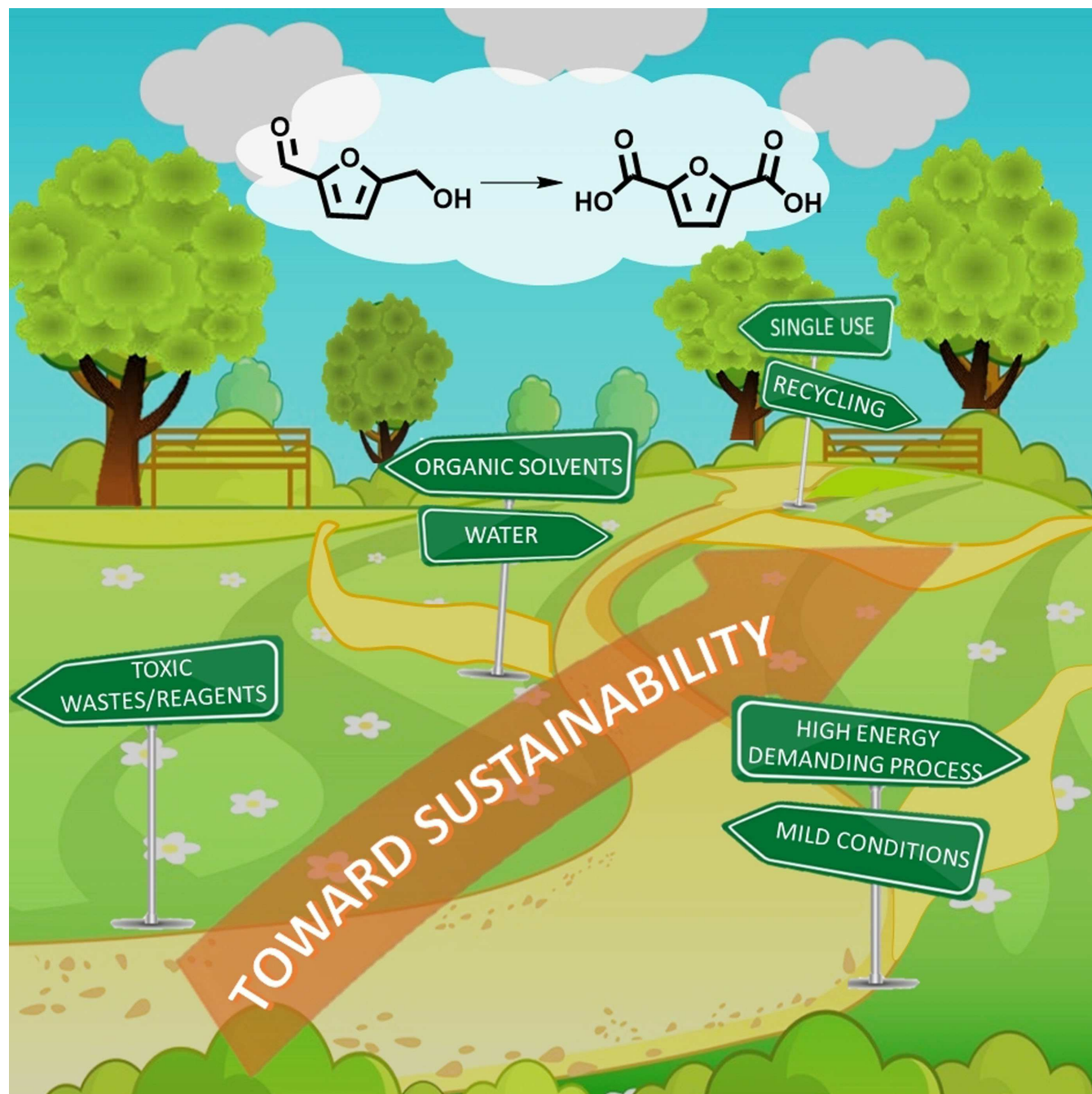




Current Advances in the Sustainable Conversion of 5-Hydroxymethylfurfural into 2,5-Furandicarboxylic Acid

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2,5-Furandicarboxylic acid (FDCA) is currently considered one of the most relevant bio-sourced building blocks, representing a fully sustainable competitor for terephthalic acid as well as the main component in green polymers such as poly(ethylene 2,5-furandicarboxylate) (PEF). The oxidation of biobased 5-hydroxymethylfurfural (HMF) represents the most straightforward approach to obtain FDCA, thus attracting the attention of both academia and industries, as testified by Avantium with the creation of a new plant expected to produce 5000 tons per

year. Several approaches allow the oxidation of HMF to FDCA. Metal-mediated homogeneous and heterogeneous catalysis, metal-free catalysis, electrochemical approaches, light-mediated procedures, as well as biocatalytic processes share the target to achieve FDCA in high yield and mild conditions. This Review aims to give an up-to-date overview of the current developments in the main synthetic pathways to obtain FDCA from HMF, with a specific focus on process sustainability.


1. Introduction

The main cause of global warming that scientists and civil society are tackling in recent years is the large amount of anthropogenic CO₂ emissions, which should be urgently reduced. The use of biomass as a monomer source can substantially contribute to solving this concern since biomass removes the atmospheric CO₂ by fixing the carbon during its growth.^[1] In this context, all monomers deriving from biomass are becoming more attractive, and their exploitation represents a challenge for the scientific community. Among all, 5-hydroxymethylfurfural (HMF), prepared by dehydration of abundant C₆ carbohydrates,^[2] represents a versatile intermediate to obtain active pharmaceutical ingredients,^[3] as well as important bio-based commodity chemicals for the synthesis of various commercially useful acids, aldehydes, alcohols, and amines.^[4] The most appealing derivatives are 2,5-dimethylfuran (DMF), a promising bio-fuel with great energy content, and 2,5-furandicarboxylic acid (FDCA), which is considered the bio-based counter-part of terephthalic acid. Indeed, FDCA has been mainly used to produce poly(ethylene 2,5-furandicarboxylic acid) (PEF), which could soon replace poly(ethylene terephthalate) (PET) in the packaging market thanks to its greater sustainability and outstanding barrier properties.^[5] The relevance of this key building block is underlined by the new plant for PEF commercialization, planned by the Dutch Company Avantium for the industrial/massive production of FDCA. The world's first flagship plant for the FDCA synthesis is currently under construction at Delfzijl and will be operational in 2024. This facility is expected to produce 5000 tons/year of FDCA, exploiting the YXY technology patented by the Company,

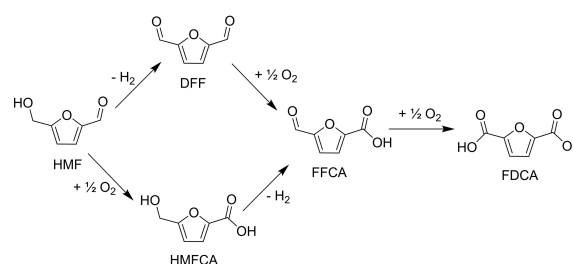
which uses fructose as a starting material.^[6] In this context, the development of a fully sustainable route to transform HMF into FDCA is important. This conversion consists of a step-wise reaction that can follow two different oxidation pathways, through 2,5-diformylfuran (DFF) or 5-hydroxymethyl-2-furan carboxylic acid (HMFCFA) (Scheme 1), which both lead to the production of FDCA.

Only a few life-cycle analysis (LCA) studies have been performed to quantify the environmental impact of FDCA synthesis.^[7–12] The reported studies point out that, comparing the production of FDCA with its direct oil-based competitor, terephthalic acid (TPA), the first one contributes to climate change with 1.60 kg of CO₂ for each kg of FDCA, while the latter one reaches the value of 1.80 kg of CO₂ per equivalent, and the fossil depletion values of FDCA and TPA are 0.44 and 1.17 kg oil equivalent, respectively.^[10] The impact of different scenarios of FDCA purification has been also evaluated,^[11] demonstrating the high effect of energy-demanding techniques such as flash separation and distillation. Very recently, Avantium with Nova Institute has reported a detailed LCA analysis regarding the production of 250 mL bottles of PEF compared with those of PET, concluding that the PEF-based products lead to a 33% decrease in greenhouse gas emission.^[6] However, these studies are characterized by high specificity, strongly influenced by the overall process analyzed, comprehensive of the characteristics of the production site, the presence of existing infrastructures, the transportation impact for feedstock supply, the availability of power supply, and so on. In any case, all the LCAs reported in the literature agree on the conclusion that the largest contribution to the environmental impact derives from the energy demand.^[9,12] Furthermore, in the sustainability perspective, biomass should be used as feedstock, toxic reagents and/or wastes should be avoided, organic solvents limited in favor of water, and the energy consumption reduced by preferring

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Scheme 1. General synthetic pathways for FDCA production from HMF

processes occurring at low temperatures or pressures and for short times.

This Review will present an overview of the most recent processes developed to convert HMF into FDCA, focusing on the sustainability of the reaction conditions. Since homogeneous catalysis requires additional steps for catalyst recovery and regeneration, which are energy-consuming, only heterogeneous and highly efficient catalytic systems will be considered. Particular attention will be paid to the highly efficient metal-based catalysis and mainly to the innovative base-free processes. Additionally, this Review will give an update on the most recent developments regarding electrochemical and photochemical catalysis, as well as enzymatic and fermentative processes, which are economic and green techniques, since they need mild reaction conditions and do not require chemical oxidants.

2. Metal-Based Catalysis

2.1. Noble metals

The synthesis of FDCA from HMF promoted by noble metals in heterogeneous catalysis represents the current benchmark for FDCA production. The huge relevance and interest in this subject are testified by the constitution of industrial processes by pioneer leaders, marking the beginning of the commercial production of FDCA.

BASF and Avantium,^[13,14] for example, designed a process in an autoclave, using a Pt/C catalyst in deuterated water. The synthesis was conducted at 100 °C for 20 h in presence of air at 10 MPa. FDCA was finally obtained with a 95% yield and the catalyst was successfully recycled. In another remarkable example, Novamont developed an optimized synthesis of FDCA exploiting a Pt/C catalyst in presence of NaHCO₃ in water at 100 °C for 4 h with 0.5 MPa oxygen. Also in this case, the desired product was obtained with a 95% yield; however, after recovery, the heterogeneous catalyst showed a decrease in reactivity.^[15]

The reported examples represent the efforts the industrial sector is devoting toward the achievement of reliable methods for FDCA production. However, important aspects such as catalyst recycling, mild reaction conditions, and overall sustainability remain key challenges. Such issues are the main targets for the current academic research in the field of supported metal catalysts. Indeed, an accurate design, as well as a controlled morphology of the catalytic system are mandatory features to conjugate the high productivity and the sustainable conditions of the reaction. The heterogeneous catalysis based on supported noble metals, such as platinum (Pt),^[16,17] gold (Au),^[18–21] ruthenium (Ru),^[22,23] and palladium (Pd),^[24,25] represents one of the most extensively studied approaches due to their good catalytic activity, and recyclability. Generally, the catalyst is assisted by bases that favor both the deprotonation of alcoholic functionalities and the hydration of aldehyde groups, facilitating the oxidation process. Very often oxygen is used as oxidant species. Table 1 shows only a selection of the most recent and relevant examples to maximize FDCA production through mild and sustainable conditions.

Outstanding results in terms of FDCA yield were obtained by carefully studying the catalytic species along with their interaction with their support. Yu et al., for example, developed an efficient catalyst by combining polyvinylpyrrolidone-capped Pt nanoparticles with chitosan-based high-surface carbon obtaining a 99% FDCA yield.^[17] The catalyst was recycled 10 times, and its activity was retained 5 times before decreasing due to nanoparticle aggregation. Also, a bimetallic Au–Pd system demonstrated high activity (97.6% yield) when supported on hierarchical bowl-like nitrogen-doped carbon (AuPd/pBNxC). In this case, the nitrogen sites provided anchoring for metals and favored HMF adsorption.^[26]

Megías-Sayago et al.^[27] and Saxena et al.^[28] respectively managed to develop very efficient catalytic systems able to work in mild temperature conditions (60–70 °C). While in the first example a simple Au/Al₂O₃ catalytic system prepared by the direct anionic exchange was studied, in the second one Saxena et al. developed metal nanoparticles encapsulated into hollow zeolites. In both cases, the yield was almost quantitative,



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Micaela Vannini graduated in Industrial Chemistry at the University of Bologna and obtained a Ph.D. in Industrial Chemistry from the same university. Her skills mainly concern the preparation and characterization of novel polymeric materials with peculiar final properties, usually polycondensates like polyesters and polyamides (especially focused on the synthesis from monomers and NMR characterization), composites, and nanocomposites. The main topic of her research is the derivation from biomasses of monomers and additives to obtain biopolymers and biocomposites. She is co-author of more than 50 publications in peer-reviewed international journals and is involved in H2020 projects (NoAW, PROLiFiC, Usable Packaging, and Preserve).

Table 1. Current advances in metal-based HMF oxidation.

Catalyst	Solvent	Base	Oxidant	<i>P</i> [Mpa]	<i>T</i> [°C]	<i>t</i> [h]	Conv. [%]	Yield [%]	Recycling [cycles]	Ref.
Pt/C	H ₂ O	NaHCO ₃	O ₂	1	110	5	99	99	5	[17]
AuPd/pBNxC	H ₂ O	Na ₂ CO ₃	O ₂	3	100	24	100	97.6	5	[26]
Au/Al ₂ O ₃	H ₂ O	NaOH	O ₂	1	70	4	100	99	5	[27]
Au Zeolite	H ₂ O	NaOH	O ₂	3	60	6	100	99	3	[28]
Au/ZrO ₂ /MgO	H ₂ O	NaOH	O ₂	0.1	35/95	4	n.d. ^[a]	95	n.d.	[29]
Pt/β-zeolite	H ₂ O	Na ₂ CO ₃	O ₂	0.1	90	24	99	90	5	[16]
Au–Pd/ Co oxide MoF	H ₂ O	NaOH or Na ₂ CO ₃	H ₂ O ₂	0.1	90	1	100	95	10	[30]
MnO ₂	H ₂ O	NaHCO ₃	O ₂	1	100	24	> 99	93	3	[32]
Mn ₂ O ₃	H ₂ O	NaHCO ₃	O ₂	1.4	100	24	100	99.5	5	[34]
Co–Mn	H ₂ O	NaHCO ₃	O ₂	1	120	5	> 99	95.2	5	[37]
Co (NP)	H ₂ O	NaHCO ₃	O ₂	0.1	100	8	100	96	n.d.	[39]
Co–lignin	H ₂ O	Na ₂ CO ₃	O ₂	0.1	85	8	100	99.5	n.d.	[40]
Co–Mn–lignin	H ₂ O	Na ₂ CO ₃	O ₂	0.1	85	10	99.7	96.1	6	[41]
Mn–Co–VC	H ₂ O	NaHCO ₃	air	1.5	130	3	100	94	6	[42]
Au/HT-AC	H ₂ O	/	O ₂	0.5	100	12	100	> 99	6	[53]
Au/MgSi-ZSM-12	H ₂ O	/	O ₂	0.1	90	24	> 99	87	5	[54]
Ru–NaY	H ₂ O	/	O ₂	1	120	8	100	94	5	[56]
AuxPd _y /NC	H ₂ O	/	O ₂	2	140	12	100	96.7	5	[59]
AuPd/nNiO	H ₂ O	/	O ₂	1	90	6	95	70	3	[60]
Pt/nNiO	H ₂ O	/	O ₂	1	100	12	100	100	5	[61]
Ru ₂ CoO _y (OH)	H ₂ O	/	O ₂	1	140	18	100	> 99	7	[63]
Pt _t Pd _r Ru/CNT	H ₂ O	/	O ₂	3	100	12	100	> 93	5	[66]
Co ₃ O ₄ /MnXCo	H ₂ O	/	O ₂	0.1	140	24	100	> 99	6	[67]

[a] n.d.: not determined.

and the catalyst offered the possibility to be recycled up to 5 times.

Extensive work was also directed toward milder conditions in terms of pressure. Rabee et al.^[29] for example, studied a series of gold-based catalysts supported on monoclinic tetragonal ZrO₂ and Mg-modified zirconia at atmospheric pressure and mild temperature, achieving FDCA with 95% yield. Liu et al.^[16] reported the successful application of β-zeolite/encapsulated Pt nanoparticles, obtaining FDCA at 90 °C and 0.1 MPa with a yield up to 90%. Specifically, the encapsulation process enhanced the thermal stability of the nanoparticles inhibiting Pt leaching, thus allowing catalyst recycling at least 5 times without reducing the activity.

Liao et al. engineered and studied Au–Pd alloy nanoparticles supported by cobalt oxide obtained via calcination of a composite of NPs encapsulated in metal–organic frameworks. The results demonstrated that in presence of hydrogen peroxide as oxidant, the alloy/support interface promotes the formation of hydroperoxyl radicals and dioxygen molecules, thus accelerating the oxidation of HMF to FDCA. As a result, 95% yield was achieved at 90 °C in 1 h while such a catalytic system demonstrated outstanding stability allowing up to 10 catalytic recycles without losing activity.^[30]

Finally, it is worth mentioning the work reported by Naim et al. where they studied the oxidation of HMF to FDCA promoted by Au/ZrO₂ focusing on the effect of common contaminants and byproducts, such as unconverted sugars, levulinic acid, and formic acid, in “realistic” conditions. The author reported that in most of the cases FDCA was produced quantitatively while only levulinic acid led to catalyst poisoning.^[31]

2.2. Non-noble metals

Non-noble metals are less expensive and more widely available than noble metals, but usually less efficient in terms of catalytic activity. To compensate for this lack of performance, the reaction conditions are usually harsher in terms of temperatures and reaction times. Non-noble metals, like their classical counterparts, often require a base addition. However, recent papers demonstrated that this performance gap was partially overcome, and catalysts based on non-noble metals could also lead to impressive results.

Among a variety of catalytic systems, manganese-based catalysts turned out to be the most active, due to the different oxidation states and the high oxygen storage of the metal, in addition to more rapid absorption and reduction of the oxygen. Mn led to remarkable results both in terms of HMF conversion and FDCA selectivity, used as it is or combined with other metals (see Table 1). Hayashi et al. demonstrated that β-MnO₂ was the most effective crystalline form of manganese oxide, achieving 93% yield of FDCA.^[32] Furthermore, even the morphology of the β-MnO₂ can affect the catalytic activity.^[33] mesoporous β-MnO₂ nanoparticles with high surface area, prepared through a template-free low-temperature crystallization method, proved more selective than β-MnO₂ prepared with the hydrothermal method. Bao et al. also found that morphology plays a key-role, synthesizing holey MnO₂ nanoflakes to obtain higher surface area and consequently extraordinary results in both HMF conversion and FDCA selectivity.^[34] Manganese oxides can also be combined with other metal oxides able to facilitate the re-oxidation of the Mn: for example, the Ce⁴⁺ present in the catalyst used by Han et al.^[35] in the ratio

Mn/Ce 6:1 led to 98.5% conversion and 91% selectivity in just 12 h of reaction. The Cu in CuMn_2O_4 spinel oxide^[36] gave FDCA in 92.1% yield, highlighting the synergistic effect of the two metals; concerning the catalysts with those single metals, the side-reactions were inhibited and the rate-limiting step of FDCA oxidation was accelerated. Therefore, the combination of different non-noble metals (one of which is Mn) has proved more promising than the use of just one, mainly in terms of time savings (see Table 1).

Another important parameter affecting the sustainability of the process concerns the catalyst preparation method: while the co-precipitation technique requires many steps and produces a large number of wastes, the solid-state grinding seems to be a very green strategy to simply produce heterogeneous catalysts, avoiding solvents, and presenting an easily scalable procedure.

In this context, Rao et al.^[37] claimed the preparation of a catalyst composed of a mixture of Mn and Co oxides, by grinding in the solid state, with further drying and calcination: this catalyst, characterized by high oxygen mobility, led to over 99% conversion and 95.2% selectivity after just 5 h of reaction. Instead, the La-MnO_2 , obtained through the more classic hydrothermal method, showed that the incorporation of the La ion^[38] increased the oxygen mobility, improving the catalytic activity and producing FDCA with 95.4% yield, after only 4 h at half working pressure. In both cases, the catalytic systems were recycled and reused at least five times without significant decrease in their performance, demonstrating once again the synergic combination of Mn with a second metal. However, considering their global availability and the sustainability of their extraction process, the use of cobalt should be preferred. And it is precisely a cobalt-based catalyst that Yang et al.^[39] focused their activities on, developing a catalytic system consisting of two different cobalt active sites: the Co single atoms and the highly dispersed Co nanoparticles. The former favored the oxidation of the alcoholic group to the aldehyde functionality, while the latter promoted the oxidation of aldehyde groups to carboxylic derivatives, thanks to the different acidity of the two active sites. The combination of these sites allowed to reach very high selectivity, even if working at ambient pressure. The efficiency of catalysts composed of Co single atoms was already exploited by Zhou et al.^[40] who further used the lignin to prepare N-doped supports: the developed metal-lignin complex gave 100% conversion and 99.5% selectivity in mild conditions, such as 85 °C for 8 h at ambient pressure. Moreover, the lignin was also exploited as a macromolecular ligand in metal-organic complexes containing Co nanoparticles:^[41] still working at low temperature and atmospheric pressure, it was possible to reach 96% conversion, and the catalyst was re-used at least 6 times without evident decrease in its activity since the N-doped carbon shell and the nanotubes protect the Co nanoparticles from leaching and deactivation. In any case, the combination of Mn and Co proved the most effective among those reported till now. Indeed, Liu et al.^[42] described the preparation of vitamin C-assisted mesoporous Mn–Co spinel oxides obtained by solid-state grinding and its use in HMF oxidation in air. This approach was fully

sustainable and very innovative, as well as easily scalable at the industrial level. According to the described strategy, vitamin C increased the concentration of oxygen vacancy (O_v) of the Mn–Co oxide, weakening the Mn–O bond intensity in the proximity of O_v and therefore increasing the lattice oxygen (O_l) reactivity, resulting in a very efficient HMF oxidation with air. Furthermore, the catalyst was recycled up to 6 times with retention of its activity, after simple regeneration at 200 °C for 2 h. In summary, catalysts based on non-noble metals are under development, and the most promising ones consist of Mn and Co, which allow obtaining high conversions and selectivity, even in very mild oxidation conditions.

2.3. Base-free catalytic systems

As mentioned before, the classical synthesis of FDCA through HMF oxidation proceeds often at high temperatures and pressure employing a variety of catalytic systems in alkaline media. The drawback of using an excess of homogeneous bases is that the processes require further acidification and purification for the subsequent use of FDCA, thus leading to a considerable amount of mineral waste and increasing the risk of reactor corrosion, hampering the green footprint of the process.^[43] The aerobic oxidation in the absence of a homogeneous base has been increasingly envisaged for large-scale industrial applications. In this sense, a variety of recoverable solid bases like hydrotalcite, used for dispersing metal nanoparticles, carbon-based materials, carbon nanotubes, graphene oxides, carbon black, or a series of basic metal oxide, like hydroxyapatite and MgAlO , were applied as basic support for heterogeneous catalysis mainly based on noble metals.^[44] Despite a relatively shorter time required for the reaction, the acidic nature of the produced FDCA might compromise the stability of the basic support, deactivating the catalyst and therefore requiring the development of dedicated strategies.^[45] A first line of research to overcome this issue deals with the use of organic solvents to prevent catalyst deactivation and erosion; however, due to safety and environmental concerns, it will not be discussed further in this Review.^[46–51] A second is focused on the design of specific catalytic systems composed of supports or co-catalysts able to withstand the reaction conditions through some recycling processes. Several active species based on Au, Pd, Pt, Ag, and Ru have been investigated under base-free conditions. In particular, many examples concern the assessment of the catalytic performances over basic supports. For instance, Sun et al.^[52] and Gao et al.^[53] investigated hydrotalcite-activated carbon support for Au nanoparticles able to impart synergistic effect thanks to the basic sites and oxygen-containing functional groups attached to the catalyst surface. Complete conversion and quantitative yield to FDCA were achieved after 12 h, 0.5 MPa O_2 at 100 °C. The influence of reaction parameters and the catalyst structure–activity relationship were also investigated, and good recyclability (6 cycles) was demonstrated. Another basic support for Au catalyst, based on Mg-bearing all-silica zeolite, was developed by Chen et al.^[54] After Mg incorporation, an almost complete conversion (> 99%)

of HMF and a high yield (87%) in FDCA was achieved at atmospheric pressure, 90 °C for 24 h. Recently, also zeolites were reported as supports for other noble-metal-based catalysts. For example, highly dispersed Pt nanoparticles were incorporated on alkaline-exchanged hierarchical ZSM-5. A total conversion of HMF with 80% of FDCA yield was achieved at 100 °C and 2.0 MPa of air.^[55] NaY zeolites were used as support for Ru nanoparticles. The 3 wt% Ru-NaY catalyst demonstrated excellent catalytic performance with complete HMF conversion and 94% yield of FDCA in 8 h (1 MPa O₂, 120 °C) and good recyclability (4 cycles).^[56] Conversely, Cai et al.^[57] prepared, by a simple colloidal method, an Au/Mg(OH)₂ catalyst, achieving high conversion and 92.6% of FDCA yield (2 h, at 0.5 MPa O₂, 110 °C). Yang et al.^[58] studied a series of base-free Au/TiO₂ catalysts modified with transition metal oxides (Fe, Co, Ni). They achieved a FDCA yield of 71.2% with low Au loading (0.5 wt%) thanks to the catalyst's ability to promote electron transfer and generation of Au^{δ-}-O_v-Ti³⁺ interface, which accelerated the adsorption and activation of the reactants.

Several papers reported also the use of Au alloyed with Pd for preventing Au deactivation promoted by the irreversible adsorption of intermediates over the Au surface. Guan et al.^[59] developed a novel hierarchical porous nitrogen-doped carbon-supported bimetallic Au/Pd catalyst possessing high basicity and efficient catalytic behavior. The maximum yield in FDCA reached 96.7% in 12 h (2 MPa and 140 °C), good recyclability was also demonstrated (5 catalytic cycles). Au/Pd alloy supported on nNiO was prepared by Bonincontro et al.^[60] The authors reported a high conversion (95%), a high yield in FDCA (70%), and a good level of stability using 1 MPa O₂ at 90 °C in 6 h. NiO was also used as support for Pt-based catalyst by Zhang et al.^[61] The catalyst reached the highest values ever reported among all the supported Pt catalysts in terms of FDCA productivity (22.2 mol mol_{Pt}⁻¹ h⁻¹) and high stability (5 catalytic cycles) in water, 1 MPa O₂ at 100 °C. Promising results in base-free aqueous conditions (5 bar O₂, 110 °C) were achieved also using Pt and Pt/Sn nanoparticles prepared from carbonyl cluster precursor on TiO₂ as support.^[62] The specific preparation enables the formation of metal particles with well-controlled dimensions, relatively low particle size distribution, and higher stability with respect to their counterpart synthesized via metal salt impregnation.

Regarding ruthenium-based catalysts, Gao et al.^[63] prepared a novel Ru-Co composite, which gave a productivity of 3.3 mol_{FDCA} mol_{Ru}⁻¹ h⁻¹ with 99.9% yield of FDCA at 140 °C and 1 MPa O₂ after 18 h.

Among noble metals, Ag catalysts, with lower prices, allow satisfactory results. Fu et al.^[64] tested CoO_x-Ag/CeO₂ in base-free conditions obtaining a yield of 71.2% (2 MPa O₂, 130 °C).

A solvent and base-free method was also proposed recently by Yu et al.^[65] employing PdO/AlPO₄-5 catalyst at 80 °C, 0.5 MPa O₂. In 5 h a conversion of 38.8% of HMF and 83.6% selectivity in FDCA were obtained.

An interesting comparative research study was conducted by Sharma et al.^[66] who analyzed the catalytic performance in 12 h in water at 100 °C and 1 MPa O₂ of Pt, Pd, Ru, Co, and Ni supported on carbon nanotubes. They found out that the

support prevented the leaching of the metals, improving recyclability (5 cycle tests). Moreover, they observed that noble metals were the most active and selective towards FDCA with a conversion of 100% of HMF and a selectivity > 93% in FDCA. In contrast, Co and Ni reached a conversion of 97.5 and 94.5%, respectively, and they were selective towards DFF.

In these last years, interesting results on the use of transition metals in base-free conditions were achieved. A remarkable example sees the exploitation of Mn-Co mixed oxide with a new morphology, which corresponds to Co₃O₄ nanoparticles decorated Mn-Co-O solid solution. The catalyst, as reported by Gao et al.,^[67] in the presence of oxygen (0.1 MPa) and water, showed high conversion (> 99%) and satisfactory performance in selectivity; however, the reaction temperature was quite high (140 °C) respect to reported Co-Mn-based benchmark catalysts and a minor activity loss was observed during recycling tests.

Although significant achievements have been made in the base-free aerobic oxidation of HMF, at the moment the noble metals based on Au, Pt, or bimetallic Pd-Au catalysts give the highest performances and comparable activities. However, the differences among the above-mentioned metals mainly lie in the effect of the alkaline catalyst support and its stability, which can shorten the reaction time and improve recycling.

2.4. Continuous-flow systems

Continuous catalytic systems for HMF oxidation are still poorly investigated despite the huge impact a reliable continuous process would have on the industrial field. However, a few remarkable examples are paving the way for a more widespread future line of research.^[44]

Lilga et al., over a decade ago, developed a continuous base-free process in a stainless-steel upflow three-phase fixed-bed reactor using air at 1 MPa and 100 °C.^[68] Among all the different Pt-based catalytic systems investigated, Pt/ZrO₂ was the best performing system, showing 98% yield of FDCA at 3 h⁻¹ of liquid hourly space velocity (LHSV).

Danielli da Fonseca Ferreira et al. performed HMF oxidation over a Ru/Al₂O₃ using O₂ in a trickle-bed reactor.^[23] FDCA was obtained with 98% yield, working at 140 °C, 3 MPa of O₂, pH 11, gas hourly space velocity (GHSV) = 900 h⁻¹, and weight hourly space velocity (WHSV) = 1 h⁻¹. In this condition, the catalyst showed high stability, retaining activity after 12 cycles and being reactivated by simple hydrothermal treatment.

It is worth mentioning the work presented by Zhao et al., combining a continuous-flow system and microwave-assisted heating on a Ru/C catalyst.^[22] While the reaction produced elevated yields in a batch setup (88% in only 30 min), the continuous process demonstrated only a partial HMF oxidation resulting in a mixture of 38% 5-formyl-2-furancarboxylic acid (FFCA) and 47% FDCA.

Finally, Liguori et al. designed a process based on a heterogenous resin-supported Pt catalyst, obtaining FDCA in 99% yield at 120 °C and 303 s of residence time.^[69] Remarkably,

the product was isolated with a space-time-yield of $46.0 \text{ g L}^{-1} \text{ h}^{-1}$ without purification steps.

3. Metal-Free Catalysis

To overcome the problems related to the use of metal-based catalysts for the direct oxidation of HMF to FDCA, such as the high cost of noble metal catalysts and their leaching that induces environmental contamination, some research studies on sustainable, cost-effective, metal-free alternatives are reported in the literature.

Specifically, heteroatom-doped (N, P, and S) carbon-based catalysts proved to be very interesting due to their high catalytic activity, low cost, simple preparation, and sustainability. The presence of heteroatoms in a carbon matrix usually causes surface defects, due to the differences in atomic radius and bond length, which can act as active catalytic sites.^[70] Among different doped carbon structures, nitrogen-doped carbon (NC) was used as metal-free heterogeneous catalyst for different reactions, including oxidations.^[71] In particular, the recent strategies tend to exploit graphitized carbon structures that are doped with N-atoms.

Nguyen et al.^[72] reported that an N-doped nanoporous graphitic carbon (NCC) catalyst could efficiently be used for oxidation of HMF to FDCA at 80°C under aerobic conditions with yields up to 80%. The authors underline the importance of the presence of nitrogen and the control of its amount and configuration in the nanoporous carbon framework. The pyrolysis of zeolitic imidazole ZIF-8 nanoparticles allowed the NNC to contain a significant amount of nitrogen, especially quaternary nitrogen (N–Q), which was regarded as graphitic N acting as a catalytic active site for aerobic oxidation. The mechanism of aerobic oxidation is supposed to be a radical process, where the N–Q sites can help generate oxygen radicals for oxidation, and the pathway of the conversion results in the sequence HMF-to-HMFA (fast step) to FFCA-to-FDCA according to Scheme 2.

In 2017 Verma et al.^[73] developed a chitosan-based solid catalyst for aerial oxidation of HMF to FDCA. A chitosan-derived, porous carbon nitride (PCNx) catalyst was obtained by calcination of chitosan, derived from marine waste, at 300°C for 4 h under a nitrogen atmosphere: the structure sees the presence of graphitized carbon at a high degree of crystallinity and glassy carbon known as graphite nitrate in a porous system with various defects. Tests on the activity of carbonaceous materials, such as graphite, graphene oxide, carbon nanotubes, and

carbon nanofibers, for the aerial oxidation of HMF to FDCA at different temperatures, confirmed the practically zero efficiency of these systems. On the other hand, the presence of graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) induced a certain conversion, whereas PCNx yields up to 80% at 70°C .

Recently, Rao et al.^[70] produced an inexpensive nitrogen-doped carbon material by carbonization of bamboo sawdust mixed with melamine and K_2CO_3 . The carbonization temperature of the catalyst controlled the amount of graphitic N and the related lattice defects in the carbon matrix and influenced the conversion of HMF to FDCA, thus confirming previous literature results.

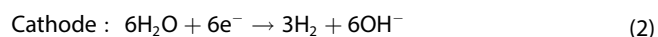
It is also interesting to underline the efforts to obtain these catalysts from biomass and waste, according to the necessity of decreasing costs, and also the efforts to demonstrate the possibility of recovering them after use. For example, PCNx catalyst^[73] can be recovered using membrane filters and reused up to 5 times without any loss in its activity.

In conclusion, it is clear that this approach, based on green and cheap metal-free catalysts, can have a significant impact on the application of HMF oxidation at the industrial level, and further studies on this promising field are expected.

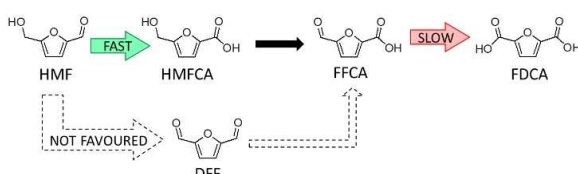
4. Electrochemical and Photocatalytic Methods

4.1. Electrochemical oxidation

Electrocatalytic oxidation reaction of HMF (HMF-EOR) is a very promising process for clean and green conversion of HMF to FDCA,^[74] particularly in a perspective in which renewable energy will gain a predominant role. The synthetic process is driven, through electron migration under mild conditions, by the electrochemical potential, thus eliminating the need for any external oxidant.^[75] The development of HMF electrochemical oxidation is gaining increasing importance since it mainly needs non-noble metal catalysts at ambient temperature. Another important feature of this process, which makes it even more interesting from an environmental point of view, is the concomitant production of H_2 that occurs at the cathode during the HMF anodic oxidation according to the following process [Eqs. (1)–(3)]:



Indeed, the H_2 gas produced by water splitting on the cathode can be recovered and exploited as a clean and green source of energy.^[76] Moreover, the cathodic reaction can be also used to reduce chemical reagents to obtain intermediates and monomers.^[75,77] The ranking of the efficiency of catalytic systems for HMF oxidation, in this case, must also consider the faradaic efficiency (FE) that describes the efficiency of the



Scheme 2. Aerobic oxidation mechanism of HMF.

electric charge transfer in the system that causes the electro-oxidation reaction.

The process generally uses heterogeneous catalysts to obtain high conversion and yields, but homogeneous catalysis can also be used by means of a mediator. Indeed, homogeneous catalysts can get in close contact with the reactants, thus providing higher yields and better FE without any pH adjustment.^[75] Choi et al.^[78] have reported that the use of 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO) as a mediator greatly reduced the overpotential requirements for HMF oxidation by suppressing water oxidation, obtaining a 98% yield with more than 93% of FE. However, a noble metallic electrode (Au) and excess TEMPO were used, causing a high cost of the process. More recently, the same authors^[79] replaced TEMPO with the less expensive 4-acetamido-TEMPO (ACT) and used carbon felt instead of Au as the electrode, with a 99.8% HMF conversion and 91.5% FDCA yield. Li and co-workers^[77] showed the concurrent electrocatalytic conversion of HMF to FDCA at the anode and to 2,5-bis(hydroxymethyl)furan (BHMF) at the cathode with a yield of 98% for FDCA and of 85% for BHMF. This work showed that HMF can be simultaneously converted into two important biobased polymer precursors in one cell.

The problems concerning the difficult separation of reaction products can be tackled with heterogeneous catalytic systems based on noble metals such as Pt, Pd, and Au. For example, Pt-containing catalysts based on PtNiS_x/carbon black were used to produce FDCA with 100% HMF conversion, FDCA yield up to 99%, and a FE of 98%.^[80]

The presence of the alkaline electrolyte provides the possibility for the use of non-noble transition metal-based compounds as catalysts for HMF-EOR. In the last few years, researchers are focusing almost all their efforts on the development of non-noble metal catalysts due to their lower costs and better catalytic performances. Non-noble metal-based catalysts comprise phosphides, sulfides, borides, nitrides, hydroxides, oxyhydroxides, and oxides. Indeed, a very large number of examples^[75] of these catalysts were published in the last decade; however, this Review will just report the most recent advances.

Nickel- and cobalt-based catalysts were deeply investigated in the last years. For example, Co–P catalysts^[81] were recently prepared in water and deep eutectic solvents (DES) obtaining more stable catalysts with a FDCA yield of 85.3%. Wang and co-workers^[82] modified the NiB_x catalyst by doping different amounts of phosphorus and demonstrated that NiB_x-P_{0.07} reached a maximum yield of FDCA (90.6%) and FE (92.5%). Poerwoprajitno et al.^[83] reported in 2020 the use of Ni-based catalysts for HMF-EOR, fabricating cubic-core and hexagonal-branched 3D Ni nanoparticles that outperformed amorphous Ni sphere nanoparticles.

Non-noble metals hydroxides, oxyhydroxides, and oxides were also deeply investigated. In particular, Zhang et al.^[84] synthesized NiCoFe layered double hydroxide (LDH) nanosheets comparing them with NiCo and NiFe LDHs. NiCoFe LDH outperformed the other two catalysts with an 84.9% yield and a conversion of 95.5%. In 2019 Choi and co-workers^[85] compared

the intrinsic catalytic properties and investigated the reaction mechanisms of NiOOH, CoOOH, and FeOOH. The highest conversion (99.8%), FDCA yield (96%), and FE (96%) were obtained with NiOOH as catalysts. Chen et al.^[86] prepared a Cu–Ni bimetallic catalyst obtaining 100% conversion of HMF with 93.3% yield. Zhou et al.^[87] reported a modified cobalt oxide catalyst with needle-like shaped Co₃O₄ nanowires that were in-situ anchored on nickel foam, forming a 3D monolithic electrode, obtaining 100% HMF conversion with 96.8% yield and 96.6% FE. In 2020, Holzhäuser et al.^[88] synthesized meso-structured NiO catalysts that proved to be more efficient with respect to bulk NiO catalysts, achieving 60% HMF conversion and 100% selectivity. A 3D highly ordered mesoporous Co₃O₄/nickel foam electrode has also been recently tested^[89] obtaining a full conversion of HMF and >99.8% yield of FDCA with an outstanding almost full FE. Lu et al.^[90] developed a CuCo₂O₄ catalyst grown on 3D porous Ni foam, achieving 93.7% FDCA yield and 94% FE.

The use of core-shell structures has also been widely investigated, and since 2018 a growing number of papers have been published on this subject since these catalysts possess active sites and conductive species at the same time.^[75] Zhang et al.^[91] reported that a carbon-coupled nickel nitride nanosheet electrode provides a 98% FDCA yield with a FE of almost 99% even after 6 successive electrolysis cycles, highlighting the excellent stability of this catalyst. Recently, Deng et al.^[92] prepared copper sulfide nanowires/NiCo-LDH nanoarrays. The copper sulfide core possesses superior conductivity and the porous NiCo-LDH provided sufficient active sites, providing an outstanding electrocatalytic activity. Also, NiSe was converted into a core-shell structure, covered by a nickel oxide/hydroxide shell, proving to have good catalytic activity and superior stability for water splitting and methanol oxidation.^[93] Wang et al.^[94] recently reported Ni/NiO nanoparticles encapsulated in oxygen-doped graphene as multifunctional electrocatalysts for hydrogen evolution, urea oxidation, and HMF-EOR. The oxygen-graphene shell plays a fundamental role in increasing the stability and activity of Ni/NiO since protects the Ni-based catalyst from the alkaline electrolyte and provides active sites for the reaction.

4.2. Photocatalytic reactions

Along with electrocatalysis, photocatalysis is a promising method to realize the conversion of HMF into FDCA in mild conditions.^[95] In general, the photocatalytic process is initiated by light irradiation with energy equivalent to, or greater than the bandgap (E_g) of a semiconductor (used as a catalyst). As a result, electrons in the valence band (VB) are excited into the conduction band (CB), leaving holes in the VB. Reduction and oxidation reactions are induced by such photo-generated electrons and holes. Superoxide and hydroxyl radicals (O_2^- and OH^\bullet) seem to be the key reactive species in photo-oxidative catalysis in presence of water: the photo-generated electrons can reduce the O₂ molecules to form O_2^- , and the photo-

generated holes may extract electrons from organic substrates or produce $\bullet\text{OH}$.^[96]

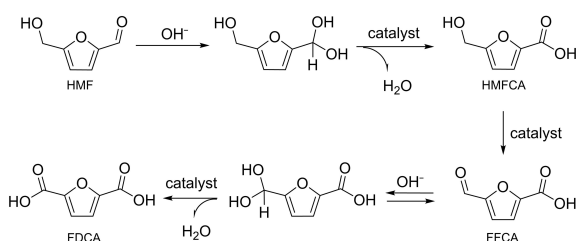
The mechanism of HMF oxidation to FDCA by photocatalysis is still a matter of discussion; however, the stepwise oxidation of HMF to FDCA in alkaline aqueous media, a combination of chemical and electrochemical studies, proposed by Li and Na, is described in Scheme 3.^[96]

The nucleophilic addition between HMF and a hydroxide ion determines the formation of a diol intermediate. In the presence of hydroxide ions and catalysts, HMFCFA is formed, which can be further oxidized to FFCA. FDCA is obtained following another nucleophilic addition between a hydroxide ion and FFCA.

Xu et al.^[97] used cobalt thiopyrphazine (CoPz) dispersed on $g\text{-C}_3\text{N}_4$ in an aqueous solution (pH 9.18) using O_2 molecules from the air as the oxidant. The use of composite with respect to CoPz alone is advantageous since the yield of FDCA increases (96.1 vs. 36.2%) since $g\text{-C}_3\text{N}_4$ ($E_g = 2.7$ eV) can inhibit the aggregation of CoPz and increase the active sites available. Moreover, a high pH seems to favor the FDCA selectivity, and CoPz/ $g\text{-C}_3\text{N}_4$ can be recycled 5 times without a noticeable decrease in either conversion of HMF or the selectivity towards FDCA.^[95] Literature also reported a few examples of photocatalytic oxidation of HMF coupled with hydrogen production. Han et al.,^[98] for example, prepared Ni loaded on ultrathin CdS nanosheets (Ni/CdS) to achieve HMF oxidation coupled with H_2 production under visible light. The authors demonstrated that, in alkaline aqueous media, a quantitative conversion of HMF into FDCA can be obtained, due to the Cannizzaro mechanism. In addition, Ni/CdS can be recycled 4 times without any decrease in photocatalytic performance.

Two examples of TEMPO-mediated HMF oxidation are reported by Cha et al.^[99] and Chadderon et al.^[100] TEMPO-mediated HMF oxidation could be initiated by an n-type BiVO_4 photoanode, achieving a quantitative conversion of HMF into FDCA (yield 100%) at the photoanode while H_2 is produced at the cathode. If cobalt phosphate is deposited on nanoporous BiVO_4 film, the charge separation in the photoanode should be favored, and FDCA is obtained with a yield of 88% after the total conversion of HMF.^[100]

In summary, electro- and photocatalytic oxidation of bio-based HMF into FDCA has shown excellent efficiency in terms of conversion, selectivity, yield, and reuse, highlighting those systems as very promising at a laboratory scale.



Scheme 3. Mechanism of HMF oxidation to FDCA in alkaline aqueous media, proposed by Li and Na.^[96]

5. Biocatalytic Methods

The interest in biological methods, such as the whole-cell and enzymatic catalysis, for the production of FDCA, is due to the mild reaction conditions, the high selectivity, and the environmentally friendly process (aqueous solvent, benign oxidant, biodegradable catalysts, low energy costs).

The biological production of FDCA involves mainly microorganisms or enzymes, and recent studies have focused on new enzymes and microorganisms with oxidative activity to produce FDCA from HMF.

5.1. Whole-cell catalysis

The whole-cell biocatalytic process is based on the natural detoxification mechanism of microorganisms. Aldehydes, such as HMF, are toxic molecules for living organisms; some microorganisms, like bacteria and fungi, developed detoxification mechanisms to convert toxic HMF to “non-toxic” molecules, and this mechanism can be exploited for FDCA production. This biotransformation process has important advantages and is receiving increasing attention in recent years.^[101–110] In fact, the whole-cell catalysts are often robust, benefitting from a protective barrier, reactive substrates, endogenous cofactors, and enzymes that perpetuate catalytic pathways and inhibit by-products.^[111,112] In the last years, several microorganisms involved in HMF conversion to FDCA have been studied.^[113–116] In particular, *Burkholderia cepacia* H-2^[113] and *Methylobacterium radiotolerans* G-2^[110] proved to be robust, showing their capacity to maintain HMF conversion even in the presence of microbial inhibitors and unfavorable media conditions. However, the FDCA production obtained with these biocatalysts was low, indicating the importance of genetic engineering approaches for the bioconversion of HMF.

In general, different approaches were attempted to increase FDCA production by whole-cell catalysis, such as parameter optimization (media conditions),^[110,113,117,118] genetic engineering,^[119–121] and the use of integrated strategy.^[101,122–124]

Regarding the genetic engineering approach, the highest FDCA production was obtained via the expression of two genes (HmfH and HMFO) in the *R. ornithinolytica* BF60 strain.^[119]

A tandem whole-cell cascade was reported by Tan et al.^[122] The combination of *P. Putida* and *E. Coli* led to full bioconversion of HMF to FDCA with a bioconversion rate much faster than other reported biocatalysts.

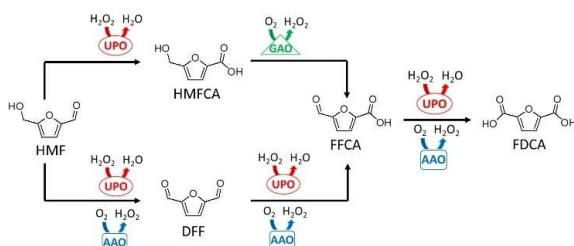
Although the whole-cell catalysis can be considered a promising system for future applications, some aspects still have to be improved, such as the low product recovery and the continuous carbon source feeding. Recently, the studies on the whole catalysis also addressed filamentous fungi, which possess unique characteristics and may have more advantages than bacteria. Indeed, filamentous fungi are particularly robust, they can tolerate a wide range of reaction conditions, and accept a broad scope of carbon sources.^[125]

5.2. Enzymatic catalysis

Compared to whole-cell processes, the use of pure enzymes allows highly efficient reactions, since there are neither impure products nor competing reactions due to other components. On the other hand, the isolation and purification of proteins are expensive, and enzymes can be more sensitive to temperature and pH than microorganisms.^[104,126]

When it comes to the oxidation of HMF into FDCA, most of the time, a single enzyme is not able to catalyze the oxidation of both the alcoholic and aldehydic moieties since its activity is limited to either alcohol oxidation or aldehyde oxidation; therefore, multi-enzyme cascade reactions, cofactors, mediators, or mutation are required.^[102] More in-depth, many efforts were devoted to studying the synthetic pathways promoted by different enzymes. Cajnko et al.^[127] tested six different enzymes against HMF and its oxidation products in order to develop a kinetic model and understand the action mechanisms of different enzymes. Some of the enzymes that showed activity against these products were fungal aryl-alcohol oxidases (AAOs), unspecific peroxygenases (UPOs), galactose oxidase (GAOs), laccases, and catalases. If the mechanism of a single enzyme is relatively easy to study, when it comes to multi-enzyme cascade reactions the mechanism becomes more complicated, since enzyme-enzyme interactions need to be considered. Different aryl-alcohol oxidases were used in multi-enzyme cascade reactions. AAOs are flavoproteins that are active on benzylic alcohol and hydrated aldehydes, therefore are able to oxidize HMF and its derivative DFF producing FFCA while reducing molecular oxygen to hydrogen peroxide. Karich et al.^[128] developed a multi-enzyme process using three fungal enzymes, i.e. wild-type AAO, a wild-type peroxygenase from *Agrocybe aegerita* (*AaeUPO*), and recombinant galactose oxidase (GAO) described in Scheme 4. However, the amount of UPO used was far from being realistic and the oxidase needed to be minimized in order to keep H₂O₂ at levels that did not damage UPO.

Similarly, AAO from *Moesziomyces antarcticus* (MaAAO) was combined with unspecific peroxygenase completing the conversion of HMF into FDCA within 144 h.^[129] In particular, MaAAO oxidized HMF to DFF and FFCA, while UPO completed the conversion of FFCA into FDCA. H₂O₂ produced during the oxidation of HMF to DFF and FFCA was found to have an inhibitory effect on AAO, causing a lack of activity on FFCA. By adding catalase that removed H₂O₂ from the reaction mixture,



Scheme 4. Multi-enzyme cascade pathway for FDCA synthesis.

an AAO from the white-rot fungus *Pleurotus eryngii* was used to obtain FDCA directly from HMF.^[130] An AAO from *Ustilago maydis* was coupled with a glyoxal oxidase (PciGLOX3) from the *Basidiomycete fungus Pycnoporus cinnabarinus* to increase the yield of FDCA. Indeed, FDCA was detected only when PciGLOX3 was added to the reaction, reaching a 16% yield after 24 h, in the presence of catalase, which removed the self-inhibition influence of H₂O₂.^[131]

Catalase was also used to improve the activity of a 5-hydroxymethylfurfural oxidase (HMFO), which is reported as a promising biocatalyst for FDCA production but is highly susceptible to hydrogen peroxide concentration and FFCA intermediate in a pH-dependent way.^[132] Indeed, the addition of catalase to remove H₂O₂ and the controlled dosage of the substrate to keep the amount of FFCA formed under control allowed to overcome these limitations. HMFO is one of the few enzymes able to catalyze the three consecutive oxidation steps for the production of FDCA from HMF. Viñambres et al.^[133] identified and purified a new HMFO from *Pseudomonas nitroreducens*, which exhibited good performance in wide pH and temperature ranges, high tolerance for the hydrogen peroxide formed, and high yields. HMFO was also used in cascade reactions for the oxidation of HMF into DFF and FFCA and coupled with a lipase Novozym 435, which completed the conversion of FFCA into FDCA.^[134]

Galactose oxidase (GAO) was used in different cascade reactions in combination with other enzymes. Birmingham et al.^[135] coupled it with UPO to create an oxidative cascade from HMF to FDCA. The combination of GAO with alcohol dehydrogenase (ADH) and horseradish peroxidase (HRP) implemented the process to obtain FFCA and FDCA from HMF by internal recycling of H₂O₂.^[136]

Laccase is a blue multi-copper oxidase able to oxidize alcohols in the presence of mediators (e.g., TEMPO), under mild conditions. This catalytic system was used to produce FDCA from HMF in 28 h with a yield up to 97%, using air as the oxidant and producing water as the sole by-product, but with a very low substrate concentration (HMF up to 100 mM).^[137] A tandem reaction was developed by Chang et al., used laccase (CotA-TJ102@UIO-66-NH₂) and lipase Novozym 435. Laccase oxidized HMF to FFCA, then the lipase was added to complete the oxidation to FDCA. Both enzymes exhibited high recyclability. The enzymatic production of FDCA from HMF could be more advantageous if the enzymes could be reused. The immobilization of enzymes could prevent loss of activity and could be a good technique to recover from economic loss for industries.^[102,103] A laccase-TEMPO was immobilized on magnetic particles to obtain FDCA with complete HMF conversion after 96 h, exhibiting good recyclability and stability, despite the long reaction time.^[138]

Enzyme engineering could also be a solution for the direct oxidation of HMF to FDCA, preventing the use of multi-enzyme cascade reactions. Indeed, an AAO was engineered to improve its activity and used to perform the entire three consecutive oxidation cascade.^[139] The variant of 8BxHFMO from *Methylovorus sp.* MP688 was engineered to improve its stabilization since it is one of the few reported enzymes able to catalyze the complete oxidation of FDCA from HMF.^[140]

5.3. Integrated processes

Several recent types of research employ a combination of enzymes and whole-cell biocatalysts intending to match the advantages of the two methods.^[101,123,124] For example, one-pot synthesis of FDCA from HMF by utilizing the complementary catalytic activities of *Comamonas testosteroni* SC1588 cells and laccase/TEMPO system was reported by Yang et al.^[123] The new chemo-enzymatic approach to FDCA production was developed and the problematic TEMPO toxicity towards microbial cells that was described can be solved by continuous-flow technology and solvent engineering.^[141] Zou et al.^[124] used TEMPO/laccase system coupled with *Pseudomonas Putida* KT2440 to obtain 100% HMF conversion and selectivity of FDCA under mild conditions, without complex gene modification, enzyme purification, or expensive cofactor addition.

More recently, a cascade system comprising *T. reesei* whole cells (filamentous fungal strain) coupled with laccase-TEMPO was used for the production of FDCA from HMF, with a molar yield of 88% in 80 h.^[125]

6. Conclusions and Perspectives

This Review tackles the challenge to give a comprehensive overview of the most recent developments for the sustainable transformation of 5-hydroxymethylfurfural (HMF) into 2,5-furandicarboxylic acid (FDCA) and portrays an ever-evolving field for this industrially relevant reaction.

The enormous relevance of this synthesis, driven by industrial and academic interests, is testified by the development of a variety of several complementary pathways emerging to combine high production and sustainability.

Up to date, the specific design of the heterogeneous metal-based catalyst architectures helps to develop processes presenting outstanding yields and involving cheap metals even in absence of alkaline conditions, avoiding undesired byproducts and favoring catalyst recycling.

Electro- and photocatalysis show excellent performance in the laboratory stage. In particular, in a perspective in which renewable energy will gain a predominant role, the electrocatalytic oxidation reaction constitutes a very promising process for clean and green conversion of HMF to FDCA. Moreover, the oxidation process simultaneously produces H₂ that can be used as fuel or reactant. However, the components of electro- and photocatalytic devices have not been standardized, and the costs are high. Therefore, efforts should be made in the transfer of such catalytic processes from laboratory to industrial scale, trying to maximize the catalyst recovery in order to minimize the overall production costs.

Biotechnological transformations involving cells and enzymes are attracting an increasing interest due to presenting the best performances in extremely mild conditions. Unfortunately, the complexity of the reaction environment, as well as the difficulties in FDCA isolation and purification currently undermine the viability of such an approach for large-scale production.

Finally, it is worth underlining the evolution of new frontier approaches: heterogeneous metal-free catalysis and continuous HMF oxidation are still poorly explored despite their outstanding potential.

Although the technologies hereby discussed objectively differ in key parameters such as reaction conditions, scale, productivity, time of reaction, costs of execution, product isolation, and the technology readiness level (TRL) to be unambiguously compared from a techno-economical point of view, some relevant trends can be evinced. While the current technological advancement seems to crown metal-based heterogeneous catalysis as the most suitable industrial approach due to the high productivity and the reliability of the catalytic systems, electrocatalytic processes are gaining tremendous attention, in particular when in correlation with renewable energies exploitation.

Indeed, synthetic pathways involving metal-free systems, light, and biocatalysts currently do not constitute viable alternatives from an industrial perspective, but on the other hand they represent the newborn academic approaches aiming at future safe and sustainable processes for FDCA production.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: 2,5-furandicarboxylic acid · biocatalysis · electrocatalysis · heterogeneous catalysis · photocatalysis

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