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Chapter 3

Catalytic Conversions of Biomass-Derived Furaldehydes Toward Biofuels

Shun Nishimura and Kohki Ebitani

Additional information is available at the end of the chapter

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Abstract

Upgrading of biomass resources toward high-energy compounds (biofuel) is a crucial technology for sustainable development because utilizations of biomass resources can contribute to the low CO_2 emission on the basis of carbon neutral concept. In this chapter, recent advances on catalytic hydrogenation and hydrogenolysis of biomass-derived furaldehydes, dehydration products of saccharides, for example, called as hydroxymethylfuran (HMF) and furfural, toward biofuels over heterogeneous catalytic system are introduced. Some approaches on mechanistic study and reactor design are also mentioned in this chapter.

Keywords: biomass, furaldehydes, biofuel, hydrogenation, hydrogenolysis

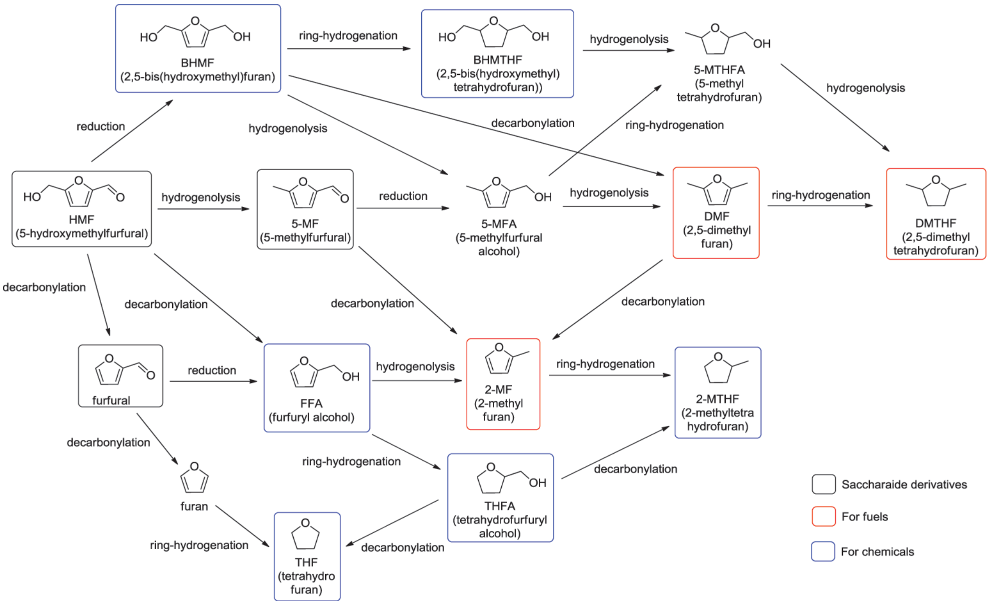
1. Introduction

In the past decades, owing to the rise of a living standard through social infrastructure development in the world, the energy demand growth has been stronger with increase of global gross domestic product (GDP), and it would rise further 30% till 2040 [1, 2]. While concerns on global warming derived from CO_2 emission have been debated in Intergovernmental Panel on Climate Change (IPCC) and Conference of the Parties (COP), they established global guidelines to participate in a sustainable development toward "zero emission." New energy sources and technologies have been current; however, it is still a great challenge to fabricate a low carbon society where high quality of life is constructed with low CO_2 emission. The rate of renewable energy including solar, geothermal, waste, wind, biofuels, wood, and hydroelectric power was only below 10% in the total primary energy consumption diagram still now [1].

A facile transformation of biomass-based resources is one of the crucial technologies to reduce the emission of CO_2 according to the carbon neutral concept; that is, the amount of CO_2 emission owing to biomass consumption (burning) is equal to the amount of CO_2 storage during its growth (photosynthesis). Thus, the balance of CO_2 concentration in the atmosphere on the basis of biomass utilization process is scarcely influenced. A lot of efforts have put into the investigations of new biomass transformation processes and derived technologies (e.g., see [3–8]). In this chapter, recent advanced catalytic transformations of biomass-based furaldehydes (furfurals) toward biofuels *via* hydrogenation/hydrogenolysis are introduced.

2. Transfer hydrogenation of furaldehydes to biofuels

A schematic reaction pathway for transfer hydrogenation/hydrogenolysis of biomass-based furaldehydes toward biofuels and chemicals is summarized in **Scheme 1**. Investigations on the synthesis of tetrahydrofuran (THF), tetrahydrofurfuryl alcohol (THFA) [9, 10], and 2-methyltetrahydrofuran (2-MTHF) [11] are attractive to serve biomass-based green solvent and precursor for aliphatic alcohols such as 1-butanol, 1,5-poentandiol, and 2-pentanol, respectively [12]. Moreover, furaldehyde-based diols of 2,5-bis(hydroxymethyl)furan (BHMF) [13–15] and 2,5-bis(hydroxymethyl)tetrahydrofuran (BHMTHF) [16–18] are the candidate for biomass-derived monomer source. Note, BHMF is also called as 2,5-dihydroxymethylfuran (DHMF) as a popular style. Accordingly, the strategy to rule such competitive reactions among reduction,



Scheme 1. Schematic reaction pathway for transfer hydrogenation/hydrogenolysis of biomass-based furaldehydes toward biofuels and chemicals.

ring-hydrogenation, hydrogenolysis, and decarbonylation is the key factor in the biorefinery on the transfer hydrogenation of furaldehydes.

The products of 2-methylfuran (2-MF), 2,5-dimethylfuran (DMF), and 2,5-dimethyltetrahydrofuran (DMTHF) have been counted on as biomass-based fuels (biofuels) as well as conventional biomass-derived transportation fuels such as bioethanol and biodiesel. These furan-based biofuels possess high-energy density [lower heating value (LHV): 28–32 MJ L^{-1}], low volatility [higher bp. (336–367 K) compared to ethanol], and good combustibility [research octane number (RON): 82–131]. Additionally, these are immiscible with water and stable compound in stage and thus would be an easier blender in gasoline than bioethanol. The DMF applications as automotive fuel have been challenged on a single-cylinder or multicylinder gasoline engines [19–21].

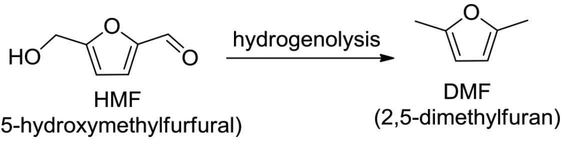
2.1. Synthesis of DMF by HMF hydrogenolysis

Synthesis of DMF from HMF is one of major researches for biofuel productions. First of all, studies on the synthesis of DMF from HMF hydrogenolysis (**Scheme 2**) have been introduced in the following five contents.

2.1.1. At pressurized hydrogen condition

Chidambaran and Bell provided 15% yield of DMF from hydroxymethylfuran (HMF) over Pd/C catalyst in ionic liquid/acetonitrile mixed solution under pressured H_2 (6.2 MPa) [22]. Recently, Saha and co-workers achieved 85% yield for DMF from HMF *via* BHMF intermediate with combined use of Pd/C and Lewis acid $ZnCl_2$ at lower pressurized H_2 (0.8 MPa) [23]. The improvement induced by $ZnCl_2$ agent was due to the facilitation on the rate-determinating step of BHMF to DMF *via* cleavage of C─O bonds. The synergism with Zn^{2+} was varied by the metal center: Pd/C/$ZnCl_2$ was faster than Ru/C/$ZnCl_2$, and Ni/C shows poor synergism. Interestingly, BHMF was identified as an intermediate product during the reaction, and it was 52% yield at maximum with the Ru/C/$ZnCl_2$ system.

Ru-supported catalyst is examined by several groups in HMF hydrogenation at pressurized H_2 in recent days. Zu *et al.* investigated Ru/Co_3O_4 catalyst and conducted 93% yield for DMF at 403 K and 0.7 MPa H_2 [24]. In this system, Ru is responsible for hydrogenation, while CoO_x works for the adsorption of hydrogenation product and then breaks the C─O bond. Nagpure *et al.* suggested Ru-NaY zeolite composed with Ru particles (Av. 2.8 nm) on the external surface served 78% yield of DMF under H_2 (1.5 MPa) at 493 K in a short duration of the reaction (1 h) [25]. According to the TOF value in DMF production at the



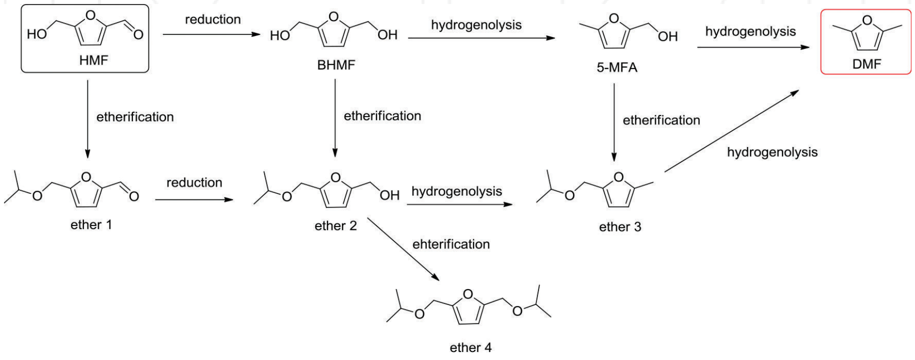
Scheme 2. Synthesis of DMF from HMF hydrogenolysis.

same condition, the reactivity of metal was expected as following order Ni (5.2 h^{-1}) < Cu (6.4 h^{-1}) < Au (16.4 h^{-1}) < Pt (60.8 h^{-1}) < Rh (80.2 h^{-1}) < Pd (98.6 h^{-1}) < Ru (156.0 h^{-1}), though the detailed information of size or surface area of other metals was not shown. The Lewis acidity of NaY zeolite was expected to increase deoxygenation ability and helped to improve the DMF yield in the reaction. On the other hand, Hu *et al.* gave 95% for DMF production over Ru/C catalyst at 473 K and 2 MPa H_2 [26]. The acid sites on carbon support supposedly promoted the hydrogenation of HMF to DMF. In addition, the authors also examined a combined use of ionic liquid (1-butyl-3-methylimidazolium chloride) and cellulose-derived sulfonated carbonaceous catalyst for HMF production from biomass-derived carbohydrates and successive hydrogenation of the extracted HMF to DMF over Ru/C catalyst, and then, more than 82% DMF yield was successfully obtained. It was generally known in the case of Ru catalyst that the reactivation by heating under H_2 flow is required to remove the depositions of high-molecular-weight by-products blocking the active Ru sites [26, 27].

In the case of Ni catalyst, the acidity of support is also expected to be the key function for deoxygenation step. Huang *et al.* explained the Ni particles mainly played a role in the hydrogenation step but had limited deoxygenation, whereas W_2C particles mainly promoted the deoxygenation step of hydroxymethyl group but had limited hydrogenation ability. They have served 96% yield of DMF by using the synergy between Ni and W_2C particles at 4 MPa H_2 [28]. It should be noted that the observed major intermediate was not BHMF but 5-MF in this study.

2.1.2. *With hydrogen donor agent*

Because the concentration of other undesirable byproducts *via* ring-open and ring hydrogenation such as BHMTHF, 5-methyltetrahydrofuran (5-MTHFA), DMTHF, and hexanediol increased at higher H_2 pressure [24, 29, 30], several approaches instead of the utilization of pressurized H_2 agent had been examined to build up further possible way in the catalytic system. Jae *et al.* applied 2-propanol as a hydride donor for Ru/C-catalyzed HMF hydrogenation and gave 81% yield for DMF at 463 K under pressurized N_2 (2.04 MPa) [27]. Two ethers *via* etherification of 2-propanol and BHMF or 5-MFA (denoted as ethers 2 and 3 in **Scheme 3**) were detected in the reaction, and the expected reaction network in the presence of 2-propanol



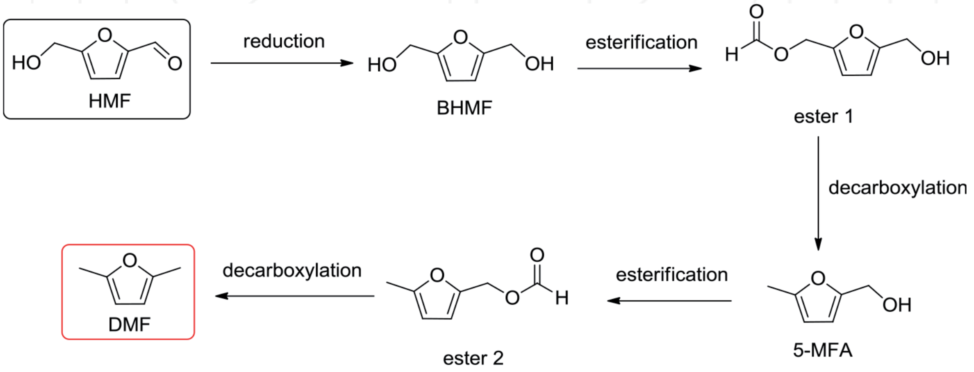
Scheme 3. Reaction network of the hydrogenation of HMF into DMF in the presence of 2-propanol.

is described in **Scheme 3**. Nagpure *et al.* demonstrated Ru-Mg(Al)O catalyst with 58% yield of DMF at 493 K for 4 h at 1 MPa H_2 assisted by hydrogen transfer from 2-propanol solvent [30]. Continuous-flow transfer hydrogenation/hydrogenolysis of HMF in 2-propanol yielded 72% DMF with Pd/Fe_2O_3 catalyst at 2.5 MPa pressure and 453 K through BHMF production at an initial stage (70% sel. at 50% conv.) [31]. Utilization of hydrogen donor agent would be a versatile strategy for the reaction.

One of the dramatic effects was found when the formic acid (HCOOH) agent was applied for the reaction. Rauchfuss *et al.* had surprisingly announced that decarbonylation of HMF to DMF (>95% yield) *via* BHMF formation route was proceeded by Pd/C catalyst and formic acid (10 equiv.) in refluxing THF/H_2SO_4 (0.13 equiv.) or dioxane (at 393 K) through diformate ester form (**Scheme 4**). The formic acid agent plays the multiroles, inhibits the decarbonylation and ring-hydrogenation, and serves mild hydrogen source and a precursor to formate ester [32, 33]. De *et al.* described Ru/C-catalyzed DMF formation from fructose with similar catalytic system, and 30% yield was obtained [34]. They also announced the positive effect of irradiation treatment (at 300 W) during reaction to significantly decrease the time for reaction.

2.1.3. Under supercritical conditions

As a different approach, Chatterjee *et al.* investigated the Pd/C catalyst under supercritical carbon dioxide ($scCO_2$) condition with various operation conditions [29]. Interestingly, they found that the $scCO_2$ pressure strongly contributed the selectivity for the HMF hydrogenation at 353 K and 1 MPa H_2 for 2 h (**Figure 1**). The selectivity for DMF was increased from 42 to 100% along with $scCO_2$ pressure increased from 4 to 10 MPa. 5-MTHFA was formed with a comparatively higher selectivity of 58% at 4 MPa and then decreased with pressure. At higher pressure (>14 MPa), DMTHF became the dominant product with about 70% selectivity. Controlled experiments with different CO_2/H_2O molar ratio indicated that (*i*) in the absence of H_2O or CO_2, the reaction proceeds through the path of HMF → 5-MFA → 5-MTHFA, and (*ii*) combined effect of CO_2 and H_2O forced the reaction to move in the direct of HMF → DMF. Weak acidic condition derived from CO_2 dissolved in water would be one of the crucial factors



Scheme 4. Reaction network of the hydrogenation of HMF into DMF in the presence of formic acid.

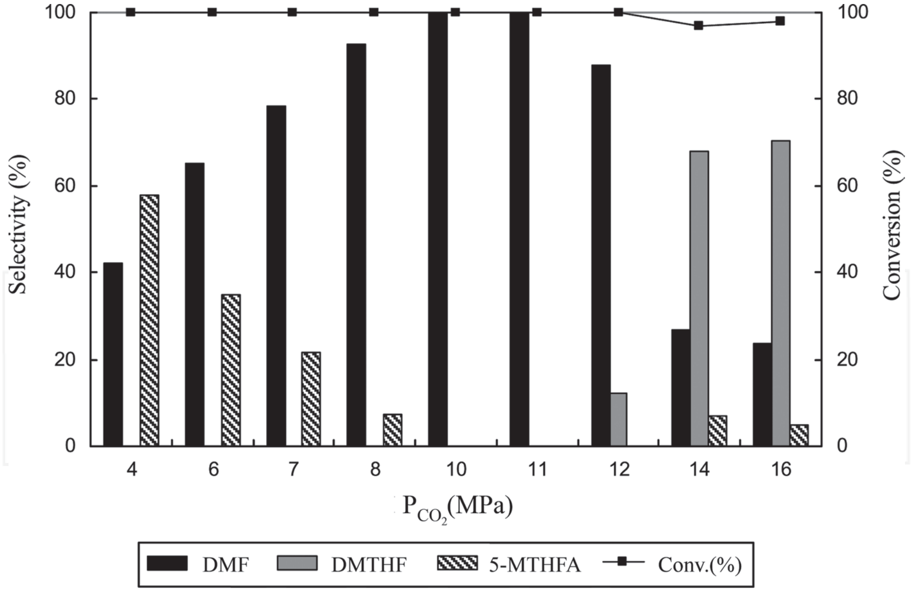


Figure 1. Effect of CO_2 pressure on the conversion and product profile. Reaction conditions: catalyst: substrate = 1:5, 353 K, 2 h, 1 MPa (H_2), water (1 mL). Reproduced with permission from The Royal Society of Chemical (RSC) of Ref. [29].

behind the hydrogenation of HMF to DMF. This catalytic system could be applied for furfural hydrogenation and 100% yield of 5-MF or 2-MTHF was achieved under optimized condition.

Hansen *et al.* demonstrated Cu-doped porous Mg-Al-O_x (Cu-PMO) catalyst with supercritical methanol in a stainless steel bomb reactor [35]. According to their concept, the rapid deoxygenation of HMF in the presence of Cu-PMO drastically diminished undesired side reactions such as polymerizations and condensations. Total yield of three main products of DMF, DMTHF, and 2-hexanol was reached to be 61%. The maximum yield for DMF was 48% at 533 K for 3 h reaction.

2.1.4. Under ambient operation conditions

In order to decrease the operation risks owing to the utilization of pressurized and/or high-temperature conditions, application of ambient condition for the target reaction is an ideal system. Moreover, as an additional issue, the undesired formation of insoluble humin is often observed and decreased the yield in furaldehyde utilizations at elevated reaction temperature [36]. One of impressive approaches under ambient operation conditions was reported by Bekkum *et al.* They have studied HMF hydrogenolysis under atmospheric H_2 at 333 K with Pd/C catalyst and gave 35.7% yield of DMF in 1-propanol solvent through propyl ether intermediates formation; the 2-methyl-5-(propoxymethyl)furan was detected in the initial stage with high yield (>80%) [37], while in 1,4-dioxane, mainly BHMF is formed with 80% yield at the same reaction condition.

Bimetallic catalysts for upgrading of biomass resources into high-value fuels and chemicals were the one of research interests in biomass conversion in the last decade [38–40]. Such movements motivated researchers to investigate bimetallic catalytic system for HMF hydrogenation with an atmospheric pressurized H_2.

Ebitani *et al.* prepared the PdAu bimetallic nanoparticles supported carbon (Pd_xAu_y/C) catalysts with different Pd/Au molar ratio (*x*/*y*) and applied to the HMF hydrogenation in an atmospheric H_2 in the presence of HCl agent [41]. In the monometallic catalysts, Pd_{100}/C and Au_{100}/C gave 60 and 0% yield for DMF yield, respectively. While, in the bimetallic PdAu series, increasing the Au contents in Pd_xAu_y leads to increase the DMF yield till Pd/Au = 50/50 (presumption) and then slightly decrease; that is, positive effect on the coexistence of Au in Pd active center in the reaction was observed. With consideration of XRD experiments, they proposed that the highest yield for DMF, 96% at ambient H_2 condition with HCl agent at 333 K, would be served over the $Pd_{73}Au_{27}$ sites formed on as-prepared $Pd_{50}Au_{50}/C$ catalyst. It is expected that electronic and/or geometric changes in Pd, that is, the internal electronic transfer from Pd to another atom in agreement with the Pauling electronegativity scale and/or the modification of Pd-Pd atomic distance due to the insertion of another atom would play a crucial role for Pd-alloy mediated reactions [42, 43]; however, the detailed mechanism is a subject for a further study in HMF hydrogenation over PdAu/C catalyst.

2.1.5. Over bimetallic active sites

Approaches with bimetallic catalyst have been also investigated by other researches. Dumesic and coworkers studied the bimetallic Ru catalytic system for the reaction. The 46% yield of DMF from HMF was produced over RuSn/C catalyst at 473 K in the presence of lactone using a Parr reactor [44]. They also reported a systematic production of DMF using bimetallic RuCu/C catalyst in 1-butanol phase to afford 71% yield for 10 h at 393 K and 0.68 MPa H_2. This vapor-phase hydrogenolysis is capable for a two-step reaction from fructose connected with biphasic reactor for *in-situ* formed HMF feeder [45].

Interestingly, Yu *et al.* found the combination of low-selective Ni species in high conversion and inactive Fe species for HMF hydrogenation by alloying contributed to the significant catalytic performance at 3.0 MPa H_2 in *n*-butanol [46]. The selectivity to DMF showed a volcano-type behavior with increasing Fe loading, and the Ni_2Fe_1/CNT catalyst gave the highest 91% yield for DMF at 473 K for 3 h. The author also reported 96% yield toward BHMF production at lower temperature (393 K); that is, the reaction temperature markedly affected the product distribution. It was expected that the longer C─O bond on Ni-Fe than that on Ni might facilitate the conversion of HMF to DMF as the main route. Wang *et al.* also induced the favorable adsorption of the C═O or C─O bond over that of the C═C by applying PtCo bimetallic sites. They achieved 98% yield of DMF formation from HMF at 453 K and 1 MPa H_2 over PtCo encapsulated in hollow carbon sphere (PtCo@HCS) catalyst in 1-butanol [47]. The author also indicated that the lower reaction temperature at 393 K served 70% yield of BHMF with PtCo@HCS catalyst.

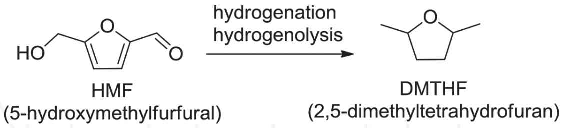
A robust and highly active CuZn nanopowder (60 mesh) catalyst for the conversion of HMF to DMF was examined by Barta and coworkers [48]. They achieved 90% yield for DMF in concentrated HMF (10 wt%) of cyclopentyl methyl ether (CPME) solution at 493 K under pressurized H_2 (20 bar). Catalytic conversion of HMF toward BHMF was also tested with same system, and >95% yield and selectivity were obtained with the CuZn nanopowder catalyst at 393 K and H_2 (70 bar) in ethanol solvent.

Recently, Yang and coworkers provided 90% yield of DMF from HMF at 483 K with formic acid in a stainless steel autoclave under self-generated pressure [49]. In this report, a reaction route involving 5-MF instead of BHMF as an intermediate has been ascertained over NiCo/C catalyst. The reaction system proceeded over alloys with non-noble metals would be a futural target for next generation.

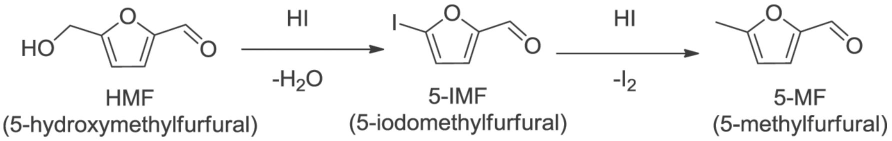
2.2. Synthesis of DMTHF from HMF hydrogenation

Owing to the ring-hydrogenation step, direct synthesis of DMTHF from HMF (**Scheme 5**) would require different strategies. Yang and Sen applied the water-soluble $RhCl_3$ species with HI acid agent in the transformation of fructose to DMTHF in chlorobenzene/water biphasic reaction system under H_2 (2.07 MPa) [50]. This powerful catalytic system served the end product of DMTHF or 2-MTHF from various saccharides such as fructose, glucose, sucrose, inulin, cellulose, and corn stover with significant activity (*ca.* 50–80% yield) at 433 K. Further mechanistic study on HMF conversion [51] revealed that the HI agent behaved as both acid catalyst for the initial dehydration of saccharides to the corresponding furans and as reducing agent in hydrogenolysis step of carbinol group in HMF *via* the formation of 5-iodomethylfurfural intermediate (**Scheme 6**). While the Rh species catalyze not only the C═O hydrogenolysis and C═C hydrogenation but also re-hydrogenation of produced iodine to HI with hydrogen. Overall, such efficient catalytic system, that is, the dehydration/reduction ability of HI combined with the hydrogenation/hydrogenolysis ability of the Rh catalyst, effectively facilitated the conversion of fructose to DMTHF.

Mitra *et al.* carefully surveyed the effects of HMF concentration, Pd loading and kinds of acidic additive in Pd/C-catalyzed hydrogenation/ hydrogenolysis of HMF at 0.21 MPa H_2 in



Scheme 5. Synthesis of DMTHF from HMF hydrogenation/hydrogenolysis.



Scheme 6. HI-assisted hydrogenolysis of carbinol group *via* formation of iodo intermediate.

dioxane. Under the optimized condition, DMTHF (>95% yield) and DMF (85% yield) was produced in the presence of acetic acid and dimethyldicarbonate, respectively. It is likely that the tendency for ring-hydrogenation against hydrogenation/hydrogenolysis was decreased in higher HMF concentration and amount of catalyst loading [32].

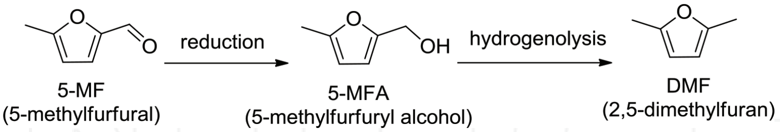
It would be noted that though at higher pressurized H_2 condition (70 bar), Pd/Al_2O_3 (>99% yield), Pd/C (89% yield), and Ru/C (88% yield) are also found to be a good catalyst for DMTHF production from HMF in ethanol solvent at 393 K, as reported by Bottari *et al.* [48].

2.3. Synthesis of DMF from 5-MF or 5-MFA hydrogenation

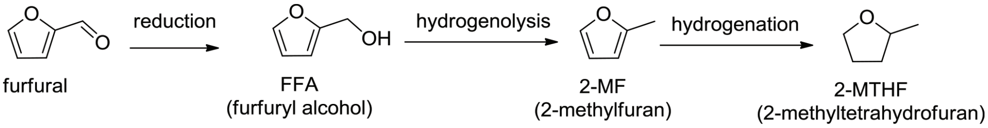
5-MF based transformations to DMF (**Scheme 7**) has received little attention. The condensed-phase C─O hydrogenolysis of 5-MFA to DMF at 493 K was carried out by the copper chromite ($CuCr_2O_4{\cdot}CuO$) catalyst pre-reduced with H_2 at various temperature (513–633 K) [52]. The authors selected the simplified system in order to examine the relationship of the Cu oxidation state and C─O hydrogenolysis activity which was the one of intermediate steps during hydrogenation/hydrogenolysis of biomass-derived HMF or 5-MF toward DMF. The surface concentration of Cu^0 and Cu^+ was varied by a reduction temperature, and reduction at 573 K caused the highest activity, an initial rate for the production of DMF and DMTHF divided by BET surface area of catalyst was 108 mmol m^{-2} min^{-1} and the highest concentration of Cu^0 and Cu^+ sites. It concluded that the Cu^0 was primarily responsible for the activity; however, unfortunately, the detailed role of Cu^+ could not be ruled out at that time.

2.4. Synthesis of 2-MF and 2-MTHF from furfural or FFA hydrogenation

Furfural derived reaction path for 2-MF and 2-MTHF production (**Scheme 8**) has attracted many scientists. The gas-phase selective cleaving the C═O bond outside the furan ring of furfural was performed on Mo_2C [53]. It was considered that the strong interaction between



Scheme 7. Synthesis of DMF from 5-MF or 5-MFA hydrogenation.



Scheme 8. Synthesis of 2-MF and 2-MTHF from furfural or FFA hydrogenation.

C─O bond of furfural in the aldehyde group and Mo_2C surface-assisted selective deoxygenation affording to 60% selectivity for 2-MF production, although the conversion of furfural seems to be low. Zhu *et al.* investigated a fixed-bed reactor test of furfural hydrogenation over a commercial catalyst (Cu/Zn/Al/Ca/Na = 59/33/61/1/1, atomic ratio) [54]. The 87% yield from furfural and 93% yield from FFA were obtained toward 2-MF formation at 523 K. In the same group, recently, further advanced examination on a continuous two-step fixed-bed reactor system over catalysts utilizing a combination of acidic Hβ-zeolite for the former dehydrogenation step of xylose to furfural and $Cu/ZnO/Al_2O_3$ for the latter hydrogenation steps of produced furfural in a mixture of γ-butyrolactone/water as solvent was attempted to the direct conversion of xylose to 2-MF *via* FFA formation [55]. It was observed that the main product can be simply tuned by the hydrogenation temperature, and the 87% yields of FFA and 2-MF was formed at 423 and 463 K under 0.1 MPa H_2, respectively. The 2-MF was frequently detected at higher reaction temperature in the FFA synthesis from hydrogenation of furfural with moderate yield (35%) [56].

In the FFA hydrogenation reaction, Pd/Fe_2O_3 catalyst yielded 31% for 2-MF under batch conditions at a transfer hydrogenation of FFA in 2-propanol, though the conversion of furfural to 2-MF was scarcely occurred (13% yield) at 453 K [31]. The former value reached to be 76% in a continuous-flow reactor, while the Pd/TiO_2 catalyst showed 71 and 88% yield for 2-MF for constant and continuously controlled pressured H_2 (0.3 MPa) condition in an autoclave reactor at room temperature (298 K) [57].

In order to avoid the use of high H_2 pressure, Zhu *et al.* designed a two-stage packing fixed-bed reactor system with $Cu_2Si_2O_5(OH)_2$ (copper phyllosilicate) in the upper reactor conjugated with Pd/SiO_2 catalyst in the bottom reactor [11]. The $Cu_2Si_2O_5(OH)_2$ itself possessed an outstanding hydrogenation ability and gave 84.6% yield for hydrogenation-deoxygenation of furfural toward 2 MF, while Pd/SiO_2 catalyst gave a significant hydrogenation performance for the C═C bonds in furan ring, serving 87.7% yield of ring-hydrogenation of 2 MF toward 2 MTHF at 443 K. Accordingly, such a dual solid catalyst system achieved up to 97.1% yield on the direct production for 2-MTHF with 100% conversion of furfural under atmospheric pressure (**Figure 2**). Thereafter, bimetallic CuPd-supported ZrO_2 catalyzed hydrogenation by using a batch reactor in the presence of 2-propanol as hydrogen donor was highlighted by other research group [58]. The molecular ratio of Cu/Pd gave significant influences on the yields for 2-MF and 2-MTHF; for example, the highest yield for 2-MF (63.6%) and 2-MTHF (78.8%) was obtained over $Cu_{10}Pd_1/ZrO_2$ and $Cu_{10}Pd_5/ZrO_2$ catalyst, respectively, with 2-propanol (14 mL) at 493 K in 1-mmol scale operation. It was denoted that the reaction mainly proceed through furfural → FFA → 2-MF → 2-MTHF sequence.

To clarify the crucial factor to prevent C─C bonds breaking while effectively breaking the C─O bonds in formyl group in furfural to form 2-MF, suppressing the furan formation, Resasco *et al.* studied the addition of 5-wt% Fe into 2-wt% Ni/SiO_2 catalyst with coimpregnation method formed Ni-Fe bimetallic alloys and yielded 39% of MF from furfural and *ca.* 78% from FFA on $NiFe/SiO_2$ catalyst at 523 K in vapor-phase conversion of furfural [59]. Controlled

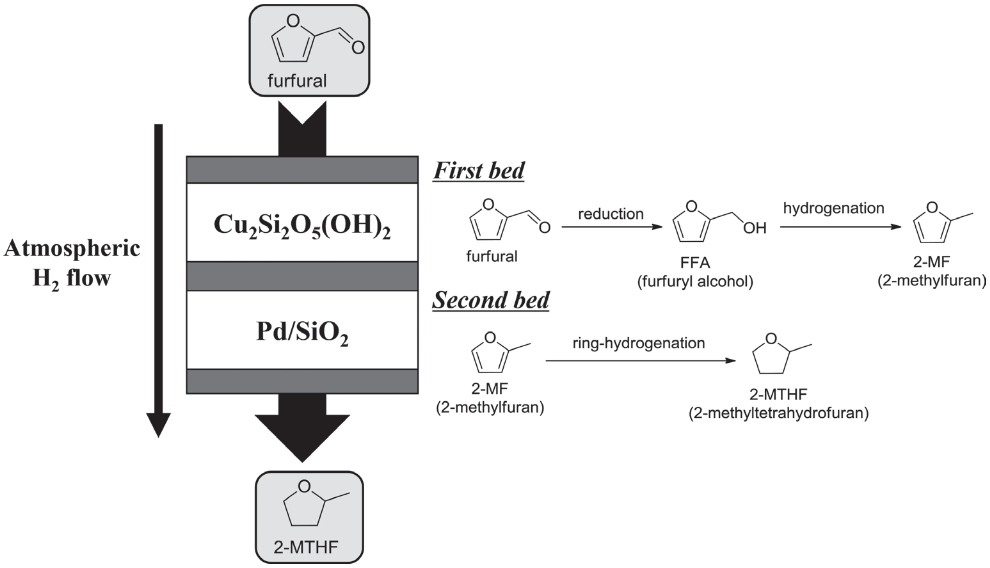


Figure 2. Systematic design for one-step conversion of furfural toward 2-MTHF with a dual solid catalyst in a fixed-bed reactor.

experiments with monitoring the yields of products in the conversion of furfural, FFA, and THFA suggested that enhancement of both hydrogenolysis and reduction in decarbonylation activity increased following to increase the Fe content in bimetallic catalyst. Notably, the authors further investigated the reaction with benzyl alcohol, which strongly supported that coexistence of Fe in Ni-Fe/SiO_2 catalyst significantly promoted the hydrogenolysis path to toluene rather than the decarbonylation path to benzene (**Figure 3**). The DFT calculation approaches determined that configuration of the adsorbed furfural on NiFe was much differed from Ni, and the significant lengthening of the C─O bond in formyl group caused on bimetallic NiFe surface would be a crucial factor to facilitate the reaction for C─O hydrogenolysis rate observed experimentally.

The same group also has claimed the importance of the differences in the molecular-surface interactions between the aldehydes and active surfaces affording to furan or FFA during furfural hydrogenation over PdCu/SiO_2 catalyst in a flow reactor [60]. In the case of PdCu/SiO_2, the formation of FFA *via* reduction gradually became dominant in the hydrogenation reaction of furfural in comparison with the formation of furan *via* decarbonylation as function of Cu loadings onto Pd/SiO_2 prepared with co-impregnation method; that is, the decarbonylation rate is greatly reduced on PdCu catalyst, but the hydrogenation (reduction) rate is increased. The changes in electron structure of PdCu alloy different from that of pure Pd resulted in a lower extent of electron back-donation to the π^* system of the aldehydes and a less stability toward the η^1(C)-acyl intermediate formation affording to furan, and these increased

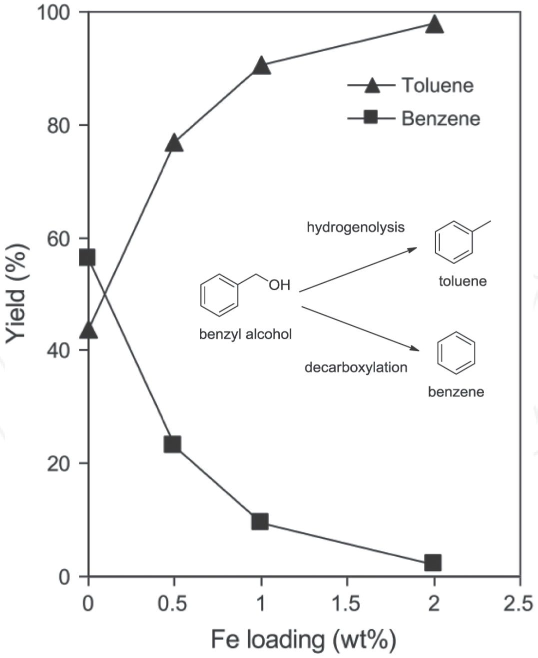


Figure 3. Yield of products from the reaction of benzyl alcohol over Ni-Fe bimetallic catalysts as a function of Fe loading. Reaction conditions: W/F = 0.1 h, H_2/Feed ratio = 25, 523 K, 1 atm. Reproduced with permission from Elsevier of Ref. [59].

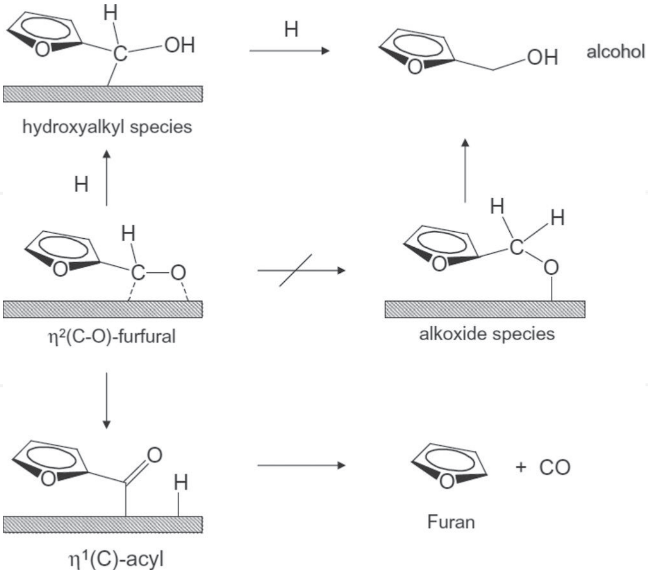


Figure 4. An expected mechanism for furfural conversion over Pd catalyst. Reproduced with permission from Elsevier of Ref. [60].

the frequency for FFA production drastically through the hydroxyalkyl intermediate path (**Figure 4**).

Mechanistic studies for understanding and controlling the reactivity for hydrogenation reactions on metal catalysts have been an attractive subject. Advanced review articles for this area would be helpful for further study (e.g., see [61, 62]).

3. Conclusions

Due to the high oxygen content in biomass resources, investigations on deoxygenation *via* hydrogenation/hydrogenolysis reaction open up a lot of insights for catalytic and systematic design on biomass upgrading toward biofuel and blender. As introduced in this chapter, bimetallic catalyst and/or utilization of transfer hydrogen donor have been a growing interest instead of conventional system using pressurized H_2 and monometalic catalyst. Mechanistic studies with systematic experiments have been a powerful tool to reveal the reaction path and optimize the reaction conditions to provide target compound selectively. As the next research generation, alloying of terminal precious sites with addition of transition metals would have been getting more attentions in hydrogenation/hydrogenolysis of furaldehydes. It needs to be underlined that pyrolysis of biomass resources toward gas, char, and/or biooil is an energetic movement [63–65]. These transformation technologies of biomass would be a key component to fabricate sustainable social design with low carbon emission.

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