

Catalyst-Based Synthesis of 2,5-Dimethylfuran from Carbohydrates as a Sustainable Biofuel Production Route

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ABSTRACT: The development of renewable energy resources is strongly urged to recoup the shortage of fossil-based energy and its associated pollution issues. Energy production from carbohydrate materials has recently been of great interest due to the availability, reliability, and abundance of carbohydrate sources. Significantly, the catalytic transformation of waste carbohydrates into furan-based biofuels, specifically 2,5-dimethylfuran (DMF), appears to be an attractive solution to the aforementioned energy and environmental issues. The potential of DMF as a renewable fuel is prospective, with its physicochemical properties that are similar to those of fossil fuels. Therefore, the current work focuses on the production of DMF, with the important aspects for enhanced DMF yield being summarized herein. Notably, the significant catalysts derived from zeolite, noble-metal, non-noble-metal, metal–organic framework, and electrocatalytic materials are discussed, alongside their effects in deriving carbohydrates to DMF. Furthermore, the mechanisms of DMF production were clarified too, followed by the scrutinization of the effects from reaction conditions, solvents, and hydrogen donors onto the DMF yield. Finally, the purification process, commercialization potential, and economic feasibility of DMF production were incorporated too, with insightful future directions being identified at the end of our review. This review is expected to advocate DMF production from carbohydrate materials, which could alleviate the energy and environmental problems encountered presently.

KEYWORDS: 2,5-Dimethylfuran, Catalyst system, Carbohydrates, Conversion efficiency, Reaction condition, Purification, Economic feasibility



INTRODUCTION

Energy sources have been known as the cornerstone of today's industries and the prime aspect of the country's economy.^{1,2} Nonetheless, the facts of finite fossil fuel reserves and increasing environmental pollution have become the major hurdles in further advancing the economic sector.^{3–5} Therefore, the search for safe and environmentally friendly energy sources has been an increasing concern to establish sustainable development.^{6,7} In particular, biofuels originated from renewables are considered as one of the most promising energy resources for the transportation sector.^{8–11} Biofuels can be classified into four generations on the basis of the origination of feedstock nature, as well as the production methodology.^{12,13}

By employing first-generation biofuels, CO₂ emissions could be decreased along with serious cost issues and unpredicted environmental consequences.¹⁴ The augmented rates in food grains were considered as the most important drawback, owing to the reduction of fertile land for crop cultivation.¹⁵ On the other hand, the second generation biofuels focusing on

lignocellulosic biomass-based ethanol production pose no negative effect on the food cycle, concurrently exhibiting salient economic and environmental benefits.^{16–18} Nevertheless, the current situation for converting biomass into fuels is not a virtuous decision, considering the exorbitant upfront cost. Similarly, the production of third generation biofuels from algae, even microorganisms, is also infeasible, since the food and fuel competition is eliminated here.¹⁹ Compared to previous generations, the fourth generation biofuels are an emerging technology, which relies upon the genetically modified crops for the deriving purpose.²⁰ Nonetheless, the high technicality and

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Table 1. Physicochemical Properties of DMF in Comparison to Those of Other Liquid Fuels^{42–47}

physicochemical properties at 20 °C	ethanol/ <i>n</i> -butanol	gasoline	DMF	diesel	biodiesel
molecular formula	C ₂ H ₆ O/C ₄ H ₁₀ O	C ₄ –C ₁₂	C ₆ H ₈ O	C ₁₀ –C ₁₅	C _{15–17} COOCH ₃
oxygen content (%)	34.78/21.60	0	16.67	0	10–12
stoichiometric air/fuel ratio	8.95/11.20	14.70	10.72	14.30	14.00
latent heat of vaporization (kJ/kg)	920/708	351	389	270–301	252–258
energy density (MJ/L)	18.4–21.2/29.2	32–34.8	30	40.3	33.3–35.7
boiling point (°C)	77/117	27–225	93	282–338	340–375
autoignition temperature (°C)	434/385	420	286	246	374–449
research octane number	110/98	90–100	119		
cetane number	8/25	10–15	9	40–45	46–60

expenses required appear to be the stumbling stone for its wide adoption. Surmising from these, biofuel production from carbohydrate-based sources, of which lignocellulosic biomass is one of the main carbohydrate sources, seems to be a feasible option for long-term sustainable development, potentially solving the energy crisis at the present era.^{21,22}

Carbohydrates are undeniably vital feedstock for fuel and chemical synthesis. With the abundance of nonedible carbohydrates on Earth,^{23,24} it sustains the synthesis of high-value chemicals and biofuels, in a way, leading to better energy security.^{25,26} As such, second-generation biofuels based on carbohydrates are gaining momentum to fulfill increasing energy demands. In particular, furan-derived biofuels are favored for their applicability in both compression-ignition and spark-ignition engines.^{27–32} Being a derivative of furan, dimethylfuran (DMF) is attracting scientific attention with its benign physicochemical properties, which presents enabling features in powering transportation.^{33,34} Moreover, mass production of DMF from carbohydrates is possible, with multiple highly efficient conversion techniques being already developed.^{35–37} At the same time, more ongoing works are presently focused on the development of reactive solvent and catalyst to technoeconomically optimize DMF synthesis.^{38–41} Table 1 shows the physicochemical properties of DMF as compared to gasoline, diesel, and other biofuels (ethanol, *n*-butanol).

Recently, several studies have also confirmed the aptness of DMF for internal combustion engines (ICEs), without the need for further engine modification,^{48–56} suggesting that DMF could be a potential biofuel in the future. In the literature, there are some reviews over the DMF synthesis as well as the use of DMF for ICEs as an alternative fuel. Indeed, Lu and co-workers⁵⁷ presented the pathway of DMF synthesis from biomass, but the role of catalysts, reaction conditions, and economic characteristics was not comprehensively analyzed. In another review, Wang et al.⁵⁸ published a review work on recent advances of biomass conversion to DMF through the catalytic route, but the reaction mechanism for forming DMF, purification technologies, and progress of developing high-performance catalysts were not mentioned. In a recent study, Tuan Hoang et al.⁵⁹ carried out their review work on the combustion and emission characteristics of ICEs running on DMF, indicating that DMF could be used to blend with gasoline or diesel to provide promising results of reducing toxic emissions and pollutants while the engine performance was insignificantly decreased. They suggested that the DMF synthesis process from biomass should be further developed, aiming to produce DMF with low cost and high conversion efficiency to make DMF suitable for commercial biofuel in the future. In recent years, innovations are still constantly implemented to further improve energy efficiency in this area of research. In this context, this review

brought to the readers a comprehensive analysis of the strategy of DMF production from various carbohydrate sources through the catalyst pathway. This review is expected to contribute toward the premise of advanced catalysts and optimized reaction conditions, aiming to have a thorough analysis and evaluation over the production process of DMF from carbohydrates. Additionally, the purification process and economic perspective were also presented to provide insights to advanced DMF production, as well as its developing strategy in the following years. Significantly, this review paper also suggests that producing and upscaling of active and non-emission catalysts should be further investigated for a more prospective development of carbohydrate-derived fuels and chemicals.

Feedstock for DMF Production. The conversion from carbohydrate-based sources to glucose/fructose and followed by DMF has been explored as a potential and biorenewable platform chemical. The carbohydrate-based sources, including the agricultural or forestry residues, industry wastes from paper and cotton manufacturing, municipal solid waste, and stock manure, could serve as the feedstock for DMF production.⁶⁰ Among these, agricultural residues are commonly used as fuel for daily life, animal feed, and composting material.^{61,62} The projected production for several agricultural wastes by 2025 includes 1267 million tons/year of rice straw, 1111 million tons/year of heat straw, 666 million tons/year of sugar cane bagasse, and 1639 million tons/year of corn stover.⁶³ The above-mentioned figures demonstrate the potential of agricultural residues in producing biofuels, which could help to reduce around 50% of greenhouse gas (GHG) emissions while alleviating the reliance on fossil energy up to 80%.⁶⁴ As for forestry residues, they are expected to hit 6 billion tons/year (inclusive of wood chips, saw dust, and unused woods) by 2050. Such huge forestry and agricultural residues, if not appropriately utilized, are very profuse, which could be transformed into a burden for waste management.

Reportedly, 1 million tons of wood residues are annually generated during forestry activities. They are prevalently burnt to generate steam and, therefore, are regarded as one of the main causes for environmental pollution and, occasionally, forest fires.⁵ In particular, the burning of high-moisture biomass-based residues is often associated with high GHG and PM emissions, causing detriment for human life.⁶⁵ These biomass sources from agricultural and forestry products could be subjected to DMF synthesis, ascribed to their high lignocellulosic content. Similarly, algae are also considered as a potential source with high fuel yield, ca. 30 times higher than those of lignocellulosic biomass. Furthermore, the cultivation of algae is relatively easy, in which brackish water or even wastewater could be adopted for nurturing purposes. Some algae could be fed on CO₂ or nitrous oxide, thereby contributing to the reduction of environmental

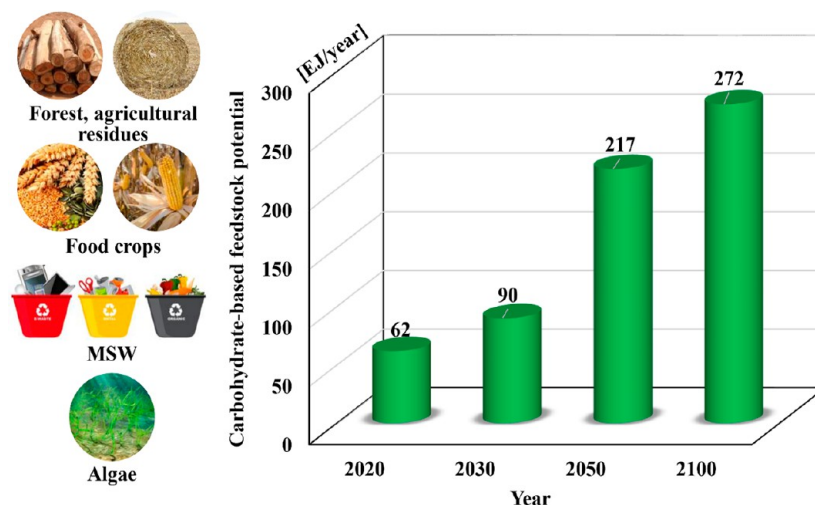


Figure 1. Potential feedstock based on carbohydrates for DMF production.

pollution.⁶⁶ However, the deployment of algae for biofuel production is still in its infancy and requires further investigation for much higher commercial value. Meanwhile, municipal solid waste (MSW) is also considered as another feasible carbohydrate source, ascribed to the paper, cotton, starch-rich foods, garden, and vegetable waste in it. The amount of MSW is often correlated to the population of a particular region. In this sense, dense countries like China and India are expected to generate enormous MSW, considering their largest population in the world. Statistically, India is estimated to release around 300 million tons/year of MSW by 2051,⁶⁷ while China is anticipated to release 480 million tons/year by 2030.⁶⁸ Out of different waste in MSW, the starch-rich waste food contributed to the most carbohydrate content, accounting for nearly 416 million/year by 2025 in Asian countries.⁶⁹ The hydrolysis process of starch-containing MSW can break the glycoside bonds, maltodextrins, or monosaccharides, resulting in valuable products through fermentation. Also, with 35.5–69% of sugar, starch-containing MSW could be valorized to high-value products, where the biobased fuel is widely accepted as a prospective product.⁷⁰ It is believed that the conversion of food waste to biofuels exhibits an economic prospective of 200–400 USD/ton, which is higher than that of electricity and animal feed (60–150 and 70–200 USD/ton, respectively). Other valorized products, such as bioplastics, organic acids, and enzymes, could reach up to 1000 USD/ton.⁷¹

Past research has evidenced the potential of converting carbohydrate-based feedstock into energy and high-end chemicals.^{72,73} Therefore, good management and planned exploitation of carbohydrate-based feedstock (such as glucose, fructose, cellulose, starch, algae, MSW, etc.) for fuel production are sure to not only bring large economic-social benefits but also contribute to improved energy security. Significantly, the typical carbohydrate-based feedstock for biofuel production is illustrated in Figure 1.

Pretreatment Process. Lignocellulosic biomass, such as crops, wood, and grasses, is touted as an ideal precursor for DMF production. Similarly, waste materials containing carbohydrates, such as starch-rich waste food, chitosan from crustacean shells, tree or fruit peel, and straw, could also be employed for DMF synthesis. Nonetheless, the direct conversion of these species to DMF is daunting due to the recalcitrance of lignocellulosic biomass. Fortunately, an appropriate pretreatment could reduce

cellulose crystallinity while promoting pore developments in the process, thereby enhancing the supply of sugar from biomass for better DMF yield.⁷⁴ This, at the same time, reduces the costs to extract useful chemicals from biomass. In general, Figure 2

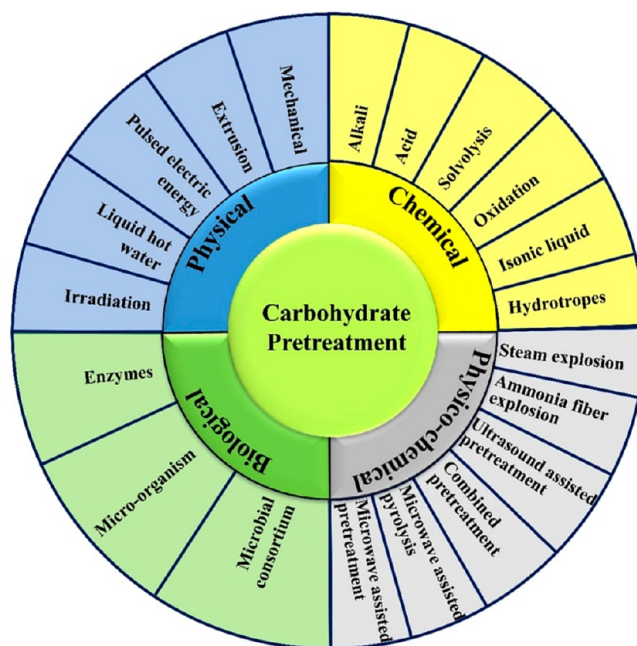


Figure 2. Applied methods in the process of carbohydrate pretreatment.

illustrates four basic methods for the pretreatment process of input materials for DMF production, which can be categorized as biological, physical, chemical, and physio-chemical pretreatment.⁷⁵ From the economic consideration, a viable pretreatment should satisfy several central criteria, such as facile removal of lignin, adoption of reusable reagents, and low operational difficulties.

Essentially, the physical approach is favored for its simplicity. The conventional physical pretreatment involves the application of water as an agent under high temperatures or high pressures to induce steam explosion and autohydrolysis toward the precursors.^{76,77} Such stringent conditions enable breaking of

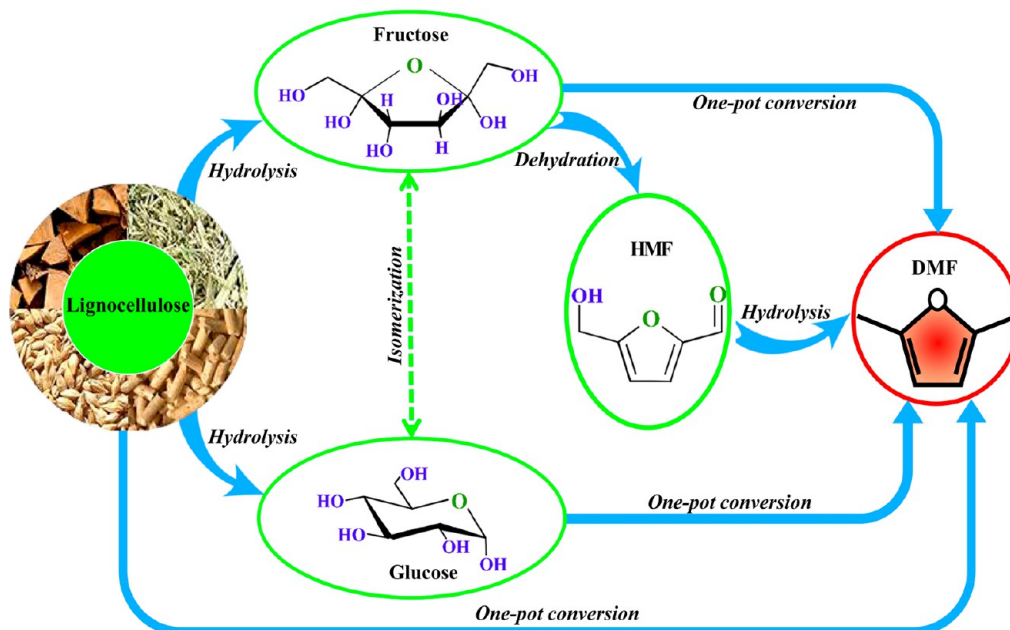


Figure 3. Scheme of DMF production from carbohydrates.¹⁰⁹

polymeric biomass bondings even with a short duration of exposure, thereby facilitating conversion of biomass to hydroxymethylfurfural (HMF; an intermediate of DMF synthesis).⁷⁸ In addition to water, pretreatment by organic solvents can also boost the readiness of sugar while increasing the DMF yield from biomass. Evidently, an additional methanol pretreatment step gives rise to 18% HMF yield from biomass, which recorded a remarkable improvement as compared to the case of untreated biomass (yield <1%).⁷⁹ On the other hand, the application of ultrasound can also expand crystalline cellulose areas of biomass, breaking down its lignin groups, thereby improving the cellulose availability and chemical reactivity of biomass precursors.⁸⁰ Similarly, hemicellulose could be decomposed by the ultrasonic treatment too, resulting in a reduced fiber-to-surface area for facilitated hydrolysis and HMF synthesis.⁸¹ With an optimum set of operating conditions, the incorporation of ultrasonics recorded a significant improvement in the conversion process, promoting the yield to 53.2% from 24.5% of the unsonicated sample.⁸² Several current physical approaches for carbohydrate pretreatment were also reported in the past literature, referenced herein.^{83–89}

Identically, chemical pretreatment could positively enhance the subsequent conversion process too. Inorganic acids (HNO_3 , H_2SO_4 , H_3PO_4 , and HCl) and organic acids ($\text{C}_2\text{H}_5\text{COOH}$, CH_3COOH , and HCOOH) are widely applied in acid pretreatment.⁹⁰ This is attributed to the susceptibility of cellulosic components to acid hydrolysis, which in turn yields xylose and/or glucose under the aid of the H^+ .⁹¹ The effectiveness of base pretreatment, however, relies on the lignin's solubility efficiency in the base solution. The primary action of base pretreatment is associated with bond-breaking of ester and glycosidic molecular dissolution of lignin. For the pretreatment of lignocellulose, NaOH , $\text{Ca}(\text{OH})_2$, KOH , and NH_4OH are ideal candidates, as the ester bonds that bind hemicellulose and other elements are highly receptive to saponification reaction.⁹² As reported, the maximum DMF yielded from wood chips could reach up to 80% after being pretreated with diluted NaOH , as opposed to only 41% of the untreated biomass.⁹³ Meanwhile, some metal salts can also

catalyze the destruction of lignocellulosic biomass,⁹⁴ which act as Lewis acids and rupture the glucosidic bond of hemicelluloses for xylose formation.⁹⁵ Alternatively, ionic liquids (ILs) and organosolv pretreatment techniques were also researched as carbohydrate pretreatment due to their cellulose-dissolving attributes that could facilitate hydrolysis of carbohydrates.^{96,97}

Physico-chemical pretreatment integrated both physical and chemical methods, aiming to attain synergisms from these approaches. Representatively, the coupled pretreatment of ultrasound and acidification prompts a synergistic biomass conversion, which is 35 and 19% higher than that of only acid pretreatment and ultrasound pretreatment.⁹⁸ In addition, another pretreatment such as the coupling of ultrasound with alkaline,⁹⁹ ionic liquid,¹⁰⁰ organic solvent,¹⁰¹ and ammonia in combination with salt¹⁰² also demonstrated promising output. In addition to ultrasonics, the integrations of other intensification approaches, such as gamma¹⁰³ and microwave irradiations, are also equally prospective as they combined with chemical pretreatment.^{104,105}

Biological pretreatment is considered as a green solution in the future with its non-emissive, low cost, and non-chemical-consuming attributes.¹⁰⁶ However, biological biomass pretreatment is presently hurdled at laboratory explorations, and its large-scale investigation is rather limited due to its long incubation period, strict condition for microbial growth, and space-consuming features.^{107,108} Generally, biological pretreatment involves selective degradation of lignin and hemicellulose through various micro-organisms, such as brown/white fungi, soft-rot fungi, or enzymes, thereby enhancing the biomass saccharification, as well as subsequent production of biofuels.

Role of Catalysts and Reaction Mechanism. DMF production from the different carbohydrate feedstocks, whether cellulosic biomass, starch-rich MSW, or algae, requires a complicated physicochemical transformation. Most of the time, the input carbohydrate will be undergoing a hydrolysis process to obtain fructose or glucose, as depicted in Figure 3.¹⁰⁹

It can be inferred from Figure 3 that the initial step of DMF production from cellulosic biomass could originate from the glucose or fructose that is produced upon hydrolysis of

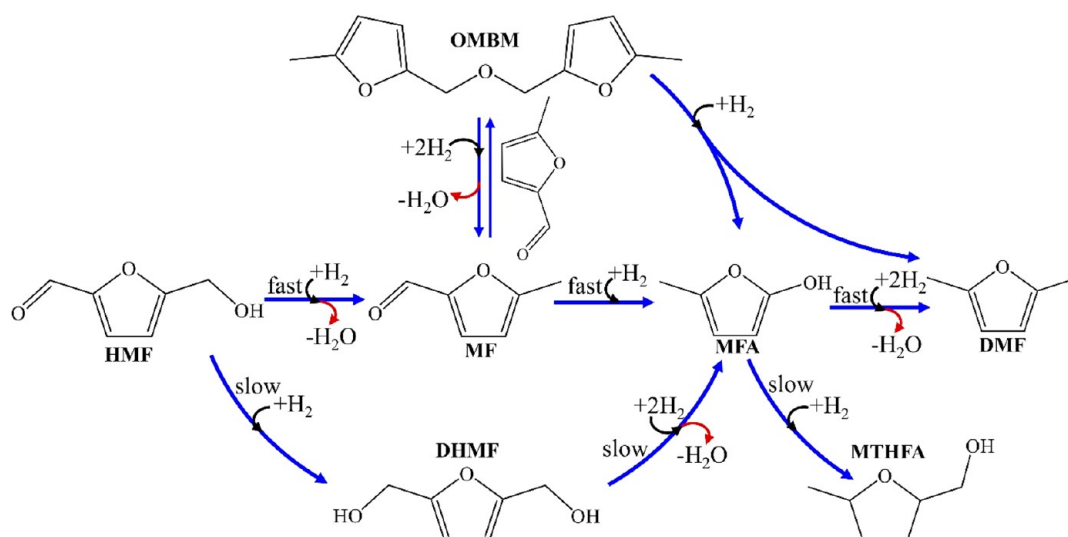


Figure 4. Conversion pathways from HMF to DMF through the hydrodeoxygenation reaction.¹²⁵

pretreated biomass, in which HMF was produced upon dehydrating glucose or fructose, followed by an HDO step to obtain DMF. Various catalysts with different surface mechanisms have been developed for the aforesaid hydrodeoxygenation (HDO) of HMF to DMF. There are three types of catalysts for these processes including Brønsted and Lewis acids as well as bifunctional catalysts. Typically, these catalysts are designed to increase the efficiency of hydrolysis, isomerization, and dehydration reaction while hindering undesirable rehydration and polymerization.

In particular, Brønsted acid catalysts are known to facilitate the hydrolysis of glucan and the dehydration of fructose and glucose, with its activity correlated to its acidity. Based on the support of the Brønsted acid catalyst, C–O–C glycosidic bonds would be weakened as the hydrolysis of polysaccharides involved the attacking of the bridging oxygen atom by protons.¹¹⁰ For fructose dehydration, the proton will normally be attached to the C₂ atom of the hydroxyl group to eliminate the water molecule, leading to a carbonium ion and the formation of a ring intermediate with five carbon members that are ready for dehydrating. After eliminating the water molecule, fructose will be transformed into an enol, further dehydrated to HMF in a subsequent step.¹¹¹ A recent study showed that some Brønsted-acid-based catalysts could prompt one-step glucose dehydration to HMF, bypassing the isomerization of glucose to fructose. Nonetheless, the activation energy for the dehydration of glucose, corresponding to 36.4 kcal·mol⁻¹, in such a direct conversion path is much higher than that of fructose (29.4 kcal·mol⁻¹). Also, it was demonstrated that the HMF yield is highly varied with the acidity of the catalyst. For Brønsted acid catalyst with pH 2, the HMF yield was 15%, while this yield was decreased to 4% as the pH was elevated to 2.3.¹¹² Notably, both organic acids (acetic, lactic, formic, acetic, boric, malic, mandelic, salicylic, succinic, oxalic, maleic, etc.) and inorganic acids (HCl, H₂SO₄, HNO₃, HCl, H₃PO₄, etc.) are functional as Brønsted-acid-based catalysts for these processes.

Lewis-acid-based catalysts are also explored in the isomerization of glucose into fructose. This isomerization is an important step that converts polymeric carbohydrates (starch, algae, biomass) to glucose as the alternative glucose-producing route; i.e., the hydrolysis of glucan is difficult due to its highly stable six-membered pyranose structure.¹¹³ The mechanisms of

catalytic isomerization of glucose in a water-bearing system can be found in the literature based on the aspects of molecular dynamics,¹¹⁴ isotope labeling, NMR spectroscopy,¹¹⁵ and DFT simulation.¹¹⁶ Lewis-acid-based catalysts generally initiate the reaction via glucose ring-opening while forming a complex containing the acyclic glucose at the oxygen position of the hydroxyl group at the C₁ and C₂ sites. Due to this coordination (inducing deficient electron of Lewis acids), it results in the polarization of the carbonyl group at C₁. The hydride transfer from C₂ to C₁ is thus promoted to form fructose. Metal- and mineral-based Lewis acid catalysts including CrCl₃, AlCl₃, GaCl₃, and InCl₃, Ti⁴⁺- and Zr⁴⁺-doped tungstite (W), and Sn-containing zeolite have also been investigated in catalyzing such a reaction.^{116,117} Nonetheless, the hydride shift while using ionic liquids occurs under a different mechanism, whereby the Lewis acid metal chlorides are used to drive the hydride transfer to C₁.⁴⁰

Lewis-acid-based catalysts appear to be more effective to induce polymerization reactions than Brønsted-acid-based catalysts.¹¹⁸ As analyzed above, Brønsted acid catalysts typically prompt effective hydrolysis and dehydration, while Lewis acid catalysts facilitate isomerization. Therefore, developing catalysts with adequate Brønsted and Lewis acid sites is vital for the one-step conversion of starch or cellulose into glucose, thereby enhancing the productivity of HMF. In this context, an optimum Lewis-to-Brønsted acid site ratio on catalyst would promote the HMF yield. The strength of these acid sites should also be carefully considered for the conversion of polymeric carbohydrates. In the cases of employing silica–alumina composite and Nb oxides as catalysts,^{119,120} weak acid sites (Lewis and Brønsted) were detected on the catalytic surface, thus selectively promoting the desirable reactions for glucose and fructose. Another work indicated an establishment of 21% HMF yield from bread waste and glucose over SnCl₄ catalyst having moderate Lewis acidity and strong Brønsted acidity in 21 min of reaction time.¹¹² The combination of metal chloride and mineral acid has been currently suggested to produce HMF from glucose or cellulose. As a result, 40% of HMF yield from cellulose was reported in the case of employing Amberlyst-38 and CrCl₃, or 42% of HMF yield from glucose was given with a Lewis–Brønsted acid catalyst based on HZSM-5 zeolite.¹²¹

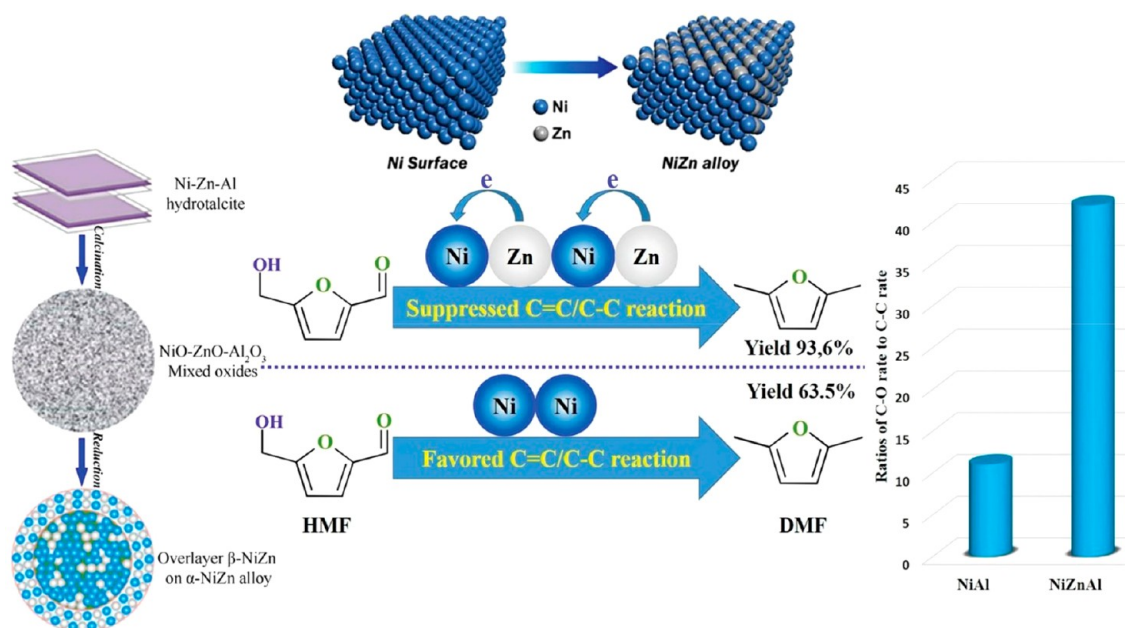


Figure 5. Conversion of fructose to DMF by using the zeolite-derived catalyst NiZnAl hydrotalcite and NiAl catalyst.¹³⁵ Reprinted with permission from ref 135. Copyright 2017 American Chemical Society.

HMF is an important precursor for various chemicals, additives, and fuels,¹²² with its susceptibility to various reaction pathways including HDO, hydrogenolysis, rehydration, esterification, etherification, and aldol condensation.¹²³ Significantly, the production of DMF by HDO of HMF takes place through various intermediates, including methyl furan (MF), methyl furfural alcohol (MFA), and dihydroxymethylfuran (DHMF).¹²⁴ The plausible reaction network for conversion of HMF to DMF, with respective relative rates of each path, is illustrated in Figure 4.

The DMF yield from HDO of HMF over suitable catalysts exhibits a close correlation to reaction time. Notably, HMF, with a dual-functional group of aldehyde and hydroxyl, could be involved in a complicated reaction network for its hydrogenolysis/hydrogenation. One of the paths involves the hydrogenation of the —CHO group in HMF while generating DHMF as the intermediate (Figure 4), which is subsequently being transformed to MFA, and finally the DMF by the two-step hydrogenolysis.¹²⁶ As for the second pathway, the formation of MF from HMF hydrogenolysis is first prompted, which then undergoes hydrogenation of its C=O group to produce DMF. Research indicates that the reaction equilibrium constant (K_p) and the activation energy needed for the second pathway (HMF–MF–MFA–DMF) were much higher than those of the first pathway (HMF–DHMF–MF–DMF).¹²⁷

The role of catalysts is undeniably crucial in prompting high DMF yield. A bifunctional catalyst is usually preferred, while some researchers manifested the effectiveness of hydrogenated metallic components and deoxygenated components for effective DMF generation. In the case of metal–acid catalysts, metal–acid synergisms are deemed to be one of the core factors for enhanced HMF dehydrogenation. In the transformation of HMF to DMF, evenly distributed metallic ions or atoms could function as extra sites based on metal–acid correlation, which in turn improve DMF yields.¹²⁸ In metal–acid catalysts, Lewis sites are more active for the dehydration of C–OH groups in HMF, thereby accelerating C–O bond cleavage for the subsequent reaction.¹²⁹ Single-phase metals (for instance, Pt, Cu, Mo, and

Ru) and bimetallic-system-based catalysts (for instance, Ru–Cu, Ni–Co, and Pt–Au) are some typical catalytic systems that could give rise to high DMF production. Comparably, transition metal oxides are favored for selectivity enhancement due to the predominance of Lewis acid sites in their structure that can enhance adsorption of OH^- radical in alcohols and CHO^- radical in aldehydes, resulting in increased DMF selectivity. In general, laboratory investigation on DMF production, whether from HMF or carbohydrates, involves either molecular hydrogen or chemical hydrogen reagents as the hydrogen supply for the HDO process. In the case of using molecular hydrogen, hydrogen gas will be supplied to the reactive system, whereas the HDO prompted by chemical hydrogen reagents is facilitated by proton H^+ from H-bearing chemicals (liquid). Indeed, the yield of DMF is significantly affected by input components; furthermore, it also depends largely on the types of solvents and catalysts used, as well as the reaction conditions such as temperature and pressure.

■ EFFECTS OF CATALYST TYPES ON DMF SYNTHESIS

Zeolite Catalysts. Zeolite-based materials are regarded as promising candidates for HDO of HMF. They manifested an excellent nature including augmented shape selectivity, as well as the ability to maintain hydrothermal stability, which made them an ideal catalyst for multiple reactions.¹³⁰ For instance, a zeolite catalyst built on Ni/ZrP was proposed by Zhu et al. and applied in the HDO of HMF.¹³¹ The authors claimed that the Ni ions in Ni/ZrP, with their metallic nature, could activate the hydrogen ions while the ZrP phase activates CH_2OH with its acidic attribute. Microscopically, the activation of CH_2OH mainly involves its C-bonded O atom, mainly contributed by the Zr^{4+} Lewis acidic sites because of its vacant orbital. Similarly, the oxygen present in the carbonyl group of MF could also be activated by such Zr^{4+} species under the same mechanistic framework.

A highly dispersed Ru supported on NaY zeolite was studied by Nagpure et al.¹³² in the production of DMF from HMF. Under optimum parameter sets, a peak DMF production of 78%

and HMF conversion of 100% were reported in the reaction. Furthermore, the authors also confirmed the high stability of the Ru—NaY catalyst over a five-consecutive reaction in the recyclability test. Other zeolites such as HY could function as a ring opener which breaks the furanic C—O bond, thereby permitting the transformation of fructose to DMF over the hydrotalcite (HT)—Cu/ZnO/Al₂O₃-coalesced HY. During the reaction, the dehydration process of fructose to form HMF has occurred after using the optimistic outcome of HY zeolite and γ -butyrolactone solvent, which subsequently yielded an improved DMF output of 48.2% at 140 °C and 40.6% at 240 °C.¹³³ Other catalysts including γ -Al₂O₃ and FAU zeolite with the presence of Pd—Ru (0.5%) were also found active for DMF generation.¹³⁴ In another study, Kong et al.¹³⁵ synthesized NiZn alloy catalyst supported on Al₂O₃ through a two-step process (Figure 5), and subsequently disclosed a straight conversion from fructose to DMF in the fixed-bed reactor. Accordingly, as-obtained catalyst exhibited a core—shell heterostructure, with β 1-NiZn overlaying on the α -NiZn core (Figure 5). The authors reported that incorporated Zn atoms induce the geometrical isolation to Ni atoms while they electronically modify the composite catalyst. As a result, the hydrogenolysis rate of C=O/C—O over C=C/C—C hydrogenation in the case of using NiZnAl-supported catalyst was increased around 3 times compared to the case of using a monometallic catalyst based on Ni, leading to a DMF yield of 93.6%. In a recent study of Guo et al.,¹³⁶ they found that ZSM-5 could play a vital role in promoting the hydrogenolysis process of HMF, while Ni could promote the hydrogenation reaction when 40% Ni was combined with ZSM-5 in Ni/ZSM-5 catalysts. As a result, an excellent selective yield of DMF could reach 96.2%. In the modern study of Chen et al.,¹³⁷ the system based on siliceous *BEA zeolite-supported Co with an open channel (Co/beta-DA) was suggested to be a potential catalyst for the conversion of HMF to DMF. They found that the presence of CoOx on the zeolite surface could improve the hydrogenolysis reaction on the basis of robust metal—support interaction. For a catalytic sample containing 20 wt % Co at 723 K, it exhibited an efficient hydrogenolysis process, inducing a high DMF productivity of 1.108 h⁻¹.

Noble-Metal-Based Catalyst. Earlier research works have shown that catalytic structures focused on single metals such as Pd, Ru, Ni, or Pt were employed for the HDO of HMF.¹³⁸ In order to evaluate the effects of carbon-supported metal catalysts on the DMF yield through the three-phase HDO of HMF, six metal-based catalysts, namely, Pt, Pd, Ir, Ru, Ni, and Co, were synthesized and subjected to the aforesaid reaction. Accordingly, the selective conversion reaction of HMF into DMF greatly depends on catalyst types. In particular, Pd catalyst gives rise to a major production of DMTHF, while a mixture of DMTHF and open-ring products was formed over Ir catalysts. In the analysis of DMF yield, the carbon balance (maximum for Pt) in the product stream was found to be paramount for catalytic poisoning.¹³⁹ DMF yield could be pushed after complete HMF conversion by employing Ru-based catalysts.¹⁴⁰ Meanwhile, non-noble metal catalysts may also generate high DMF yields/selectivities.¹⁴¹ The use of heterogeneous Fe-based catalysts supported on activated carbon was also reported to achieve 86.2% selectivity of DMF.¹⁴² Similarly, Cu-doped porous metal oxides also demonstrated high efficiency in HDO of HMF under the support of supercritical methanol, despite the overall yield of DMF being highly influenced by DMTHF and 2-hexanol.¹⁴³

Noble-metal-based catalyst system studies are unceasingly advancing to improve the transformation yields of HMF to DMF. Chidambaram et al.¹²⁵ studied the two-step process involved in the conversion of glucose to DMF. Their research showed that using C₆H₁₁N₂Cl as the ionic fluid for the reaction resulted in a low DMF yield, reasonably due to the insolubility of H₂ in the ionic liquid. A maximum of only 47% HMF conversion and 32% DMF yield was achieved under optimized reaction conditions over Pd/C. In spite of the less satisfactory outputs, they managed to identify the formation of unprecedented intermediates such as 2-methyl furfural (MFf) and 2,5-bis(hydroxymethyl) furan (BHMF) in the reaction. Significantly, MFf was recognized as the main intermediate, which is then transformed to DMF in the reaction with 5-methylfurfyl alcohol (MFA). In a separate study, an in situ domino process using hydrophobic Pd/C-based catalyst systems and H₂ donor from polymethylhydrosiloxane for the DMF synthesis from fructose was developed by Li et al.¹⁴⁴ The conversion reaction was maintained at 120 °C in *n*-butanol without the separation of unstable intermediates. Gratifyingly, they found that hydrophobic Pd/C-TMS (trimethylchlorosilane-modified Pd/C) catalyst has afforded the highest yield of DMF, up to 94%. Moreover, they also confirmed the competency of alcohols as solvent, although they give rise to lower DMF yields (64–82%) as compared to that of polymethylhydrosiloxane. More importantly, Pd was proven as an active, yet sustainable catalyst for the deoxygenation process, due to its good recyclability. Interestingly, the employment of hydrophobic catalysts could eliminate the attachment of water to the catalytic surface, thereby alleviating side reactions while reserving the reactive sites to targeted reactants for enhanced outputs. Such hydrophobicity-induced positive effects were clarified by Ji et al.,¹⁴⁵ who have developed hydrophobic Pd/PDVB-S-143 for the conversion of fructose to DMF. They reported weakened subreactions on the hydrophobic surface of the Pd catalyst, which could be explained by the facilitated H-component adsorption. Among the as-prepared catalysts in their study, Pd/PDVB-S-143 manifested the best catalytic activity, with the highest DMF yield recorded at 94.2%. While the catalyst delivers similar activity for five consecutive reaction cycles, it could also convert fructose into DMF through a one-step process, in which the common intermediate, the HMF, is basically absent in the product stream. This virtue realizes the reductions in both organic solvent used and operational costs associated with the purification of products. In addition, the conversion efficiency of the whole process can be increased too, with polymethylhydrosiloxane being the hydrogen donor.

Similarly, Talpade et al.¹⁴⁶ also employed a Pd-based catalyst (Fe—Pd/C) for DMF production, however, in the system that adopts H₂ as the hydrogenation reagent at 20 bar in the liquid-acid-free environment. The results indicated that the enhanced selective hydrogenation of HMF to DMF is realizable by Fe—Pd/C bimetallic nanocatalyst, which provided a DMF yield of 96% at 150 °C within 2 h. Zhang et al.¹⁴⁷ incorporated Pd into their catalyst, namely, graphitized-carbon (GC)-assisted Pd—Au_{*x*} (*x* = 1–4), with various molar ratios of Au/Pd. The optimum catalyst, PdAu₄/GC800, delivered an excellent DMF selectivity of 94.4%, ascribed to the strong interaction of Au and Pd nanoparticles in the catalyst. Interestingly, active Pd⁰ species are enhanced with Au content, thereby suggesting that Au—Pd interactions could stabilize Pd metal against oxidation. Graphitized carbon is rendered with a large number of large π -systems and sp² hybridized graphite-like carbon, which may

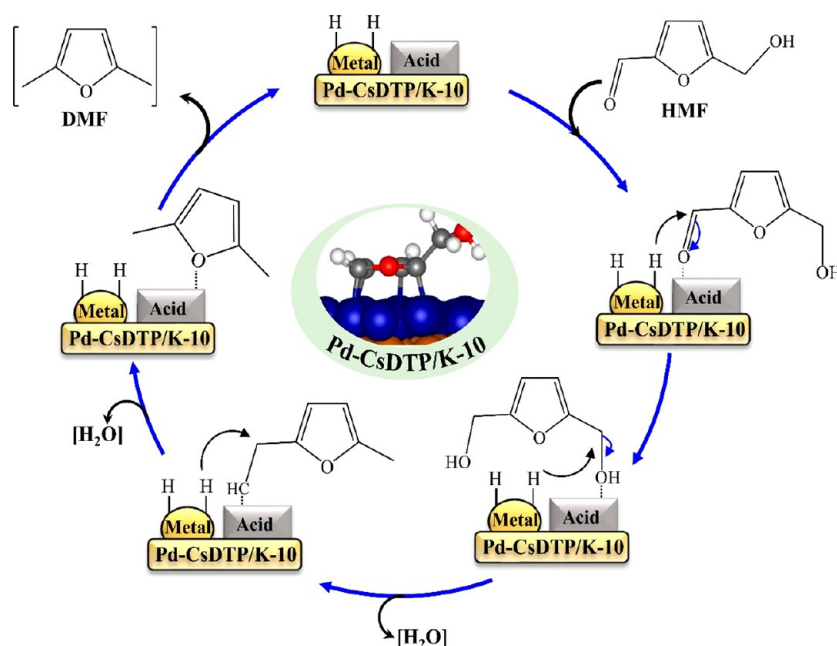


Figure 6. Postulated hydrogenation mechanism of HMF conversion to DMF through Pd-based catalyst systems.¹⁵¹ Reprinted with permission from ref 151. Copyright 2016 American Chemical Society.

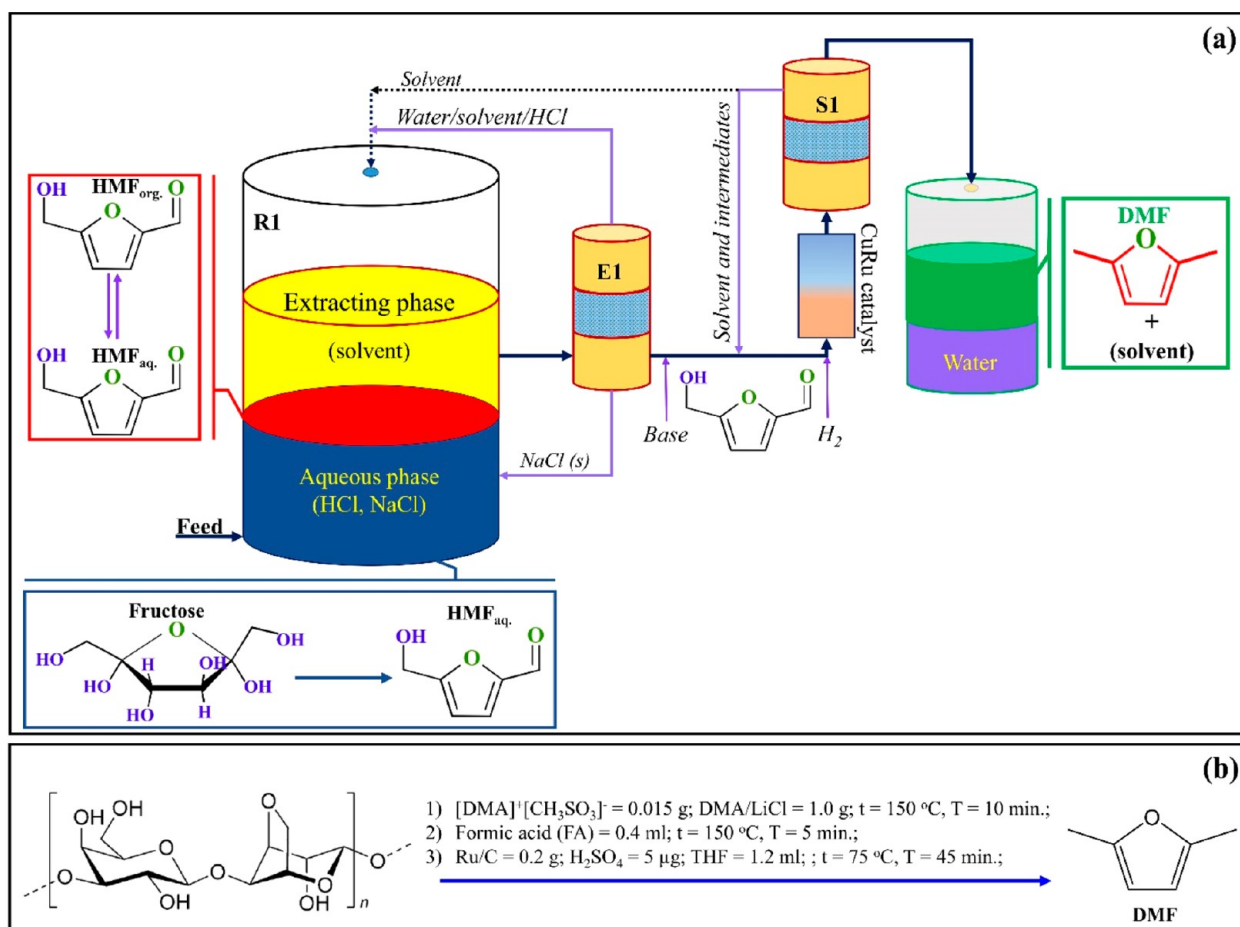


Figure 7. Scheme of the conversion process of feedstock to DMF with various reactors: (a) from fructose to DMF with biphasic reactors;¹⁵³ (b) from lignocellulosic and algal biomass to DMF with a one-pot reactor.¹⁵⁴

promote reactant–graphene interactions. This facilitates the deposition of HMF onto the activated carbon surface through

the formation of H-bonding with the OH– and CHO– groups in HMF,¹⁴⁸ which is promotional for DMF generation. Notably,

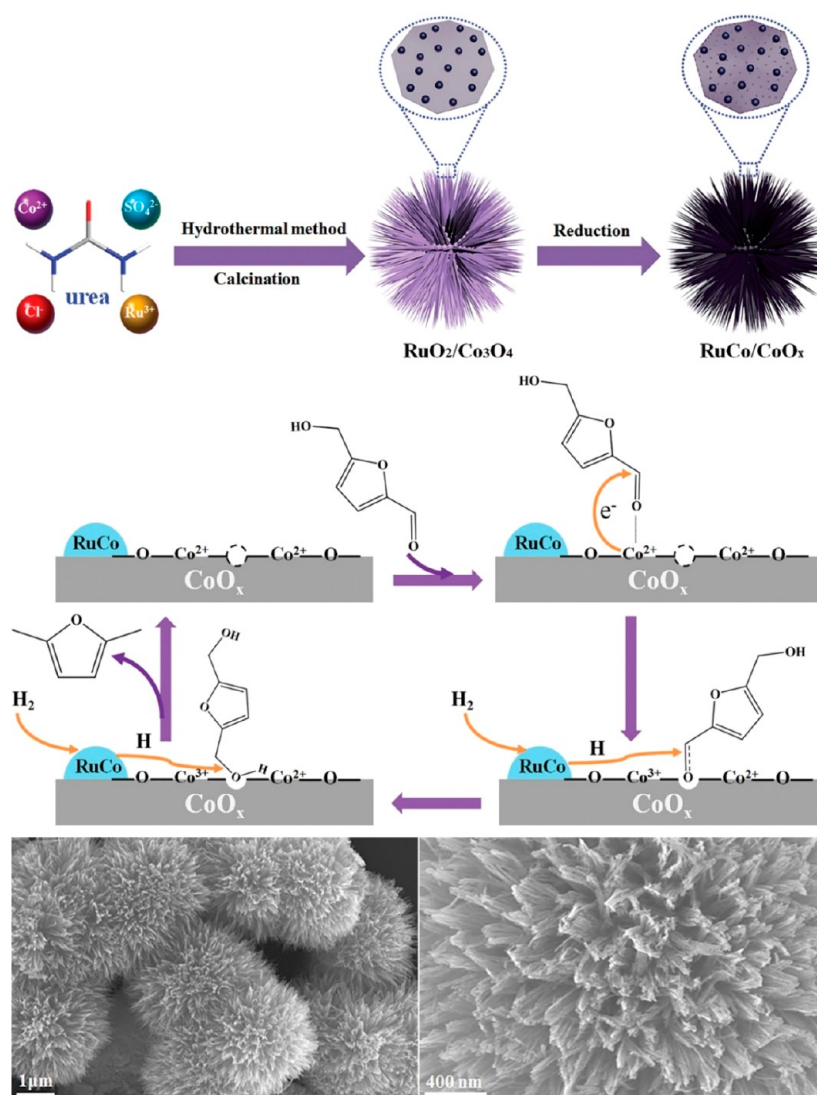


Figure 8. Activity mechanism of RuCo/CoO_x catalyst.¹⁵⁸ Reprinted with permission from ref 158. Copyright 2018 Elsevier.

DMF produced in the reaction corresponded to the increment of Pd in catalyst, implying its dominating role in the hydrogenation of HMF to DMF.

Saha et al.¹⁴⁹ suggested replacing the exorbitant Au promoter with Zn, which in turn prompted comparable promotional effects to Pd-based catalysts. Their results indicate that the incorporation of Zn(II) imparted Lewis acidic sites to the bimetallic Zn–Pd catalyst while realizing an optimum DMF yield of 85% from the HMF HDO process under the most conducive conditions. In comparison, the monometallic Pd catalyst delivered a lower DMF (60%) under the same condition, which, however, still outperformed ZnCl₂ that exhibited no catalytic effects. Although the production process of DMF from fructose over the two-step path demonstrated high DMF, this approach is usually shadowed by the high energy requirement and coexistence of an intermediate (HMF) in the product stream. These may incur additional costs for DMF production. Meanwhile, the addition of acid was also found to enhance the conversion efficiency of DMF. Therefore, it is necessary to design a robust catalyst system, with potential reactor corrosion, waste acid treatment, and product separation being considered.¹⁵⁰ Significantly, the bifunctional metal–acid catalyst system of Pd–Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10 could be the

solution to the aforesaid problems.¹⁵¹ While the catalytic feature of Pd was elucidated in previous studies, the adoption of K-10 is rationalized by its acidic attribute for promoted DMF production. Upon incorporating the constituents, Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10 could activate the OH groups in DHMF, thereby prompting its hydrogenolysis reaction to produce DMF (Figure 6). As a result of the synergisms of Pd and Cs_{2.5}H_{0.5}PW₁₂O₄₀/K-10, 81% of the DMF yield was obtained after 2 h of reaction. In addition, Liao and co-workers have also investigated the employment of sulfur-modified Pd–Co catalyst (Pd–Co₉S₈/S-CNT) for selective catalytic hydrogenolysis of HMF to DMF.¹⁵² The results confirmed the high activity of the PdCo₈/S-CNT catalyst that yields 96.0% HMF conversion with 83.7% DMF selectivity at 120 °C after 13 h of reaction. More importantly, from the role-determining reaction, they revealed that Pd plays a key part in catalyzing the hydrogenation of the CHO[−] group while the Co₉S₈ phase induces hydrogenolysis of the OH[−] group in HMF. Meanwhile, the authors also attribute the improvements of the hydrogenation/hydrogenolysis activity of the bifunctional Pd–Co₉S₈/S-CNT-based catalyst to the high dispersion of metallic particles and enhanced adsorption of reactants.

Ru-based catalysts have also been extensively investigated as monometallic and bimetallic catalysts for the HDO of HMF to DMF.¹⁵³ Román-Leshkov and co-workers¹⁵³ suggested the production of DMF based upon the catalytic conversion of fructose that is directly obtained from lignocellulosic biomass or glucose-to-fructose isomerization (shown in Figure 7a). Initially, HMF was produced using a biphasic reactor that employed *n*-butanol as a pulled-out organic in an aqueous phase of HCl/NaCl. The addition of NaCl maintains the high biphasic ratio of its aqueous medium, which at the same time induces the salting-out effect to facilitate the conversion of fructose to HMF. The adoption of NaCl salt results in an extraction ratio of 3.3 in conjunction with the improved HMF selectivity of 79%. The conversion of fructose to HMF was followed by hydrogenolysis of purified HMF over the CuRu/C catalyst for DMF production. In spite of its activity, the employment of the Cu–Ru/C catalyst is shadowed by its adverse reaction with chloride ions, which could lead to the development of the vapor phase hydrogenolysis process. However, NaCl does not evaporate with the reactants and reside in the liquid phase; therefore, its reaction with the catalyst was prevented. To conduct the new hydrogenolysis process, a flow reactor was designed, which realized a DMF yield of 76–79%. By using a one-pot reactor in combination with the multicomponent catalytic method, De et al.¹⁵⁴ successfully produced DMF from biomass through a one-pot operation in the single-vessel reactors. Specifically, [DMA]⁺[CH₃SO₃][−] was utilized as the catalyst to convert untreated biomass into HMF on the account of hydrolysis and dehydration processes. HMF was subsequently converted into DMF over Ru/C, as illustrated in Figure 7b. It is worth noting that different types of lignocellulose-based biomass, including fructose, α -cellulose, sugar cane bagasse, and agar, were adopted as the substrates in this investigation. However, only 32% of DMF yield was obtained from this method under the optimum setting, which is far lower than that of the case where a two-vessel reactor was employed. Further investigations are required to improve the feasibility of single-vessel reactors. In addition, the impact of reactor configuration on the efficiency of the catalytic hydrogenation process in transforming HMF into DMF was investigated by Luo et al.,¹⁵⁵ who compared the performance of the batch reactor to that of the continuous-flow reactor over the same catalyst. Compared to the batch reactor, the DMF yield was increased to 60% in the case of using the continuous-flow reactor.

In the study by Zu et al.,¹⁵⁶ Ru/Co₃O₄ was employed for the HMF HDO reaction to synthesize DMF in the presence of both tetrahydrofuran and H₂. The authors confirmed the accountability of Ru for hydrogenation, while Co₃O₄ contributed a major part to the hydrogenolysis of OH groups through C–O cleaving. Various reaction conditions including temperatures, pressures, and Ru percentages were analyzed. The use of Ru/Co₃O₄ catalyst at 130 °C with a hydrogen pressure of 7 bar provided an improved DMF yield up to 24 h. The synergistic effect of Ru and Co is attributed to the increased HMF-to-DMF conversion.¹⁵⁶ This is consistent with the results obtained by Esen et al.¹⁵⁷ that stated the advocacy of reduction reactions in the presence of both Ru and Co.¹⁵⁷ In detail, the effects of three catalysts, namely, Ru/SiO₂, Co/SiO₂, and Ru–Co/SiO₂, were evaluated for DMF production. Bimetallic Ru–Co/SiO₂ provided quantitative DMF yields at 140 °C. Ru and Co interactions could be clearly seen in Figure 8, where the Co²⁺ species in the surface of Ru–Co/CoO_x was believed to play an important role in the adsorption of the C=O group in HMF.

Upon adsorbing, electron transfer from the catalyst would be prompted, resulting in the formation of Co³⁺ species and weakening of HMF's C=O bond. The O atom of the weakened C=O group could be seated into the oxygen vacancy next to Co³⁺. Meanwhile, Ru–Co nanoparticles exhibit considerable activity in dissociating H₂, leading to the generation of active hydrogen species, which would rapidly spill to the support surface. Along with the oxygen vacancies, the formation of ROH was further activated to enhance DMF conversion.¹⁵⁸ In the case of Ru–Co/CoO_x catalyst, two important synergistic effects, namely, (i) Ru–Co nanoparticles and the high density of defective sites on the surface and (ii) the unique dandelion-like nanostructuring of Ru–Co nanoparticles and the spillover effect of hydrogen, collectively improve the DMF production rate.¹⁵⁹ Cu–Ru/C could also provide 71% DMF yield after 10 h of batch reaction in the presence of 1-butanol under optimum conditions (220 °C, 6.8 bar of H₂ pressure).¹⁶⁰ In general, molecular H₂ was considered as the H₂ source in reactions of HMF HDO, although the employment of hydrogen-transfer reagents was thought to be relatively safer.¹⁶¹ As for the case of using a Ru/C-based catalyst, formic acid was regarded as the hydrogen source for the HDO reactions of HMF, lignocellulose, and fructose. Representatively, a mixture of products (37% DMF, 3% LA, and 43% 5-formylxymethyl furfural (FMF)) was obtained while using HMF as the initial substrate.

In another example, HMF was derived from the direct conversion of substrates that originated from lignocellulose and carbohydrate via a Brønsted acid IL pathway. Such HMF was subsequently converted to DMF through a FMF intermediate over a Ru/C-based catalyst with formic acid being the hydrogen source. Interestingly, the input feedstock was found to be the major determinant for DMF yield, whereby only 10% of sugar was converted to DMF.¹⁵⁴ The employment of cellulose and pure HMF could improve that figure to 16 and 37%, respectively, which, however, are far lower than that of the investigation utilizing 2,5-bis(hydroxymethyl)-furfural as feedstock (81%). Moreover, the use of isopropyl alcohol as a hydrogen source was also investigated in the HMF-to-DMF investigation over Ru/C.¹⁶² The effects of Ru, in the form of Ru/C and RuO₂, on the DMF selectivity were further investigated by Jae et al.¹⁶³ They found that the DMF yield was lower (<30%) in the case of using either of the Ru catalysts. However, with both Ru/C and RuO₂ incorporated, the DMF yield can reach up to 70%. In another study, the promotional effects of ZnCl₂ onto Ru/C and Pd/C catalyst systems were also investigated in converting HMF to DMF.¹⁴⁹ The catalyst system of Ru/C with ZnCl₂ incorporated (Ru/C/ZnCl₂) gives rise to 41% DMF yield alongside 52% DHMF, which is more superior to the catalyst system of only Ru/C. This can be attributed to the capability of Zn²⁺ in Ru/C/ZnCl₂ in enhancing the deoxygenation of BHMF, and hence the overall yield of DMF. Similarly, Pd/C/ZnCl₂ also delivered a better DMF yield as compared to its Zn-absent counterpart. Pd/C/ZnCl₂ was also proven to outperform Ru/C/ZnCl₂,¹⁴⁹ owing to a sturdy interaction between ZnCl₂ and Pd/C. Meanwhile, the Ru–ZrO₂–MCM-41 catalyst obtained from the blending of Ru and ZrO₂–MCM-41 delivered a motivating outcome of 90% DMF yield in a diminutive reaction time of 1 h. Likewise, the elevated yield was associated with the high activity of spheroidal Ru nanoparticles (<20 nm) on the ZrO₂–MCM-41 catalyst, which augmented the selective HDO of HMF and, sequentially, the DMF yield.¹⁶⁴ In general, the combination of Ru and Co afforded an unprecedented conversion efficiency of HMF to DMF, although H₂ was usually

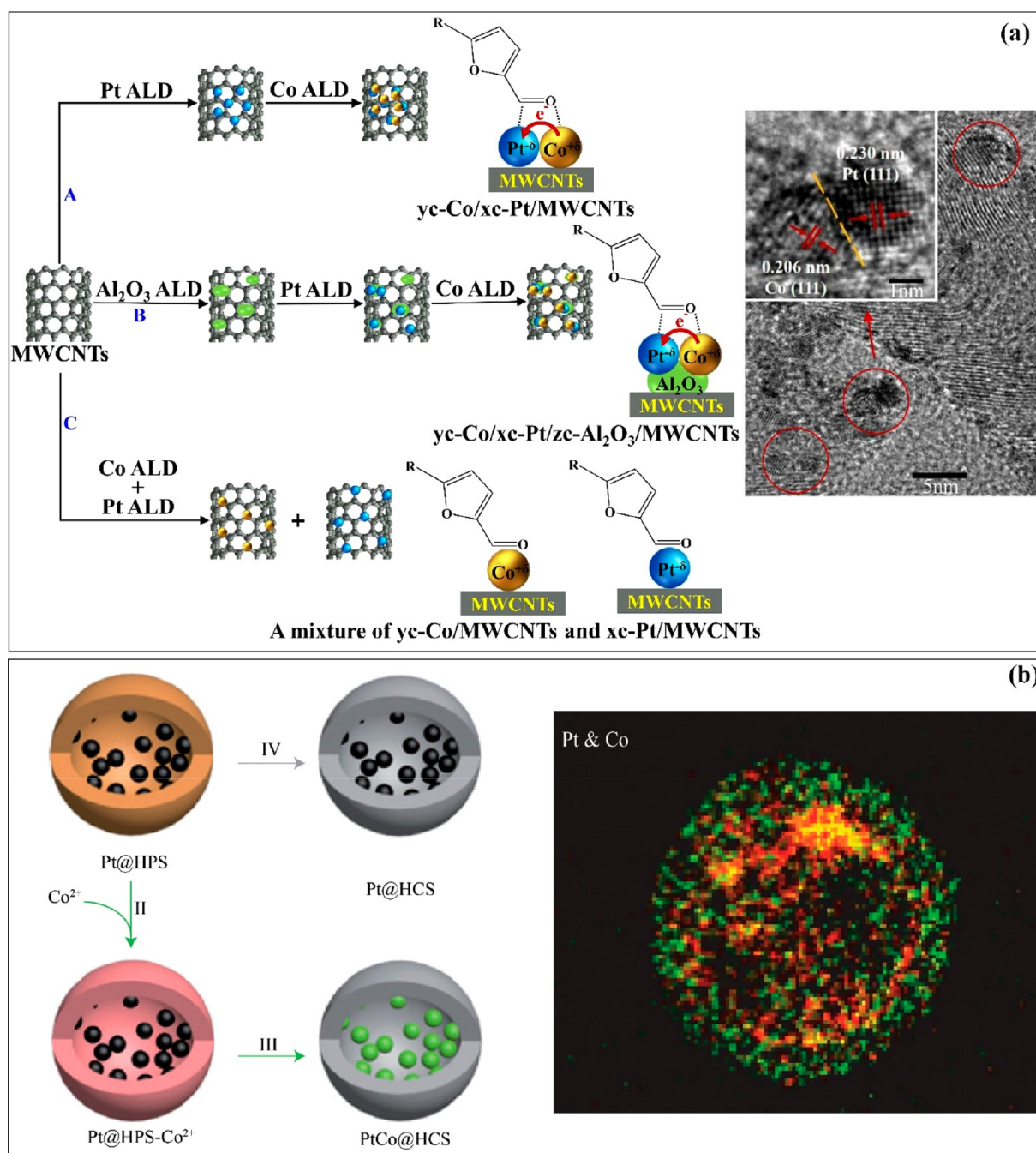


Figure 9. (a) Catalyst activity mechanism of the Pt–Co/5c-Al₂O₃/multiwalled-carbon-nanotube-based catalyst.¹⁶⁷ Reproduced from ref 167 with permission. Copyright 2018 Royal Society of Chemistry. (b) Synthesis mechanism of PtCo@HCS (left) and STEM of PtCo@HCS-500 (right).¹⁶⁶ Reprinted with permission of ref 166. Copyright 2014 Springer-Nature.

used as a donor. In the future, other donors should be developed to not only ensure safety but also improve DMF yield.

Platinum (Pt) is known for its high selectivity for the hydrogenation of the C=O. Nonetheless, it is quite difficult to control the hydrogenation rate with its active characteristic. Pt-based monometallic catalyst is seldom employed in the HDO of HMF.⁵⁸ One of the representative studies involves the synthesis of high-surface-area Pt₃Co BNN catalyst from the reduction of the complex double-metal salt of [Co(NH₃)₅Cl][PtCl₄].¹⁶⁵ Succinctly, the authors reported a high DMF selectivity of nearly 80% in the HDO of HMF. Wang et al.¹⁶⁷ studied the catalytic effect of the bimetallic Pt–Co catalyst coated on multi-walled

carbon nanotubes (MWCNTs) for DMF generation. Figure 9a shows the synergistic outcomes of Pt–Co with the sustenance of Al₂O₃. From the synergetic effects of Pt–Co with an Al₂O₃ coating, it can be observed that the electron was transferred directly from Co to Pt, instead of passing through the MWCNTs due to the presence of isolated Pt–Co nanoparticles. However, the hydrogenation of the furan ring present could not be prevented due to the low charge density of the bimetallic catalyst system. This resulted in a low DMF yield and high production of byproducts from the reaction because a low charge density enhanced the selectivity of the C=O group. In the case of using MWCNTs, they acted as a “bridge” to connect Pt with Co,

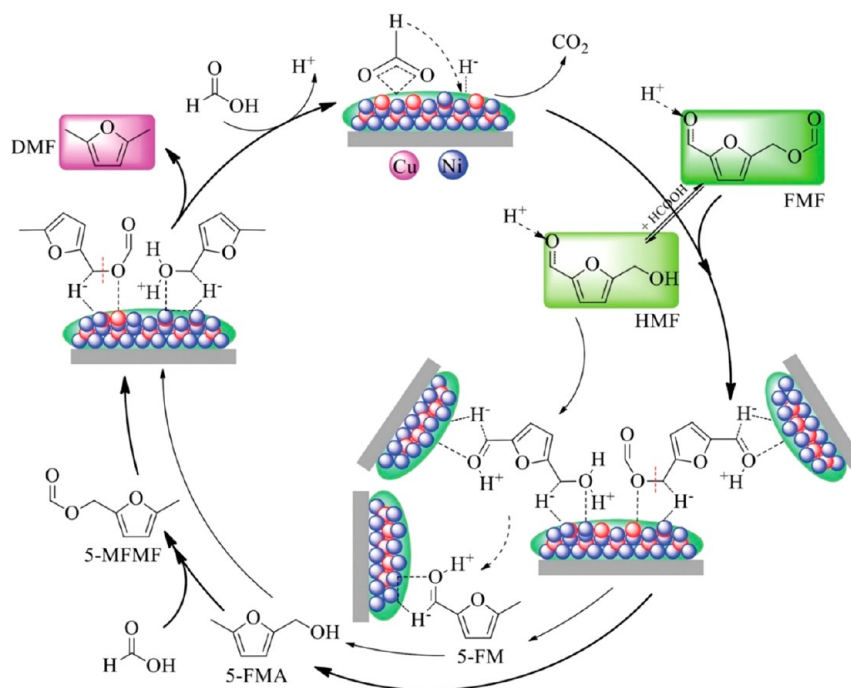


Figure 10. Synthesis scheme of DMF by using Ni—Cu/SBA-15 catalyst.¹⁷⁴ Reprinted with permission from ref 174. Copyright 2019 American Chemical Society.

aiming to promote the electronic transfer from Co to Pt, resulting in the rise in the charge density on metal Pt—Co nanoparticles. In the reaction of HMF hydrogenolysis, the achieved results from the enhancement of charge density on bimetallic Pt—Co nanoparticles were demonstrated to increase both the rate of adsorption and dissociation for the C=O group at $\text{Pt}^{\delta-}$ — $\text{Co}^{\delta+}$ sites (Figure 9b, left). The synergistic effect of the bimetallic catalyst on Pt—Co nanoparticles and MWCNTs boosted DMF selectivity. This disclosed a critical Pt and Co interaction in the hydrogenolysis of HMF in the bimetallic catalyst to improve the selective HDO of HMF and consequently the DMF yield. These results were similar to those of Wang et al.,¹⁶⁶ who have reported a novel bimetallic catalyst system based on Pt—Co/HCS, which was operated on Pt—Co nanoparticles supported by hollow carbon nanospheres, to convert HMF to DMF under a temperature of 180 °C with the support of 1-butanol. Pt—Co/HCS provided up to 98% of DMF yield, although this DMF yield was reduced to 72% after the third cycle. The conversion efficiency of the bimetallic catalyst system of P—Co/HCS was found to be much higher than that of the monometallic catalyst system. Such results were attributed to the shells containing part of the cobalt ions, while larger particles were contained in the hollow core. Surprisingly, Pt and Co elements in HCS almost overlap, leading to the formation of a concomitant lattice contraction when Co was incorporated into the Pt(fcc) structure (Figure 9b, right). Interesting effects were believed to increase DMF yields, although only 9 and 56% yields were obtained when using a monometallic catalyst system of Pt/activated carbon nanoparticles and Pt/graphitic carbon nanoparticles, respectively.

The effects of noble metal on the conversion efficiency of HMF to DMF were also various. For instance, the use of an Ir/SiO₂-based noble metal catalyst supported by H₂SO₄ in THF was only given 23% of DMF yield from HMF under the optimal conditions.¹⁶⁸ However, Pd-based catalyst showed some excellent results in relation to HMF HDO to DMF. Chatterjee

et al.¹⁶⁹ have utilized a commercial Pd/C catalyst for the HDO reaction of HMF. A maximum DMF yield of 100% after 2 h of reaction time was achieved in the case of using supercritical carbon dioxide—water under a temperature of 80 °C. The combination of CO₂ and water has increased the acidity in the CO₂—water system, enhancing the DMF synthesis efficiency. It can be observed that the best catalytic performance for the conversion of HMF to DMF via HDO can be attained when noble metallic chemical catalysts are used. Although it has the highest performance among the catalysts, process optimization of the reaction conditions and catalyst preparation are also required for further improved performance.

Non-Noble-Metal-Based Catalysts. Current developments and research are recently focused on non-noble catalysts because the production costs of noble catalysts are high. Some bifunctional catalysts such as the Ni/C and ZnCl₂/Ni/C catalysts displayed a lower conversion efficiency during the hydrogenation process of the reaction. The reason for this is the presence of a noneffective hydrogenation metal such as Ni. The Ni ions that are present interact with the Zn²⁺ Lewis acid, which results in a low transformation efficiency. The conversion efficiency was observed to be improved as the temperature was increased (88% at 180 °C).¹⁷⁰ Other bifunctional catalysts including nickel—tungsten carbide (Ni—W₂C) supported on activated carbon (AC) showed excellent conversion efficiency from HMF to DMF. High synergistic interactions between W₂C and Ni improved the deoxygenation and hydrogenation process of the conversion. A very high DMF yield of 96% was achieved by using such catalysts.¹⁷¹ Bifunctional catalysts including Ru—MoOx/C-based catalyst provided a similar performance as Ni—W₂C, able to achieve a DMF yield of 79.4%.¹⁷² The high yield from Ni-based catalysts is justified in Ni selectively hydrogenating C—O, C=O, and C=C bonds. The synergistic effect of Ni with other metals was demonstrated by using Ni—Al₂O₃ catalysts for selective conversion to DMF from HMF with 91.5% DMF yield.¹⁷³ The synergistic effect of Ni and Cu was further

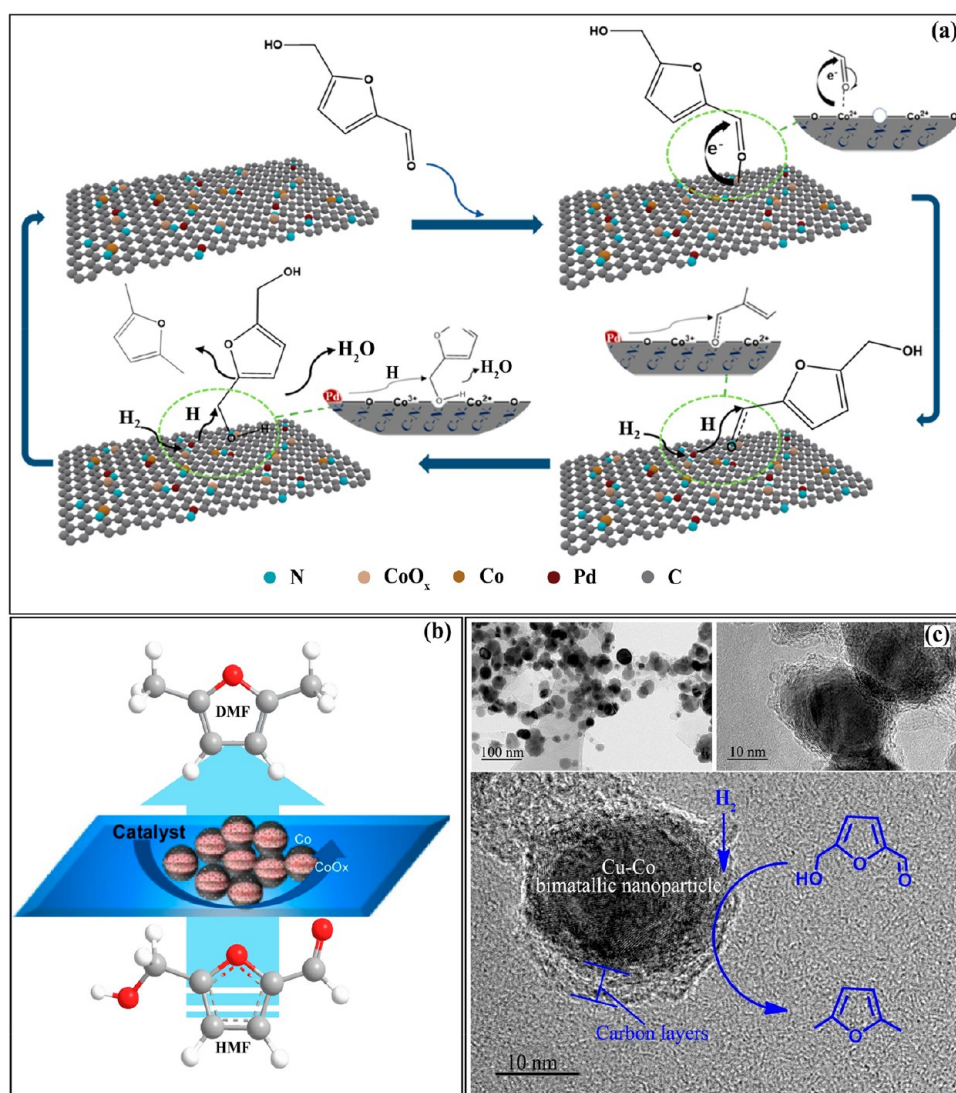


Figure 11. Synergistic mechanism of bifunctional catalysts. (a) Reaction mechanism of the PCNC catalyst for DMF synthesis from HMF hydrogenolysis.¹⁷⁷ Reprinted with permission from ref 177. Copyright 2020 American Chemical Society. (b) Synergistic effect of Co–CoO_x in HMF HDO to DMF.¹⁷⁸ Reprinted with permission from ref 178. Copyright 2019 Elsevier. (c) TEM of the Cu–Co@carbon nanoparticle catalyst and the route of DMF formation from HMF through support of Cu–Co@carbon nanoparticles.¹⁷⁹ Reprinted with permission from ref 179. Copyright 2017 Elsevier.

interpreted in the case of using Ni–Cu/SBA-15 as a catalyst for FMF conversion to DMF, in which FMF was known as a product of the esterification reaction between HMF and FA (Figure 10). The yield of DMF was revealed to reach 71.0% along with the excellent recyclability of catalyst. Finally, the bilateral incorporation of Ni–Cu was found to boost the hydrogenolysis selectivity toward the ester bond of C–O for a new strategy of producing DMF from FMF with high productivity.¹⁷⁴

A catalytic system developed on available and inexpensive metals such as Cu and Zn was reported by Brzezińska et al.¹⁷⁵ CuZnO could further activate the reaction conversion of HMF HDO in a suitable environment. High HMF conversion to DMF was obtained due to the presence of Cu²⁺ and Cu⁰ sites, where Cu²⁺ enhanced the HMF adsorption through the C=O bond and H₂ dissociation and reduction was allowed by Cu⁰. As a result, the highest DMF yield was achieved with 79% after 5 h of reaction time and under a temperature of 493 K. In addition, the abundant occurrence and financial aspects of Fe as compared

with Cu or Ni suggest that Fe-based catalysts could be considered for mass production, through employing instantaneous thermolysis of g-C₃N₄ and Fe/AC to prepare Fe-derived heterogeneous catalysts aiming to produce DMF from the HDO of HMF. Resultantly, an augmented rate of DMF yield (≈85.7%) was recorded.¹⁷⁶

Cobalt (Co) displayed remarkable effects on the DMF production in bimetallic catalysts. The combination of Pd and Co with MOF was also investigated by Shang et al.¹⁷⁷ A novel catalyst based on Co–CoO_x@N-doped C catalyst from pyrolysis of ZIF-67 after immobilizing a series of Pd was developed to apply in HMF hydrogenolysis to DMF. Surprisingly, Pd/Co–CoO_x@N-doped C has brought not only an excellent selectivity yield of DMF up to 97.8% but also the ability of a magnetically recyclable nature and high stability. This result was attributed to the high surface area, suitable porosity, and abundant oxygen vacancies in Co species generated in situ with highly dispersed characteristics, facilitating the fast transfer of electron and mass in doped

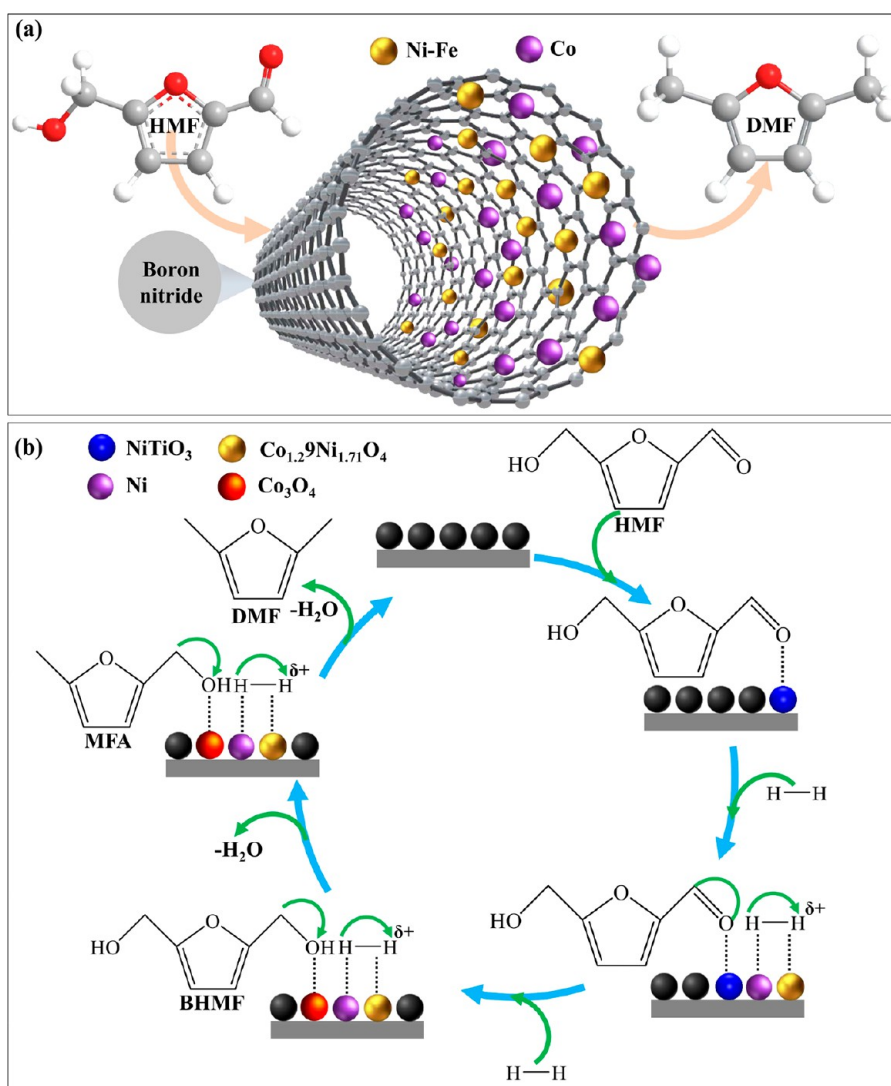


Figure 12. Synergistic mechanism of multifunctional catalysts. (a) SEM images of Fe–Co–Ni/BN and h-BN and the reaction mechanism of HMF HDO to DMF using Fe–Co–Ni/BN.¹⁸¹ Reprinted with permission from ref 181. Copyright 2020 Elsevier. (b) The NiCoTi-8-catalyst-based reaction pathway of HMF hydrogenation for DMF synthesis.¹⁸³ Reprinted with permission from ref 183. Copyright 2021 Springer-Nature.

carbon materials (Figure 11a). Moreover, uniform Pd anchoring in N-doped C nanographene along with a large number of topological-imperfection surface defects derived from N-doped C nanographene was considered a favorable factor for polarizing the C=O and removing the –OH bond. However, most studies have reported that the cost of MOF was still too high and it was thus difficult to employ under the current conditions. More clearly, the catalytic mechanism of Co–CoO_x could be explained in Figure 11b, in which the Co²⁺ species were found to adjoin O_v on the support surface, leading to oxygen atom fixation on the C=O bond of HMF via electron transfer. Co³⁺ species were formed, and the C=O bond was reduced. After that, O_v adjoining Co²⁺ could be taken up by the carboxylate oxygen in HMF. Remarkably, the chemical adsorption of HMF could be motivated by the interaction of the defect structure on the Co²⁺–O_v–Co²⁺ surface and HMF, facilitating the C=O bond hydrogenation of HMF. Finally, the conversion reaction of HMF to DMF benefited from such a superior electron transfer nature. It is evident that the bilateral effect between metallic Co and acidic CoO_x in the bifunctional Co–CoO_x catalyst system

has promoted the selective HDO of HMF, leading to the increase in the yield of DMF to 83%.¹⁷⁸

Earlier research works also pointed out that bimetallic nanoparticles built on Cu–Co supported by a carbon layer coating were a peak efficiency catalyst in the DMF synthesis reaction through the HMF HDO, leading to a high yield of 99.4% at 180 °C by using ethyl alcohol as the hydrogen donor.¹⁷⁹ Cu–Co bimetallic nanoparticles coated with carbon of 10–60 nm in size were uniformly distributed along with a graphene-layer-like carbon coating. This has the effect of protection against oxidation and deactivation and helped to increase the DMF conversion efficiency (Figure 11c). Even with Mn, although it is not a noble metal, the achieved performance in the conversion of HMF to DMF was also quite high in the case of combining with Co under the ratio of Mn/Co (50%/50% of mass). This result was also proven by Akmaz et al.,¹⁸⁰ who showed the highest DMF yield (around 91.8%) obtained after 4 h of reaction at a temperature of 180 °C. The DMF yield from the bimetallic Mn–Co catalyst system was even much higher than that from Ru–Co.

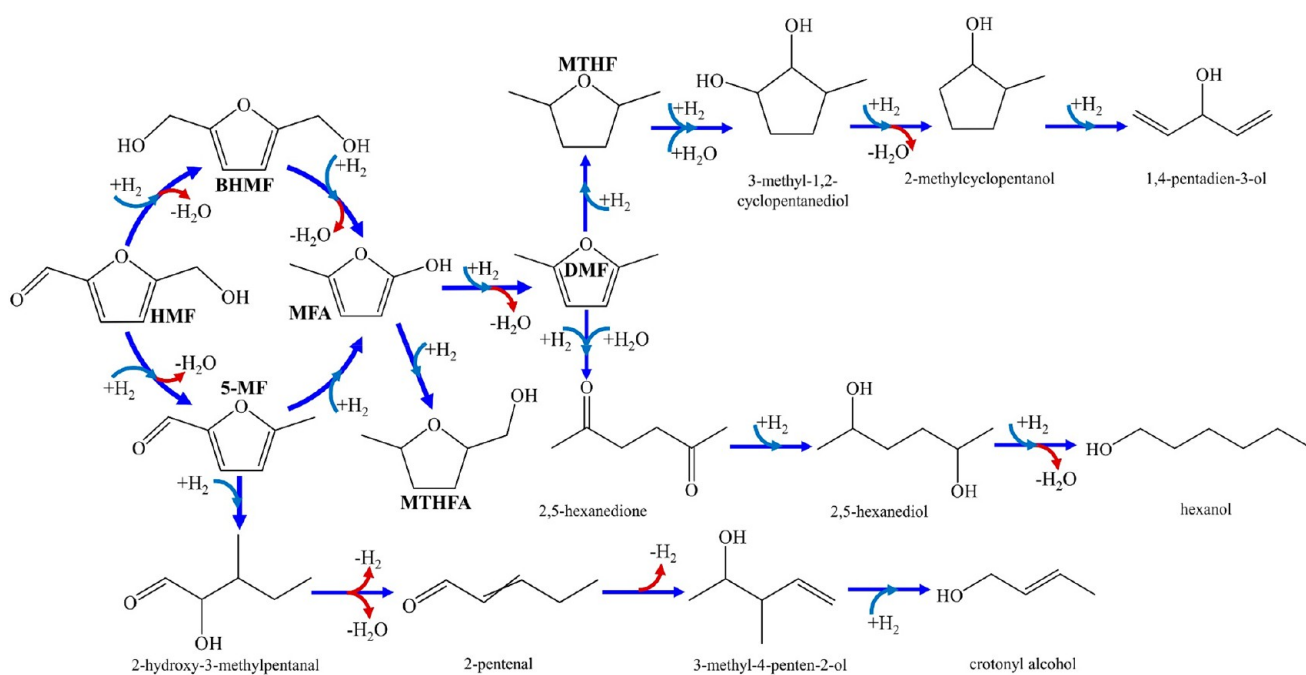


Figure 13. Reaction pathway for the hydrogenation of HMF on the Cu/Nb₂O₅-Al₂O₃-623 catalyst.¹⁸⁴ Reprinted with permission from ref 184. Copyright 2020 Elsevier.

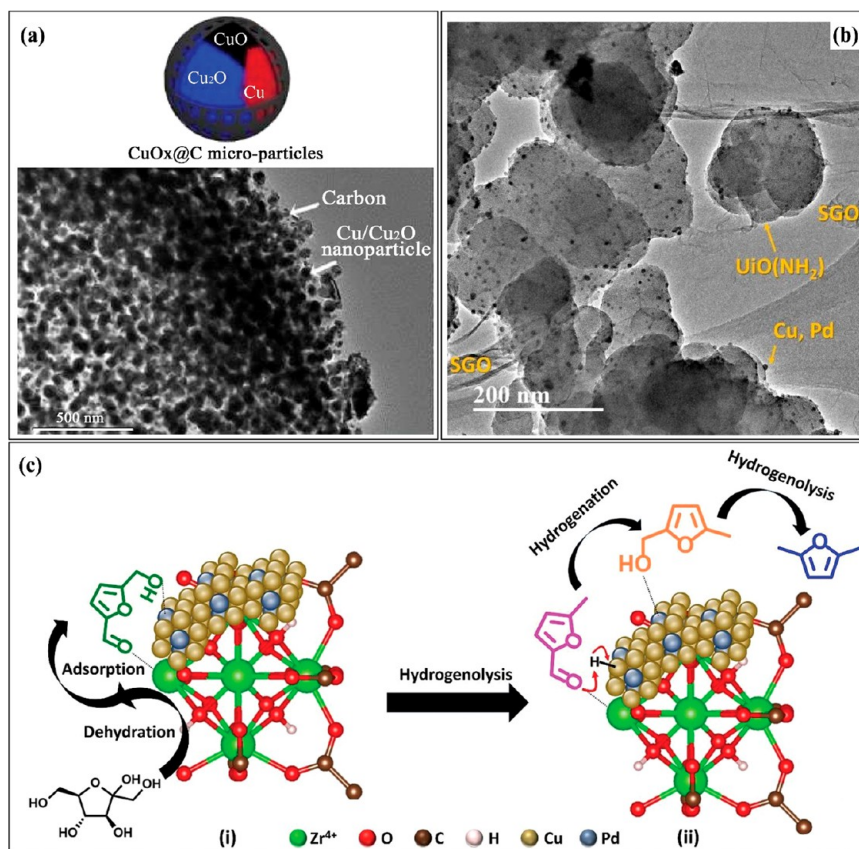


Figure 14. Synergistic mechanism of bifunctional catalysts. (a) HRTEM and structure of Cu-BTC-MOF.¹⁸⁵ Reprinted with permission from ref 181. Copyright 2020 Wiley-VCH. (b) HR-TEM images of 10Cu-1Pd/U50S50. (c) Plausible transformation of HMF to DMF.¹⁸⁷ Reprinted with permission from ref 187. Copyright 2019 Elsevier.

In present research works, multifunctional catalysts were found to offer a quite high selective yield of DMF from the HDO reaction of HMF. For example, the Fe_{0.8}-Co_{3.0}-Ni_{1.9}/h-BN

catalyst was observed to be a high-efficiency catalyst for an augmented production rate of DMF (≈94%), in which sequestered Co and Ni-Fe alloy species were homogeneously

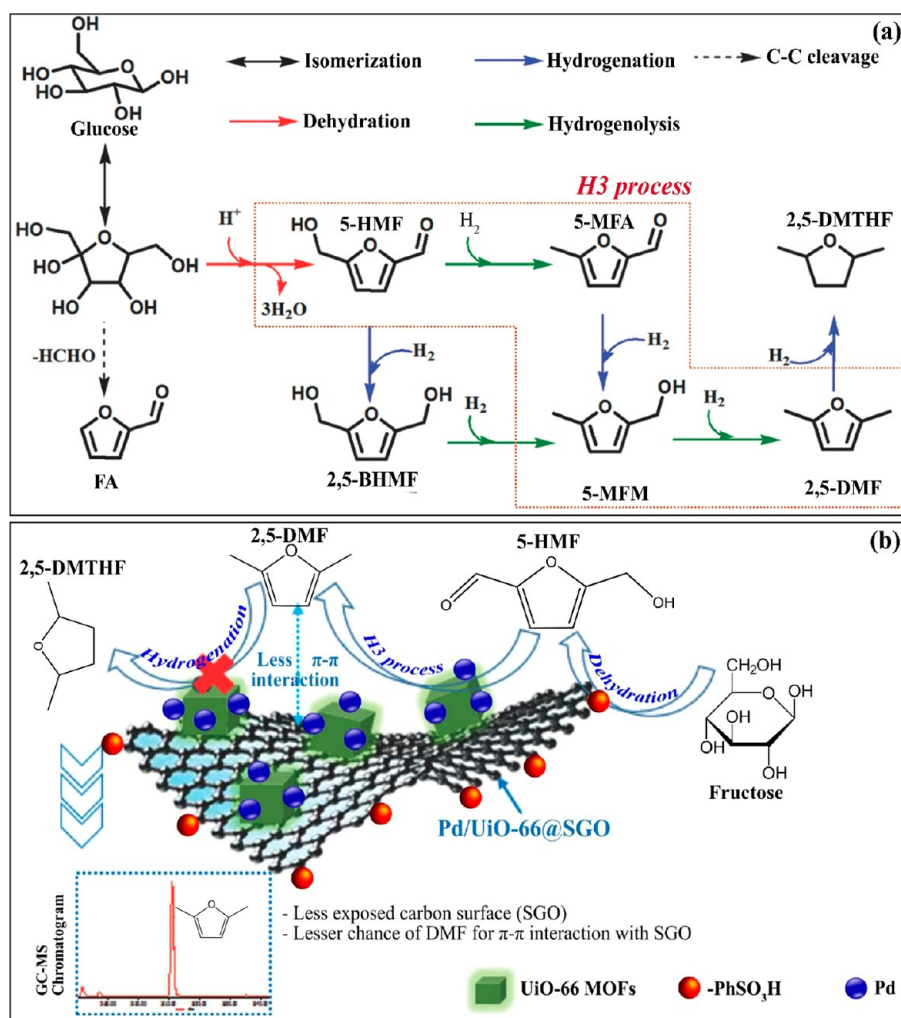


Figure 15. Scheme of the Pd/Uio-66@SGO catalyst surface with the conversion route of glucose to DMF.¹⁸⁸ Reproduced from ref 188 with permission. Copyright 2017 Royal Society of Chemistry.

distributed on the BN surface because of the deposition precipitation, indicating the peak activity for enhancing the DMF synthesis performance through HDO of HMF (Figure 12a).¹⁸¹ The achieved results have shown the synergistic and excellent effects of bifunctional catalysts supported by suitable metal with an optimal ratio. In another study, Seemala et al.¹⁸² proved this, where they employed Cu–Ni/TiO₂ catalyst for the conversion. The strong interaction between Ni and TiO₂ was found to be selective, which resulted in the development of active structures. The use of the catalyst resulted in a DMF yield of 90%. Due to this, the selectivity during HDO was high, which resulted in higher conversion efficiency. Furthermore, the interaction between Ni and TiO₂ was so sturdy that the bimetallic particles were efficiently attached to the TiO₂ present in the catalyst. This reduced the catalyst degradation by a huge degree and improved the regeneration and reusability of the catalyst. In the next study of Ma et al.,¹⁸³ they further studied the role of multifunctional catalysts like NiCoTi-8 in the conversion reaction of HMF to DMF. Interestingly, they explored that the oxygen in the carbonyl group of HMF was activated by Lewis acidic sites of NiTiO₃, promoting the hydrogenation reaction of HMF to form BHMF. In addition, Co²⁺ on the Co₃O₄ surface could adsorb HMF, while Co₃O₄ could activate the hydroxyl oxygen of BHMF to produce DMF (Figure 12b).

Esteves et al.¹⁸⁴ recently reported the synergistic effect of Cu and Nb to significantly increase DMF production. A high dispersion of Cu with Lewis acid sites played an important role in the oxygen activation of OH– groups in HMF and BHMF, aiming to promote DMF formation. In this way, Cu/Nb₂O₅–Al₂O₃-623 was employed under mild reaction conditions to synthesize DMF from HMF. Surprisingly, the promising DMF yield (around 90%) was achieved after 10 h of reaction. More importantly, reaction pathways were provided for the hydrogenation of HMF on Cu/Nb₂O₅–Al₂O₃-623 (Figure 13) as well as the potential of Nb₂O₅–Al₂O₃-623-supported Cu-based catalyst as an environmentally benign and relatively inexpensive catalytic alternative for DMF production.

MOF-Based Catalysts. A metal–organic framework (MOF) is known as a crystalline material, which possesses permanent porosity due to the special architecture of the metal ions and the organic bridging ligand, widely employed in storage, separation, and catalysis applications with promising prospective outputs. In a recent study, Zhang and co-workers¹⁸⁵ developed a series of monometallic Cu catalysts through the controlled thermolysis of Cu–BTC metal–organic frameworks (MOFs), in which a Cu–BTC (BTC as 1,3,5-benzenetricarboxylic acid)-derived porous carbon matrix was synthesized to enwrap CuOx@C catalyst with Cu₂O/Cu composites (Figure 14a). The content of Cu⁺ in the catalyst was increased, thereby

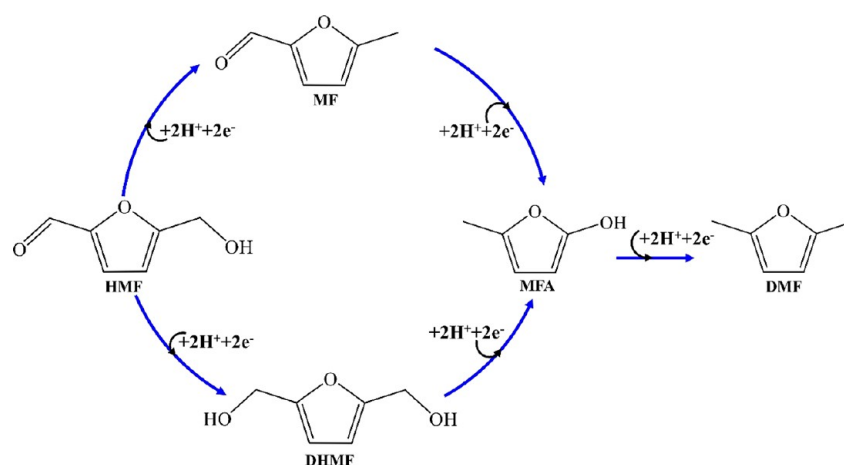


Figure 16. Technique for DMF production from HMF based on electrocatalytic hydrogenation.¹⁹²

improving the activity of the catalyst. This was also because of the synergetic effect between Cu^0 and Cu^+ , which is evidenced in HRTEM images (Figure 14a, below). Based on Figure 14a, the incorporation of dispersed $\text{Cu}/\text{Cu}_2\text{O}$ nanoparticles, as well as a large number of $\text{CuOx}@C$ microparticles, can be observed in the porous-structure carbonaceous substrate. Such a catalyst prompted a high DMF selectivity of 92% at 180 °C under a hydrogen pressure of 30 bar. Similarly, Sarkar et al.¹⁸⁶ also reported a Cu/MOF -based catalyst loaded with Pd through the impregnation process, which exhibited an excellent catalytic efficiency of 96.5% DMF yield. More interestingly, they detected that the intrinsic synergistic effect between Cu and Pd in $\text{Cu}-\text{Pd}@C-B$ (MOF) catalyst caused by the electronic interaction was significant. In this context, the Pd–Pd bond length was increased in conjunction with a decreased Cu–Cu length, thereby enhancing the catalytic activity while increasing DMF yields.

Heterogeneous bimetallic catalysts such as Cu/Pd on $\text{UiO}-66(\text{NH}_2)$ have also been reported by Insyani et al.¹⁸⁷ for DMF production from polysaccharide-based sources via a one-pot reaction. The authors discovered that Cu/Pd -originated bimetallic catalysts promoted the hydrogenolysis of C–OH and C=O groups successively. Meanwhile, the synergistic effects of Brønsted (SO_3H^- groups in SGO and $\text{Zr}(\text{IV})-\text{OH}$ species in $\text{UiO}-66(\text{NH}_2)$) and Lewis acid sites (Zr^{4+} species in $\text{UiO}-66(\text{NH}_2)$) were augmented because of employing an optimized $\text{UiO}-66(\text{NH}_2)/\text{SGO}$ ratio, thereby improving the cleavage of glycosidic linkage, dehydration, and isomerization of polysaccharides. From Figure 14b,c, C=O groups in molecular HMF tend to bind the unsaturated Zr^{4+} nodes in $\text{UiO}-66(\text{NH}_2)$, while the hydrogenolysis process over $\text{Cu}-\text{Pd}$ sites was believed to prompt the removal of C–OH in HMF to form MFA.¹⁸⁷ After that, DMF was formed through MFA via hydrogenolysis of the C–OH group. More interestingly, the desorption of as-obtained DMF from the catalyst surface was easy due to the absence of both C=O and C–OH groups. Moreover, the interaction between C=C bonds of DMF with the surface of $\text{Cu}(111)$ and the Cu_3Pd phase caused by the Cu_3Pd atomic crystalline arrangement was unfavorable, thereby hindering furan-ring-opening reactions. Overall, a DMF yield of around 73.4% is recorded with the reaction at 200 °C and 10 bar in 3 h.

In the recent study of Insyani and co-workers,¹⁸⁸ a novel $\text{Pd}/\text{UiO}-66@\text{SGO}$ catalyst was designed by loading Pd on a metal–organic framework ($\text{UiO}-66$) based on Zr deposited on

sulfonated graphene oxide. As a result, a direct conversion reaction of fructose/glucose to DMF with an unprecedentedly high yield through a one-pot approach without HMF purification was reported when using a catalyst of $\text{Pd}/\text{UiO}-66@\text{SGO}$ in THF solvent under 160–180 °C of temperature and 10 bar of H_2 pressure for 3 h. This exceptional phenomenon was attributed to the crystal structure of $\text{UiO}-66$, in which the structural defects and in-plane vibration of the sp^2 carbons could be seen (Figure 15a). This imperfection in the crystal structure of $\text{UiO}-66$ was believed to cause a large surface area, resulting in a higher total acidity.¹⁸⁹ Moreover, such a large surface area of defected $\text{UiO}-66$ caused by uncoordinated Zr_6 -cluster nodes could result in a synergetic effect of Lewis acid at the Zr^{4+} metal center and Brønsted acid at the $\text{Zr}-\text{OH}$ site or $\text{Zr}-\text{OH}_2$ site.¹⁹⁰ Moreover, the $\pi-\pi$ interaction of the C=C sp^2 in graphene and the unsaturated ring of furan could facilitate DMF adsorption on the SGO surface, leading to an excellent performance (99.2% DMF yield from HMF), outperforming that of fructose (70.5%) and glucose (45.3%). More importantly, a plausible reaction pathway for the direct conversion of fructose/glucose to DMF over $\text{Pd}/\text{UiO}-66@\text{SGO}$ catalyst was also proposed (Figure 15b). In general, the activity of Pd is intrinsically high for the hydrogenation of the furan ring instead of the C=O bond. This is due to the intensive interaction of π bonds in the furan ring and the narrow d band in the Pd molecule, resulting in the reduction of the selectivity yield to DMF in conjunction to the subreactions.

Electrocatalysts. Electrocatalytic techniques are a new promising alternative to the conventional catalytic reactions used for conversion of HMF which could lead to large-scale industrial applications in DMF production. Electrocatalysis could be employed for both oxidation and hydrogenation processes while maintaining mild to moderate reaction conditions.¹⁹¹ The process used the technique of ion shifting, where a non-catalytic reaction occurs while a proton is unswervingly transferred from water molecules present in the electrolytic solution. Nilges et al.¹⁹² used H_2SO_4 with a concoction of water and ethyl alcohol as the electrolyte to convert HMF to DMF during the electrocatalysis reaction (Figure 16). A maximum DMF yield of 34.6% was observed during the reaction. Other methods such as the utilization of ZrO_2 -doped graphite as the electrode during the reaction resulted in a low conversion efficiency of just 30.7%.¹⁹³ Using a CuNi bimetallic electrode resulted in a very high DMF yield of 91.1%.¹⁹⁴ Although the process of electrocatalysis resulted in

Table 2. Solvent Types for HMF Conversion from Carbohydrates

solvent	explanation	operating conditions	characteristics
polar protic	subcritical water; alcohol (methanol, ethanol, propanol, butanol); acetone; 1,4-dioxane	100–374 °C	- providing protons and high polarity - low conversion efficiency
polar aprotic	methyl isobutyl ketone (MIBK); dimethyl sulfoxide (DMSO); dichloromethane (DCM); tetrahydrofuran (THF); <i>N,N</i> -dimethylacetamide (DMA); biomass-based solvents (MTHF, DMF, γ -GVL...)	120–180 °C	- moderate polarity - non-acidic hydrogen - quite high conversion efficiency
ionic liquids (ILs)	salts in liquid state or the combination of salts and acid, composed of large organic cations	moderate temperature, around 100 °C	- disrupting and dissolving the polysaccharide macrostructure - low melting point and suitable viscosity - high conversion efficiency
biphasic/binary systems	at least two solvents	<200 °C	- lower-solubility solvent in water is more suitable - using secondary solvent to increase the partitioning coefficient - increasing the extractive phase volume, resulting in accelerating the diffusion rate of HMF

low yields, it was considered an ecofriendly alternative to the conventional utilization of catalysts. The reaction showed other great advantages such as the capability to continue the reaction at room temperature where the hydrogenation process for conversion of HMF to DMF was achieved by proton addition from water. The scope of research in this field is to develop a new electrode material that has a higher yield and conversion efficiency. Recently, photocatalysts like CoPz/g-C₃N₄ and WO₃/g-C₃N₄ were established, which used a different pathway compared to conventional DMF production. These new catalysts could produce DMF by using selective oxidation reactions of HMF with the continuous support of oxygen. This technique is believed as a green novel route for the synthesis of DMF.^{195,196} Moreover, using biocatalytic techniques for production by using enzymes and whole cells could result in a very high DMF yield and will be considered as green production of DMF.^{197,198}

DMF Synthesis from Other Intermediates. In other methods of production, CMF could be converted to DMF. CMF is a highly reactive chemical used as a vital precursor for various chemical compounds used in industries. The production of DMF from CMF has been paid less attention due to the feasibility of the conversion process from CMF to DMF. CMF contains chlorine, which adds an extra process of separating chlorine from CMF. Initially, Mascal et al. tried to synthesize DMF from CMF by using Pd/C as the catalyst but resulted in very low DMF yields.¹⁹⁹ Other studies have shown that conversion of CMF into EMF or EL in alcohol or into HMF or LA in water was more efficient than conversion into DMF. Recently, a new three-step approach to conversion of CMF to DMF was developed. Initially, MFf was produced from CMF in toluene/water using the hydrogenation process, followed by condensation of MFf with 4-tertbutyl aniline in the solvent of *N,N*-dimethylformamide/acetic acid. After this, hydrogenation of the product from the second step using a Pd/C catalyst was conducted to produce DMF. The three-step process resulted in a DMF yield of 65% from CMF. Although the process had a moderate yield, the separation process after each step was a huge challenge.²⁰⁰ This made the conversion of CMF to DMF

inefficient when compared to converting from HMF. Although CMF to DMF conversion has been disregarded due to the high cost and low efficiency, conversion of CMF to EMF has been studied and yields greater than 90% have been achieved.²⁰¹

The effects of reaction conditions (temperature and pressure), catalyst, solvent, and feedstock are very different. For example, with the same catalyst Pd/C and reaction conditions but with two varying solvents, a DMF yield of 32% was achieved by using EMIMCl/acetonitrile, while EMIMCl gave only 12% DMF yield.²⁰² In another instance with the same catalyst Pd/C, a DMF synthesis reaction from HMF was conducted with two solvents including [EMIM]Cl–MeCN and ScCO₂–H₂O and various H₂ pressures (10 and 62 bar). However, a surprising result was reported that the synthesis reaction of DMF with ScCO₂–H₂O and a H₂ pressure of 10 bar gave the maximum DMF yield of 100% compared to 32% of the remaining case.¹⁶⁹ In the case of using HMF as a precursor for DMF production, organic solvents and ILs were widely employed in the HDO reaction. While ILs were usually used in the biomass conversion, this result was demonstrated when using the [BMIM]Cl system along with the catalyst system based on both non-noble and noble metal like Ni, Ru, Pt, and Ir. The change in DMF yield from 34.0 to 89.3% has indicated that ILs play a vital role in cellulose hydrolysis.⁵⁸ Furthermore, the water– γ -butyrolactone-based solvent system was found to be most suitable for directly converting fructose to DMF as using catalyst supported by HY zeolite and hydrotalcite–Cu/ZnO/Al₂O₃.¹³⁵ Besides, the application of formic acid as solvent was explored to provide a formyl group for the HMF HDO, helping to increase DMF yields.²⁰³ Due to this result, the study on the effects of solvents, H₂ donor sources, and reaction conditions will be further discussed in the next section.

Effect of Solvents on DMF Synthesis. For the conversion reaction to DMF from direct biomass or the derivatives, some processes are involved including HDO, hydrolysis, and isomerization. Therefore, in addition to catalyst, the solvent is typically used to enhance the efficiency of conversion from a feedstock for HMF/DMF production. The solvent is known for a critical role in dissolving the components in reactionlike substrates and

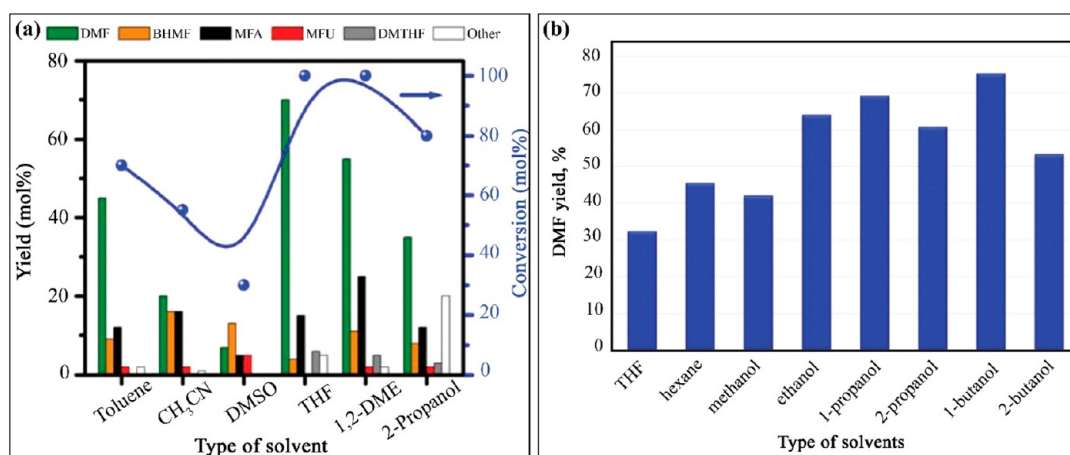


Figure 17. Effects of solvents on conversion efficiency to DMF. (a) Catalyst of Ru–NaY under a temperature of 220 °C, a H₂ pressure of 10 bar, and a reaction time of 1 h.¹³² Reprinted with permission from ref 132. Copyright 2015 American Chemical Society. (b) Catalyst of Fe-L1/C-800 after 12 h of reaction (drawn from data in ref 142). Reprinted with permission from ref 142. Copyright 2017 Wiley-VCH.

catalysts, stabilizing the components before and after reaction to form the thermodynamic equilibrium, acting as the secondary catalyst. Generally, the solvent types and their features have been summarized in Table 2.

At high temperatures and pressures, the unique properties of water were found to play a vital part in the hydrothermal conversion of cellulosic biomass. Hot water was considered as the catalyst for both acid- and base-based reactions due to its capacity of self-dissociation to ions of H⁺ and OH⁻. As reported, the ionic constant for water was $K_w = [H^+][OH^-] = 10^{-14}$; however, this ionic constant was increased by a thousand times at a reaction temperature of 200–300 °C,²⁰⁴ resulting in a certain favorability for HMF and DMF synthesis. Also, the activity of each catalyst is believed to strongly associate with the as-used solvents. Interestingly, for the HMF conversion process, the performance of polar protic solvents has been demonstrated to be more superior to that of non-polar or polar aprotic solvents. For example, the HMF conversion in the case of using Pt/MCM-41 catalyst with different solvents was reported as follows: 100% for water > 72.1% for methanol > 55.6% for ethanol > 27.2% for propanol > 24.4% for butanol > 12.0% for acetone > 10.1% for hexane under the same reaction conditions.²⁰⁵

The use of polar aprotic-based solvents in the synthesis process of HMF and DMF could improve the conversion yield. The most common polar aprotic-based solvents are divided into two main groups. One group, like DMSO, is miscible with water and considered as the co-solvents or modifiers. Another group, like MIBK, DCM, or THF, is not soluble in water, even salted out to create the biphasic system. Ionic liquids (ILs) with some special properties listed in Table 2 are known as “green solvents” and are typically used for synthesis reactions. Some types of ILs for DMF production can include [ASBI][Tf], [BMIM]Cl, [BMIM][BF₄], [EMIM][Cl], [HMIM]Cl, and [NMM][CH₃SO₃]. Additionally, renewable ILs could be considered as potential solvents. Indeed, for DMF synthesis from HMF, monophasic solvents such as organic solvents and ILs could be widely utilized in HMF HDO. Especially, the IL solvent could be found to bring a high conversion efficiency of biomass into value chemicals.²⁰⁶ This was confirmed in the work of Cai et al.,²⁰⁷ who have investigated the furan synthesis process from biomass under the mild condition with the support of heterogeneous catalysts based on Ni, Ru, Pt, and Ir metal and in the monophasic

[BMIM]Cl system. As a result, the significant influence of ILs on the reaction efficiency of cellulose hydrolysis was reported as the conversion efficiency ranged from 34.0 to 89.3%.

In another research work of Chidambaram et al.,¹²⁵ the authors found that the peak yield of DMF for the case of using EMIMCl–CH₃CN solvent was obtained at approximately 15%. The influence of solvent on the catalytic activity in the HMF hydrogenolysis conversion to DMF under a temperature of 220 °C, a H₂ pressure of 7 bar, and Ru-based catalyst was also studied by Nagpure et al.²⁰⁸ They have evaluated the effects of different solvents such as 2-propanol (protic type), THF (aprotic polar), and 1,2-DME and toluene (nonpolar) on the hydrogenolysis reaction and the selectivity yield of DMF. The obtained result has shown a strong dependence of catalyst activity on solvents, in which the order for the catalytic activity as toluene < 1,2-DME ≈ THF < 2-propanol could be seen. The lower hydrogenolysis activity of HMF to DMF in toluene solvent was because of the overlap degree of the d bands in Ru metal with the carbon π molecular orbitals,²⁰⁹ reducing the hydrogenolysis activity of HMF. A similar result was also reported in another study as using a Ru–NaY catalyst for the hydrogenolysis process of HMF to DMF.¹³²

It could be clearly seen that the catalytic activity was remarkably dependent on the solvent characteristics, following the order DMSO < CH₃CN < 2-propanol < toluene < 1,2-DME < THF. Indeed, Wei et al.²¹⁰ have found that THF was the most suitable solvent among as-used solvents, such as [BMIM]Cl, 1,4-dioxane, DMSO, *N,N*-dimethylformamide, THF, methanol, ethanol, isopropanol, and 1-butanol, with the highest yield of 90.1% being for the THF case in the HMF conversion reaction to DMF by using Ru/C as a catalyst. Obviously, the negative effects of DMSO, CH₃CN, and toluene solvents on Ru-based catalyst systems were further demonstrated. In addition, the Ru-based catalyst system was deactivated by the impacts of solvents containing sulfur or nitrogen such as DMSO and CH₃CN. Meanwhile, the synergistic effects between THF and Ru–NaY provided the highest conversion yield of 69.5%, which was illustrated in Figure 17a. Similarly, the effects of solvents on the DMF yield were also evaluated by Li et al.,¹⁴² employing various solvents such as THF, hexane, methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol for the catalyst conversion of HMF to DMF through Fe-L1/C-800. As a result, 2-propanol

was found to be the best solvent, yielding the highest efficiency of 75.3% (Figure 17b).

In the conversion reactions of cellulose/fructose/glucose or sugars to DMF, biphasic solvents have been reported to be a better selection because this direct conversion was conducted through the dehydration of sugars to HMF in the first step. Roman-Leshkov et al.¹⁵³ have found that adding NaCl in the second step of the DMF synthesis from cellulose has yielded the highest DMF conversion efficiency under the support of Cu–Ru/C catalyst. In addition, DMF synthesis from fructose by the one-step process was also reported by Li et al.²¹¹ They used a biphasic solvent system ([BMIM]Cl/THF) in water along with a Ru-based modified catalyst. Resultantly, the highest DMF yield (around 66%) was achieved, while the water amount in the solvent mixture was explored to have a strong effect on the DMF yield. In summary, the bilateral effect of catalyst and solvent on the conversion efficiency and yield of DMF was self-evident, suggesting the investigation on the reasonable selection of solvent for each catalyst system.

Effects of H₂ Donor on DMF Synthesis. Results show that H₂, FA, alkanol (methanol, ethanol, isopropanol, butanol), cyclohexanol, 1,4-butanediol, water, and even HMF can be employed as a hydrogen donor for the selective conversion to DMF. Recent studies used electrocatalytic hydrogenation for the HMF synthesis, and the achieved results were very surprising.²¹² For H₂ as a donor, usually is it used for catalyst systems of HMF HDO to DMF due to its availability and easy activation on the catalyst surface. Nonetheless, a number of challenges of using H₂ as a donor are also pointed out as a transport issue, economic factor, safety, and sustainability, in which the safety issue is the top because the solubility of molecular hydrogen is low in most solvents, leading to the requirement on high pressure in the catalyst systems.²¹³ Many studies have tried using other donors replacing H₂; some substances such as FA, alcohol, hydrocarbon, ammonia, and hydrazine were found to be potential H-donors with low cost and safety.²⁰⁶

FA was found to have three roles in catalyst-based HDO reactions for converting HMF to DMF. On the one hand, it played a role as a hydrogen source in the hydrogenation process. On the other hand, it could be considered as the acid catalyst for converting fructose to HMF through the dehydration process, and its third role was known as a reagent for the deoxygenation reaction of furanyl methanol. Using FA as an H₂ donor was believed to address and overcome the challenge associated with the durability of material and catalyst as using other strong acids such as H₂SO₄, HCl, and HNO₃. In the study of Yang et al.,²¹⁴ Ni–Co/C catalyst was employed for HMF hydrogenation to DMF in FA as the H₂ donor and THF as the solvent, with the highest yield of DMF (around 90%) reported when the reaction was conducted at a temperature of 120 °C. Furthermore, FA was also considered as a H-donor for the DMF synthesis from fructose and HMF through using Pd/C as a catalyst in THF as solvent.²¹⁵ Surprisingly, a high DMF yield could be achieved from HMF, corresponding to 95%, although a DMF yield of only 51% was obtained from fructose. In a recent study, Sun et al.¹⁷⁴ have also reported the effect of FA and the synergistic effect of Ni–Cu catalyst on the DMF yield. However, they found that 5-formyloxymethylfurfural has exhibited a better advantage than HMF in the DMF production under the above-mentioned catalyst system. Obviously, FA could be considered as the promising hydrogen donor; however, it runs into some problems relating to the corrosion of an acid in large-scale applications. This has suggested a better H-donor base, and the alkanol family

was thought to be a potential candidate when they have not caused any corrosion phenomenon to metal.

Jae et al.^{162,163} adopted 2-propanol as a H-donor for DMF synthesis by using a Ru-based catalyst. They realized that 2-propanol appeared to be more suitable for Ru/C than Ru/C + RuO₂ when the Ru/C-based catalyst system afforded a higher DMF yield than with the Ru/C + RuO₂-based catalyst. Similarly, Scholz et al.²¹⁶ utilized 2-propanol in a synthesis reaction of HMF to DMF with the support of Pd/Fe₂O₃ catalyst. In this case, 2-propanol was considered as both a hydrogen donor and solvent. They reported that a DMF yield of 72% could be achieved. Hansen and co-workers¹⁴³ have used methanol as a solvent in the Cu-doped porous-metal-oxide-based catalyst reaction of HMF HDO to DMF; they have detected that the highest yield of DMF of 48% could only be achieved after 3 h of reaction and at 260 °C.

Furthermore, Zhang et al.²¹⁷ reported that the catalytic activity of Cu/Al₂O₃-based catalyst was the best in the process of in situ H₂ production from methanol, which is associated with the DMF yield of 75%. In a recent study of Nagpure et al.,²¹⁸ they have conducted an overall evaluation of the effects of hydrogen donors originated from alkanol including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, and 2-butanol on the DMF yield as using 2 wt % Ru–NMC-3 catalyst at a temperature of 160 °C. The obtained results illustrated in Figure 18a have shown the profound dependence of the activity on the as-used hydrogen donor. The conversion efficiency to DMF was increased from 10% (for the methanol case) to 84% (for the 2-

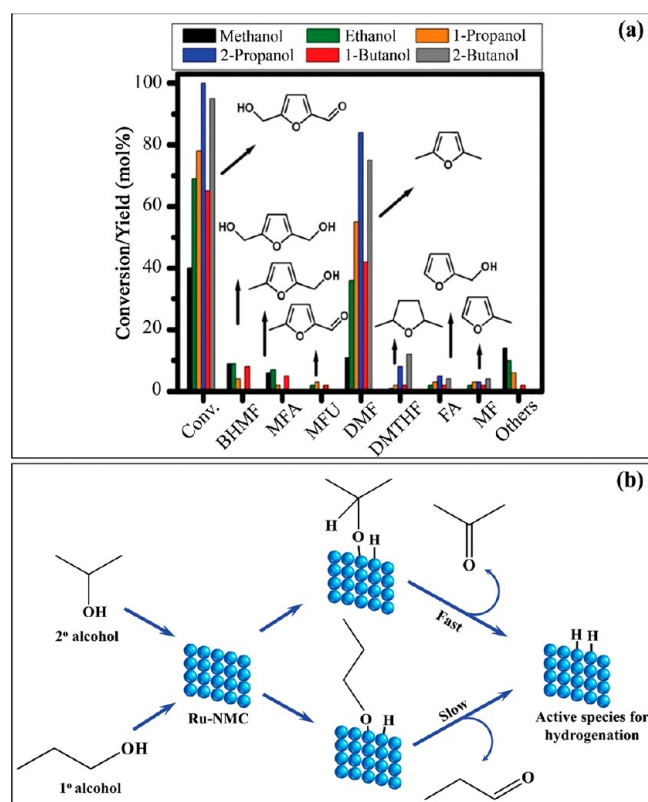


Figure 18. (a) Effects of hydrogen donor originated alkanol on the conversion efficiency to DMF. (b) The route of active species for hydrogenation under the secondary and primary alcohols.²¹⁸ Reproduced from ref 218 with permission. Copyright 2020 Royal Society of Chemistry.

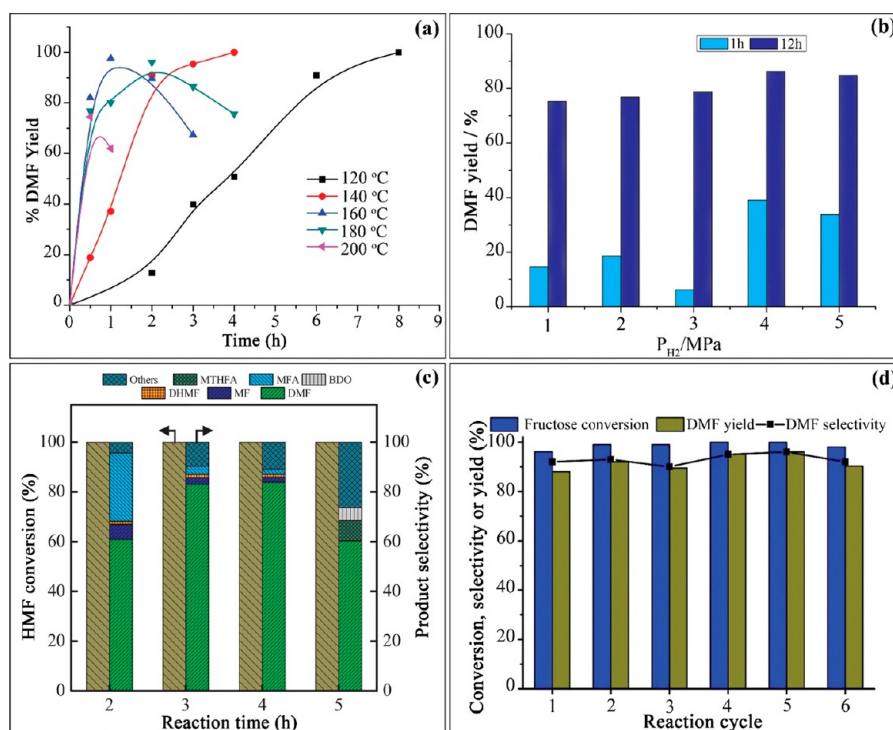


Figure 19. Effects of reaction conditions on the DMF yield. (a) Effects of the reaction temperature in the case of Ru–Co/SiO₂ catalyst.¹⁵⁷ Reprinted with permission from ref 157. Copyright 2019 Springer-Nature. (b) Effects of H₂ pressure in the case of Fe–L1/C-800 catalyst.¹⁴² Reprinted with permission from ref 142. Copyright 2017 Wiley-VCH. (c) Time-dependent HMF conversion to DMF with 20Co/beta-DA-C723R catalyst.¹³⁷ Reprinted with permission from ref 137. Copyright 2020 Elsevier. (d) Reuse cycle of Pd/C–SO₃H–TMS catalyst for the direct DMF production from fructose.¹⁴⁴ Reproduced from ref 144 with permission. Copyright 2017 Royal Society of Chemistry.

propanol case). The reactivity order could be seen as follows: 2-propanol > 2-butanol > 1-propanol > ethanol > 1-butanol > methanol.²¹⁸ Obviously, the tendency of hydrogen release from the secondary alcohols such as 2-propanol and 2-butanol was higher than that with the primary alcohols, indicating that dialkyl ketone possesses the higher reduction potential, while the etherification reaction was detected to favor primary alcohols.²¹⁹ As a result, the formation of active species for the hydrogenation process from the secondary alcohols was faster than that of the primary alcohols over Ru–NMC (Figure 18b).

As mentioned above, the finding route of catalyst or solvent and hydrogen donor to convert HMF to DMF should satisfy the requirement of green access and sustainability, which has put out a challenge for DMF production with no or little toxic release. Unfortunately, the use of 2-propanol or methanol for the HMF HDO process to synthesize DMF was difficult to separate the products, pulling the idea over the use of a green hydrogen donor, but it is also easy to separate. Indeed, Li et al.¹⁴² have used *n*-butanol as a solvent and an additional hydrogen source; they found that *n*-butanol had an evident effect in the hydrogenation of the C=O bond in HMF, leading to quite a high DMF yield as using Fe–L1/C-800 catalyst, corresponding to 86.2%. In a recent study, Li and co-workers have explored a pathway of DMF production without any external oxygen and hydrogen supply.²²⁰ They have used highly efficient vapor-phase dehydrogenation–hydrogenation combined with bimetallic Ni–Cu nanocatalysts to synchronize the DMF and phenol production. Unprecedentedly, the DMF yield could be achieved to 99% from HMF. Interestingly, such a coupling process with efficient, eco-friendly, and versatile characteristics was found to apply in the synchronized production of phenol and DMF, showing a promising process based on the criteria of green

chemistry and sustainable development. In addition, Gao et al.²²¹ have evaluated the effects of cyclohexanol as a hydrogen source on the DMF yield when using NC-decorated Cu-based catalyst, indicating a DMF yield of 96.1%. The use of polymethylhydrosiloxane (PMHS) as the hydrogen donor was also found to offer quite a high DMF yield, even if it was applied to synthesize DMF from fructose.^{144,222} Generally, H₂ was typically used under high pressure for the catalyst reaction to produce DMF. Moreover, it has high dispersion, high cost, and flammability, resulting in concerns about the safety. Therefore, the development of other hydrogen sources to meet the requirements of high efficiency, high degree of safety, and environment friendliness is imperative.

EFFECTS OF REACTION CONDITIONS ON DMF SYNTHESIS

Since temperature plays a critical part in chemical reactions based on catalysts, the optimization of the reaction temperature in HMF conversion is very necessary to achieve the best yield. There are several methods to heat the equipment and vessel in a reaction such as conventional heating (oil bath or bath, aluminum heating block, autoclave) and microwave.

Among conventional heating methods, using an oil bath is more popular, where stirring is usually used to enhance the mass transfer of the reactive phases.²²³ However, conventional heating has the disadvantages such as a long time for reaction and a low heat transfer efficiency. In recent years, the microwave is emerging as a more efficient method for heating in the conversion reaction of biomass. Its noticeable advantages such as shortening reaction time, improving conversion productivity, and diminishing the side reactions were reported. For instance, with the same catalyst and solvent, a 91% HMF yield was

Table 3. Conversion Efficiency to DMF under Various Feedstock/Catalyst/Solvent/Reaction Conditions

feedstock	catalyst	solvent	H ₂ donor/pressure (MPa)	temperature (K)	time (h)	yield (%)	ref	
HMF	Ru/Co ₃ O ₄	THF	molecular H ₂ /0.7	403	24	94	156	
	Ru/C	isopropanol	molecular H ₂ /0.5	398	1	69.5	140	
	Ru–Co/SiO ₂	THF	molecular H ₂ /2	413	6	100	157	
	Ru/SiO ₂		molecular H ₂ /1.5	453	2	96		
	RuCo/CoO _x	1,4-dioxane	molecular H ₂ /0.5	473	2	96.5	158	
	Ru–ZrO ₂ –MCM-41	THF		molecular H ₂ /1.5	433	1	90	164
		<i>n</i> -butanol					70	
		4-dioxane					58	
	Ru/CNTs	dioxane		molecular H ₂ / <2	423	1	83.5	229
	Ru/CoFe–LDO	THF		molecular H ₂ /1	453	6	98.2	230
	Pt–Co/MWCNTs	1-butanol		molecular H ₂ /1	433	8	92.3	167
	PtCo@HCS	1-BuOH		molecular H ₂ /1	453	2	98	166
	Pt ₃ Ni/C	1-propanol		molecular H ₂ /3.3	473		98	231
	Pt ₃ Co ₂ /C	1-propanol		molecular H ₂ /3.3	433		98	232
	PdAu ₄ /GC800	THF		molecular H ₂ /1	423	6	94.4	147
	Pd–Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ /K-10	THF		molecular H ₂ /1	363	2	81	151
	Pd–Co ₉ S ₈ /S-CNT	THF		molecular H ₂ /0.3	393	13	83.7	152
	Pd/C	dioxane + formic acid/CH ₃ COOH		molecular H ₂ /0.2	393	15	85	203
	Pd/Fe ₂ O ₃	2-propanol		2-propanol	453	0.4	72	216
	PdCl ₂ /HCl	ethanol		PMHS	298	0.5	89.7	222
	Pd–Fe/C	THF		molecular H ₂ /2	423	2	88	146
	Ni–OMD ₃	water		molecular H ₂ /3	473	6	98.7	127
	Ni–W ₂ C/AC	THF		molecular H ₂ /1	453	3	96	171
	36Ni–12Cu/SBA-15	THF		FA	493	5	71	174
	Ni–Co/C	THF		2-propanol	483	24	20	214
				FA			90	
				molecular H ₂ /1.5			60	
	Ni–Co/C	THF		molecular H ₂ /1	403	71	90	233
	Ni/SBA-15	1,4-dioxane		molecular H ₂ /3	453	0.5	71	234
	NiCu ₃ /C	1-propanol		molecular H ₂ /3	453		98.7	235
	NiO/WO ₃	water		molecular H ₂ /1	453	6	95	236
	Cu–PMO	methanol		methanol	433	3	48	143
	Cu–BTC-MOFs	IPA		molecular H ₂ /3	453	4	73	185
	Cu–Co@C (Cu:Co = 1:3)	ethanol		molecular H ₂ /5	453	8	99.4	179
	CuZnO	dioxane		molecular H ₂ /2	493	5	79	175
	Cu/Al ₂ O ₃	methanol		methanol	513	6	75	217
	Cu–NC/MgAlO	cyclohexanol		cyclohexanol	493	0.5	96.1	221
	Cu–Ni/BC	THF		molecular H ₂ /4	493	12	93.5	237
	Cu/Nb ₂ O ₅ –Al ₂ O ₃ -773	THF		molecular H ₂ /2	423	10	90	184
	Cu–CuFe ₂ O ₄	2-propanol		molecular H ₂ /3	443	6	93	238
	CuCo@NGr/ α -Al ₂ O ₃	THF		molecular H ₂ /1	413	16	99	239
	Co/ β -DA	THF		molecular H ₂ /1.5	423	3	83.1	137
	Co/SiO ₂	THF		molecular H ₂ /1.5	453	2	96	157
	Co _{1,0} /rGO	ethanol		molecular H ₂ /2	493	1	94.1	240
	Fe-L1/C-800	<i>n</i> -butanol		<i>N</i> -butanol, molecular H ₂ /4	513	5	86.2	142
Fe _{0.8} –Co _{3.0} –Ni _{1.9} /h-BN	THF		molecular H ₂ /2	453	4.5	94	181	
4.8Pd/UiO-66@SGO (MOF)	THF		molecular H ₂ /1	433	3	99.2	188	
4.8Pd/SGO (MOF)						68		
CuPd@C–B (MOF) (reduction route using solid-phase H ₂)	THF		molecular H ₂ /1.5	393	7	96.5	186	
Pd/Co–CoO _x @N-doped C	dioxane		molecular H ₂ /1.5	453	2	97.8	177	
fructose	Pd/C	THF	formic acid	353	15	51	215	
	Pd/C	<i>n</i> -butanol	PMHS	393	1.5	84	144	
	Pd/C–trimethylchlorosilane (TMS)				1.5	94		
	Pd/C–SO ₃ H				2	77		
	Pd/C–SO ₃ H–TMS				2	92		
	Pd/PDVB–S-143	<i>n</i> -butanol		molecular H ₂ /1	393	6	94.2	145
	2.4Pd/UiO-66@SGO	THF		molecular H ₂ /1	433	1	25.9	188
	4.8Pd/SGO					3	38.5	

Table 3. continued

feedstock	catalyst	solvent	H ₂ donor/pressure (MPa)	temperature (K)	time (h)	yield (%)	ref
glucose	Ru/C	[BMIM]ClTHF	molecular H ₂ /5	403	0.5	50	211
	Amberlyst 15/Ni@WC	ethanol	formic acid	423	~0.3	38.5	241
	4.8Pd/UiO-66@SGO	THF	molecular H ₂ /1	453	3	43.5	188
	Pd/C-SO ₃ H-TMS	<i>n</i> -butanol	PMHS	393	4	55	144
sucrose	10Cu-1Pd/U50SS0	THF	molecular H ₂ /1	473	3	79.9	187
	Pd/C-SO ₃ H-TMS	<i>n</i> -butanol	PMHS	393	3	72	144
	10Cu-1Pd/U50SS0		molecular H ₂ /1	473	3	73.4	187
cellobiose	4.8Pd/UiO-66@SGO	THF	molecular H ₂ /1	473	3	38.1	187
	Pd/C-SO ₃ H-TMS	<i>n</i> -butanol	PMHS	393	5	53	144
	10Cu-1Pd/U50SS0	THF	molecular H ₂ /1	473	3	67.7	187
	4.8Pd/UiO-66@SGO	THF	molecular H ₂ /1	473	3	29	187
inulin	Pd/C-SO ₃ H-TMS	<i>n</i> -butanol	PMHS	393	3	82	144
starch	10Cu-1Pd/U50SS0	THF	molecular H ₂ /1	473	5	53.6	187
	4.8Pd/UiO-66@SGO	THF	molecular H ₂ /1	473	5	19.5	187
cellulose	10Cu-1Pd/U50SS0	THF	molecular H ₂ /1	473	3	29.8	187
	4.8Pd/UiO-66@SGO	THF	molecular H ₂ /1	473	3	10.3	187

obtained from fructose under microwave heating and 1 min of reaction time, while the reaction time for oil bath heating was 40 min and achieved only a 79% HMF yield.²²⁴ Besides, the interaction of the photons produced by microwave and CH₂OH group in cellulose molecular promoting the conversion process faster was also revealed.²²⁵ Furthermore, the use of microwave heating is indicated to save up to 85% of energy in comparison to conventional heating methods, although the reaction medium could be an agent to hinder the irradiation absorption.

Indeed, the effects of reaction temperature versus the reaction time on the DMF yield as using with Ru-Co/SiO₂ catalyst could be illustrated in Figure 19a. It could be observed that the time for reaching a DMF yield >99.9% was longer, corresponding to 8 h, at a low temperature of 120 °C. Nonetheless, the reaction time was seen to be shorter at higher temperatures; for instance, a DMF yield >99.9% was obtained for only 4 h at a temperature of 140 °C. If the reaction temperature was continuously increased, the DMF yield was decreased. The reason for the lessening of DMF as augmenting the temperature was attributed to further formation of byproducts from DMF synthesis at higher temperatures. Similarly, most studies have reported the significant effects of reaction temperature on the DMF yield.^{145,186,226} However, this effect was different between catalyst types. Nishimura et al.²²⁷ have declared the highest DMF yield of 99.96% with Pd-Au/C catalyst under a mild reaction temperature of 60 °C, while Gao et al.²²¹ found the highest DMF yield of 96.5% with Ru-Co/CoO_x at a temperature of 200 °C. In general, the reaction temperatures can be changed in a large range, from room temperature to 250 °C.

For the effect of H₂ pressure on DMF yield, it was reported that it is difficult for H₂ to cause remarkable activity on the catalyst surface. Due to this reason, the pressure of H₂ is typically to increase the catalyst capacity as H₂ is considered as a donor. Similar to the reaction temperature, the increase in H₂ pressure could lead to an increase in DMF yield. However, if the pressure was higher than the optimized value, it could cause a decrease in DMF yield. This result was due to the increase in the yield of intermediates and byproducts. Moreover, the combined effect of H₂ pressure and reaction time plotted in Figure 19b was absolutely demonstrated in most studies,^{142,177} suggesting that the optimization of reaction conditions is very important.

As illustrated in Figure 19b, the highest DMF yield could be achieved at a H₂ pressure of 4 MPa after 12 h of reaction, but the DMF yield tended to decrease with the elevation of H₂ pressure. For instance, Nagpure et al.¹³² have indicated that, in the case of using Ru-NaY catalyst, the highest DMF yield of nearly 80% was obtained in 1 h, under 15 bar of H₂ pressure. However, beyond 3 h, a H₂ pressure of 5 or 10 bar was found to induce maximized DMF yield, corresponding to 67%. Similarly, Shang et al.¹⁷⁷ concluded that the highest DMF yield was nearly 100% when the H₂ pressure was 1.5 MPa; however, the DMF yield was seen to decrease along with increasing H₂ pressure. Generally, changing tendencies of DMF yield in the correlation with H₂ pressure were also reported in the literature.^{127,210} In addition to reaction temperature and H₂ pressure, the DMF yield was also found to have a high sensitivity to the reaction time; this was self-evident in Figure 19c.¹³⁷ A maximum DMF yield could be reached within 3–4 h, while a shorter or longer reaction time is detrimental for the DMF yield, judging from its declining trend reported. It was confirmed in most studies that the ratio of byproducts was increased, reducing the selectivity yield of DMF.^{144,174} Furthermore, from the analysis of the core relationship between the reaction conditions and the DMF yield, it was found that the reaction conditions play an important role in getting the highest yield of DMF. Due to this reason, Srivastava et al.²²⁸ have suggested a Taguchi method to optimize the DMF production process. In their study, five factors such as reaction temperature, reaction time, H₂ pressure, catalyst dosage, and HMF conversion were selected as the input data for the optimization using Cu-Co/Al₂O₃ catalyst. As a result, they found the reaction conditions (temperature = 220 °C, H₂ pressure = 30 bar, reaction time = 6 h, catalyst loading = 0.5 g, and HMF concentration = 0.2% weigh) could offer the maximum DMF yield of 87%. This method has opened a new approach to optimize the technical features of the DMF production based on catalyst. Besides, the number of reaction cycles was used to evaluate the economic factor and the stability level of the catalyst (Figure 19d).¹⁴⁴ Normally, the greater the number of reaction cycles, the higher the economic feature and the stability level of catalyst, and vice versa. Thus, developing catalyst systems with high techno-economic index, excellent stability, and environmental friendliness is necessary before pushing DMF production to the industrial scale. In summary,

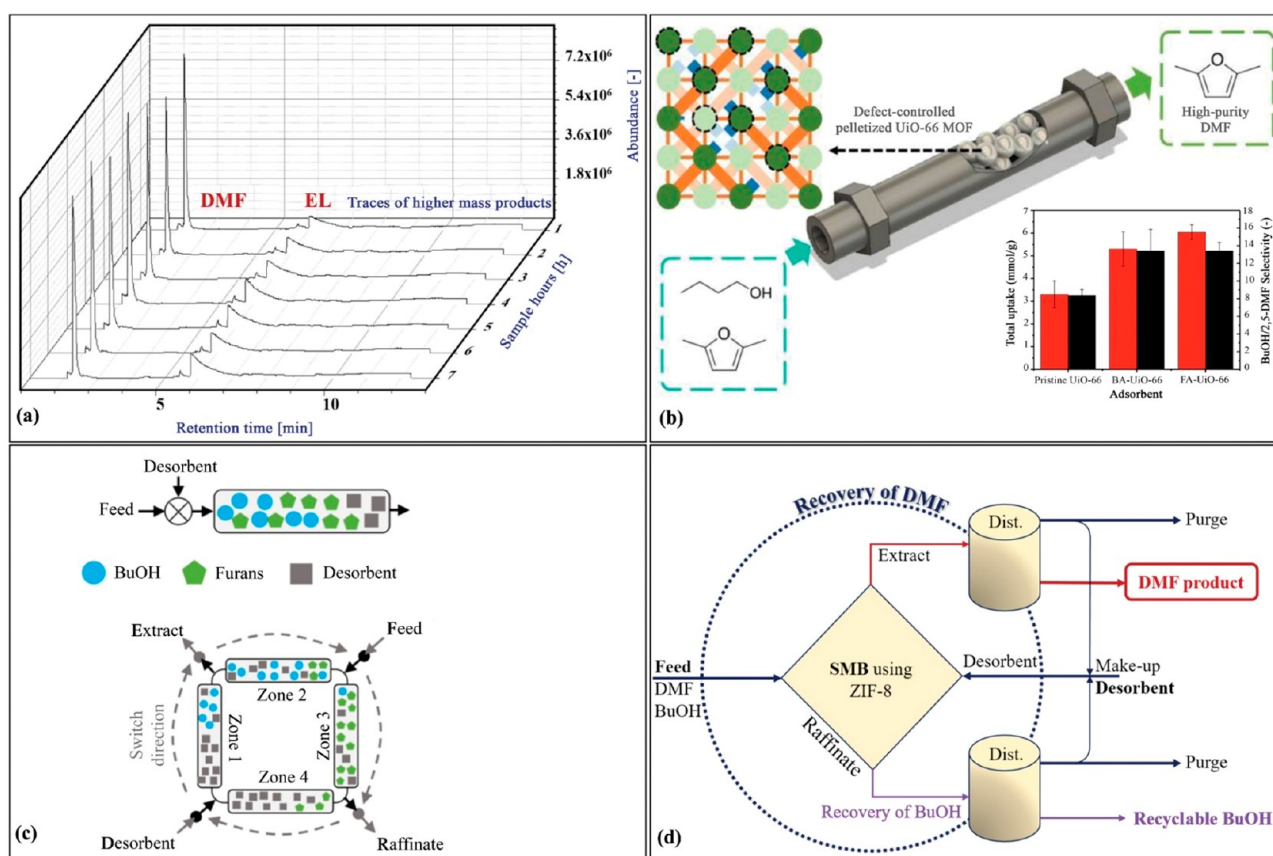


Figure 20. Technology for DMF purification after the synthesis process. (a) Distillation method based on the difference of boiling point for DMF separation from a mixture of DMF–EL.²⁴¹ Reproduced from ref 241 with permission. Copyright 2017 Royal Society of Chemistry. (b) Separation of DMF from *n*-butanol solvent by using defect UiO-66 MOF.²⁴² Reprinted with permission from ref 242. Copyright 2018 American Chemical Society. (c) Continuously operated simulated moving bed process based on zeolite-imidazolized framework-8 (ZIP-8). Reprinted with permission from ref 242. Copyright 2018 American Chemical Society. (d) Closed-loop SMB-integrated purification based on adsorption for DMF with high purity.²⁴³ Reprinted with permission from ref 243. Copyright 2019 American Chemical Society

the DMF synthesis via HMF or direct conversion based on various techniques (reaction conditions, catalyst, solvent, H₂ source) and carbohydrate-rich raw materials was shown in Table 3.

PURIFICATION PROCESS OF DMF

For DMF purification, the removal of impurities after the production is extremely critical.²⁴² By exploiting the difference of boiling points, Braun and co-workers²⁴¹ suggested an economic method to separate DMF from the mixture consisting of DMF, ethyl levulinate (EL), and ethanol. Notably, the boiling points of DMF, EL, and ethanol are 95, 205, and 109 °C, respectively. Moreover, the evaporation energy of ethanol is 3 times higher than that of DMF. Therefore, they have used distillation to isolate the molecules. However, it is mentioned that their method is to target the production of DMF and EL from fructose through the combination between dehydration and hydrodeoxygenation in a continuous flow reactor. As a result, all DMF was found in the distillation process, while EL stayed in the bottom of the flask; this purification process could be illustrated in Figure 20a.

In another way, DMF production from fructose using *n*-butanol also afforded to provide a high DMF yield, but effective *n*-butanol recovery from the products mixture is essential to sustain the production process. Significantly, Chiang et al.²⁴² have synthesized the zirconium terephthalate (UiO-66) MOF

for the selective adsorption of *n*-butanol from the product stream from DMF generation. This complements the conventional distillation process for its incompetency in recovering pure DMF from the mixture stream. In their study, polar defects created by monoacid modulators in UiO-66 promoted a significant increase in *n*-butanol selectivity. They have compared the capacity of separation for DMF in *n*-butanol of three types of UiO-66 such as pristine UiO-66 MOFs, UiO-66-MOF-modulated BA (BA - benzoic acid), and UiO-66-MOF-modulated FA (FA - formic acid). As a result, the adsorption behavior of UiO-66 in FA showed the highest performance with 99% purification of DMF (see Figure 20b). Obviously, the use of defect-engineered UiO-66 for the absorption of *n*-butanol in the final purification process was demonstrated to bring a high selective efficiency for the already concentrated/upgraded DMF stream, while the distillation method was shown to be inefficient in this range because of forming a azeotrope component although the differences in pure-component boiling points between DMF and *n*-butanol were remarkable. The nonideality of the DMF/*n*-butanol mixture was believed to make the difference in pure-component boiling points less relevant as usually in the case of polar mixtures.²⁴² Due to this reason, upgrading the diluted-reaction product before removing *n*-butanol is still a challenging task, requiring a stronger solution for DMF-selective adsorption. By exploiting the noticeable differences in the dipole moment and the logarithmic partition

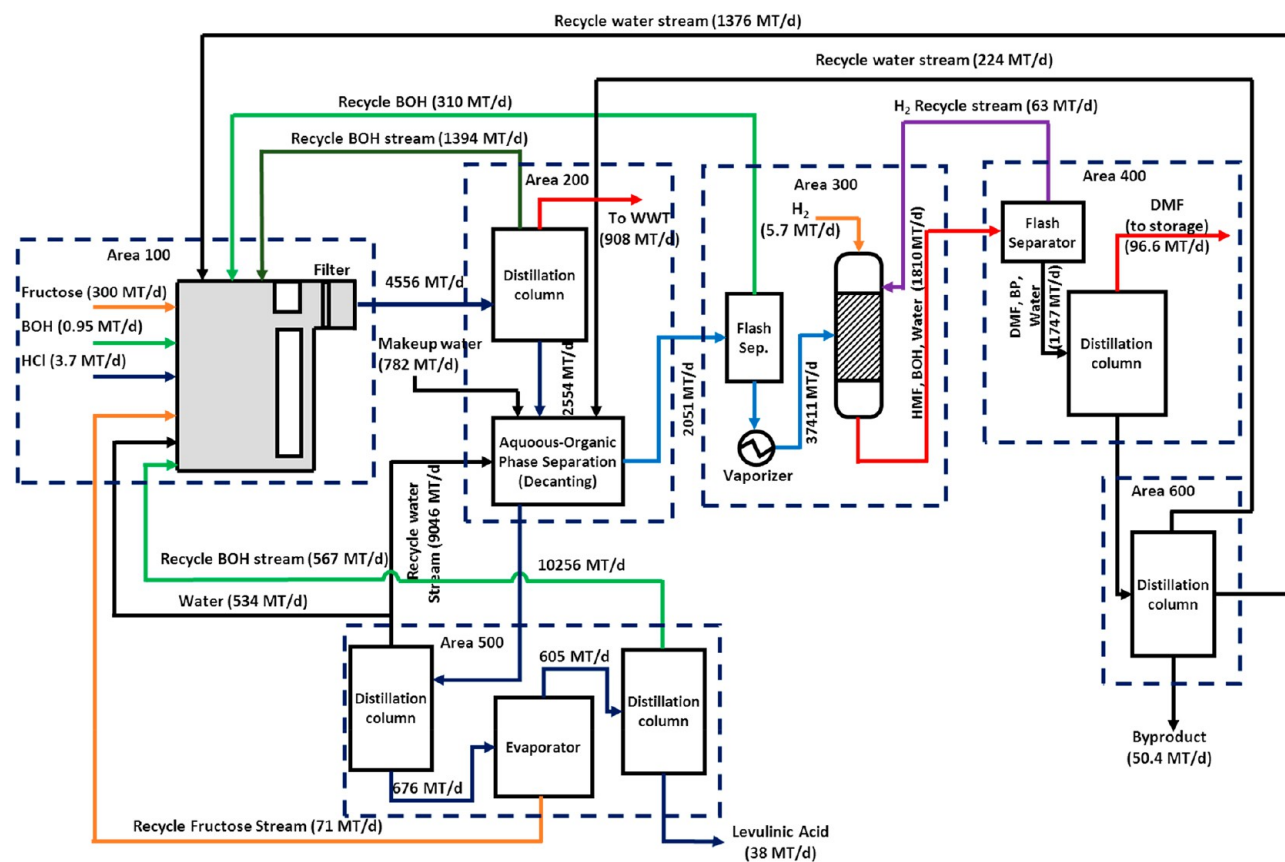


Figure 21. DMF production process with fructose as input material.²⁴⁵ Reprinted with permission from ref 245. Copyright 2011 Elsevier.

coefficient of octanol/water between DMF and *n*-butanol, Chiang et al.²⁴³ have developed a separation process of DMF based on hydrophobic MOFs with the adsorption mechanism of zeolitic imidazolate framework-8 (ZIF-8). The process of DMF separation and *n*-butanol recovery based on the absorption mechanism could be illustrated in Figure 20c,d. In addition, they found that fixed-bed adsorption processes should only apply to remove the minor components because of their restrictions relating to the selectivity limitation in multicomponent systems.²⁴³ Furthermore, the use efficiency of the solid bed and desorbent could be reduced by using cyclic operation, which was found to switch between the cycles of adsorption, desorption, or regeneration aiming to ensure the continuous running process. A simulated moving bed process (Figure 20c) was suggested for continuous operation.²⁴⁴ In their suggested process, high-purity DMF along with a recycling stream of *n*-butanol was analyzed. The results indicate that the purification process based on the simulated moving bed in combination with ZIF-8 has given a high DMF productivity >100 kg of DMF/m³ of adsorbent during an hour (Figure 20d). More interestingly, they have reported that this DMF purification process could be applied to realistic mass transfer as the mini-plant simulated moving bed was successfully built and trialed.

COMMERCIALIZATION AND ECONOMIC ASPECT

There is a lack of a full report on the process economy for DMF production, whether it is with a direct or indirect path. For the indirect production methods, DMF could be produced from HMF, while carbohydrates were used for the direct production methods. Most of the production processes were undertaken under pilot or laboratory scale; the information on industrial-

scale processes is rather limited presently. In the modeling of two-step dehydration of fructose to DMF by using (HCl + biphasic) solvent (Figure 21), some works from Dumesic et al.^{153,245,246} identified fructose feedstock as the largest economic hindrance to large-scale DMF production, which corresponded to 47% of the overall operation cost. Other costs include the expenses associated with the pretreatment of raw material, reactor and catalyst systems, the product purification process, and so forth. This, therefore, confirmed the impracticality of employing fructose for large-scale DMF production. Cheaper alternatives should be explored for a better chance of industrialization. In this sense, carbohydrate-based waste or cellulosic/lignocellulosic biomass could be the suitable material with their low sourcing costs.

Significantly, the two-step process depicted in Figure 21, with a DMF capacity of 96.9 MT/day, requires a capital cost of around 121.9 million US dollars for its setting up. The organic phase obtained from the first-half process is expected to consist of 58% HMF, which then is transferred to the aqueous–organic phase separator and flashed for solvent removal in the flash separator. Next, the purified HMF will be vaporized and flown into the plug-flow tubular reactor for DMF production over the Cu–Ru/C catalyst. Significantly, Ru-based catalyst is costly, with an estimated initial cost of 36.4 million US dollars and a biennial cost of 0.2585 million US dollars for the replacement of catalysts.²⁴⁵

Furthermore, it is also confirmed that the regeneration of Cu–Ru/C must be periodically performed, preferably once after every 10 reaction cycles, with H₂ being the regenerating agent. The costs incurred from such a regeneration step could not be overlooked in the long run. Meanwhile, the side production of

LA and unidentified products (38 and 50.4 MT/day, respectively) could also lead to considerable handling costs in the DMF production. With the high materials and production costs, the minimum support price (MSP) for DMF is expected to lie at 7.63 US dollars/gallon, which is much higher than that of corn-derived ethanol (2.3 US dollar/gallon) and cellulosic-based ethanol.²⁴⁷ According to the sensitivity analysis, with the proposed DMF production in Figure 21, the change in cost for fructose is roughly 20%, which may lead to a 9.3% fluctuation of MSP for DMF. On the other hand, a 20% increased DMF yield would lead to an MSP reduction of 16.7%, in spite of the slight increment in catalyst cost due to altered throughput. In this context, the adoption of selective catalysts, as reported in Table 3, including Ni-OMD₃ (yield = 98.7%),¹²⁷ Cu-Co@C (yield = 99.4%),¹⁷⁹ Ru-Co/SiO₂ (yield = 100%),¹⁵⁷ Pt₃Ni/C (yield = 98%),²³¹ or CuCo@/NGr/ α -Al₂O₃ (yield = 99%),²³⁹ is advantageous for cost reduction.

In general, all production process for DMF were shifted toward the exploration of low-cost feedstocks and high-yield catalyst systems. Due to this reason, the one-step DMF production process from carbohydrate-based sources, especially waste carbohydrates, with the presence of befitting catalysts should be investigated. The commercialization strategy for DMF in engine application can only be realized when the DMF price is comparably low to that of ethanol. Therefore, research directions in the future should concentrate on high-efficiency solutions to convert biomass or carbohydrate in waste to DMF over an optimized catalyst system. In addition, technologies for the storage and pretreatment of biomass should be endeavored too, to reduce the processing time while cutting the cost for DMF production. In addition to the economic aspects, the environmental sustainability in DMF production processes should also be taken into serious consideration. The deployment of various established sustainability assessment tools, including life cycle assessment,²⁴⁸ exergy, and economy-based criteria analysis,^{249,250} could be useful to achieve that.

CONCLUSIONS AND FUTURE DIRECTIONS

DMF could be viewed as the impending and novel second-generation biofuel with many benefits, making it a promising candidate for engine applications. This contribution was aimed to provide a broad and comprehensive overview for DMF production, from pretreatments of input material to catalyst reactions and types of systems. The latest progress in the HMF hydrogenolysis for DMF production was thoroughly analyzed and compared in the aspect of utilized catalysts, reaction pathways, and mechanisms. Summarizing from these prospects, some specific conclusions could be drawn as follows:

- DMF yields up to ~100% are possible with the appropriate processing of feedstock/biomass and optimized catalyst system, solvent, hydrogen donor, and reaction conditions.
- A two-step production path, with HMF/CMF as the intermediates, could deliver a high DMF yield. Compared to cellulosic and starchy biomass, the catalytic conversion of glucose or fructose for DMF production in ILs is preferred in the sense of higher DMF yield. However, algae, starch-rich wastes, and lignocellulosic/cellulosic biomass are cheaper and more sustainable for the commercial DMF production process.
- Bifunctional catalyst systems supported by hydrogenated metal generally give rise to a higher selectivity of DMF, as

compared to those monometallic catalysts. Most of the time, noble-metal-based bifunctional catalysts could promote the conversion of intermediate species as compared to the non-noble metallic systems. However, a facile catalyst preparatory framework should be developed to advocate the industrialization of DMF production.

- The optimization of reaction conditions for DMF production is imperative. While maximizing the DMF yield, the corresponding reaction conditions, such as temperature and pressure, must be within the practical range. Different hydrogenation reagents should be investigated too, to reduce the dependence on H₂ while enhancing the production systems in the aspects of reactivity and safety. Moreover, the exploration of suitable green solvent should be focused too, as the conventional solvent is corrosive due to its high acidity. Also, the utilization of existing reactors for DMF production appears to be laborious and time-consuming; therefore, the development of advanced reactors with robust reaction engineering analysis must be performed prior to the implementation process.
- The purification of DMF and the economic feature of DMF production should be comprehensively evaluated. Information in regard to these aforesaid aspects is rather limited. Therefore, future studies are suggested to close these knowledge gaps for a more facilitated DMF industrialization later.

In general, materials with carbohydrate-like molecular structures, such as starch, fructose, and glucose, have been studied for the production of DMF. Meanwhile, the advancement of catalytic technology has also permitted a prospective output from the conversion process. Even though the flourishing of biomass-transfer technology enables the synthesis of DMF as a modern generation biofuel, there are several unresolved problems that have not been addressed. In particular, the selection of a one-pot reactor or biphasic reactor for DMF production is an arguable issue, whereby its influences could even be extended to the DMF yield and its recovery from product streams, as well as the handling of byproducts from the reaction. Another unsolved issue is the selection of catalysts for the reaction. A high-yield catalyst is desired to improve the production rate of DMF, but its synthesis is normally difficult and costly. Another issue lies in the selection of input material, which depends upon various factors such as its availability, composition, and cost. For the production of DMF, a high carbohydrate content in the input material is preferable, as it would increase the yield from the reaction. In such a sense, biomass appears to be an ideal candidate for DMF production, with its high carbohydrate content (75%) and renewable feature.

Overall, the current work highlighted the green and sustainable production of DMF, which is regarded as a novel class of biofuel. Better than ever, the sleeping giant DMF should be awakened as soon as possible to harmonize the benefitting relationships of energy, environment, and carbohydrate-based economy. That idea is not beyond the pure intended to reduce the dependence on fossil fuels and to maintain sustainable development.

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Zuohua Huang is professor of Xi'an Jiaotong University, China. He received his Ph.D. in 1994. He is vice-director of the Combustion Section of the Chinese Society of Engineering Thermo-physics. He is Principal Editor of FUEL and Fellow of the Combustion Institute, Director of Board of the Combustion Institute. His research interests are combustion and energy science. He has published over 400 papers in international journals and is a highly cited scholar in engineering.



Rafael Luque is Profesor Titular de Universidad from Departamento de Quimica Organica, Universidad de Cordoba. He has been leading research from group FQM-383 (NanoVal) at Universidad de Cordoba since 2009. He has close to 600 publications (*h*-index 87; ca. 34,000 citations) and several patents (7) as well as numerous prizes and awards including the most recent 2018 ACS Sustainable Chemistry & Engineering Lectureship Award from the American Chemical Society and Tongjiang Distinguished Scholarship from Quanzhou Normal University (2021). Prof. Luque was also named 2018, 2019, 2020, and 2021 Highly Cited Researcher (Clarivate Analytics).



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H. Hadiyanto is Full Professor at the Chemical Engineering Department, Diponegoro University, Indonesia. He completed his Master and Ph.D. degrees in Bioprocess Engineering from Wageningen University in The Netherlands in 2003 and 2007, respectively. His main research focus is on biomass and bioenergy development including

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Van Viet Pham received his Ph.D degree in 2019. He is interested in the research areas of energy conservation, renewable energy resources, alternative fuels, internal combustion engines, and engineering transport. He has published more than 40 articles in international journals with an *h*-index of 15. He has been a main member in Progress of Applied Technology and Engineering in Transport Research Group (PATET) at Ho Chi Minh City University of Transport since 2019.

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