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Catalytic Methods to Produce 2,5-Furandicarboxylic Acid from Glucose

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Abstract

The new avenue in the realm of catalysis and in chemical industry is the paradigm shift from fossil based to biobased inventory, including the feedstock. Biomass is found to be a promising substitute to petroleum-based feedstock. Almost all the chemicals that could be derived from the conventional petro-refinery can be obtained from the bio-refinery with the intelligent use of Catalysis for the conversion of biomass selectively to the target product in an atom and energy efficient way. Conversion of glucose to 2,5-furandicarboxylic acid is such a challenge to catalyst chemists. There are two key steps involved in the conversion of biomass (cellulose) to 2,5-FDCA. One is to stop the conversion of cellulose at the intermediate stage of the formation of 5-hydroxymethylfurfural avoiding the most feasible product, i.e., the levulinic acid and then converting the key intermediate of the cellulose hydrolysis process via glucose isomerization and dehydration, namely, the 5-HMF to 2,5-FDCA using a potential redox catalyst. Of course, we all know that noble metals (Pt, Pd, Au on carbon or TiO_2 or some other inert support) are the best for this purpose. But chemical industry does not have the luxury of using noble metal catalyst for producing 2,5-FDCA. So, the obvious next choice is to go for non-noble metal-based metal oxides. Enormous work is done on this issue and such efforts are highlighted. An insight into the significant progress in the understanding of the catalytic pathways and the reaction mechanisms for the selective conversion of glucose to 2,5-FDCA is provided. Essentially, a fine balance between the basicity (alkalinity) and redox property of the catalyst appears to be the key for the selective conversion of glucose to 2,5-FDCA. Novel catalytic system, like the ammonium salt of molybdophosphoric acid, remains to be explored for the application.

Keywords: 2,5-furandicarboxylic acid, 2,5-FDCA, glucose valorization, 5-hydroxy methyl furfural, catalyst, polyethylene furanoate, climate action, renewable energy

INTRODUCTION

2,5-Furandicarboxylic acid (2,5-FDCA) has emerged as a pivotal bio-based platform chemical for sustainable polymer production, particularly as a renewable replacement for petroleum-derived terephthalic acid in the synthesis of polyethylene furanoate (PEF), a high performance polymer used for packaging and carrying applications [1, 2] A comprehensive analysis of catalytic methods for 2,5-FDCA production from glucose, encompassing both direct one-pot conversion strategies and sequential two-step approaches involving 5-hydroxymethylfurfural (5-HMF) as an intermediate [3, 4]. The transformation pathway typically involves glucose isomerization to fructose, dehydration to HMF, and subsequent oxidation to 2,5-FDCA through various intermediates including 2,5-diformylfuran (DFF), 5-hydroxymethyl-2-furancarboxylic acid (HFCA), and 5-formyl-2-furancarboxylic acid (FFCA) [5].

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Recent advances in heterogeneous catalysis have shown remarkable progress in developing sustainable, cost-effective alternatives to noble metal catalysts. Traditional catalytic systems based on Au, Pt, and Pd supported materials have demonstrated impressive 2,5-FDCA yields exceeding 90% [6, 7], while emerging non-noble metal catalysts, particularly nickel-based systems (S and P doped FeNi layered double hydroxides), showed promising performance with yields reaching ~83% under optimized conditions. Noble metal catalysts, such as Au-Pd bimetallic systems on activated carbon, have achieved exceptional selectivity with 99% 2,5-FDCA yield and excellent recyclability over multiple cycles [8] though their high cost and limited availability pose significant challenges for industrial scalability. Interestingly, recent investigations into nickel oxide (NiO_x) catalysts have revealed yields of 34.14% with 42.57% selectivity under remarkably mild conditions at just 25°C. What makes these nickel catalysts particularly exciting is their ability to maintain catalytic activity when processing crude 5-HMF derived directly from glucose, demonstrating practical applicability to real biomass feedstock without extensive purification [1].

This review examines the critical process parameters that can make or break 2,5-FDCA production, including reaction temperature, oxidant selection (O_2, air, H_2O_2, NaClO), base concentration, catalyst loading, and solvent systems [9–11]. Multiphase reaction systems employing biphasic and triphasic configurations have shown particularly impressive results by facilitating 5-HMF extraction and preventing unwanted side reactions [3]. For direct glucose-to-2,5-FDCA conversion, researchers have achieved yields of 52–78% using integrated catalytic systems with acid catalysts for dehydration (HCl, $AlCl_3$, Amberlyst-15, $CrCl_3$) coupled with oxidation catalysts [5, 12], while two-step processes with intermediate purification can push yields up to an impressive 98% [6, 8]. The key insight here is that process intensification strategies, including controlled oxidant dosing and optimized catalyst-support interactions, have proven essential for maximizing 2,5-FDCA selectivity while minimizing humin formation and other undesired by-products [12–14].

Looking ahead, this review highlights the importance of developing integrated catalytic systems that strike the right balance between efficiency, sustainability, and economic feasibility. The path forward involves designing multifunctional catalysts capable of performing both dehydration and oxidation reactions, developing green solvents and separation technologies, and successfully scaling up processes from laboratory to industrial production [15–20]. The transition from fossil-based to bio-based polymer precursors will require continued innovation in catalyst design, process optimization, and downstream purification to establish 2,5-FDCA as a commercially viable building block for the circular bioeconomy.

The global transition toward sustainable materials and renewable resources has sparked intense research into bio-based platform chemicals derived from abundant biomass feedstock. Among these emerging materials, 2,5-FDCA has captured considerable attention as a promising renewable substitute for petroleum-derived terephthalic acid in polymer synthesis. What makes 2,5-FDCA particularly interesting is its role as a key monomer in producing polyethylene furanoate (PEF), a biopolymer that actually outperforms conventional polyethylene terephthalate (PET) in terms of thermal stability and barrier properties [2]. This superior performance has opened up exciting applications in food packaging, textiles, electronics, and automotive manufacturing, suggesting that 2,5-FDCA could play a crucial role in the materials of tomorrow.

However, synthesizing 2,5-FDCA from glucose is far from straightforward. The process represents a complex multi-step transformation involving sequential dehydration and oxidation reactions [3–5]. Glucose, as the primary building block of cellulosic biomass, must first undergo isomerization to fructose, followed by acid-catalyzed dehydration to yield 5-HMF, which then undergoes selective oxidation to produce 2,5-FDCA [6, 12]. This conversion pathway presents several significant technical hurdles, including the frustrating formation of unwanted by-products like humins and levulinic acid, catalyst deactivation over time, and the challenge of achieving selective oxidation under mild conditions. These complexities have driven extensive research efforts into developing efficient catalytic systems capable of maximizing 2,5-FDCA yields while minimizing environmental impact and keeping production costs reasonable.

The industrial interest in 2,5-FDCA production is quite real and growing. Major chemical companies have made significant investments in this technology, with production capacities projected to reach an impressive 120,000 tons per year. Companies, such as Avantium, AVA Biochem, Origin Materials, Corbion-BASF, and DuPont-ADM, have each developed their own process technologies, though achieving economically viable large-scale production remains a challenge that the industry is still working to overcome [2, 10]. The bottom line is that cost-effectiveness depends critically on three factors: catalyst performance, product purification efficiency, and the ability to process crude biomass-derived feedstock without requiring extensive intermediate purification steps.

REACTION PATHWAYS AND MECHANISMS

Conversion of Glucose to 5-HMF via Isomerization and Dehydration

Converting glucose to HMF is a bit more complicated than it might first appear. The process proceeds through a two-stage mechanism that requires initial isomerization to fructose followed by triple dehydration [3, 12]. Unlike fructose, which can undergo direct acid-catalyzed dehydration through a cyclic pathway, glucose needs an additional isomerization step, typically catalyzed by Lewis's acids or base catalysts. Researchers have explored various catalysts for this transformation, including chromium chloride ($CrCl_3$), aluminum chloride ($AlCl_3$), mineral acids (HCl, H_2SO_4), solid acid catalysts (Amberlyst-15, niobium phosphate), and ionic liquids. This isomerization step often becomes the bottleneck in glucose-to-2,5-FDCA processes, with fructose yielding 5-HMF much more efficiently due to its more favorable ring structure.

The major challenge in 5-HMF production from glucose is the competing formation of undesired by-products, particularly humins. Humins are the insoluble polymeric materials formed through condensation reactions of furanic intermediates which will reduce the yield of the target product. Humin formation gets worse under acidic conditions and elevated temperatures, which means researchers need to carefully walk a tightrope when optimizing reaction parameters. Solvent selection turns out to play a crucial role here, with biphasic systems (water/organic solvent) showing much better results by continuously extracting HMF from the aqueous phase, effectively protecting it from degradation and preventing humin formation.

5-HMF Oxidation to 2,5-FDCA

The oxidation of 5-HMF to 2,5-FDCA can take two quite different routes, depending on whether you have base present in the reaction system. In base-catalyzed oxidation, the aldehyde group of HMF gets oxidized first to form 5-hydroxymethyl-2-furancarboxylic acid (HFCA) as the initial intermediate, which then oxidizes further to 5-formyl-2-furancarboxylic acid (FFCA), and finally makes it all the way to 2,5-FDCA. This pathway dominates in alkaline media and is characterized by rapid HFCA formation followed by a somewhat slower oxidation to the final 2,5-FDCA product.

In base-free oxidation systems, things work differently – the hydroxymethyl group gets oxidized preferentially to form 2,5-diformylfuran (DFF) as the primary intermediate [14, 15]. This pathway has been elegantly confirmed through isotope labeling studies, which revealed the surprising fact that oxygen atoms in the carboxylic groups actually come from water rather than molecular oxygen [7, 15]. The mechanism involves reversible hydration of aldehyde groups to germinal diols, followed by hydride abstraction and transfer to the metal catalyst surface, with subsequent formation of carboxylic groups through water-mediated proton regeneration.

CATALYTIC SYSTEMS FOR 2,5-FDCA PRODUCTION

Noble Metal Catalysts

Gold-based catalysts have proven to be real stars in 5-HMF oxidation, with supported gold nanoparticles on hydrotalcite (Au/HT) achieving impressive 2,5-FDCA yields up to 98.8% under the right conditions. The exceptional selectivity of gold catalysts stems from their unique electronic properties and remarkable ability to activate molecular oxygen at relatively low temperatures. However, there's a catch – monometallic Au catalysts tend to suffer from deactivation due to irreversible adsorption of intermediates and gold particle agglomeration, which limits their long-term stability and recyclability.

Bimetallic Au-Pd catalysts have emerged as superior alternatives, cleverly combining the high activity of gold with the stability of palladium. Researchers have found that an 8:2 molar ratio of AuPd on activated carbon hits the sweet spot, achieving an outstanding 99% 2,5-FDCA yield with excellent recyclability over five consecutive cycles [8]. The synergistic effect between Au and Pd enhances electron transfer processes and prevents catalyst deactivation, making these systems commercially attractive despite their admittedly high cost.

Platinum-based catalysts have also delivered promising results, with Pt/C achieving a respectable 81% 2,5-FDCA yield under notably mild conditions – just 1 bar O_2 at 25°C – in alkaline medium [7]. Adding promoters, such as lead into Pt/C catalysts, can push the activity even further by modifying electronic properties and improving resistance to poisoning. Ruthenium catalysts offer yet another interesting option, particularly when paired with hydrogen peroxide as the oxidant, demonstrating 91% 2,5-FDCA yields [11]. This approach provides an alternative to oxygen-based systems and enables reactions under even milder conditions.

Non-Noble Metal Catalysts

The development of earth-abundant transition metal catalysts represents what many consider the holy grail for economically viable 2,5-FDCA production. Nickel-based catalysts have emerged as particularly promising alternatives to noble metals, offering significant cost advantages while maintaining reasonable catalytic performance [1, 9, 14]. Recent studies on nickel oxide (NiO_x) catalysts have demonstrated quite a range of 2,5-FDCA yields – from 34% to an impressive 97% – depending on synthesis method, reaction conditions, and oxidant selection.

A particularly thorough study on NiO_x catalysts revealed an interesting finding: how you make the catalyst matters a lot. Catalysts prepared without thermal treatment showed surprisingly better activity compared to their thermally treated counterparts, achieving 34.14% 2,5-FDCA yield with 42.57% selectivity at just 25°C using a NaClO:HMF molar ratio of 12:1 and 6% catalyst loading. The ability to operate at room temperature represents a significant practical advantage over noble metal systems, cutting energy requirements and operational costs substantially. What's even more encouraging is that these catalysts demonstrated excellent recyclability, maintaining their activity over five consecutive cycles. Perhaps, most importantly from a practical standpoint, they showed catalytic activity when processing crude 5-HMF derived directly from glucose dehydration, confirming that they can handle real biomass feedstock without needing extensive purification [1].

Manganese-based catalysts have also shown considerable promise, with Mn^{3+}-containing oxides demonstrating enhanced catalytic activity thanks to their favorable redox properties. Researchers have investigated other transition metal catalysts including cobalt, copper, and iron as well, though these generally exhibit lower selectivity compared to nickel systems [13, 16, 18]. The main challenge with non-noble metal catalysts boils down to achieving high selectivity while maintaining stability under the harsh oxidative conditions these reactions require, as these materials tend to be more susceptible to leaching and structural degradation over time.

Metal-Free and Organocatalytic Systems

Emerging research has explored metal-free catalytic systems based on organic catalysts and photocatalytic approaches using carbon nanodots as catalysts which are indeed at their infancy [21]. While these systems offer environmental advantages and eliminate concerns about metal leaching, they generally exhibit lower reaction rates and yields compared to metal-based catalysts. Photocatalytic oxidation using visible light and organic photosensitizers represents an intriguing sustainable approach, though scalability and quantum efficiency remain significant challenges for industrial implementation.

PROCESS STRATEGIES AND OPTIMIZATION

One-Pot versus Two-Step Processes

Two primary process configurations have been developed for glucose-to-2,5-FDCA conversion: integrated one-pot systems and sequential two-step approaches. Two-step processes involving HMF purification between dehydration and oxidation stages consistently achieve higher FDCA yields (90–98%) but incur additional separation and purification costs. The major challenge with HMF as an isolated intermediate is its sensitivity to pH, light, heat, and oxygen, which can lead to degradation and necessitate careful storage and handling [22].

One-pot processes eliminate intermediate purification steps, reducing process complexity and capital costs. However, maximum 2,5-FDCA yields in single-phase one-pot systems without phase separation are limited to approximately 72%, due to competing reactions and catalyst incompatibility between dehydration and oxidation steps. The incorporation of multiphase separation strategies has significantly improved one-pot yields, with triphasic systems achieving 78% FDCA yield from fructose and 50% from glucose [23].

Multiphase Reaction Systems

Biphasic solvent systems employing water and immiscible organic solvents (tetrahydrofuran, methyl isobutyl ketone, toluene) have proven effective in enhancing HMF yields and preventing degradation. The organic phase continuously extracts HMF from the aqueous reaction medium, protecting it from acid-catalyzed rehydration to levulinic acid and minimizing humin formation. Water/THF biphasic systems with HCl and $AlCl_3$ catalysts have achieved 52% 2,5-FDCA yield from glucose [24].

Triphasic systems represent an advanced configuration with three distinct phases: aqueous dehydration phase, HMF-rich organic transfer phase, and aqueous oxidation phase. This design enables spatial separation of incompatible catalysts while facilitating continuous HMF transfer to the oxidation zone. The limitation of triphasic systems is the mass transfer resistance between phases, which can become rate-limiting and reduce overall process efficiency. Optimization of phase volumes, stirring rates, and interfacial properties are crucial for maximizing triphasic system performance.

CRITICAL PROCESS PARAMETERS

Temperature optimization represents a critical balance between reaction kinetics and selectivity. Higher temperatures (>150°C) accelerate dehydration but promote side reactions and humin formation. Oxidation reactions typically proceed more selectively at moderate temperatures (25–100°C), though reaction rates may be compromised. Recent studies on nickel catalysts have demonstrated that room temperature oxidation is feasible, offering significant energy savings compared to traditional high-temperature processes [25].

Oxidant selection profoundly influences both 2,5-FDCA yield and process sustainability. Molecular oxygen and air represent the most environmentally benign oxidants, though they often require elevated pressures and base catalysis. Hydrogen peroxide offers high reactivity at atmospheric pressure but generates water as the only by-product. Sodium hypochlorite (NaClO), while effective, produces chloride waste and requires careful handling. Studies have shown that controlled addition of NaClO can enhance 2,5-FDCA yields by 2.28-fold compared to single-dose addition, highlighting the importance of oxidant dosing strategy [26]. Base concentration affects both reaction kinetics and selectivity in oxidation reactions. Alkaline conditions (NaOH, Na_2CO_3, $NaHCO_3$) facilitate aldehyde oxidation and enhance 2,5-FDCA solubility but can also promote substrate degradation. Optimal base concentrations typically range from 0.1 to 2 M, depending on the catalyst system and substrate concentration. Recent research has explored base-free oxidation routes to simplify product separation and reduce salt waste, though these systems generally exhibit lower activity.

Catalyst Design and Support Effects

The choice of support material significantly influences catalyst performance through effects on metal dispersion, particle size, electronic properties, and resistance to sintering. Activated carbon remains the most widely used support due to its high surface area, chemical stability, and ease of metal impregnation in Table 1. However, carbon support can be susceptible to oxidation under harsh reaction conditions, leading to catalyst degradation and metal leaching. Hydrotalcite (layered double hydroxide) has emerged as an excellent support for gold catalysts, providing basic sites that enhance oxidation activity while offering superior thermal stability [27]. The layered structure of hydrotalcite facilitates metal dispersion and prevents nanoparticle agglomeration, contributing to enhanced catalyst longevity. Ceria-based supports have also shown promise due to their oxygen storage capacity and ability to facilitate redox cycles in Figure 1.

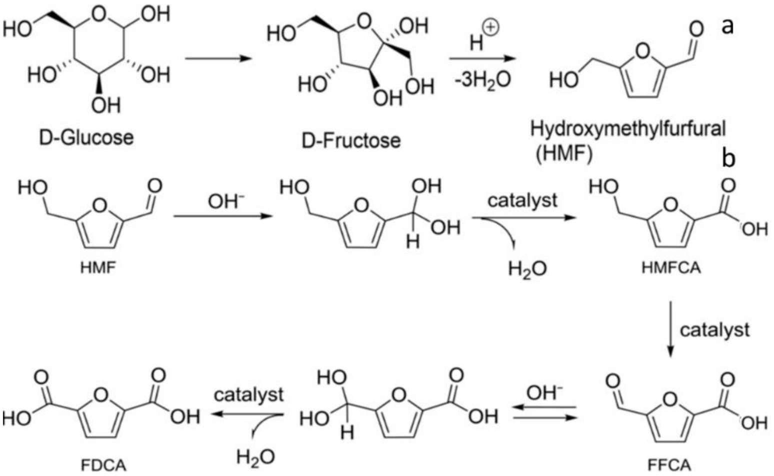

Figure 1. (a) Production of 5-HMF from glucose [22]; (b) Mechanism for the oxidation of 5-HMF to 2,5-FDCA in aqeous alkaline medium [23].

Table 1. Novel catalysts developed for the selective conversion of 5-hydroxy methylfurfural (5-HMF) to 2,5-furandicarboxylic acid (2,5-FDCA).

Catalyst type	Specific catalyst	Reaction conditions	2,5-FDCA yield (wt.%)	Key features	References
Noble Metal	Au/HT	Base-catalyzed oxidation, O_2	98.8	High selectivity; catalyst prone to deactivation.	[2, 7]
Noble Metal	Au–Pad on AC	O_2 oxidation, alkaline medium	99	Excellent recyclability.	[8]
Noble Metal	Pt/C	1 bar O_2, 25°C, alkaline	81	Mild conditions.	[7]
Noble Metal	Pt/C	Modified electronic properties	Enhanced	Improved resistance to poisoning.	[7]
Noble Metal	Ru + H_2O_2	H_2O_2 oxidant, mild conditions	91	Alternative to O_2 systems.	[11]
Non-Noble Metal	NO_x	25°C, Nalo, RT	34.14	Room temperature, recyclable.	[1]
Non-Noble Metal	NO_x (optimized)	Various conditions	97	Works with crude HMF.	[9, 14]
Non-Noble Metal	LDH	Base-free aerobic oxidation	High	High selectivity.	[14]
Integrated System	HCl/$AuCl_3$ + Oxidation	Water/THF biphasic	52	No HMF purification.	[5]
Two-Step Process	Various catalysts	Separate steps	90–98	Higher yield, costly separation.	[6, 8]

FUTURE DIRECTIONS AND RESEARCH OPPORTUNITIES

The development of multifunctional catalysts capable of performing both dehydration and oxidation reactions in a single system represents a promising avenue for process simplification. Such catalysts could eliminate the need for separate catalyst systems and enable true one-pot conversion with minimal phase separation requirements. Functional materials incorporating acid sites for dehydration and redox-active metals for oxidation on a single support are being explored, though achieving the appropriate balance of acid-base-redox properties remains challenging. Expanding substrate utilization beyond pure glucose to encompass complex polysaccharides and lignocellulose biomass would significantly enhance the sustainability and economic appeal of 2,5-FDCA production. Direct processing of cellulose, hemicellulose, or entire biomass streams without extensive pretreatment could reduce upstream costs. However, this requires catalysts tolerant to impurities, such as lignin degradation products, ash components, and proteins, that may poison active sites or interfere with reactions [28].

Alternative reaction media, including ionic liquids, deep eutectic solvents, and supercritical fluids, offer potential advantages in substrate solubility, catalyst stability, and product separation. Ionic liquids have demonstrated enhanced HMF yields from glucose through stabilization of reaction intermediates and favorable solvation properties. However, the high cost and environmental concerns associated with ionic liquids necessitate development of recyclable systems with minimal losses. Process intensification through continuous flow reactors, microreactor technology, and membrane reactors could significantly improve productivity and energy efficiency. Continuous processes enable better heat management, reduced reactor volumes, and enhanced mass transfer compared to batch operations. Membrane reactors combining reaction and separation in a single unit could simplify downstream processing and improve overall yields by shifting equilibria through product removal [29].

Integration of biological and chemical catalysis represents an emerging hybrid approach leveraging the selectivity of enzymes with the robustness of chemical catalysts. Enzymatic oxidation of 5-HMF to 2,5-FDCA using oxidases and dehydrogenases has achieved high yields under mild conditions, though enzyme stability and cofactor requirements pose challenges for industrial implementation. Combining enzymatic glucose isomerization with chemical HMF dehydration and oxidation could optimize each transformation step while minimizing undesired side reactions. The catalytic conversion of glucose to 2,5-FDCA represents a critical technology for building a truly sustainable bioeconomy based on renewable polymer materials [30].

CONCLUSION

Noble metal catalysts, particularly Au-Pd bimetallic systems, have demonstrated truly exceptional performance with 2,5-FDCA yields approaching 99%, though economic realities strongly favor the development of earth-abundant alternatives that won't break the bank. Recent advances in nickel-based catalysts show that non-noble metals can deliver competitive performance while offering substantial cost advantages. The fact that NiO_x catalysts can successfully process crude HMF derived directly from glucose represents an important milestone toward real-world, practical implementation. That said, we still need further improvements in yield, selectivity, and catalyst stability to truly match the performance of noble metal systems and make this technology ready for prime time. Moving from laboratory research to industrial-scale 2,5-FDCA production will require integrated solutions that address catalyst development, process design, product purification, and economic viability all at once. This is clearly a multidisciplinary challenge that will need expertise from catalysis, chemical engineering, materials science, and process economics working together. With continued innovation and investment, 2,5-FDCA-based polymers genuinely have the potential to displace petroleum-derived materials in numerous applications, helping to reduce greenhouse gas emissions and enhance resource sustainability. The path forward involves more than just technical optimization – we also need to consider broader sustainability metrics including life cycle assessment, carbon footprint analysis, and how this all fits into circular economy principles. As research moves toward commercialization, we should emphasize developing processes that are not only technically feasible but also environmentally beneficial and economically competitive in the global marketplace. That is the real test that will determine whether 2,5-FDCA becomes the game-changer it promises to be.

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