

Recent advances in the production of 2,5-furandicarboxylic acid from biorenewable resources

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ARTICLE INFO

Article history:

Received 20 February 2023

Revised 17 April 2023

Accepted 17 April 2023

Available online 22 April 2023

Keywords:

HMF

FDCA

Bio-based chemicals

Biorenewable resources

Chemical routes

ABSTRACT

Bio-based renewable resources have emerged as strong contenders to produce fuels and chemicals via carbon-neutral and eco-friendly methods. In particular, 2,5 furandicarboxylic acid (FDCA) which is listed among the top 12 platform molecules, can be used to produce bio-based polymer as an alternative to polyethylene terephthalate (PET). Notably, FDCA can be produced from an array of biorenewable resources using catalytic materials. However, biomass-derived 5-hydroxymethylfurfural (HMF) remains the primary feedstock to produce FDCA. Thus, the current review focuses on the recent advances in FDCA application and production via catalytic routes, particularly from HMF and other biorenewable feedstocks. Accordingly, the effect of different noble metal and noble metal-free catalytic materials on feedstock conversion and FDCA yield has been discussed. Moreover, the effect of operating conditions such as solvent, bases, oxygen sources, temperature and pressure has been discussed.

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1. Introduction

Disproportionate fossil fuel exploitation has caused severe environmental damage and adverse effects [1–3]. As a result, the quest to find fossil fuel alternatives has gained momentum since the beginning of this century. In this regard, biorenewable resources such as agricultural residue, forest residue, kitchen waste, waste biomass, and derived chemicals have been suggested as alternative feedstocks to produce fuels and chemicals [4–9]. Notably, the US Department of Energy (DOE) has identified the top 12 value-added chemicals that can be considered as a replacement for several fossil fuel-derived chemicals and fuels [10–13]. One such molecule is 2,5 furan dicarboxylic acid (FDCA), which is listed among the top 12 chemicals and can be used to produce biopolymers [14–17]. FDCA is a biobased organic molecule consisting of two carboxylic acid groups bonded to a central furan ring. It has a higher melting point of 342 °C, which makes it thermally stable and suitable for polymeric applications. Indeed, FDCA can replace petroleum-based terephthalic acid for the production of biobased plastic polyethylene furandicarboxylate (PEF) due to the similarity in its functional group with terephthalic acid [18,19].

The PEF has better mechanical strength, higher thermal stability, and high gas barrier than petroleum-based PET. For example,

PEF thermal stability is around 260 °C, higher than PET thermal stability temperature of 220 °C [21]. Similarly, oxygen diffusivity, CO₂, and water permeability are 11, 31, and 5 times lesser in FDCA-derived PEF than PET [22]. One possible reason for such a high gas barrier can be attributed to the presence of a furan ring in the FDCA, which provides rigidity to PEF. The rigidity of the polymer may be due to the non-linear axis of rotation of the furan ring associated with heterocycles dipolarity, which restricts the flipping of the furan ring and makes the PEF-based polymer more rigid than PET-based polymer [22]. More importantly, biobased plastic PEF produced using FDCA is biodegradable; thus, it can be used commercially [15,18,23,24]. Indeed, several companies such as Coca-Cola, Avantium, Danone, and ALPLA have plans to produce FDCA-derived PEF plastic bottles on a commercial scale [14,23,25–27]. Moreover, FDCA and derived molecules have applications in packaging, clothing, disposable items, polyamide, polyurethanes, thermosetting, resins, polyesters, plasticizers, fungicides, macrocyclic ligands, dipentyl furan-2,5-carboxylate, thiolene films and several daily life applications [28]. Furthermore, FDCA can be used as a feedstock to produce a wide range of chemicals and intermediates such as succinic acid, adipic acid, furan, 2,5-bis(hydroxymethyl)furan, FDCA ester, 2,5-bis(aminomethyl) tetrahydrofuran, as shown in Fig. 1 [20,29]. As a result, FDCA had a market value of USD 441.5 million in 2020, which is expected to almost double (USD 857.3 million) by 2028 [30]. Moreover, FDCA can be produced via different routes, such as chemo-catalytic, electrochemical, and

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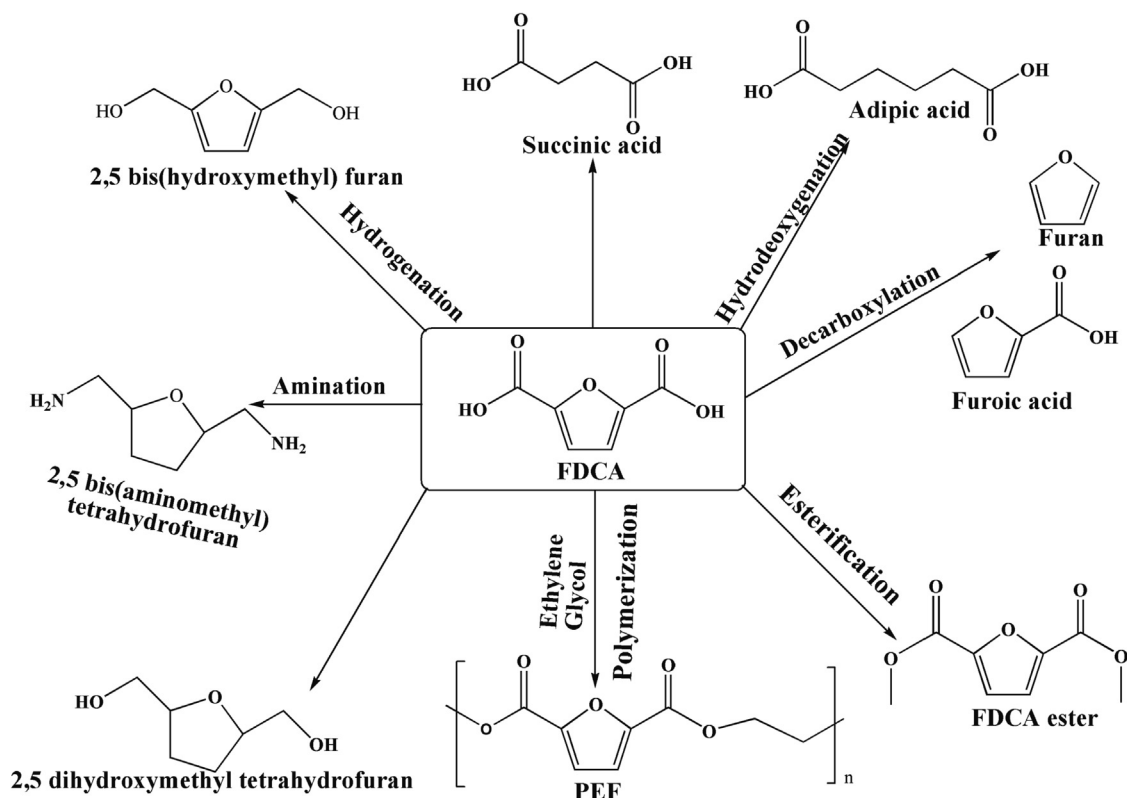


Fig. 1. Potential chemicals produced from FDCA [20].

biocatalytic routes, as shown in Fig. 2, using biomass-derived feedstock such as HMF, which makes it unique and worthy of investigation. As one-pot conversion of sugars like glucose, and fructose into FDCA has advantages such as energy and time-saving because there is no need for separation of HMF, as it is directly converted to FDCA. For example, Yan et al. applied Amberlyst-15/ $\text{Fe}_{0.6}\text{Zr}_{0.4}\text{O}_2$ for the conversion of fructose to FDCA and measured 46% FDCA yield in the presence of O_2 in 24 h [31]. However, it is noteworthy that HMF production from lignocellulosic biomass is a well-known process; thus, production of FDCA directly from HMF can be integrated with the existing processes for commercial applications. In general, depolymerization of lignocellulosic biomass results in the forma-

tion of C_6 sugars followed by its hydrolysis to yield glucose. After that, isomerization of glucose in the presence of an acid catalyst to yield fructose, followed by dehydration into 5-hydroxymethylfuran(HMF), as shown in Fig. 3 [32–36]. The HMF is then further converted to FDCA via oxidation reaction. Indeed, a few researchers have reviewed the FDCA molecule though the mechanistic and its economics have not been discussed [37–39]. Thus, the present review focuses on developing a catalytic and mechanistic insight into FDCA production from biomass-derived HMF. Moreover, the present study also discusses the current market scenario and the effect of different feedstocks on the production of FDCA.

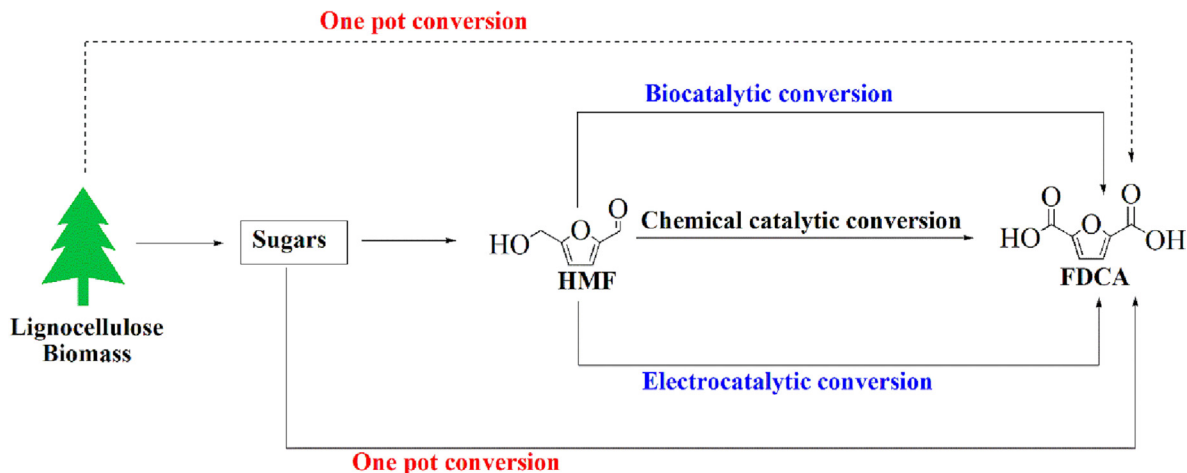


Fig. 2. Overall routes for FDCA production from biorenewable resources.

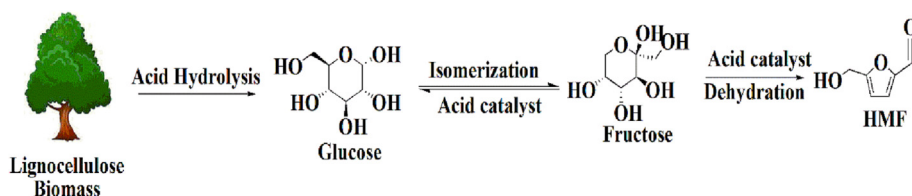


Fig. 3. Schematic for conversion of biomass into HMF [32].

2. Biocatalytic production of FDCA from HMF

Biocatalytic processes for FDCA production from HMF using enzymes or microorganisms, in general, are preferred due to their requirement of ambient temperature and atmospheric pressure [40]. Moreover, intermediates and byproducts produced via biocatalytic processes are mostly non-toxic and biodegradable, which makes the overall process green [41]. On the contrary, the biocatalytic method faces significant challenges in lower FDCA yield and complex purification requirements [42]. In general, biocatalytic processes for FDCA production can be broadly categorized into two major classes, namely enzymatic catalysis, and whole-cell catalysis, which are discussed in the subsequent sections.

2.1. Enzymatic catalysis

There are three enzymatic routes, as shown in Fig. 4 via which FDCA can be produced from HMF, as the latter contains both alcohol and aldehyde groups. Interestingly, each of these routes further follows different catalytic pathways, thereby leading to several plausible mechanisms for FDCA production from HMF. For example, Yuan et al. reported three sequential oxidation steps via which FDCA can be produced from HMF [43]. The authors noted that FDCA production via the proposed mechanism could further take two pathways. In the first route, FDCA is produced via intermediate 5-hydroxymethyl-2-furoic acid (HMFCA), which is formed due to the oxidation of the aldehyde group of HMF. Subsequently, the

alcohol group oxidizes to yield intermediate 5-formyl-2-furoic acid (FFCA), which further oxidizes to yield FDCA. On the contrary, the latter proceeds via oxidation of the HMF alcohol group to form DFF, which has two aldehyde groups, followed by double oxidation to yield FDCA. Noteworthy that most of the enzymes involved in HMF conversion catalyze either alcohol or aldehyde groups but not both simultaneously. In contrast, alcohol and aldehyde must be oxidized simultaneously to facilitate the complete HMF conversion to FDCA [43]. Therefore, multiple enzymes are used for the biosynthesis of FDCA from HMF in a process known as cascade catalysis, wherein at least two catalysts are used to accomplish the reaction [44]. For example, Krystof et al. used 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO)-lipase and *Candida Antarctica* (CAL-B) measured 93% FDCA yield (Table 1, Entry1) at 40 °C in 24 h of HMF oxidation [45]. Similarly, McKenna et al. used galactose oxidase (GO M₃₋₅) and *peri*-plasmic aldehyde oxidase (PaoABC) to establish a one-pot enzyme cascade reaction for converting 100% HMF to >99% FDCA (Table 1, Entry 2) at 37 °C in 10 h [46,47]. Moreover, the authors added catalase (CAT) to the reaction media to produce O₂ from H₂O₂. As a result, more oxygen is provided to the reaction. Furthermore, the authors also studied FDCA production by employing different types of catalysts (GO M₃₋₅, HRP, PaoABC, and CAL) in a continuous one-pot reaction system. The authors observed that PaoABC catalyst primarily oxidizes DFF due to the presence of highly active carbonyl electrophile of DFF (attacked by the molybdenum OH nucleophile). As a result, 100% FDCA yield can be achieved using PaoABC at the optimum concentration (Table 1, Entry 3) [46].

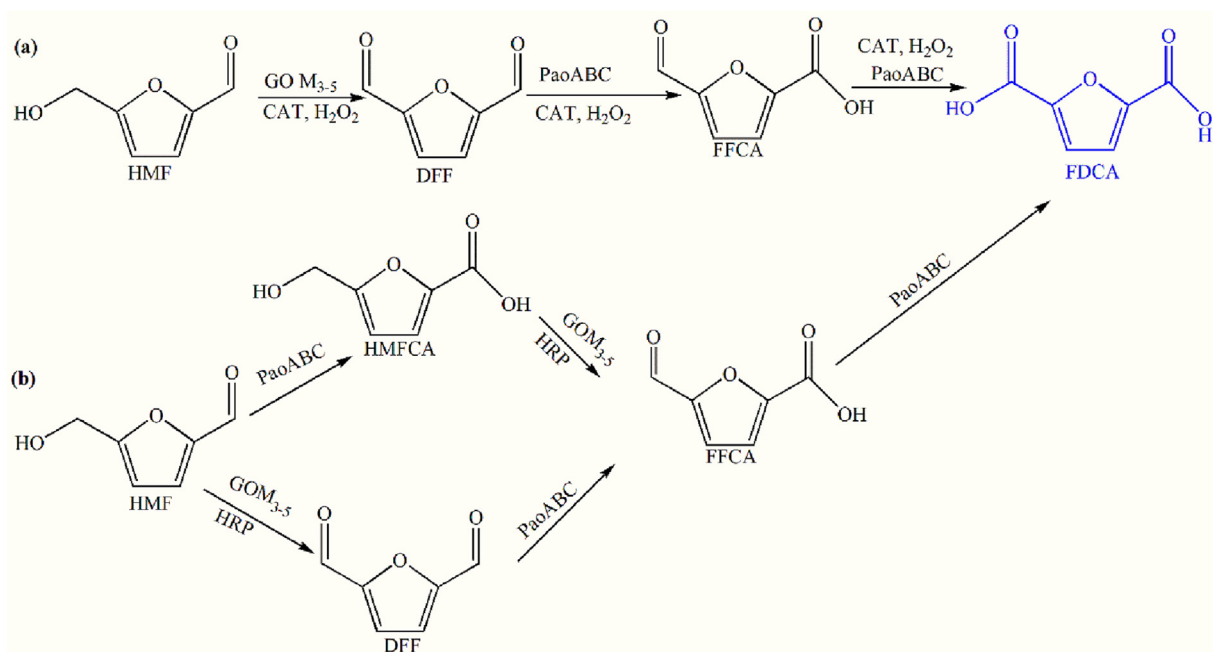


Fig. 4. Schematic diagram of HMF conversion to FDCA via enzymatic routes [46].

Table 1
HMF oxidation using enzymatic catalysts.

Entry	Catalyst	Oxidant	Temp (°C)	HMF (mM)	Time (h)	Conv. (%)	Yield (%)	Ref.
1	TEMPO/CAL-B	H ₂ O ₂	40	50	24	–	93	[45]
2	GO M ₃₋₅ /PaoABC	O ₂	37	100	10	100	>99	[46]
3	GO M ₃₋₅ + HRP + CAL + PaoABC	O ₂	37	100	6	100	100	[46]
4	GAO + AAO + UPO	H ₂ O ₂	25	10	24	100	80	[48]
5	HMFO	O ₂	25	4	24	100	95	[49]

HRP-horse radish peroxidase.

Similarly, Karich et al. used a combination of three fungal enzymes: wild-type aryl alcohol (AAO), wild-type peroxygenase obtained from *Agroclybe* (AaeUPO), and galactose oxidase (GAO) to measure 80% FDCA yield (Table 1, Entry 4) at 25 °C in 24 h. Relatively lower FDCA yield, in this case, can be attributed to the formation of 2 equivalents of H₂O₂ during the oxidation of HMF to DFF by AAO, which might inhibit the oxidation of FFCA to FDCA [48]. Thus, attempts have been made to find a single enzyme that can oxidize both alcohol and aldehyde groups simultaneously and cause comparative FDCA yield. In this regard, Dijkman et al. reported the use of HMF oxidase (HMFO) taken from the family of glucose-methanol-choline oxidoreductase as a single enzyme that oxidizes both alcohols as well as aldehyde functional group to yield up to 95% FDCA from HMF at 25 °C in 24 h (Table 1, Entry 5) [49]. Thus, this area of research can be promising for FDCA production from HMF and require extensive effort.

2.2. Whole-cell catalysis

Whole-cell catalysis is another important biocatalytic pathway to produce FDCA from HMF using microorganisms such as fungi and bacterial species instead of enzymes. The primary advantage of the whole-cell biocatalytic process is FDCA production from HMF in one step, unlike enzymatic processes, which usually require two or more steps. Also, whole-cell catalysis operational cost is lower than enzymatic processes, possibly due to the low prices of raw materials [50]. However, whole-cell catalytic processes require a longer reaction time than enzymatic catalysis. Moreover, the whole cell catalysis route is yet to be explored in detail and has limited availability of literature reports to deduce any conclusive decision. Rajesh et al. examined the production of FDCA from HMF using a fungal strain called *Aspergillus flavus* APLS-1 to measure 67% FDCA yield [51]. The lower FDCA yield can be attributed to toxicity to microorganisms due to a higher concentration of substrate HMF >1 g/L and reduction of oxygen due to higher growth of cell concentration [51]. Similarly, Yang and Huang et al. found that *Burkholderia cepacia* H-2 and *Methylobacterium radiotolerans* G-2 strains cause higher FDCA yield. These two strains were among five strains that were examined in that study. *B. cepacia* H-2 produced 989.5 mg/L of FDCA, whereas 97.4 mg/L was obtained by *M. radiotolerans* [52]. Nevertheless, there is still little research into the biocatalytic HMF conversion to FDCA. After implementing stricter environmental standards, researchers need to give more attention to biocatalytic conversion to overcome the challenges such as low FDCA yield and realize economic feasibility.

3. Electrochemical oxidation of HMF to FDCA

HMF oxidation through the electrochemical pathway to produce FDCA is considered a green process; it has recently received more scientific attention [40]. The mechanism of this process is

that the oxidation process is driven by the electrochemical potential of the electrode, substituting the oxidant with electrons. As a result, the overall waste of this process is less [42]. Another advantage of electrochemical oxidation is that the oxidation rate can be controlled, which improves the reaction rate [14]. According to Sajid et al., an additional benefit of using the electrochemical oxidation process to produce FDCA is that a clean H₂ is produced as a by-product. However, poor yields were obtained, and this route has not generally been well characterized. Product recovery is another challenge, mainly when used in a basic medium [40]. Initially, the oxidation of HMF using the electrochemical pathway to produce FDCA was described in an H-shaped cell [53]. The alkaline medium was NaOH solution, and nickel oxide/hydroxide was used as the anode. After 4 h, the FDCA yield was 71% at a current density of 0.016 A/cm². A carbon black-supported noble metal catalyst was examined by Chadderdon et al. in an alkaline medium to produce FDCA, shown in Fig. 5. When Au/C catalyst was used, fast aldehyde oxidation occurred, but with slower oxidation of the alcohol group. For favoured alcohol oxidation, a higher electrochemical potential is necessary; thus, the electrode and electrode potential are essential to producing 5-formyl-2-furan carboxylic acid (FFCA) shown in Fig. 5. A lower electrode potential can produce HMFCA under a lower electrode using Au/C, but a higher potential is needed in HMFCA(5-hydroxymethyl-2-furoic acid) oxidation to produce FDCA. Pd/C-catalyzed reactions, on the other hand, take two paths with different electrode potentials. A lower aldehyde oxidation rate occurred at low electrode potential on Pd/C than Au/C; however, the aldehyde oxidation dramatically increases with increased potential. HMF easily converted into HMFCA on the Au/C catalyst, indicating that aldehyde oxidation is preferable over alcohol oxidation. The reaction pathway of HMF oxidation on Pd/C differs from Au/C and it is dependent on the applied potential. It was observed that DFF route was favoured at low potentials while the HMFCA route required greater potential [54]. Another way to overcome the product recovery problem is using acidic media instead of alkaline media. Kubota and Choi et al. found that a 53.8% FDCA yield was obtained in acidic media with a large by-product formation [55]. Vuyyuru et al. examined the usage of Pt electrodes along with a current density of + 0.44 mA/cm². The result showed a meager FDCA yield (18%) with only 70% HMF conversion [56]. Although the electrochemical oxidation route involves minimal pollution, it has not been thoroughly investigated, and more research is required. The yield can be enhanced by using more stable and active electrocatalysts. Also, it is noteworthy that noble metal catalysts are expensive and poses challenge in the commercialization of the process. As a result, it is of utmost importance to develop inexpensive alternatives to these noble metal catalysts. Some possible alternatives can be Ni, Co, Cu, Mn, and V which have shown significant activity in the electrochemical production of FDCA from HMF [57,58].

Recently Pang et al. prepared Ni-MOF/Ag electrode using 1 M KOH electrolyte to measure complete conversion of HMF and 99.8% FDCA yield with 99.8% Faraday efficiency [59]. Improved

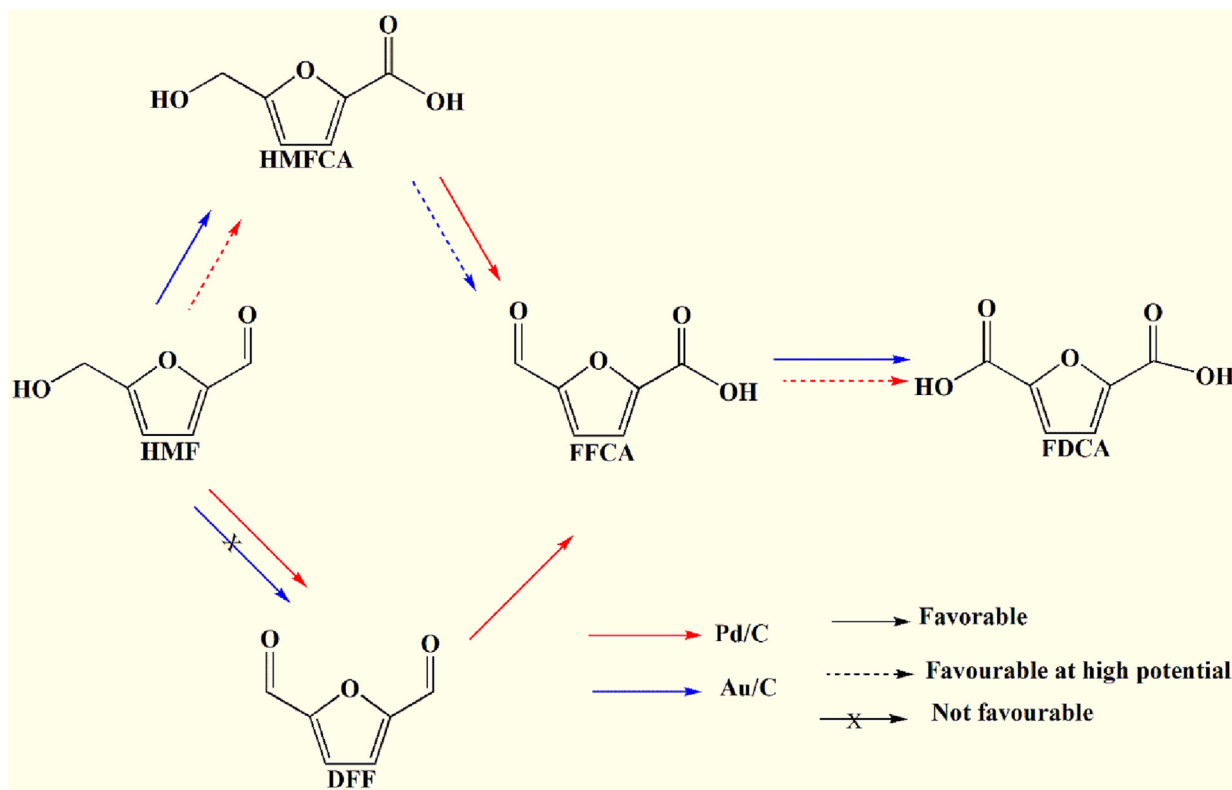


Fig. 5. The reaction pathway using two electrocatalysts (Au/C and Pd/C) for the electrochemical oxidation of HMF to produce FDCA [54].

electrocatalytic performance can be attributed to the presence of the active sites $\text{Ni}^{3+}/\text{Ag}^+$. Similarly, Liang et al. measured 96.1% FDCA yield and 97.36% HMF conversion from 5HMF using 1 M KOH electrolyte and $\text{NiN-V}_2\text{O}_3$ as a catalyst [60]. The authors observed that bifunctionality of $\text{NiN-V}_2\text{O}_3$ inhibits the adsorption of H_2 on Nickel which causes selective production of FDCA as well. Similarly, Chen et al. employed cobalt-based catalyst $\text{Co}_3\text{O}_4/\text{CF}$ for electrochemical oxidation and measured 93.2% FDCA yield along with H_2 gas at a faradaic efficiency of 99.8% [57]. Better performance of $\text{Co}_3\text{O}_4/\text{CF}$ due to its structural defects and huge active sites for electrochemical oxidation of HMF [57]. Moreover, Tao et al. measured 93% FDCA selectivity with 91% faradaic efficiency using a CuCo_3O_4 -based electrocatalyst. Here, the excellent performance of the catalyst is due to the synergistic effect of Cu and Co which changes the electronic structure of the catalyst [61].

Likewise, Wang et al. used $\delta\text{-MnO}_2$ based catalyst to measure 98% FDCA yield with 98% faradaic efficiency. The excellent catalytic activity of the $\delta\text{-MnO}_2$ catalyst is due to its high surface area of $198 \text{ m}^2/\text{g}$ which works well in both alkaline and acidic conditions maintaining stability and activity [62]. Other, interesting non-metal-based catalysts employed for the electrochemical oxidation of HMF are carbon-based catalyst and N-oxyl-based catalyst. For example, Qin et al. employed N, B doped on carbon material and measured 57% FDCA yield and 71% HMF conversion [63]. Electrochemical oxidation of HMF took place due to the doping of N and B causes point defects at grain boundaries that result in a significant number of unpaired electrons, producing frustrated Lewis pairs (FLPs). The FLPs are formed when negatively charged N atoms are combined with positively charged B atoms. Another non-metal based catalyst 2,2,6,6-tetramethylpiperidine 1-oxyl (TEMPO) was synthesized by Cha et al. to measure 99% FDCA yield with 93% faradaic efficiency at mild pH 9.2 buffer solution [64].

4. Chemical synthesis of FDCA from HMF using homogeneous catalysts

The research on HMF conversion to FDCA was first conducted through chemical catalytic methods involving homogeneous or heterogeneous catalysts. Homogeneous catalysis refers to the catalyst and reactants being in the same phase, whereas heterogeneous catalysts mean the catalyst and the reactants are in different phases [65]. To date, the chemical route has been the most extensively used for the oxidation of HMF to FDCA compared to other routes. Chemical catalytic conversion is still the most feasible and well-studied route for FDCA production from HMF [14]. Due to various difficulties with homogeneous catalysis, such as catalyst separation and recycling, it is a less appealing route than heterogeneous catalysis. Moreover, homogeneous catalysts primarily have two practical challenges: a reduced FDCA yield and the formation of the by-product. Therefore, the use of homogeneous catalysts is less studied for the oxidation of HMF to FDCA. For example, Partenheimer et al. employed Co/Mn/Br catalyst for HMF oxidation and measured 70% FDCA yield at 70 bar air pressure in 3 h at 125°C [66]. Heterogeneous catalysis, on the other hand, has numerous advantages, including easy separation and recycling due to the nature of heterogeneous catalysts [67].

5. Noble metal supported heterogeneous catalysts over the aerobic oxidation of HMF to FDCA

Several noble metals supported by heterogeneous catalysts have been identified and shown to have superior catalytic activity, recyclability, and stability. Noble metals such as platinum (Pt), gold (Au), ruthenium (Ru), and palladium (Pd) have been extensively explored and successfully employed in the HMF conversion to FDCA [14]. The authors further reported that the catalyst type, cat-

alyst support, and reaction media are primary variables that substantially impact the aerobic oxidation of HMF to FDCA. Sahu et al. reported that the purpose of using catalyst support is to improve the oxidation process of HMF by increasing the catalyst's activity [68]. Carbon materials are widely employed as support materials since they are inert, plentiful, and affordable [42].

5.1. Platinum-based catalysts

Among different noble metal catalysts, Pt has been found more promising for the sustainable production of FDCA through oxidation due to its higher activity and stability. Pt is loaded upon different supports like activated carbon, carbon nanotubes (CNT), and reduced graphene oxide due to their excellent physical and chemical properties as well as acidic and basic sites, which is essential for sustainable production of FDCA from HMF. Davis et al. measured 79% FDCA yield using Pt/C under 6.9 bar O₂ pressure at 22 °C in 6 h (Table 2, Entry 1) [69]. The authors found that if reaction time and temperature increase, FDCA yield also increases. For example, Wang et al. measured 84% FDCA yield (Table 2, Entry 10) in 24 h of reaction at 25 °C [70], whereas 89% FDCA yield (Table 2, Entry 3) was measured by Sahu et al. at 140 °C in 12 h of reaction [68]. Additionally, FDCA yield also changed when carbon-based supports were replaced with γ -Al₂O₃, TiO₂, ZrO₂, CeO₂, and PVP (polyvinylpyrrolidone). For example, Sahu et al. measured 96% and 94% (Table 2, Entries 4,7) FDCA yield using Pt/ γ -Al₂O₃ and Pt/ZrO₂ at 1 bar O₂ pressure and 140 °C in 12 h. However, at the same reaction conditions only, 2% and 8% FDCA yield was measured (Table 2, Entries 5–6) in the presence of Pt/TiO₂ and Pt/CeO₂, respectively, despite 100% HMF conversion of HMF. One possible reason for less FDCA yield could be attributed to the high oxygen storage capacity of reducible oxides such as Pt/TiO₂ and Pt/CeO₂ than non-reducible supports Pt/AC, Pt/ γ -Al₂O₃ and Pt/ZrO₂ [71]. Moreover, TiO₂ and CeO₂ have oxygen vacancies at their interface, which may lead to undesirable side products. It has also been found that the oxygen exchanging capacity of CeO₂ (194 μ mol/g) is higher than ZrO₂ (9 μ mol/g). The oxygen exchange capacity of CeO₂ such as Ce⁴⁺/Ce³⁺ act as a redox couple and a similar observation has been seen in TiO₂ as Ti⁴⁺/Ti³⁺ as a redox couple. However, using all these monometallic catalysts has some limitations, such as low stability and deactivation due to changes in

the structure of Pt metal. Notably, leaching, sintering or poisoning of the surface of metal due to the adsorption of product intermediates acids blocks the catalyst's active sites [72,73]. It has been observed that the catalytic efficiency of the bimetallic catalyst is better than the monometallic catalyst in the production of FDCA. For example, Bi incorporated with Pt helps to achieve 99% FDCA yield at 40 bar air pressure and 100 °C than 69% FDCA yield over Pt/C (Table 2, Entries 13–14). It may be due to the elimination of Pt poisoning by incorporating Bi. Moreover, Rass et al. measured 99% FDCA yield at 100% HMF conversion in 6 h at 150 °C and 10 bar O₂ pressure in the absence of base (Table 2, Entry 16) over Pt-1.5Cu/C [74]. Similarly, Zhong et al. measured 96% FDCA yield at 100% HMF conversion at 10 bar O₂ pressure and 95 °C only in 3 h. (Table 2, Entry 17) over 1.5Pt₁-Au₄/N-HNT [73]. It has been observed from the aforementioned discussion that the catalytic performance of bimetallic catalysts significantly improved than monometallic catalysts for FDCA production from HMF. It is worth mentioning that the better performance of the bimetallic catalyst can be attributed to the synergistic effect of metal alloys [73].

However, using several noble metal catalysts supported over different carriers and the presence of base for oxidation of HMF to FDCA for achieving higher yield still faces problems of formation of salt as a by-product which requires further purification of products, increasing the operational cost [75]. Therefore, it is necessary to use base-free oxidation of HMF to FDCA to overcome these limitations of using base additives. Limited research has been carried out in this context; Han et al. measured 97% FDCA yield at 100% HMF conversion through oxidation of HMF to FDCA using Pt/C-O-Mg catalyst in the absence of base (Table 2, Entry 20) [76]. The authors observed that the higher FDCA yield might be due to strong basic sites (Pt/C-O-Mg) [76]. Siankevich et al. measured 94% and 99% FDCA yield using Pt/PVP and Pt/IP at 1 bar O₂ pressure at 80 °C in 24 h (Table 2, Entries 11,12) in the base-free environment [77]. In addition, Cheng et al. measured 99% FDCA yield using bimetallic catalyst Pt-Cu_{1.5}/AC at 6 bar O₂ pressure and 150 °C in 6 h in the absence of base (Table 2, Entry 16) [74]. High FDCA yield can be due to the synergistic effect of Pt and Cu at the optimum ratio of Pt and Cu metals [74]. Similarly, Salakhum et al. measured 80.1% yield using Pt-Ca-Hie-ZSM5 at 20 bar O₂ pressure and 110 °C in 24 h in the absence of base (Table 2, Entry 18) [78]. Better catalytic performance of the catalyst due to the presence of both Pt

Table 2
HMF oxidation using Pt catalyst to yield FDCA.

Entry	Catalyst	Base	Oxidant (bar)	Temp (°C)	Time (h)	HMF Conv. (%)	FDCA yield (%)	Ref.
1	Pt/C	NaOH	6.9 O ₂	22	6	100	79	[69]
2	Pt/C	Na ₂ CO ₃	1 O ₂	75	12	100	14	[68]
3	Pt/C	Na ₂ CO ₃	1 O ₂	140	12	100	89	[68]
4	Pt/ZrO ₂	Na ₂ CO ₃	1 O ₂	140	12	100	94	[68]
5	Pt/TiO ₂	Na ₂ CO ₃	1 O ₂	140	12	96	2	[68]
6	Pt/CeO ₂	Na ₂ CO ₃	1 O ₂	140	12	100	8	[68]
7	Pt/ γ -Al ₂ O ₃	Na ₂ CO ₃	1 O ₂	140	12	96	96	[68]
9	Pt/C	pH-13	10 O ₂	50	4	100	72.81	[56]
10	Pt/C	NaOH	1.01325 O ₂	25	24	100	84	[70]
11	Pt/PVP	Base free	1 O ₂	80	24	100	94	[77]
12	Pt/IP	Base free	1 O ₂	80	24	100	99	[77]
13	Pt/C	Na ₂ CO ₃	40 air	100	6	99	69	[82]
14	Pt-Bi/C	Na ₂ CO ₃	40 air	100	6	100	>99	[82]
15	Pt-Bi/TiO ₂	Na ₂ CO ₃	40 air	100	6	>99	99	[83]
16	Pt-Cu _{1.5} /AC	Base free	10 O ₂	150	6	100	99	[74]
17	1.5Pt ₁ -Au ₄ /N-HNT	NaOH	10 O ₂	95	3	100	96	[73]
18	Pt-Ca-Hie-ZSM5	Base free	20 O ₂	110	24	100	80.1	[78]
19	Pt-NC-CeO ₂	Base free	4 O ₂	150	4	100	99.9	[80]
20	Pt/C-O-Mg	Base free	10 O ₂	110	12	100	97	[76]
21	Pt/CNT	Base free	30 O ₂	100	12	100	97.8	[79]
22	Pt/CeO ₂ @C	Na ₂ CO ₃	15 O ₂	110	1.67	100	99	[81]

lewis acid sites and cationic sites (Ca) incorporated in the hierarchical zeolite facilitates the oxidation of HMF to FDCA [78]. Sharma et al. measured 97.85% yield using Pt/CNT at 30 bar O₂ pressure and 100 °C in 12 h in the base-free environment (Table 2, Entry 21) [79]. High FDCA yield can be attributed to the functionalization of carbon nanotube with carbonyl, quinone, and phenol functional groups, which increases the adsorption of reactant HMF and intermediates that facilitates FDCA formation [79]. Ke et al. measured 99% FDCA yield using Pt-NC-CeO₂ in the absence of base at 4 bar O₂ pressure and 150 °C in 4 h (Table 2, Entry 19) [80]. High FDCA yield can be attributed to the presence of strong basic sites (due to the presence of pyridine-type nitrogen) as well as the availability of oxygen vacancies due to CeO₂ [80]. It is worth noting that a possible reason for the higher FDCA yield is not only the synergistic effect of metal but also the presence of basic and acidic sites in the catalyst. Moreover, recently, Zheng et al. measured 99% FDCA yield by employing Pt/CeO₂@C at 110 °C in 1.6 h at 15 bar O₂ pressure using base Na₂CO₃ (Table 2, Entry 22) [81]. Excellent catalytic performance of catalyst can be attributed to the carbon coating over CeO₂, O₂ molecule was activated by transferring the electrons because of redox ability of CeO₂. Whereas the carbon coating is in responsible of adsorbing HMF and able to conduct electrons between the CeO₂ core and the carbon surface [81]. However, the production of FDCA from HMF in the base-free environment by employing bimetallic catalysts also have limitations such as longer reaction time, higher temperature, leaching of supports, deactivation of catalyst due to blockage of active sites the catalyst, and due to formation of intermediates acids during a series of oxidation of HMF.

5.2. HMF oxidation based on palladium catalysts

Pd is another promising noble metal catalyst for catalytic oxidation of HMF to FDCA, whose activity varies according to the support used. Besides, the catalytic activity depends upon several factors, such as catalyst particle size, the substrate-to-metal ratio, amount of base used. For example, Devis et al. measured 71% FDCA yield at 6.9 bar O₂ pressure and 22 °C in 6 h (Table 3, Entry 1) [69]. However, the yield increases if catalyst support is replaced with metal oxide support. For example, Siyo et al. measured 90% FDCA yield using PdNPs at 1 bar O₂ pressure and 90 °C in the presence of base NaOH in 5 h of reaction (Table 3, Entry 5) [84]. Moreover, 62%, 78%, 90%, and 91% FDCA yields have been measured using Pd/TiO₂, Pd/Al₂O₃, Pd/ZrO₂/La₂O₃, and Pd/KF/Al₂O₃, respectively, at the same reaction condition in 8 h (Table 3, Entries 3–4, 6–7). High FDCA yield in the case PdNPs, Pd/ZrO₂/La₂O₃, and Pd/KF/Al₂O₃ catalyst has been measured; this can be attributed to lower byproducts formation. While in the case of Pd/TiO₂ low yield has been measured due to the high formation of byproducts; this may be due to the strong adsorption of intermediates and reactant HMF on active sites of the catalyst resulting in the blockage of active sites. The authors also reported low carbon balance; the possible reason for low carbon balance may be the formation of a high amount of by-products. Also, FDCA yield decreased during recycling from 62% to 54% in the case of Pd/TiO₂ (Table 3, Entries 2–3). The possible reason for the decrease in the yield may be due to the leaching of the catalyst [84]. Furthermore, Zhang et al. measured 92.9% FDCA yield (Table 3, Entry 8) using γ -Fe₂O₃@HAP-Pd (0) at 100 °C and 30 ml/min oxygen flow rate in 6 h [85]. Similarly, Mei et al. measured 91.8% FDCA yield using C-Fe₂O₃-Pd at 80 °C, and 30 ml/min oxygen flow rate in 4 h at 97% conversion attained [86]. Notably, these magnetic-based catalysts were used to ease the catalyst's separation without loss of catalytic activity. Like Pt catalyst, Gupta et al. used basic support for the oxidation of HMF to measure 100% HMF conversion and >99% FDCA yield in 7 h [87]. Similarly, Wang et al. developed Pd/HT-5 nanoparticles cata-

lyst supported over hydrotalcite measured 91.3%, 92.4% yield, and 99% and 99.4% HMF conversion under base-free conditions (Table 3, Entries 11, 12) [88]. Herein, HMF conversion and FDCA yield increased from 99% to 99.4% and 91.3% to 92.4%, possibly due to the hydrotalcite (Mg-Al-CO₃) basic nature. The authors also reported that approximately 60–70% HMF was adsorbed on the hydrotalcite. Besides, 10%–20% of HMFA, FFCA, and FDCA were also adsorbed on the hydrotalcite [88]. Possible reasons for the high FDCA yield are increased metal loading from 1% to 2%, increased active sites, and higher reactant adsorption on the catalyst's surface.

Recently, Xia et al. synthesized bimetallic Pd-Au/HT and measured 90% FDCA yield (Table 3, Entry 17) and 100% HMF conversion in the presence of additives NaOH at 60 °C and 60 ml/min oxygen flow rate in 6 h [89]. Possible reasons for the better catalytic performance may be due to the size effect (approximately 4.1 nm), higher metal dispersion 46.9%, electronic and structural effect, and the synergistic effect of Pd-Au/HT [89]. Similarly, Gao et al. measured 100% FDCA yield (Table 3, Entry 14) in the base-free environment using AuPd/La-CaMgAl-LDH catalyst at 120 °C in 1 h with good stability and recyclability. Possible reasons for high FDCA yield are the synergistic effect of Au and Pd and the presence of larger surface basic sites due to the presence of hydroxyl functional group in LDH and doping of rare earth metal oxide and the electronic structure of the Au-Pd/La-CaMgAl-LDH. The authors also observed that the stability of CaMgAl-LDH was poor due to the leaching of Mg-Al. However, the stability of CaMgAl-LDH has been improved by doping La. The possible reason for the stability of AuPd/La-CaMgAl-LDH can be attributed to the strong interaction of La ions with Ca²⁺, Mg²⁺, and Al³⁺ in the brucite-like structure of La-CaMgAl-LDH through the bond of La³⁺-O-M which confirm by XPS analysis. LaOx moiety prevents interaction with support and acid products such as FFCA and FDCA during the reaction. Thus, enhancing the stability of La-CaMgAl-LDH support in the aerobic oxidation of HMF to FDCA. The authors also reported minimal leaching of 0.8 wt% and 0.3 wt% of total metal content Mg, Ca. [90]. Liao et al. also measured 95% FDCA yield and 100% HMF conversion (Table 3, Entry 21) in the presence of NaOH base using Au_{0.5}Pd/Co₃O₄ only in 1 h of reaction [91]. High FDCA yield can be attributed to the metal alloy's synergistic effect and the strong interaction of Co with Au and Pd. However, it suffers from problems such as formation of salt as a by-product which requires further purification of products, thereby increasing the operational cost when base as an additive for carrying out the oxidation reaction of HMF [91].

Bonincontro et al. developed an Au-Pd-nNiO catalyst and measured 100% FDCA yield (Table 3, Entry 20) under base-free conditions at 90 °C using 10 bar O₂ pressure in 14 h of reaction [92]. It is worth mentioning that basicity is provided through nNiO in the reaction. High FDCA yield can be attributed to the basicity and optimum atomic ratio of Au and Pd (6/4). Further, Zhuang et al. have developed a zeolite-based catalyst through hydrolysis routes, in which Pd nanoparticles were encapsulated inside Beta zeolite and measured 98% FDCA yield at >99% HMF conversion (Table 3, Entry 22) using Pd/Beta catalyst at 1.0325 bar O₂ pressure and 90 °C temperature in 24 h. Possible reasons for higher FDCA yield may be attributed to the higher surface area of 589 m²/g, pore volume of 0.28 cm³/g, and smaller particle size of 1.61 nm as well as the synergistic effect of Pd and Beta zeolite but still suffer from longer reaction time of 24 h [93]. Moreover, Yan et al. have developed Pd/MnOxCo₂ (Pd/MC) by colloidal immobilization method by dispersing Pd nanoparticles on MnOxCo₂ and measured 92.5% FDCA yield at 100% HMF conversion (Table 3, Entry 23) at 110 °C and 2 bar O₂ pressure in 10 h in the presence of base additive KHCO₃ [94]. Possible reasons for higher FDCA yield and superior performance of catalyst can be attributed to the presence of a good number of oxygen vacancies in CeO₂ and low redox potential of

Table 3
HMF oxidation to FDCA using Pd catalyst.

Entry	Catalyst	Base	Oxidant (bar)	Temp. (°C)	Time (h)	HMF Conv. (%)	FDCA Yield (%)	Ref.
1	Pd/C	NaOH	6.9 O ₂	22	6	100	71	[69]
2	Pd/TiO ₂ *	NaOH	O ₂	90	8	>99	54	[84]
3	Pd/TiO ₂	NaOH	O ₂	90	7	>99	62	[84]
4	Pd/Al ₂ O ₃	NaOH	O ₂	90	8	>99	78	[84]
5	Pd-NP	NaOH	O ₂	90	5	>99	90	[84]
6	Pd/ZrO ₂ /La ₂ O ₃	NaOH	O ₂	90	8	>99	90	[84]
7	Pd/KF/Al ₂ O ₃	NaOH	O ₂	91	8	>99	91	[84]
8	γ-Fe ₂ O ₃ @HAP-Pd(0)	K ₂ CO ₃	O ₂	100	6	97	92.9	[85]
9	C-Fe ₂ O ₃ -Pd	K ₂ CO ₃	O ₂	80	4	98.2	91.8	[86]
10	HT-5	Base free	O ₂	100	7	0	0	[88]
11	1 %Pd/HT-5	Base free	O ₂	100	7	99	91.3	[88]
12	2 %Pd/HT-5	base free	O ₂	100	3	99.4	92.4	[88]
13	Pd/HPGS	NaOH	1 O ₂	50	6	99.96	83.15	[98]
14	AuPd/La-CaMgAl-LDH	Base free	5 O ₂	120	1	100	100	[90]
15	Pd/CC	K ₂ CO ₃	O ₂	140	30	–	85	[100]
16	DMF	NaOH	1.01325 O ₂	25	24	100	91	[101]
17	Pd-Au/HT	NaOH	O ₂	60	6	100	90	[89]
18	Pd/MnO ₂	K ₂ CO ₃	1 O ₂	100	4	100	88.1	[102]
19	PdNP/MnO ₂	K ₂ CO ₃	1 O ₂	100	4	100	67.8	[102]
20	AuPd-nNiO	Base free	10 O ₂	90	14	100	100	[92]
21	Au _{0.5} Pd@Co ₃ O ₄	NaOH and Na ₂ CO ₃	1.0325 H ₂ O ₂	90	1	100	95	[91]
22	Pd@Beta	Na ₂ CO ₃	1.0325 O ₂	90	24	>99	98	[93]
23	Pd/MC	KHCO ₃	2 O ₂	110	10	–	92.5	[94]
24	PdAu/Cp-NH ₄ OH	NaOH	3.03975 O ₂	60	6	100	76	[97]
25	Pd/CNT	Base free	O ₂	60	1	>99	71	[99]
26	Pd/o-CNT	Base free	O ₂	60	1	>99	93	[99]**
27	PdAu-TiO ₂	NaOH	10 O ₂	70	4	100	85	[103]

*After recycling, DMF- Dimethylformamide, ** BHMF (2,5 bis (hydroxymethyl) furan).

Ce³⁺ and Ce⁴⁺ (1.3, 1.8 eV) [95], transfer of lattice oxygen from CeO₂ to MnO₂ [96] and synergistic effect of Pd and MC [94]. The authors also reported that if the reaction temperature increases from 90 °C to 110 °C, FDCA yield increases from 77.6% to 89.8%. However, if the temperature increased to 130 °C, the FDCA yield decreased to 77.9% which could be attributed to the degradation of HMF [94]. Interestingly, bimetallic catalyst PdAu supported over modified sunit with NH₄OH (Pd-Au/Cp-NH₄OH) has been developed by German et al. and measured 76% FDCA yield (Table 3, Entry 24) at 60 °C and 3.03975 bar O₂ pressure in the presence of base NaOH [97]. The authors observed that oxidation of HMF to FDCA occurs due to Brønsted acid sites and basic centers. These acid sites and basic centers are available due to the presence of aromatic nitrogen in significant amounts. Higher active species of Pd²⁺ and Au⁺ which provide basicity in the reaction system, lead to the formation of FDCA. The author also reported that an optimum size of 4 nm was essential for the oxidation of HMF [97]. Similarly, Chen et al. observed that support of heteroatom increases the Pd²⁺ species leading to a decrease in activation energy of HMF conversion and FDCA formation [98]. Li et al. reported Pd supported over CNT modified with 30 wt% HNO₃ (Pd/o-CNT) to measure 93% FDCA yield and 99% BHMF (2,5 bis (hydroxymethyl) furan) conversion (Table 3, Entry-26) at 60 °C and 100 ml/min O₂ pressure only in 1 h [99]. However, only 71% FDCA yield was measured (Table 3, Entry-25) when unmodified CNT support was used at the same reaction condition [99]. An increase in the FDCA yield using Pd/o-CNT(modified) than Pd/CNT(unmodified) can be attributed to an increase in the ratio of PdHx to Pd⁰ in the case of Pd/o-CNT.

5.3. HMF oxidation based on Au catalyst

Among the noble catalyst, Au has been extensively employed for the oxidation of HMF and other oxidation reactions by the research community due to the high activity of Au catalysts and

stability [104–106]. Recently, the aerobic oxidation of HMF to FDCA using Au-based catalysts has received significant attention from the scientific research community. Unlike other catalysts, the performance of Au-based catalysts in HMF oxidation depends on the types of support [106]. Casanova et al. measured 44% and 15% FDCA yield at 130 °C and 10 bar air in 8 h by employing Au/C and Au/Fe₂O₃ catalysts [107]. On the contrary, Au/TiO₂ and Au/CeO₂ provided a high FDCA yield (>99%). Au/CeO₂ significantly enhanced the catalytic performance when reductively pretreated, which helped to increase the Ce³⁺ ions and enhance the oxygen vacancies in the catalyst's support. As a result, during the oxidation of the HMF alcohol group, these species Ce³⁺ have a significant impact on transferring hydride and O₂ activation during the oxidation of the OH functional group [106]. Moreover, Pasini et al. measured 99% FDCA yield at 100% HMF conversion (Table 4, Entry 5) at 95 °C and 10 bar O₂ pressure in 4 h, using a bimetallic catalyst 1.5% Au-Cu/TiO₂ [108]. The bimetallic catalyst Au-Cu/TiO₂ gives a higher yield than the monometallic catalyst Au/TiO₂. Possible reasons for the higher FDCA yield include the synergistic effect of Au-Cu alloy and the high dispersion of Au nanoparticles (increases the active sites). Similarly, Villa et al. measured 79.20% FDCA yield at 60 °C and 3 bar O₂ pressure in 6 h (Table 4, Entry 8) [109]. However, if Pd and Pt in different molar ratios (6:2 and 8:2) are incorporated in Au along with AC support, FDCA yield increases and 93.06%, 94.05%, 96.03%, and 98.01% (Table 4, Entries 9–14) in 2–4 h than monometallic catalyst Au/AC [109]. The lower yield of the monometallic catalyst Au/AC was attributed to the catalyst's deactivation due to the irreversible adsorption of intermediates on the catalyst's surface or agglomeration of Au. Moreover, higher FDCA yield in the case of Au₈Pd₂/AC can be attributed to the synergistic effect of Au and Pd. The authors also reported that Au-Pd/AC performs better than Au-Pt/AC in the atomic ratio 8:2 of Au-Pd/Pt; this can be due to the electronic properties of both catalytic systems [109]. In addition, if the atomic ratio of Au:Pd and Au:Pt increase

Table 4
HMF oxidation for FDCA production using Au catalyst.

Entry	Catalyst	Base	Oxidant (bar)	Temp. (°C)	Time (h)	HMF Conv. (%)	FDCA Yield (%)	Ref.
1	Au/Fe ₂ O ₃	NaOH	10 air	130	8	100	15	[107]
2	Au/C	NaOH	10 air	130	8	100	15	[107]
3	Au/CeO ₂	NaOH	10 air	130	8	100	>99	[107]
4	Au/TiO ₂	NaOH	10 air	130	8	100	>99	[107]
5	Au–Cu/TiO ₂	NaOH	10 O ₂	95	4	100	99	[108]
6	Au/TiO ₂	NaOH	20 O ₂	23	22	100	80	[69]
7	Au/HT	Base free	O ₂	95	7	>99	>99	[87]
8	Au/AC	NaOH	3 O ₂	60	6	>99	>79.20	[109]
9	Au ₆ Pd ₄ /AC	NaOH	3 O ₂	60	2	>99	>94.05	[109]
10	Au ₆ Pd ₄ /AC	NaOH	3 O ₂	60	4	>99	>98.01	[109]
11	Au ₈ Pd ₂ /AC	NaOH	3 O ₂	60	2	>99	>98.01	[109]
12	Au ₈ Pd ₂ /AC	NaOH	3 O ₂	60	4	>99	>98.01	[109]
13	Au ₆ Pt ₄ /AC	NaOH	3O ₂	60	4	>99	>93.06	[109]
14	Au ₈ Pt ₂ /AC	NaOH	3O ₂	60	4	>99	>96.03	[109]
15	Au–CeO ₂ @	NaOH	10 O ₂	70	4	100	92	[120]
16	Au–CeO ₂ \$	NaOH	10 O ₂	70	4	100	91	[120]
17	Au ₃ Cu ₁ –CeO ₂	NaOH	10 O ₂	70	4	100	71	[120]
18	Au–Pd/MgO	Base free	5 O ₂	100	12	100	99	[75]
19	Au–Pd/CNT	Base free	5 O ₂	100	12	100	94	[75]
20	Au–Pd/CNT ^t	Base free	5 O ₂	100	18	100	91	[75]
21	Au/Ce _{0.9} Bi _{0.1} O ₂ -δ	NaOH	10 O ₂	65	2	100	>99	[125]
22	Au–Pd/ZOC	NaHCO ₃	3O ₂	80	4	100	>99	[104]
23	Au/ZOC	NaHCO ₃	3 O ₂	80	4	>99	72.27	[104]
24	Au–CeO ₂ (calcined)	NaOH	10 O ₂	70	4	100	92	[122]
25	Au/HT–AC	Base free	5 O ₂	100	12	100	>99	[113]
26	Au/ZrO ₂	NaOH	50 air	125	5	100	89	[128]
27	Au/MgO	Base free	26 air	110	2	99	90.09	[129]
28	Au/ZrO ₂	NaOH	40 air	125	5	100	84	[126]
29	Au/GC	NaOH	7 O ₂	110	6	100	97	[130]
30	Au/ZrO ₂	NaOH	30 air	125	5	100	100	[127]
31	Au ₃ Cu–Al NPs1	NaOH	10 air	100	5	100	91 ± 1	[121]
32	Au/rod–CeO ₂		15 O ₂	120	24	100	95.6	[124]
33	Au/MgSi–ZSM–12	Base free	1 O ₂	90	24	>99	87	[115]
34	Au/Si–ZSM–	Mg(OH) ₂	1 O ₂	90	24	>99	98	[115]
35	Au/ZSM–5	NaOH	3 O ₂	60	6	100	99	[116]
36	Au/MCM–22	NaOH	3 O ₂	60	6	100	97	[116]
37	CoO _x –Au/TiO ₂	NaOH	20 O ₂	130	2.5	100	90.2	[131]
38	Au/CeO ₂		6 O ₂	90	0.0114	100	90 ^m	[123]

@- washed in reaction condition; \$ thermally treated at 300 °C, m-micropacked-bed reactor.

from 6:4 to 8:2, the yield also increases, which means the catalytic activity of both catalysts increases if Au content is enhanced. A similar observation has been made in the oxidation of alcohol and glycerol [110–112].

Like Pt and Pd, attempts have also been made to develop base-free processes using Au catalysts. For example, Gupta et al. measured >99% FDCA yield at 95 °C and 1 bar O₂ pressure in 7 h (Table 4, Entry 7) in base-free conditions over Au/HT catalyst [87]. The Au supported over hydrotalcite showed remarkable performance under the base-free condition as basicity is provided due to the presence of HCO₃[−] and OH[−] on the surface of layered clays hydrotalcite [87]. Similarly, Gao et al. measured >99% FDCA yield at 100 °C and 5 bar O₂ pressure in 12 h (Table 4, Entry 25) using Au/AC–HT [113]. The authors observed that activated carbon exhibits hydroxyl and quinone functional groups and basic sites of HT, which may accelerate the formation of FDCA [113]. Moreover, bimetallic catalysts have been used in the base-free environment to oxidize HMF to FDCA. For example, wan et al. measured 99%, 94%, and 91% FDCA (Table 4, Entries 18–20) at 100 °C and 5 bar O₂ pressure in 12 h, 18 h in the base-free condition using Au–Pd/MgO, Au–Pd/CNT and Au–Pd/CNT^t [75]. Higher FDCA yield in the case of Au–Pd/MgO than Au–Pd/CNT and Au–Pd/CNT^t can be attributed to the presence of MgO, which provides basicity in the reaction system, as well as higher adsorption of reactant HMF and FFCA due to acid–base interaction. However, it is unstable during

recycling as its selectivity decreases may be due to the leaching of MgO in the presence of FDCA in the reaction solution. On the other hand, Au–Pd/CNT exhibits excellent stability and selectivity during recycling, and better performance in terms of yield can be attributed to the adsorption of reactant HMF and intermediates due to the presence of carbonyl and quinone groups on the surface of CNT. Nevertheless, oxidation of HMF occurs at higher temperatures and takes a longer time in base-free conditions [75]. Moreover, Ferraz et al. measured 90.09% FDCA yield at 99% HMF conversion at 110 °C and 26 bar air pressure in 2 h in base-free conditions (Table 4, Entry 27) using Au/MgO [114]. Despite 90.09% yield being measured, the process suffered from leaching of MgO due to the formation of acid compounds hence decreasing the yield after recycling [114]. Interestingly, Chen et al. developed zeolite-based catalysts such as Au/MgSi–ZSM–12 and Au/Si–ZSM–12 and Mg(OH)₂ as a base measured 87%, 98% FDCA yield at 90 °C and 1 bar O₂ pressure in 24 h (Table 4, Entries 33–34) in the base free environment and the presence of base [115]. The enhancement of yield from 87% to 98% can be attributed to more hydroxide ion provided due to the addition of Mg(OH)₂, which increase the basicity in the reaction system hence facilitating the HMF conversion to FDCA. It is worth mentioning that leaching of both MgO and Mg(OH)₂ occurs and takes a long time for the complete conversion of HMF [115]. Further, Saxena et al. measured 99% and 97% FDCA yield at 60 °C and 3 bar O₂ pressure in 6 h (Table 4, Entries 35–

36) using zeolite-based catalysts Au/ZSM-5 and Au/MCM-22 with the addition of base NaOH [116]. The FDCA yield increased slightly in the case of Au/ZSM-5 due to higher metal loading 0.028 than 0.022 in the case of Au/MCM-22 as well as higher metal to HMF ratios (8.8×10^{-5} (g/g), 6.9×10^{-5} (g/g)) [116]. No resistance hindering the reactant, products, and blockage of catalyst pores occurred due to stabilizing agents used during catalyst preparation, such as PVP and sodium citrate [84,117]. Also, no leaching and agglomeration of nanoparticles occurred, and no side reaction or products formed during the reaction due to the hydrophobicity offered by zeolite [118,119].

Albonetti et al. measured 92%, 91%, and 71% FDCA yield at 70 °C and 10 bar O₂ pressure in 4 h in the presence of base additive NaOH using Au-CeO₂@, Au-CeO₂\$ (\$ denotes thermal treatment at 300 °C) and Au₃Cu₁-CeO₂ catalyst (Table 4, Entries 15–17) [120]. The authors observed FDCA higher yield in the case of Au-CeO₂@ (washed in the reaction condition denoted as Au-CeO₂@ catalyst) due to the complete removal of PVP used during the synthesis of catalyst Au-CeO₂@ and Au-CeO₂\$ as well as ceria oxide provide oxygen vacancy. Although bimetallic catalyst had better yield, stability, and recyclability when Au₃Cu₁-CeO₂ was employed for oxidation of HMF, only a maximum yield of 71% was measured. It may happen due to a more significant amount of PVP stabilizer used while preparing a bimetallic catalyst of Au-Cu. PVP cannot be removed entirely due to the strong interaction between Cu and PVP (due to the formation of complex species) through washing under reaction conditions [120]. Similarly, Uzunidis et al. measured 91% FDCA yield at 100 °C at 10 bar air pressure in 5 h in the presence of base NaOH using Au₃Cu-A1 NPs1 (Au:Cu is 3:1) supported over carbon, and stabilization was done using ionic liquids (Table 4, Entry 31). Higher FDCA yield has been reported using bimetallic catalyst Au-Cu NPs than monometallic catalyst Au NPs. If Cu content increases, the FDCA yield decreases, as TON decreases from 263 to 259 for Au₃Cu-A1 NPs1 to AuCu-A1 NPs2, indicating that Au NPs can show catalytic activity towards HMF conversion to FDCA [121]. Similarly, Lolli et al. measured 92% FDCA yield (Table 4, Entry 24) at the same reaction condition Albonetti et al. reported using Au/CeO₂ [122]. Catalytic performance can be attributed to the controlled size of the crystal, defects sites due to ceria oxide, which provide oxygen vacancy, and exposure of the crystal plane during the oxidation reaction of HMF [122]. Furthermore, Yang et al. measured 90% FDCA yield at 90 °C and 6 bar O₂ pressure in 0.01141 h (Table 4, Entry 38) using Au/CeO₂ in micro packed bed reactor [123]. Better performance of Au/CeO₂ catalyst attributed to the significant improvement of liquid mass transfer efficiency as well as CeO₂ providing oxygen vacancy leads to enhancement of HMF conversion to FDCA [123].

Although Au/CeO₂ exhibit excellent catalytic performance and stability due to high catalytic activity, this activity not only depends on oxygen vacancy available due to CeO₂ but also on the exposure of the crystal face of CeO₂. For example, Wei et al. developed nanorod-CeO₂ (1 1 0), nanocube-CeO₂ (1 0 0), and nano octahedron-CeO₂ (1 1 1) and measured 95.6% yield at 120 °C and 15 bar O₂ pressure in 24 h using Au/rod-CeO₂ (Table 4, Entry 32) [124]. It was found that the adsorption of HMF on Au/rod-CeO₂ was higher than on other crystal faces, which can be attributed to the strong interaction between oxygen vacancy of ceria ion and CHO functional group of HMF as rod-CeO₂ (1 1 0) has higher adsorption energy of E_{ads} = 1.04 eV than Cube-CeO₂ (1 0 0), Oct-CeO₂ (1 1 1) are 0.84 eV, 0.17 eV respectively [124]. Moreover, Miao et al. measured >99% FDCA yield at 65 °C and 10 bar O₂ pressure in 2 h in the presence of base NaOH using Au/Ce_{0.9}Bi_{0.1}O_{2-δ} (Table 4, Entry 21) [125]. The catalytic activity of catalyst Au/Ce_{0.9}Bi_{0.1}O_{2-δ} may be attributed to the availability of Au^{δ+} incorporation of Bi. Oxidation of alcohol and C-H activation is due to Au^{δ+} as well as hydride transfer, which is collectively assisted with Ce³⁺, Au^{δ+},

and Bi-O-Ce bonding [125]. Another interesting support ZOC (Zinc hydroxycarbonate) has been developed through the process of deposition precipitation by Gui et al. and measured >99%, 72.27% FDCA yield at 80 °C and 3 bar O₂ pressure in 4 h in the presence of base additive NaHCO₃ by employing Au-Pd/ZOC (Au:Pd is 1:1) and Au/ZOC (Table 4, Entries 22–23) respectively [104]. The better catalytic activity of the catalyst can be attributed to the basicity provided in the reaction system as well as base additive NaHCO₃ stabilizing ZOC support and preventing leaching of ZOC due to the formation of intermediates carboxylic acid products [104]. Interestingly, Schade et al. measured 84% FDCA yield at 125 °C and 40 bar air pressure in 5 h by adding 12 eq. of NaOH base in the presence of Au/ZrO₂ (Table 4, Entry 28) [126]. The authors found that increasing the base amount of 12 eq. increases the FDCA yield and can be attributed to the enhancement of basicity in the reaction system, which prevents the irreversible adsorption of intermediates carboxylic acid formed. Thus, preventing the blockage of active sites of the catalyst [126]. Similarly, Naim et al. measured 100% FDCA yield at 125 °C and 30 bar air pressure in 5 h by adding 8 eq. of NaOH base using Au/ZrO₂ (Table 4, Entry 30) [127].

5.4. HMF oxidation based on Ru

Like other precious metals, Ru-based catalyst has also been extensively used for the oxidation of HMF to FDCA. For example, Xie et al. measured 78.2% FDCA yield at 150 °C and 20 bar O₂ pressure in the presence of base additive Hydrotalcite (HT) using Ru/C (Table 5, Entry 1) [132]. The author observed that the selectivity and carbon balance were meager in the presence of strong bases such as NaOH and Ca(OH)₂ in the reaction system. In the case of the NaOH base, only a 13.65% carbon balance was found, possibly due to the high amount of OH⁻ species and the reaction temperature of the reaction system, which leads to HMF degradation [133]. In contrast, 89.6% of carbon balance and 78.6% of FDCA yield were measured in the presence of HT, possibly due to the utmost basicity provided by the solid base HT. Similarly, Lucas et al. measured 93% FDCA yield at 120 °C and 20 bar O₂ pressure in 6 h in the presence of base additive NaOH using Ru supported over K-OMS-2 (Potassium exchange octahedral molecular sieve-2) (Table 5, Entry 2) [134]. The authors observed that the oxidation of HMF to HMFA is due to the redox activity of Mn⁴⁺/Mn³⁺ followed by FDCA formation in the presence of Ru [134]. However, in the base-free condition, Artz et al. measured 77.65% FDCA yield at 140 °C and 20 bar O₂ pressure in 3 h using Ru/CTF (Table 5, Entry 3) [135]. However, the catalyst suffered recyclability issues. Similarly, Zheng et al. measured 97.03% FDCA yield at 110 °C and 10 bar O₂ pressure in 12 h in the presence of base Mg(OH)₂ using Ru/C (Table 5, Entry 6) [136]. In this case, the authors observed no leaching, possibly because basicity neutralized the acid products and facilitated HMF oxidation to FDCA [136].

On the contrary, Ramirez-Barria et al. measured 81% and 75.85% FDCA yield in base-free conditions using Ru(NN)/NrGO and Ru (NN)/rGO catalysts, respectively at 100 °C and 10 bar air pressure in 8 h (Table 5, Entries 4–5) [137]. An increase in the FDCA yield may be attributed to the presence of nitrogen which provides basic sites that facilitate the oxidation of HMF to FDCA. Similarly, Mishra et al. measured 99.1%, 82.2%, and 60.8% FDCA yield at 120 °C and 20 bar air pressure in 10 h in the base-free condition by employing Ru/MnCo₂O₄, Ru/CoMn₂O₄, and Ru/MnCo₂O₃ catalysts respectively (Table 5, Entries 7–9) [15]. Higher FDCA yield may be attributed to the presence of both lewis and Brønsted acid on the surface of the catalyst Ru/MnCo₂O₄. However, in the case of the Ru/MnCo₂O₃ catalyst, low yield may be due to the non-cubical spinal structure of Ru/MnCo₂O₃ because of the absence of oxygen molecules. Another interesting support hydroxyapatite (consists of Ca and phosphorous) has been used for the oxidation of HMF by Gao et al. to mea-

Table 5
HMF oxidation to FDCA using Ru catalyst.

Entry	Catalyst	Base	Oxidant (bar)	Temp. (°C)	Time (h)	HMF Conv. (%)	FDCA Yield (%)	Ref.
1	Ru/C	HT	20 O ₂	150	–	100	78.2	[132]
2	Ru-K-OMS-2	NaOH	20 O ₂	120	6	100	93	[134]
3	Ru/CTF	Base free	20 O ₂	140	3	100	77.6	[135]
4	Ru(NN)/NrGO	Base free	10 air	100	8	>99	81	[137]
5	Ru(NN)/rGO	Base free	10 air	100	8	100	75.8	[137]
6	Ru/C	Mg(OH) ₂	10 O ₂	110	12	100	97.3	[136]
7	Ru/MnCo ₂ O ₄	Base free	24 air	120	10	100	99.1	[15]
8	Ru/CoMn ₂ O ₄	Base free	20 air	120	10	100	82.2	[15]
9	Ru/MnCo ₂ O ₄	Base free	20 air	120	10	100	60.8	[15]
10	Ru/HAP	Base free	10 O ₂	120	24	100	99.6	[138]
11	Ru/HAP	Base free	10 O ₂	140	24	100	99.9	[138]
12	Ru/MgAlO	Base free	6.2 O ₂	140	4	100	99	[142]
13	Ru/ZrO ₂ H-aero	Base free	10 O ₂	120	16	100	97	[143]
14	Ru/ZrO ₂ H-SBA	Base free	10 O ₂	120	16	97	84.39	[143]
15	Ru/Mn ₆ Ce ₁ O ₇	Base free	10 O ₂	150	8	99	63.36	[146]
16	Ru/Mn ₆ Ce ₁ O ₇	Base free	10 O ₂	150	15	100	99.9	[146]
17	Ru/CNT		30 O ₂	100	12	100	92.8	[79]
18	Ru/C	NaHCO ₃	10 O ₂	120	24	100	91.34	[151]**
			1,4 dioxane:H ₂ O 1:4					
19	Ru/C	Na ₂ CO ₃ + NaOH	H ₂ O ₂	80	0.5	100	88	[12]
20	Ru ₄ CoOy(OH)	Base free	10 O ₂	150	24	100	>99	[148]
21	Ru-NaY	Base free	10 O ₂	120	8	100	94	[149]
22	Ru/HAP	Base free	10 O ₂	130	15	100	65	[141]*
23	Ru/C	NaHCO ₃	40 O ₂	140	3	100	98.2	[153]
			DioxaneH ₂ O					

sure 99.6% FDCA yield at 120 °C and 10 bar O₂ pressure in 24 h in the base-free environment using Ru/HAP (Table 5, Entries 10–11) [138]. The author observed that increased FDCA yield could be attributed to both acidic and basic sites on the surface of the hydroxyapatite (HAP). These acid and basic sites are available on the surface of HAP due to HPO₄^{2−} (Brønsted acid sites), OH[−] vacancies, and Ca²⁺ cation (Lewis acid sites) [139,140]. Similarly, Lin et al. measured 65% FDCA yield from 5-methoxymethylfurfural (MMF) at 130 °C and 10 bar O₂ pressure in 15 h in the base-free condition using Ru/HAP (Table 5, Entry 22) [141]. Lower FDCA yield through MMF routes could be attributed to the side reaction that resulted in the formation of humins. The authors also observed that the oxidation pathway proceeds through MMFCA (*5-methoxymethyl furan –2 carboxylic acid), HMFCa, and FFCA intermediates to form FDCA [141]. Another researcher, Antonyraj et al., measured 99% FDCA yield at 140 °C and 6.2 bar O₂ pressure in 4 h in the base-free condition by employing Ru/MgAlO (Table 5, Entry 12) [142]. Herein also, the authors observed that the very high FDCA yield could be attributed to the availability of acid sites and basic sites that play a pivotal role. However, MgAlO support dissolves in the reaction mixture due to formation of intermediates FFCA and FDCA products [142]. Pichler et al. measured 97% and 84.39% FDCA yield at 120 °C and 10 bar O₂ pressure in 16 h in the base-free condition using Ru/ZrO₂ H- and Ru/ZrO₂ H-SBA catalysts (Table 5, Entries 13–14) [143–145]. Possible reasons for high yield could be the very small size of Ru nanoparticles (0.8–1 nm) and the high surface area of Ru/ZrO₂ H-aero. Thus, the employment of Ru/ZrO₂ H-aero facilitates the oxidation of HMF to FDCA.

Another interesting support Mn₆Ce₁O₇ has been reported by Gao et al. to measure 99.9% FDCA yield at 150 °C and 10 bar O₂ pressure in 15 h in the base-free condition using Ru/Mn₆Ce₁O₇ (Table 5, Entry 16) [146]. Higher FDCA yield may be attributed to a large amount of Ru⁰, Ce³⁺, Mn⁴⁺, and oxygen vacancies. The author also reported good catalytic activity and stability of the Ru/Mn₆Ce₁O₇ catalyst due to a robust interaction between Ru⁰ and Mn₆Ce₁O₇ support. If reaction time decreases from 15 h to 8 h, then FDCA yield decreases to 63.36% (Table 5, Entry 15)

[146]. Similarly, Co metal oxide is used as support for catalytic oxidation of HMF to FDCA due to the strong interaction between Ru and Co and changing of acidic and basic sites, crystal defects, and the presence of lattice oxygen [147]. For example, Gao et al. measured >99% FDCA yield at 150 °C and 10 bar O₂ pressure in 24 h in the base-free condition using Ru₄CoOy(OH) (Table 5, Entry 21) [148]. The author observed that higher FDCA yield could be due to the presence of both acidic and basic sites, Ru⁰ metal which facilitates the adsorption of HMF and results in the formation of alkoxide intermediates and adsorbed hydrogen species. Moreover, the creation of oxygen vacancies due to Co²⁺/Co³⁺, O₂ molecules dissociate into O_{latt}. This further reacts with adsorbed hydrogen resulting in the formation of H₂O molecules. Thus close catalytic cycle was facilitated by the presence of Ru⁰, and Co²⁺/Co³⁺ redox couple. Another researcher, Kandasamy et al., measured 94% FDCA yield at 120 °C and 10 bar O₂ pressure in 8 h using Ru-NaY catalyst (Table 5, Entry 21) [149]. Higher FDCA yield can be attributed to optimum metal loading of 3 wt%, good metal dispersion, availability of acid sites and basic sites and a high amount of Ru⁰ (70%) [149]. The author also observed that if the reaction temperature increased above 120 °C, then the FDCA yield decreased may be due to the degradation of HMF at higher temperatures. Further, if metal loading increased from 3 wt% to 6 wt%, then yield also decreased. This may be due to an increase in the crystal size of the metal, resulting in unwanted side products and agglomeration of Ru nanoparticles [150].

Besides catalysts, solvents, oxidants, support, and reactant type have a significant role in FDCA production using Ru. For example, Si et al. measured 91.34% FDCA yield from 5-formylloxymethylfurfural (**FMF) at 120 °C and 10 bar O₂ pressure in 24 h in the presence of NaHCO₃ base using Ru/C (Table 5, Entry 18) [151]. Higher FDCA yield using a mixture of 1,4 dioxane and water in the ratio of 1:4 w/w can be attributed to the higher stability of FMF and the presence of 1,4 dioxane and water solvents [151]. It was observed that the low hydrogen bonding (δ_H = 7.4) and lesser polarity (δ_p = 1.8) of 1,4 dioxane may facilitate the adsorption of FMF and intermediates formed on the Ru/C catalyst

surface as well desorption of FDCA from sites of catalyst [152]. Similarly, Xie et al. used 1,4 dioxane and water in the ratio of 1:4 w/w to measure 98.2% FDCA yield in the presence of base additive NaHCO_3 at 140 °C and 40 bar O_2 pressure in 3 h (Table 5, Entry 23) [153]. Another researcher, Zhao et al., used a microwave reactor for the synthesis of FDCA from HMF and measured 88% FDCA yield at a mild temperature of 80 °C in the presence of base Na_2CO_3 and NaOH with 12 wt% of H_2O_2 as an oxidant using 5% wt of Ru/C in 0.5 h (Table 5, Entry 19) [12]. The possible reason could be uniform heating of the reaction mixture using a microwave reactor [154] and oxidant H_2O_2 .

As per aforementioned noble metals, Au catalysts have been found to be more effective at oxidising aldehyde groups. On the contrary, Pt and Pd catalysts are more effective at oxidising alcohol groups. Also, Pt and Pd catalysts requires less harsh operating conditions than Au. Indeed, Au catalysts are typically used at high temperatures for better performance [69,107]. This pattern is in line with an earlier comparative study that showed Pt and Pd catalysts to be more FDCA-selective, with 79% and 71% FDCA yield, respectively, whereas Au catalysts needed higher O_2 pressures, higher base concentrations, and a longer reaction time to achieve a similar FDCA selectivity [69,126]. Similarly, Ru catalysts exhibit low rates of HMF conversion and FDCA production, indicating that their mass activities require improvement. Ru catalysts, however, continue to be economically advantageous due to their low price, which is often 4% lesser than Au and Pt cost per gram [135].

6. Non-noble metal supported heterogeneous catalysts over the aerobic oxidation of HMF to FDCA

In general, catalysts based on noble- metals have been extensively employed for the catalytic oxidation of HMF to FDCA due to excellent catalytic performance, stability, and recyclability. However, their high cost and non-availability limit the FDCA production process commercialization. Therefore, attempts have been made to non-noble metal-based catalysts which are less expensive and readily available. In this regard, Sahu et al. measured 85% FDCA yield at 100 °C and 10 bar O_2 pressure in the absence of base additive in 10 h (Table 6, Entry 1) using Fe(III) POP catalyst [155]. The authors also observed that the HMF oxidation could be accelerated by forming a radical chain mechanism. The possible reasons for higher FDCA yield can be attributed to the high surface area and active metal sites of Fe(III) POP catalyst [155]. Similarly, Gao

et al. measured 90.4% FDCA yield at 100 °C and 24 bar O_2 pressure in the presence of solvent CH_3CN in 24 h using Merified resin cobalt(II) meso-tetra (4-pyridyl) porphyrin (MR-Co-Py) (Table 6, Entry 2) [1]. The author reported that the main reaction pathway is oxidation of HMF to DFF subsequently to FDCA. Similar trends have been reported on HMF oxidation to FDCA using $\text{Fe}_3\text{O}_4\text{-CoO}_x$ as a catalyst [2]. Moreover, high conversion and yield using CH_3CN solvent and t-BuOOH as an oxidant have been reported, whereas low conversion and yield FDCA measured using solvent H_2O , DMSO, and toluene. The possible reasons for good yield can be attributed to polarity, acid-base properties, a dielectric constant, and steric hindrance in the CH_3CN and t-BuOOH solvent. These properties also significantly affect the HMF oxidation in the presence of MR-Co-Py catalyst [1]. Furthermore, Jain et al. reported spinel-mixed metal oxide catalyst $\text{Li}_2\text{Co-Mn}_3\text{O}_8$ to measure 80% FDCA yield at 150 °C and 55 bar O_2 pressure by employing $\text{CH}_3\text{-COOH}$ as an additive in 8 h (Table 6, Entry 3) and sodium bromide as a co-catalyst [156]. Similarly, magnetic-based nanocatalyst $\text{Fe}_3\text{O}_4\text{-CoO}_x$ has been reported by Wang et al. to measure 68.6% FDCA yield at 80 °C in the presence of t-BuOOH as an oxidant in 12 h (Table 6, Entry 4) [2]. The authors reported that the main routes of HMF oxidation to FDCA followed DFF to FDCA; however, HMFA also formed in a minor amount, which indicates that both OH and aldehyde groups of HMF oxidized simultaneously. Similarly, transition metal oxides catalysts in different proportions of Ce, Zr, and Fe have been used to measure 13.8%, 23.2%, and 44.2% FDCA yield, respectively, at 140 °C and 20 bar O_2 pressure in the base-free environment using 1-butyl-3 methylimidazolium chloride [Bmim]Cl ionic liquid solvent in 24 h (Table 6, Entries 5–7) [157]. FDCA yield increased because a solid solution of ceria generates huge oxygen vacancies resulting in the enhancement of redox properties and catalytic activity [158,159]. The authors also observed that ILs act as solvent and co-catalyst due to the formation of hydrogen bonds between HMF and ILs [160,161], which play a crucial role in HMF oxidation.

Furthermore, Hayashi et al. measured 91% FDCA yield at 100 °C and 10 bar O_2 pressure using NaHCO_3 as a base additive in 24 h over MnO_2 catalyst (Table 6, Entry 9) [162]. The authors observed that oxidation of HMF was carried out in the presence of strong bases NaOH, carbonates, and phosphates, leading to a decrease in the FDCA yield (91% to 14%), although >99 HMF conversion was achieved in each case. It has also been reported that the oxidation of FFCA to FDCA may be the rate-determining step, as the rate of

Table 6
HMF oxidation to FDCA using non-noble metal catalysts.

Entry	Catalyst	Additives	Oxidant (bar)	Temp (°C)	Time (h)	HMF Conv. (%)	FDCA Yield (%)	Ref.
1	Fe(III) POP	Base free	10 O_2	100	10	100	85	[155]
2	MR-Co-Py	CH_3CN	t-BuOOH	100	24	95.6	90.4	[1]
3	$\text{Li}_2\text{Co-Mn}_3\text{O}_8$	CH_3COOH	55 O_2	150	8	100	80	[156]
4	$\text{Fe}_3\text{O}_4\text{-CoO}_x$	–	t-BuOOH	80	12	97.2	68.6	[2]
5	$\text{Ce}_{0.5}\text{Fe}_{0.5}\text{O}_2$	Base free	20 O_2	140	24	98.4	13.8	[157]
6	$\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$	Base free	20 O_2	140	24	96.1	23.2	[157]
7	$\text{Ce}_{0.5}\text{Fe}_{0.15}\text{Zr}_{0.35}\text{O}_2$	Base free	20 O_2	140	24	99.9	44.2	[157]
8	$\text{Fe}_{0.6}\text{Zr}_{0.4}\text{O}_2$	Base free	20 O_2	160	24	99.9	60.6	[172]
9	MnO_2	NaHCO_3	10 O_2	100	24	>99	91	[162]
10	$\text{MOF-Mn}_2\text{O}_3$	NaHCO_3	14 O_2	100	24	100	99.5	[163]
11	$\text{MnO}_x\text{-CeO}_2$	KHCO_3	20 O_2	110	6	98	91	[96]
12	MnCo_2O_4	KHCO_3	10 O_2	100	24	99.5	70.9	[166]
13	$\text{Co}_3\text{O}_4/\text{Mn}_x\text{Co}$	Base free	1 O_2	140	24	100	>99	[167]
14	$\text{Mn}_3\text{Co}_2\text{O}_x\text{-0.3VC}$	NaHCO_3	30 air	130	3	100	96	[168]
15	MnO_2/CF	NaHCO_3	3 O_2	100	2	99.8	97	[169]
16	CuMnO_4	Base free	t-BuOOH	80	16	100	96.4	[170]
17	CuOx-CoOy-PVP/G	Base free	NaClO	40	1	100	91.3	[171]

PVP- polyvinylpyrrolidone, G- Graphene.

formation of FDCA is greater than FDCA. Moreover, Bao et al. measured 99.5% FDCA yield at 14 bar O_2 pressure and 100 °C in the presence of $NaHCO_3$ as a base additive in 24 h using metal–organic framework manganese-based catalyst ($MOF-Mn_2O_3$) (Table 6, Entry 10) [163]. The excellent catalytic performance of the catalyst can be attributed to the presence of a large number of surface pores, as the redox properties of the catalyst increase the active sites and facilitate the diffusion of reactants. Similarly, Han et al. reported a MnO_x-CeO_2 catalyst to measure 91% yield at 110 °C and 20 bar O_2 pressure in 6 h in the presence of base additive $KHCO_3$ (Table 6, Entry 11) [96]. It can be attributed to the presence of high oxygen vacancies in CeO_2 due to the presence of Ce^{3+} , which transfers molecular oxygen to active sites of MnO_2 [164], hence accelerating the oxidation of HMF to FDCA. The authors also observed that the presence of a strong base such as NaOH reduces FDCA yield decreases may be due to the degradation of HMF to insoluble humins. Moreover, at high temperatures above 130 °C, selectivity decreased to 19.5%; this may be due to the degradation of HMF at high temperatures [150,165].

Similarly, Zhang et al. measured 70.9% FDCA yield at 100 °C and 10 bar O_2 pressure in the presence of $KHCO_3$ for 24 h using $MnCo_2O_4$ catalyst (Table 6, Entry 12) [166]. The authors found that the excellent catalytic performance of the catalyst might be due to the presence of surface oxygen molecules that forms lattice oxygen and the Mn^{3+}/Mn^{2+} redox cycle of $MnCo_2O_4$ which facilitates the oxidation of HMF to FDCA [166]. Similarly, Gao et al. measured >99% FDCA yield at 140 °C and 1 bar O_2 pressure in the base-free environment for 24 h (Table 6, Entry 13) [167]. The excellent catalytic performance of the catalyst could be attributed to the enormous amount of Lewis acid and Brønsted acid sites available in $Co_3O_4/Mn_{0.2}Co$, which accelerated the oxygen mobility and facilitated the HMF conversion to FDCA. These Lewis acid sites are available due to Mn^{4+}/Mn^{3+} ions, and Brønsted acid sites are available due to $Co-O-H^+$ [167]. The authors also reported that Lewis acid sites facilitated the adsorption of HMF while Brønsted active sites can accelerate the formation of the COOH group of FDCA. Furthermore, Liu et al. measured 96% FDCA yield at 100% HMF conversion in the presence of base $NaHCO_3$ at 130 °C and 15 bar air pressure in 3 h using $Mn_3Co_2O_x-0.3VC$ catalyst (Table 6, Entry 14) [168]. The author observed that the excellent performance of the catalytic system could be attributed to the enhancement of lattice oxygen concentration due to the presence of solid vitamin C in the catalytic system as $Mn_3Co_2O_x-0.3VC$. Similarly, Jiang et al. measured 97% FDCA yield at 100 °C and 3 bar O_2 in the presence of base additive $NaHCO_3$ in 2 h using MnO_2 -based porous carbon foam (Table 6, Entry 15) [169]. The better performance of the catalyst could be attributed to the high specific surface area, O_2 vacancies concentration, acidic sites, basic sites, and mobility of transfer charge of FDCA [169]. Moreover, recently, Wang et al. measured 96.4% FDCA yield at 80 °C and t-BuOOH as an oxidant in the base-free condition in 16 h using $CuMnO_4$ (Table 6, Entry 16) [170]. Better catalytic activity can be attributed to the synergistic effect of Cu and Mn speeding up the redox cycle and enabling the conversion of HMF to FDCA [170]. Another researcher Rao et al. measured 91.3% FDCA yield at 40 °C in 1 h using NaClO as an oxidant by employing $CuOx-CoOy-PVP/G$ catalyst (Table 6, Entry 17) [171]. The heterostructure of the catalyst controlled the electronic state and facilitated the charge transfer process, resulting in remarkable catalytic performance.

7. Mechanism of HMF oxidation into FDCA using non-noble metal and noble metal-based catalytic system

As discussed, HMF oxidation may follow different routes based on the active sites of the catalyst, base, and solvent used. For exam-

ple, researchers have suggested that Mn^{4+} acts as an active site of the catalyst in which the adsorption of HMF occurs, as shown in Fig. 6 [147,167]. Transformation of oxygen occurs through the redox cycle of Mn and Ce oxide. Therefore, the reaction gets initiated by the adsorption of HMF on the surface of the active site of the catalyst (Mn^{4+}) accomplished via transferring hydrogen on the surface of the catalyst by cleavage of OH bond simultaneously forming metal oxide intermediate. After that base hydroxyl group (OH^-) deprotonates the proton from the β position (concerning metal), simultaneously accepting electrons by Mn^{4+} and liberating the water molecule by depositing electrons on the surface of the catalyst resulting in the formation of the aldehyde group. These deposited electrons on the catalyst's surface are scavenged by the redox cycle of Ce^{4+} to Ce^{3+} [146]. Herein, oxygen adsorbed on the catalyst surface is dissociated into chemisorbed oxygen simultaneously to lattice oxygen [O^{2-}] via a redox cycle of Ce^{4+} to Ce^{3+} , as shown in Fig. 6 [96]. Furthermore, this lattice [O^{2-}] is transferred to the lattice of MnO_2 , which reacts with already adsorbed hydrogen and forms water or hydroxyl ions. Moreover, H_2O as a nucleophile gives lone pair of the electron to the carbonyl carbon of the resulting aldehyde chain and forms geminal diol; further, deprotonation occurs through the base ($2OH^-$), resulting in the dehydrogenation and formation of carboxylic acid. Furthermore, desorption of FDCA is accomplished through Mn^{4+} and liberation of H_2O , as shown in Fig. 6. So in the above reaction mechanism, Mn^{4+} acts as lewis acid [167], which enhances the reaction and base used for deprotonation. Besides that, Ce converted the oxygen into lattice oxygen through the redox cycle.

Moreover, in the case of noble metal in the presence of a base, reactions were initiated by hydroxyl ion, and transfer of proton by H_2O takes place. Initially, geminal diol was produced by the nucleophilic addition of water (hydroxide ion) to the carbonyl. The alcohol side chain of HMF was then activated by OH^- in the presence of Au or Pt metal catalysts, leading to the oxidation of intermediate aldehydes to yield final diacid products shown in the Fig. 7. Furthermore, deprotonated hydrogen is adsorbed on the catalyst's surface, and deposited electrons are consumed by $1/2O_2$ [173].

8. Challenges and future outlook

It is noteworthy that FDCA can be produced from an array of biobased molecules such as 5-(chloromethyl) furfural (CMF), 5-methoxymethylfurfural (MMF), BHMF 2,5 bis (hydroxymethyl) furan, HMF, carbohydrates and lignocellulosic biomass primarily via oxidation reaction using thermocatalytic, biological, electrochemical, and photocatalytic processes as shown in Fig. 8. However, most of these routes are emerging, and limited data is available to study their feasibility. For example, only one article reports FDCA production from CMF [42]. The authors used an HNO_3 catalyst at 80 °C for 24 h to measure 59% FDCA yield [174]. Similarly, FDCA can be produced from biomass-derived MMF, which may be an exciting area of research. It is noteworthy that MMF is produced via etherification of fructose in methanol and is a thermally stable molecule, making it suitable for such applications [175,176]. Deigo et al. measured ~72% FDCA yield from MMF using Co/Mn/Br catalyst at 180 °C at 60 bar air pressure for 1 h [177]. Similarly, Lin et al. measured 65% FDCA yield at 130 °C at 10 bar O_2 pressure for 15 h using MMF as a substrate [141]. The authors observed that side reactions, such as the formation of HMFCA, suppress the desired product yield and consume a significant portion of the feedstock. Interestingly, FDCA from MMF can also be produced via biological routes about which significantly fewer details are available and need further studies [43].

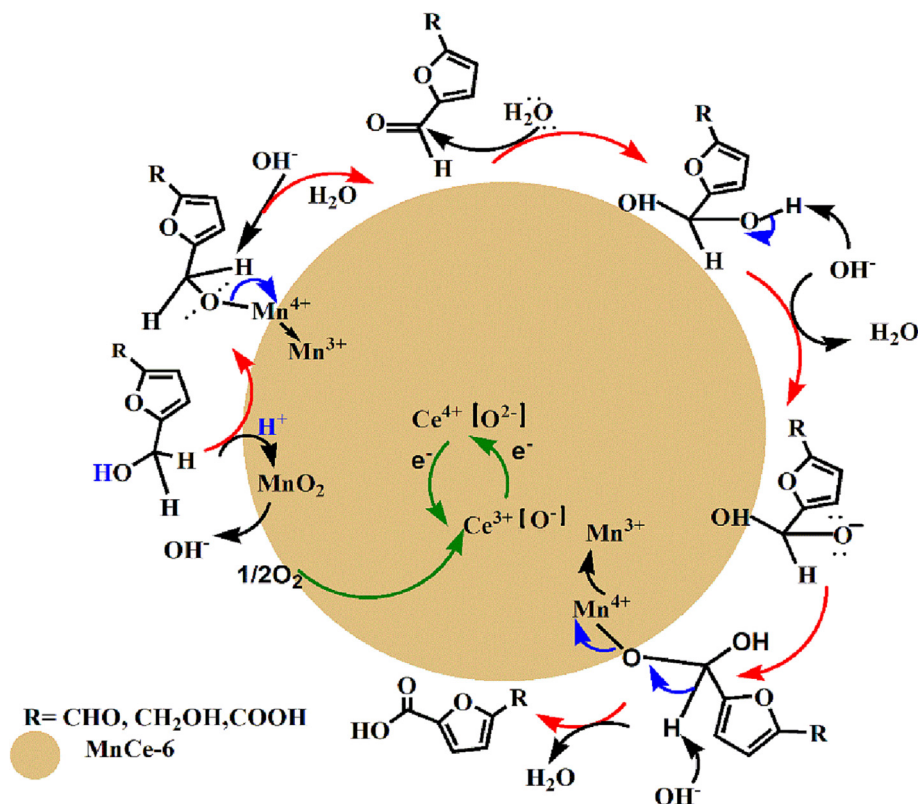


Fig. 6. A plausible mechanism of HMF oxidation into FDCA [96].

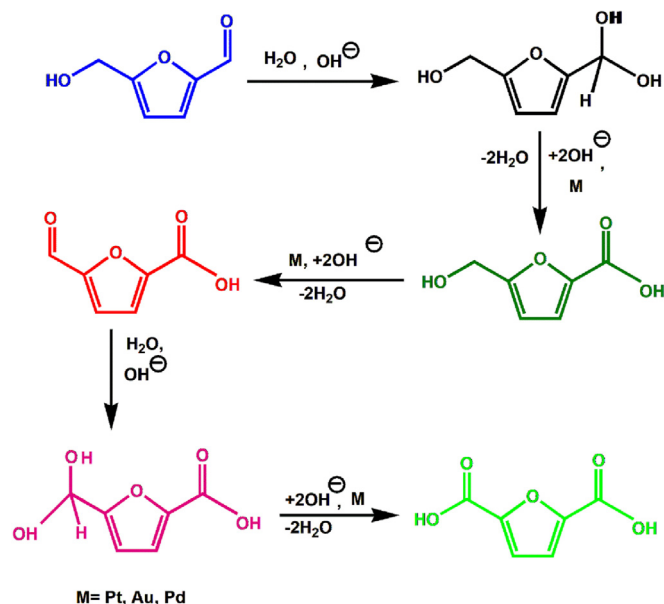


Fig. 7. A possible reaction mechanism of noble metals in the presence of base [173].

Similarly, furoic acid is another biomass-derived molecule that can be used recently to produce FDCA [178].

Although FDCA can be produced from HMF as an intermediate using different routes, such as chemical catalytic conversion, biocatalytic conversion, or electrochemical conversion. The production of FDCA directly from biomass-derived sugar (one-pot conversion) is a challenging task albeit possible. For example, a multi-functional catalysts can conduct this conversion in a one-

pot reaction with acidic, basic, and metal sites [14,42]. Also, the possibility of consecutive carbohydrate oxidation is the major difficulty with the direct conversion of sugar to FDCA [14]. However, this challenge can be partially fixed using polymeric membranes or molecular sieves in biphasic systems by Kröger et al. and Saha and Abu-Omar et al. Using a polytetrafluoroethylene membrane with a pore size of 0.45 μm and an exchange area of 70 cm^2 is the favored oxidation method for carbohydrates [155,179]. Even though FDCA yield from this one-pot process is meager and difficult to implement, it opens up a new research field for the production of FDCA [40].

Overall, the direct conversion of sugar to FDCA (one-pot step production) is promising for several reasons. The final FDCA product using this route is cheaper than producing FDCA from an intermediate, and the sugar carbohydrate substrates are readily available. Additionally, the one-pot method avoids the risk associated with the instability of intermediate products. However, using this route to produce FDCA is inefficient as the yield is very low, especially compared to the production of FDCA from an intermediate such as HMF. Interestingly, photocatalytic routes for FDCA production are also reported, which may hold a promising future [180].

It is worth noticing that thermocatalytic oxidation processes often take place at high temperatures and high oxygen pressure. Similarly, the performance of catalytic systems based on inexpensive first-row transition metal catalysts are not as promising as precious metal catalysts. As a result, enzymatic routes gained momentum owing to their low temperature operations. Nevertheless, enzymatic catalyst also suffers high cost of genetic engineering for synthesis, less activity, lower stability and recyclability [181]. Thus, photocatalytic processes can be considered promising route to produce FDCA. Biomass derived molecules such as HMF can be photo-oxidized to produce FDCA in combination with HER

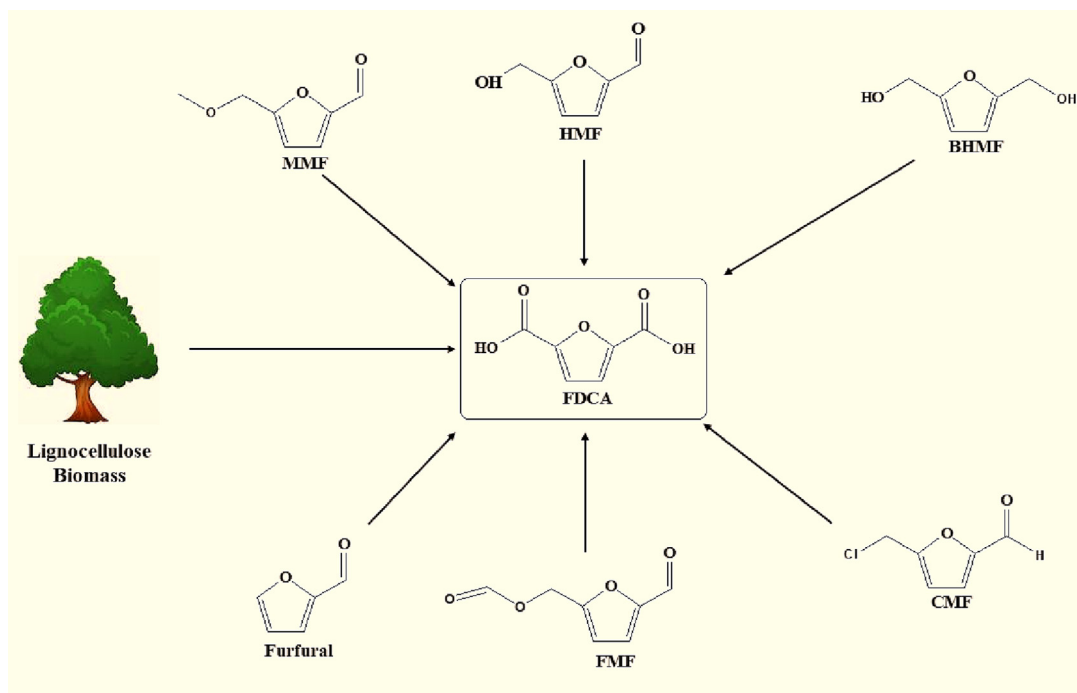


Fig. 8. Different platform chemicals for FDCA production [43].

[182]. For example, Gonzalez-Casamachin employed Zn/PPy (zinc/pyrrole) composite for photocatalytic oxidation of HMF and measured 9.12% FDCA yield and 30% HMF conversion at 40 °C [183]. Similarly, Jang et al. employed anatase TiO₂ photocatalyst NPs to measure 100% HMF oxidation and 40% FDCA yield in 24 h [184]. Moreover, Nam et al. used Fe and Cr doped CeO₂ photocatalyst to measure 40% FDCA yield from HMF [185]. In contrast, Zhu et al. employed 2.5% Au/ZnO photocatalyst to measure a relatively higher (53.9%) FDCA yield and 55.6% HMF conversion in only 5 h [180]. Nevertheless, photocatalytic production of FDCA is yet to be explored in detail and may become an interesting area of research.

9. Conclusion

FDCA production has become vital due to its wide applications in manufacturing bio-based polymers like polyamide, polyester, and polyurethanes and the synthesis of valuable biobased chemicals such as succinic acid adipic acid, furan, and FDCA ester. Notably, FDCA can be produced from a wide range of biobased feedstocks such as HMF, BHMF, CMF, FMF, MMF, and fructose, among which HMF is most widely used for the production of FDCA by the research community. In general, noble metals and precious metals such as Pt, Pd, Au, and Ru, or a combination thereof, have been used extensively as catalysts for the oxidation of HMF to FDCA. Moreover, the support of the catalyst has a crucial role in FDCA production. It is also observed that the bimetallic catalysts perform better regarding FDCA yield and recyclability. For example, Au-Pd/ZOC yielded >99% FDCA at 80 °C at 3 bar O₂ pressure in 4 h, which is significantly higher than 72.27% FDCA yield measured in the presence of monometallic catalyst Au/ZOC catalyst. However, these processes employ an excess base for achieving higher FDCA yield, leading to a more expensive method and less green synthesis approaches due to the formation of inorganic salts. Therefore, the production of FDCA in the absence of base has also been investigated and suffers from low yield, leaching of basic supports, and humins formation. It has also been observed that catalyst activity depends on various factors such as active phase,

particle size, reaction media, types of acidic and basic sites, and recyclability. Moreover, different oxidants such as O₂, air, H₂O₂, t-BuOOH, DMSO, and Dioxane can be used as oxygen sources. However, O₂ has been extensively used by the researcher because of its low cost and ease of availability. However, high pressure is required for catalytic oxidation when performed using O₂. Other oxidants such as H₂O₂, t-BuOOH, and dioxane have been employed to oxidize HMF, where safety may be a concern, especially in large-scale production. Moreover, non-noble metal heterogeneous catalysts have also been used for FDCA production. However, non-noble metal catalysts have limitations such as lower yield, longer reaction time, and high temperature and pressure.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

EA would like to thank the Science and Engineering Research Board (SERB), Government of India, for the Startup Research Grant (SRG/2020/000582) to support this work.

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2023-06-01

Elsevier

<https://doi.org/10.1016/j.mset.2023.04.005>

Prasad S, Khalid AJ, Narishetty V, et al., (2023) Recent advances in the production of 2,5-furandicarboxylic acid from biorenewable resources. Materials Science for Energy Technologies, Volume 6, June 2023, pp. 502-521