A 92% yield of FDM based on fructose was obtained. Moreover, the mixture of FDM/n-butanol was directly converted into poly(2,5-furandimethylene succinate) employing biomass-derived succinic acid as another monomer without purification of FDM, as illustrated in Scheme 13. This work provided a successful example for the production of the down-stream product of FDM from fructose, and no noble metal catalysts were used.

Compare to “one-pot, two step” method, “one-pot, one step” processes usually afford lower yield of FDM. Xiang et al. (Xiang et al. 2016) reported that the combination of HY zeolite and hydrotalcite (HT)- $\text{Cu/ZnO/Al}_2\text{O}_3$  catalyzed the one-step conversion of fructose towards FDM in a fixed-bed reactor.  $\text{H}_2$  was used as the hydrogen



**Scheme 13.** Conversion of fructose to Poly(2,5-furandimethylene succinate) without purification of FDM (Upare et al. 2018)

**Table 5** Some examples of one-pot production of FDM from hexose

Hexose	Reaction conditions	Yield (mol%, based on monosaccharide)	Refs.
Fructose	The 1st step: 20 mmol fructose, 1 mL DMSO + 10 mL THF, 2 mol formic acid, 150 °C, 5 h The 2nd step: 2 mmol triethylamine, 0.1 mmol iridium catalyst, 40 °C, 5 min, stirred. Then, a solution of formic acid (0.88 mL, 20 mmol) in THF (20 mL) was added using a syringe pump (flow rate = 2.5 mL h <sup>-1</sup> )	71 (isolated)	(Thananattanachon and Rauchfuss 2010)
Fructose	The 1st step: 1 mmol fructose, 0.5 g [BMIm]Cl, 130 °C, 20 min The 2nd step: 35 mL cool water, 50 mg 5% Ir/TiO <sub>2</sub> , 60 bar H <sub>2</sub> , 50 °C, 3 h	71	(Cai et al. 2014)
Fructose	The 1st step: 15 g fructose, 1.0 g Amberlyst-15, 85 g n-butanol, 100 °C, 5 h The 2nd step: 50 g HMF feed from the fructose dehydration, 0.5 g reduced Cu(50)-SiO <sub>2</sub> , 15 bar H <sub>2</sub> , 100 °C, 5 h	92	(Upare et al. 2018)
Fructose	WHSV (fructose) = 0.02 h <sup>-1</sup> , H <sub>2</sub> = 15 mL/min, 1 bar, 4 g HY zeolite and 5 g CuO/ZnO/Al <sub>2</sub> O <sub>3</sub> , 140 °C; fructose/water/γ-butyrolactone, w/w/w, 3/15/82	48.2	(Xiang et al. 2016)
Fructose	30 mg fructose, 20 mg Co-NC, n <sub>formic acid</sub> /n <sub>fructose</sub> = 15, 3.5 mL water-1,4-dioxane solvent (3/7), 5 bar N <sub>2</sub> , 170 °C, 3 h, 500 rpm	62	(Xu et al. 2022b)
Glucose	30 mg glucose, 20 mg Co-NC, 5 mg NiCl <sub>2</sub> , n <sub>formic acid</sub> /n <sub>fructose</sub> = 20, 3.5 mL water-1,4-dioxane solvent (3/7), 5 bar N <sub>2</sub> , 160 °C, 6 h, 500 rpm	60	(Xu et al. 2022a)

donor. At low temperature, HT-Cu/ZnO/Al<sub>2</sub>O<sub>3</sub> catalyst selectively adsorbed the aldehyde group of HMF, affording FDM as the dominant reduction product. The increase of temperature promoted the hydrogenolysis of hydroxyl group, resulting in DMF as the dominant reduction product. Under optimized conditions, a 48.2% yield of FDM and a 40.6% yield of DMF were obtained at 140 °C and 240 °C, respectively. However, the moderate HMF yield in dehydration step limited the overall yield of FDM. Xu et al. (Xu et al. 2022b) used formic acid as acid catalysts for the dehydration of fructose to HMF and hydrogen donor for hydrogenation, while heterogeneous Co catalysts supported on nitrogen-containing carbon were used as hydrogenation catalyst. Under optimized conditions (170 °C, 3 h), an enhanced FDM yield of 60.2% with full conversion was achieved. Compared to sole water or 1,4-dioxane as solvent, the use of water/1,4-dioxane medium favored the formation of FDM from

fructose by facilitating the solubility of fructose and inhibiting the undesirable condensation or polymerization of HMF or FDM. The dehydration of fructose to HMF was the rate-determining step of the cascade conversions, which has been revealed by kinetic studies. The same group (Xu et al. 2022a) reported the selective conversion of glucose to FDM using NiCl<sub>2</sub> as dehydration catalyst in a similar catalytic system, and a 60% FDM yield was afforded at 160 °C for 6 h. Moreover, moderate FDM yields of 46.4–56.1% could be obtained from di/polysaccharides, including sucrose, lactose, maltose, glucan, and cellobiose.

Some typical examples for direct conversion of carbohydrates to FDM are summarized in Table 5.

## Conclusions and perspectives

### Conclusions

FDM is an attractive biomass-derived chemical that can be applied in many fields. The synthesis of FDM from HMF, an important platform compound, has been extensively investigated. Both noble and non-noble metal catalysts have showcased good catalytic activity for the hydrogenation of HMF towards FDM in satisfactory yields in some cases. In such a hydrogenation transformation, H<sub>2</sub> is usually used as a hydrogen source. Apart from H<sub>2</sub>, formic acid and some alcohols also could act as a hydrogen donor, which avoids the use of high pressure H<sub>2</sub> and makes the reduction reaction safer. In addition to traditional thermo-catalysis, emerging technologies including photo-catalysis and electro-catalysis provide alternative approaches for the synthesis of FDM. The direct conversion of carbohydrates (typically fructose and glucose) is a much more promising strategy for the production of FDM, but only limited examples have been reported. Challenges still exist in improving FDM yield from carbohydrates.

### Perspectives

Although many interesting examples have been reported, the production of FDM on industrial scale still faces enormous challenges. Some typical issues should be addressed in the future studies. (1) Considering the high cost of HMF, future research should be focused on developing new effective catalytic systems for the direct transformation of carbohydrates to FDM. Currently, the single step either the dehydration of carbohydrates to HMF or the hydrogenation of HMF to FDM has been widely investigated, but the cascade conversion suffers from serious side-reactions. (2) To design an effective catalytic system for one pot synthesis of FDM should synthetically consider several factors, such as reaction medium, catalyst, gas atmosphere, reaction temperature, etc. How to combine these conditions is difficult but of significance. To develop effective bifunctional catalyst or combination catalysts is attractive, which might afford selective synthesis of FDM in a one-step protocol. For potential application in industry, the design of equipment also should be taken into account in accordance with respective practical situations. (3) The deep insight for the reaction mechanism of dehydration and hydrogenation steps by theoretical or experimental method will be helpful for rational design. The fundamental mechanism insights are essential to develop more efficient and stable catalysts. (4) The systematic establishment of separation technologies is important. In most cases, FDM need be separated from reaction mixture before further application. Unfortunately, previous studies mainly focused on high yield of target products. Therefore, to develop energy-efficient

separation technologies is of significance. (5) In addition to boosting catalysis efficiency, the cost and environmental influence also should be considered for potential industrial applications.

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### Author contributions

DZ, YD, CQ, YR and DJ: conceptualization, literature review, data curation, writing original draft; DJ, GX, and LF: project administration, supervision and revising the manuscript. All authors read and approved the final manuscript.

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### Availability of data and materials

Not applicable.

### Declarations

#### Ethics approval and consent to participate

Not applicable.

#### Consent for publication

Not applicable.

#### Competing interests

The authors declare that they have no competing interests.

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### References

- Arias KS, Carceller JM, Climent MJ, Corma A, Iborra S (2020) Chemoenzymatic synthesis of 5-hydroxymethylfurfural (HMF)-derived plasticizers by coupling HMF reduction with enzymatic esterification. *ChemSuschem* 13(7):1864–1875
- Arias KS, Liu L, Garcia-Ortiz A, Climent MJ, Concepcion P, Iborra S, Corma A (2021) Bimetallic CuFe nanoparticles as active and stable catalysts for chemoselective hydrogenation of biomass-derived platform molecules. *Catal Sci Technol* 11(10):3353–3363
- Arico F (2021) Synthetic approaches to 2,5-bis(hydroxymethyl)furan (BHMF): a stable bio-based diol. *Pure Appl Chem* 93(5):551–560
- Bao L, Yang SQ, Hu TL (2022) Cu-NPs@C nanosheets derived from a PVP-assisted 2D Cu-MOF with renewable ligand for high-efficient selective hydrogenation of 5-hydroxymethylfurfural. *ChemSuschem* 15(13):e202200392
- Bottari G, Kumalapatni AJ, Krawczyk KK, Feringa BL, Heeres HJ, Barta K (2015) Copper-zinc alloy nanopowder: a robust precious-metal-free

- catalyst for the conversion of 5-hydroxymethylfurfural. *Chemsuschem* 8(8):1323–1327
- Cai H, Li C, Wang A, Zhang T (2014) Biomass into chemicals: one-pot production of furan-based diols from carbohydrates via tandem reactions. *Catal Today* 234:59–65
- Cao Q, Liang W, Guan J, Wang L, Qu Q, Zhang X, Wang X, Mu X (2014) Catalytic synthesis of 2, 5-bis-methoxymethylfuran: a promising cetane number improver for diesel. *Appl Catal A* 481:49–53
- Chandrashekar VG, Natta K, Alenad AM, Alshammari AS, Kreyenschulte C, Jagadeesh RV (2022) Reductive amination, hydrogenation and hydrodeoxygenation of 5-hydroxymethylfurfural using silica-supported cobalt-nanoparticles. *ChemCatChem* 14(1):e202101234
- Chatterjee M, Ishizaka T, Kawanami H (2014) Selective hydrogenation of 5-hydroxymethylfurfural to 2,5-bis-(hydroxymethyl)furan using Pt/MCM-41 in an aqueous medium: a simple approach. *Green Chem* 16(11):4734–4739
- Chen Q, Li T, Zhou Y, Bi Y, Guo S, Liu X, Kang H, Wang M, Liu L, Xing E, Yang D (2020) Selective hydrogenation of 5-hydroxymethylfurfural via zeolite encapsulation to avoid further hydrodehydroxylation. *Ind Eng Chem Res* 59(26):12004–12012
- Chen X, Song S, Li H, Gk G, Yan N (2021) Expanding the boundary of biorefinery: organonitrogen chemicals from biomass. *Acc Chem Res* 54(7):1711–1722
- Chimentao RJ, Oliva H, Belmar J, Morales K, Maki-Arvela P, Warna J, Murzin DY, Fierro JLG, Llorca J, Ruiz D (2019) Selective hydrodeoxygenation of biomass derived 5-hydroxymethylfurfural over silica supported iridium catalysts. *Appl Catal B-Environ* 241:270–283
- Chimentao RJ, Oliva H, Russo V, Llorca J, Fierro JLG, Maki-Arvela P, Murzin DY, Ruiz D (2021) Catalytic transformation of biomass-derived 5-hydroxymethylfurfural over supported bimetallic iridium-based catalysts. *J Phys Chem C* 125(18):9657–9678
- Dai J, Li F, Fu X (2020) Towards shell biorefinery: advances in chemical-catalytic conversion of chitin biomass to organonitrogen chemicals. *Chemsuschem* 13(24):6498–6508
- de Luna GS, Ho PH, Lollí A, Ospitali F, Albonetti S, Fornasari G, Benito P (2020) Ag electrodeposited on Cu open-cell foams for the selective electroreduction of 5-hydroxymethylfurfural. *ChemElectroChem* 7(5):1238–1247
- de Luna GS, Ho PH, Sacco A, Hernandez S, Velasco-Velez J-J, Ospitali F, Paglianti A, Albonetti S, Fornasari G, Benito P (2021) AgCu bimetallic electrocatalysts for the reduction of biomass-derived compounds. *ACS Appl Mater Interfaces* 13(20):23675–23688
- Falcaro P, Ricco R, Yazdi A, Imaz I, Furukawa S, Maspoch D, Ameloot R, Evans JD, Doonan CJ (2016) Application of metal and metal oxide nanoparticles@MOFs. *Coord Chem Rev* 307:237–254
- Feng Y, Yan G, Wang T, Jia W, Zeng X, Sperry J, Sun Y, Tang X, Lei T, Lin L (2019) Cu-1-Cu-0 bicomponent CuNPs@ZIF-8 for highly selective hydrogenation of biomass derived 5-hydroxymethylfurfural. *Green Chem* 21(16):4319–4323
- Gelmini A, Albonetti S, Cavani F, Cesari C, Lollí A, Zanotti V, Mazzoni R (2016) Oxidant free one-pot transformation of bio-based 2, 5-bis-hydroxymethylfuran into  $\alpha$ -6-hydroxy-6-methyl-4-enyl-2H-pyran-3-one in water. *Appl Catal B* 180:38–43
- Guo Y, Chen J (2016) Photo-induced reduction of biomass-derived 5-hydroxymethylfurfural using graphitic carbon nitride supported metal catalysts. *RSC Adv* 6(104):101968–101973
- He J, Burt SP, Ball M, Zhao D, Hermans I, Dumesic JA, Huber GW (2018) Synthesis of 1, 6-hexanediol from cellulose derived tetrahydrofuran-dimethanol with Pt-WO<sub>3</sub>/TiO<sub>2</sub> catalysts. *ACS Catal* 8(2):1427–1439
- He Y, Deng L, Lee Y, Li K, Lee J-M (2022) A review on the critical role of H<sub>2</sub> donor in the selective hydrogenation of 5-hydroxymethylfurfural. *Chemsuschem* 15(13):e202200232
- Hou Q, Qi X, Zhen M, Qian H, Nie Y, Bai C, Zhang S, Bai X, Ju M (2021) Biorefinery roadmap based on catalytic production and upgrading 5-hydroxymethylfurfural. *Green Chem* 23(1):119–231
- Hu L, Xu J, Zhou S, He A, Tang X, Lin L, Xu J, Zhao Y (2018) Catalytic advances in the production and application of biomass-derived 2, 5-dihydroxymethylfuran. *ACS Catal* 8(4):2959–2980
- Hu L, Dai X, Li N, Tang X, Jiang Y (2019) Highly selective hydrogenation of biomass-derived 5-hydroxymethylfurfural into 2,5-bis(hydroxymethyl)furan over an acid-base bifunctional hafnium-based coordination polymer catalyst. *Sustain Energy Fuels* 3(4):1033–1041
- Hu L, He A, Shen X, Gu Q, Zheng J, Wu Z, Jiang Y, Wang X, Xu J, Kan Y, Xu F (2022) A high-efficiency zirconium-based single-atom catalyst for the transformation of biomass-derived 5 hydroxymethylfurfural to 2,5-bis(hydroxymethyl)furan with nearly 100% selectivity. *Green Chem* 24(18):6931–6944
- Huang Z, Sun X, Zhao W, Zhu X, Zeng Z, Xu Q, Liu X (2022) Selective hydroconversion of 5-hydroxymethylfurfural to 2,5-bis(hydroxy-methyl)furan using carbon nanotubes-supported nickel catalysts. *Carbon Resour Convers* 5(4):289–298
- Huang Z, Zeng Z, Zhu X, Zhao W, Lei J, Xu Q, Yang Y, Liu X (2023) Boehmite-supported CuO as a catalyst for catalytic transfer hydrogenation of 5-hydroxymethylfurfural to 2,5-bis(hydroxymethyl)furan. *Front Chem Sci Eng* 17(4):415–424
- Jae J, Mahmoud E, Lobo RF, Vlachos DG (2014) Cascade of liquid-phase catalytic transfer hydrogenation and etherification of 5-hydroxymethylfurfural to potential biodiesel components over Lewis acid zeolites. *ChemCatChem* 6(2):508–513
- Jaryal A, Venugopala Rao B, Kailasam K (2022) A light(er) approach for the selective hydrogenation of 5-hydroxymethylfurfural to 2,5-bis(hydroxymethyl)furan without external H<sub>2</sub>. *Chemsuschem* 15(13):e202200430
- Ji K, Xu M, Xu SM, Wang Y, Ge R, Hu X, Sun X, Duan H (2022) Electrocatalytic hydrogenation of 5-hydroxymethylfurfural promoted by a Ru1Cu single-atom alloy catalyst. *Angew Chem Int Ed* 61(37):e202209849
- Jiang Y, Woortman AJ, Alberda van Ekenstein GO, Petrovic DM, Loos K (2014) Enzymatic synthesis of biobased polyesters using 2, 5-bis (hydroxymethyl) furan as the building block. *Biomacromol* 15(7):2482–2493
- Kang E-S, Kim B, Kim YG (2012) Efficient preparation of DHMF and HMFA from biomass-derived HMF via a cannizzaro reaction in ionic liquids. *J Ind Eng Chem* 18(1):174–177
- Kumalaputri AJ, Bottari G, Erne PM, Heeres HJ, Barta K (2014) Tunable and selective conversion of 5-HMF to 2,5-furandimethanol and 2,5-dimethylfuran over copper-doped porous metal oxides. *Chemsuschem* 7(8):2266–2275
- Kwon Y, de Jong E, Raoufoghaddam S, Koper MT (2013) Electrocatalytic hydrogenation of 5-hydroxymethylfurfural in the absence and presence of glucose. *Chemsuschem* 6(9):1659–1667
- Kwon Y, Birdja YY, Raoufoghaddam S, Koper MT (2015) Electrocatalytic hydrogenation of 5-hydroxymethylfurfural in acidic solution. *Chemsuschem* 8(10):1745–1751
- Lewis JD, Van de Vyver S, Crisci AJ, Gunther WR, Michaelis VK, Griffin RG, Román-Leshkov Y (2014) A continuous flow strategy for the coupled transfer hydrogenation and etherification of 5-(hydroxymethyl) furfural using Lewis acid zeolites. *Chemsuschem* 7(8):2255–2265
- Li G, Sun Z, Yan Y, Zhang Y, Tang Y (2017) Direct transformation of HMF into 2, 5-diformylfuran and 2, 5-dihydroxymethylfuran without an external oxidant or reductant. *Chemsuschem* 10(3):494–498
- Lillie LM, Tolman WB, Reineke TM (2017) Structure/property relationships in copolymers comprising renewable isosorbide, glucarodilactone, and 2, 5-bis (hydroxymethyl) furan subunits. *Polym Chem* 8(24):3746–3754
- Liu Y, Mellmer MA, Alonso DM, Dumesic JA (2015) Effects of water on the copper-catalyzed conversion of hydroxymethylfurfural in tetrahydrofuran. *Chemsuschem* 8(23):3983–3986
- Long J, Zhao W, Xu Y, Li H, Yang S (2018) Carbonate-catalyzed room-temperature selective reduction of biomass-derived 5-hydroxymethylfurfural into 2,5-bis(hydroxymethyl)furan. *Catalysts* 8(12):633
- Luijckx GCA, Huck NPM, van Rantwijk F, Maat L, van Bekkum H (2009) Ether formation in the hydrogenolysis of hydroxymethylfurfural over palladium catalysts in alcoholic solution. *Heterocycles* 77(2):1037–1044
- Mondelli C, Gözaydın G, Yan N, Pérez-Ramírez J (2020) Biomass valorisation over metal-based solid catalysts from nanoparticles to single atoms. *Chem Soc Rev* 49(12):3764–3782
- Ohyama J, Esaki A, Yamamoto Y, Arai S, Satsuma A (2013) Selective hydrogenation of 2-hydroxymethyl-5-furfural to 2,5-bis(hydroxymethyl)furan over gold sub-nano clusters. *RSC Adv* 3(4):1033–1036
- Ojagh H, Achour A, Ho PH, Bernin D, Creaser D, Pajalic O, Holmberg J, Olsson L (2021) Effect of DMSO on the catalytic production of 2,5-bis(hydroxymethyl)furan from 5-hydroxymethylfurfural over Ni/SiO<sub>2</sub> catalysts. *React Chem Eng* 7(1):192–200
- Qiao S, Zhou Y, Hao H, Liu X, Zhang L, Wang W (2019) Selective hydrogenation via cascade catalysis on amorphous TiO<sub>2</sub>. *Green Chem* 21(24):6585–6589



- Rao KTV, Hu Y, Yuan Z, Zhang Y, Xu CC (2021) 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* 609:117892
- Silva WR, Matsubara EY, Rosolen JM, Donate PM, Gunnella R (2021) Pd catalysts supported on different hydrophilic or hydrophobic carbonaceous substrate for furfural and 5-(hydroxymethyl)-furfural hydrogenation in water. *Mol Catal* 504:111496
- Subbiah S, Simeonov SP, Esperança JM, Rebelo LPN, Afonso CA (2013) Direct transformation of 5-hydroxymethylfurfural to the building blocks 2, 5-dihydroxymethylfurfural (DHMF) and 5-hydroxymethyl furanoic acid (HMFA) via cannizzaro reaction. *Green Chem* 15(10):2849–2853
- Takkellapati S, Li T, Gonzalez MA (2018) An overview of biorefinery-derived platform chemicals from a cellulose and hemicellulose biorefinery. *Clean Technol Environ Policy* 20:1615–1630
- Tang X, Wei J, Ding N, Sun Y, Zeng X, Hu L, Liu S, Lei T, Lin L (2017) Chemoselective hydrogenation of biomass derived 5-hydroxymethylfurfural to diols: key intermediates for sustainable chemicals, materials and fuels. *Renew Sustain Energy Rev* 77:287–296
- Thananathanachon T, Rauchfuss TB (2010) Efficient route to hydroxymethylfurans from sugars via transfer hydrogenation. *Chemsuschem* 3(10):1139–1141
- Torres LAZ, Woiciechowski AL, de Andrade Tanobe VO, Karp SG, Lorenci LCG, Faulds C, Soccol CR (2020) Lignin as a potential source of high-added value compounds: a review. *J Clean Prod* 263:121499
- Turkin AA, Makshina EV, Sels BF (2022) Catalytic hydroconversion of 5-HMF to value-added chemicals: insights into the role of catalyst properties and feedstock purity. *Chemsuschem* 15(13):e202200412
- Upare PP, Hwang YK, Hwang DW (2018) An integrated process for the production of 2, 5-dihydroxymethylfuran and its polymer from fructose. *Green Chem* 20(4):879–885
- Vikanova KV, Chernova MS, Redina EA, Kapustin GI, Tkachenko OP, Kustov LM (2021) Heterogeneous additive-free highly selective synthesis of 2,5-bis(hydroxymethyl)furan over catalysts with ultra-low Pt content. *J Chem Technol Biotechnol* 96(9):2421–2425
- Wang Q, Feng J, Zheng L, Wang B, Bi R, He Y, Liu H, Li D (2020) Interfacial structure-determined reaction pathway and selectivity for 5-(hydroxymethyl)furfural hydrogenation over Cu-based catalysts. *ACS Catal* 10(2):1353–1365
- Wang J, Zhao J, Fu J, Miao C, Jia S, Yan P, Huang J (2022a) 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* 643:118762
- Wang L, Zuo J, Zhang Q, Peng F, Chen S, Liu Z (2022b) Catalytic transfer hydrogenation of biomass-derived 5-hydroxymethylfurfural into 2, 5-dihydroxymethylfuran over Co/U<sub>2</sub>O<sub>3</sub>-NH<sub>2</sub>. *Catal Lett* 152:361–371
- Wang T, Xie W, Pang Y, Qiu W, Feng Y, Li X, Wei J, Tang X, Lin L (2022c) Solvent-free hydrogenation of 5-hydroxymethylfurfural and furfural to furanyl alcohols and their self-condensation polymers. *Chemsuschem* 15(13):e202200186
- Wozniak B, Spannenberg A, Li Y, Hinze S, de Vries JG (2018) Cyclopentanone derivatives from 5-hydroxymethylfurfural via 1-hydroxyhexane-2, 5-dione as intermediate. *Chemsuschem* 11(2):356–359
- Xiang X, Cui J, Ding G, Zheng H, Zhu Y, Li Y (2016) One-step continuous conversion of fructose to 2, 5-dihydroxymethylfuran and 2, 5-dimethylfuran. *ACS Sustain Chem Eng* 4(9):4506–4510
- Xu L, Nie R, Chen X, Li Y, Jiang Y, Lu X (2021) Formic acid enabled selectivity boosting in transfer hydrogenation of 5-hydroxymethylfurfural to 2,5-furandimethanol on highly dispersed Co-N-x sites. *Catal Sci Technol* 11(4):1451–1457
- Xu L, Lyu X, Jiang Y, Wei X, Nie R, Lu X (2022a) Highly selective one-pot production of 2,5-furandimethanol from saccharides. *Green Chem* 24(12):4935–4940
- Xu L, Nie R, Lyu X, Jiang Y, Wei X, Lu X (2022b) One-pot production of 2,5-furandimethanol from fructose Co-catalyzed with formic acid and heterogeneous Co catalysts. *Energy Fuels* 36(1):480–487
- Yu IKM (2021) Mechanistic understanding of the catalytic hydrogenation of bio-derived aromatics. *Green Chem* 23(23):9239–9253
- Yu L, He L, Chen J, Zheng J, Ye L, Lin H, Yuan Y (2015) Robust and recyclable nonprecious bimetallic nanoparticles on carbon nanotubes for the hydrogenation and hydrogenolysis of 5-hydroxymethylfurfural. *Chem-CatChem* 7(11):1701–1707
- Zhang Y, Li T, Xie Z, Han J, Xu J, Guo B (2017) Synthesis and properties of biobased multiblock polyesters containing poly(2, 5-furandimethylene succinate) and poly(butylene succinate) blocks. *Ind Eng Chem Res* 56(14):3937–3946
- Zhang Z, Liu C, Liu D, Shang Y, Yin X, Zhang P, Mamba BB, Kuvarega AT, Gui J (2020) Hydrothermal carbon-supported Ni catalysts for selective hydrogenation of 5-hydroxymethylfurfural toward tunable products. *J Mater Sci* 55(29):14179–14196
- Zhao Z, Luo X, Peng J, Wang S, Guo T, Zheng H (2022) Complementary metal-semiconductor interactions on Ag-TiO<sub>2</sub> NT heterojunction for the efficient electrochemical reduction of 5-hydroxymethylfurfural. *Sustain Energy Fuels* 6(23):5281–5289
- Zhong Y, Ren R, Peng Y, Wang J, Ren X, Li Q, Fan Y (2022) In situ construction of hierarchical Ag-decorated Cu nanowire arrays as an efficient and durable electrocatalyst for hydrogenation of 5-hydroxymethylfurfural and furfural. *Mol Catal* 528:112487
- Zhu Y, Kong X, Zheng H, Ding G, Zhu Y, Li Y-W (2015) Efficient synthesis of 2, 5-dihydroxymethylfuran and 2, 5-dimethylfuran from 5-hydroxymethylfurfural using mineral-derived Cu catalysts as versatile catalysts. *Catal Sci Technol* 5(8):4208–4217

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