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Review

Chemical Transformation of Biomass-Derived Furan Compounds into Polyols

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Abstract: Polyols such as 1,5-pentadiol, 1,6-hexanediol, and 1,2,6-hexanetriol are crucial chemicals, traditionally derived from non-renewable fossil sources. In the pursuit of sustainable development, exploring renewable and environmentally benign routes for their production becomes imperative. Furfural and 5-hydroxymethylfurfural are C_5 and C_6 biomass-derived platform molecules, which have potential in the synthesis of various polyols through hydrogenation and hydrogenolysis reactions. Currently, there is an extensive body of literature exploring the transformation of biomass-derived furan compounds. However, a comprehensive review of the transformation of furan compounds to polyols is lacking. We summarized the literature from recent years about the ring-opening reaction involved in converting furan compounds to polyols. This article reviews the research progress on the transformation of furfural, furfuryl alcohol, and 2-methylfuran to 1,2-pentadiol, 1,4-pentadiol, 1,5-pentadiol, and 1,2,5-pentanetriol, as well as the transformation of 5-hydroxymethylfurfural to 1,2-hexanediol, 1,6-hexanediol, and 1,2,6-hexanetriol. The effects of the supported Pd, Pt, Ru, Ni, Cu, Co, and bimetallic catalysts are discussed through examining the synergistic effects of the catalysts and the effects of metal sites, acidic/basic sites, hydrogen spillover, etc. Reaction parameters like temperature, hydrogen pressure, and solvent are considered. The ring opening catalytic reaction of furan rings is summarized, and the catalytic mechanisms of single-metal and bimetallic catalysts and their catalytic processes and reaction conditions are discussed and summarized. It is believed that this review will act as a key reference and inspiration for researchers in this field.

Keywords: furfural; furfuryl alcohol; 5-hydroxymethylfurfural; pentadiol; hexanediol; 1,2,6-hexanetriol; catalysis; hydrogenolysis

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1. Introduction

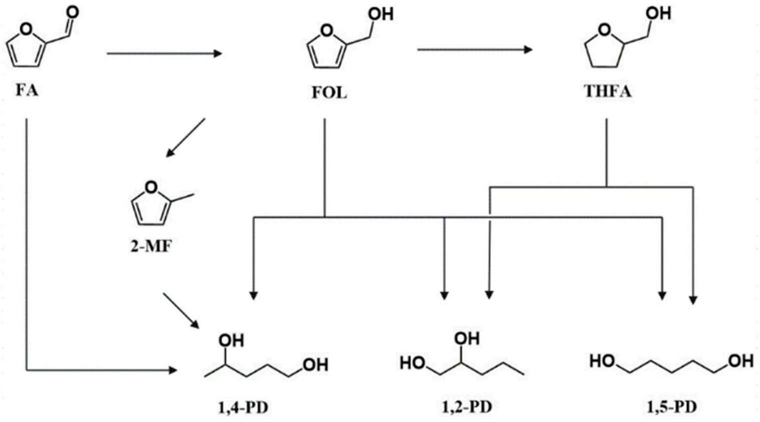
Escalating environmental pollution and the energy crisis have made the upgrading and substituting of non-renewable fossil fuels imperative. The urgent development of green and sustainable energy sources is crucial. Lignocellulosic biomass, a renewable organic carbon resource, has gained much attention due to its unique properties, such as its low cost and sustainable supply. Lignocellulose, composed of cellulose (40–60%), hemicellulose (25–35%), and lignin (15–20%) [1], is a highly abundant biomass resource, which has broad application prospects. However, its intricate and recalcitrant structure poses significant challenges to direct utilization. Through acid or enzymatic catalysis, cellulose and hemicellulose can be transformed into pivotal platform compounds such as 5-hydroxymethylfurfural (HMF) and furfural (FA) [2], serving as vital bridges between biomass resources and the chemicals industry. They are characterized by extremely high intrinsic reactivity based on their high density of organic functional groups, combining the functional groups of ether, cyclodienol, aromatic, aldehyde, and phenyl alcohol in one molecule. Under favorable conditions, these platform molecules offer diverse value-added reaction routes, including hydrogenation [3–5], oxidation [6–8], etherification [9–11], polymerization [12–14], amination, [15–17] etc., holding strong industrial application prospects.

The primary value enhancement pathways encompass the following: (1) eliminating oxygen to produce eco-friendly solvents and biofuels [3,18]; (2) preserving oxygen for the synthesis of chemical materials [19,20]; and (3) ring rearrangement into cyclic compounds. Notably, hydrogenation has emerged as an effective strategy, garnering research attention. The direct conversion of FA and HMF into polyols is highly appealing, prompting numerous researchers to delve into the ring-opening mechanism, with the goal of meeting industrial demand [21]. FA and its derivative, furfuryl alcohol (FOL), have the potential to produce plentiful value-added products, such as 1,2-pentadiol (1,2-PD), 1,5-pentadiol (1,5-PD), 1,4-pentanediol (1,4-PD), levulinic acid, and levulinates [22]. Similarly, HMF, a crucial C_6 organic biomass resource, enables the production of various downstream polyols, including 1,2-hexanediol (1,2-HD), 1,6-hexanediol (1,6-HD), and 1,2,6-hexanetriol (1,2,6-HT). However, the multistep reaction processes involved also facilitate the occurrence of side reactions (decomposition and polymerization), posing significant challenges in converting them into valuable chemicals [23]. To obtain a desired yield of target products, diverse catalytic systems have been devised to ensure high conversion and selectivity. In homogeneous catalysis, a lot of advancements have been reported. Chung [24] used $[Ru(X(CH_2PPh_2)_3\text{-}\kappa^3\text{-}P)(NCCH_3)_3](OTf)_2$ ($X{=}H_3C\text{-}C,N$) to form 1,4-PD from FA acetate. Schlaf [25] used trans-[(2,9-dipyridyl-1,10-phenanthroline) $(CH_3CN)_2Ru](OTf)_2$ to transform FA into 1,4-PD. Despite their advantages in terms of long-term stability, selectivity, and mass transport limitations [26], the challenges of recycling and reusing the catalysts and particularly the separation of catalysts from the target products hinder their widespread industrial application. Therefore, a suitable heterogeneous catalytic system, utilizing noble metals such as Pd, Pt, and Ru as the active sites, has emerged as a more appealing alternative due to the exceptional catalytic performance of these elements. However, the extensive use of noble metals is constrained by their high cost, making the exploration of non-noble metals crucial. The application of a series of transition metals (Ni, Cu, Co) has resulted in certain breakthroughs. A single active center hardly caters to the demands of complex reaction systems. Consequently, various strategies have been studied, including alloying [27], instituting strong metal-support interactions [28], and utilizing the synergistic effects between metal sites and acid/basic sites, which can enhance the selectivity for the target product and increase the reaction rate.

There have been many reviews published on the hydrogenation of FA or HMF. For example, Nakagawa et al. reported a review on the reduction of furfural or HMF with H_2 over heterogeneous catalysts to convert oxygen-rich compounds, including hydrogenation of the furan ring, C-O hydrogenolysis, rearrangement, C-C dissociation, and polymerization [29]. Jiang et al. reported advances made regarding the various transformations of HMF to furan-based polyester platform 2,5-furandicarboxylic acid (FDCA), 5-hydroxymethyl-2-furancarboxylic acid (HMFCA), 2,5-diformylfuran (DFF), and to fuels and fuel additives, including the gasoline blendstock 2,5-dimethylfuran (DMF), ethyl levulinate (EL), γ-valerolactone (GVL), methylfuran (MF), and so on [30]. However, there is currently no specialized review on the ring-opening reaction that transforms furan compounds to polyols. In this review, we summarize the past works involving ring-opening hydrogenolysis of biomass-derived furan compounds to polyols. For C_5 furan compounds, studies involving the transformation of FA, FOL, and 2-methylfuran to 1,2-PD, 1,4-PD, 1,5-PD, and 1,2,5-pentanetriol over supported Pd, Pt, Ru, Ni, Cu, Co, and bimetallic catalysts are considered. For C_6 furan compounds, research examining the transformation of HMF and its derivatives to 1,2-HD, 1,6-HD, and 1,2,6-HT is reviewed. The synergistic effects of catalysts, the effects of metal sites and acidic/basic sites, and the effects of reaction conditions, including temperature, solvent, and hydrogen pressure, are also reviewed comprehensively.

2. The Ring Opening of Furfural and Its Furan Derivatives

Furfural (FA), a biomass-derived C_5 source, can be transformed into pentadiols, which are the most meaningful target products. In the industry, 1,2-PD is utilized as an antibacterial agent in cosmetics and as an important intermediate for the synthesis of propiconazole [31], which is derived from n-pentene [32]. 1,4-PD, an important monomer for the synthesis of polyester and plaster, which can be synthesized via the condensation of hydroquinone and acetic anhydride with catalysts of NaOH or H_2SO_4 [33]. 1,5-PD has also been used in the synthesis of polyester, polyurethane, and pharmaceuticals from glutaraldehyde [34] or dimethyl glutarate [35]. However, conventional methods often involve the use of excess acids, bases, salts, toxic organic reagents, and expensive feed, all of which deviate from the path of sustainable development. The hydrogenolysis of FA or its derivatives provides a greener and more sustainable route to pentadiols (Scheme 1). The ring-opening process is crucial in converting FA to pentadiols. Also, several reaction routes have been proposed and are summarized in Scheme 1. We will provide a detailed description of the results obtained for the synthesis of different target polyols using FA or FOL as raw materials on supported metal catalysts.



Scheme 1. The ring-opening route from FA to pentadiols.

2.1. The Production of 1,2-PD

Two main reaction routes have been proposed for the conversion of FA into 1,2-pentanediol (1,2-PD), an acidic and a basic catalysis process, respectively. On the basic support, firstly, a carbonyl group is transformed into a hydroxyl group. FOL molecules are adsorbed on the surface of the basic catalyst in a tilted configuration, forming alcoholate species. Subsequently, the furan ring is directly broken to produce penta-2,4-diene-1,2-diol [36] or through the formation of partially hydrogenated species that open the ring to produce 1-hydroxy-2-pentanone [37]. Both intermediates can be transformed into 1,2-PD easily under H_2 atmosphere. On the acidic support, similar routes occur but with H^+ providing the driving force for ring opening instead of alcoholate species [38]. The results of various studies investigating the conversion of FA and FOL into 1,2-PD are listed in Table 1.

2.1.1. The Noble-Metal Catalyst

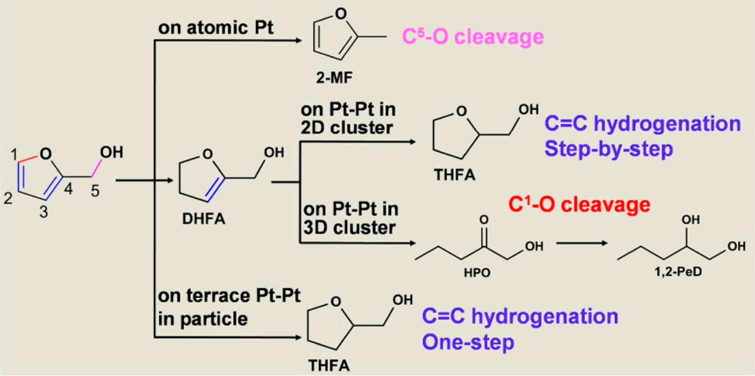
Wang's group synthesized a Pt/CeO_2 catalyst with a 59.9% yield of 1,2-PD from FA. They proposed that the basic sites of CeO_2 play an important role in the reaction [39]. One year later, they explored the impact of different crystal planes of CeO_2 on the hydrogenolysis of FOL to 1,2-PD [40]. Pt^0 is beneficial for ring opening, but it is hard to reduce Pt on nanorod CeO_2 due to the strong Pt-O-Ce bond controlled by oxygen vacancy formation energy. On the octahedron CeO_2, the metal-support interaction is too low to suppress the growth of particles, which decreases the 1,2-PD yield. Over a CeO_2-nanocube exposed with the (100) facet, the highest yield of 1,2-PD was achieved due to the appropriate metal-support interaction that regulated the electronic state and particle size of Pt. Zhang's group successfully converted FA to 1,2-PD under ambient hydrogen pressure, with Pt-Fe/MT (magnesium titanate) achieving an 81% yield of 1,2-PD [5]. The addition of Fe made Pt electron rich, so that ring hydrogenation at Pt sites was suppressed, and the low-valence Fe^{2+} sites could selectively adsorb and activate oxygen-containing groups, facilitating C-O bond breakage. In addition, the reaction produces the desired yield of the ring-opening product only in water, which may be attributed to the fact that water can greatly accelerate hydrogen spillover.

Yadav's group [41] reported a Ru/OMS-2 catalyst that transformed FA to 1,2-PD with an 87% yield. They proved that the kinetic model is in accordance with a dual-site Langmuir-Hinshelwood-Hougen-Watson mechanism. Hwang's group [27] synthesized the Ru-Sn/ZnO catalyst, which yielded 84% of 1,2-PD from FA. Through a direct reduction without calcination, a Ru-Sn alloy phase is synthesized, along with a SnO_x dispersion on the boundary of the alloy fringe. On the one hand, the electronic interaction of Sn^0 with Ru metal helps to suppress excessive hydrogenation activity. On the other hand, the SnO_x generates more C-O adsorption sites and may polarize oxygen moieties in FA, creating a more favorable environment for selective C-O scission on the Lewis acid sites of SnO_x species. From the perspective of hydrogen solubility, 2-propanol is a suitable solvent for solubilizing hydrogen. DFT calculations show that there is a significantly lower energy barrier for the C-O bond activation at the C_5 position compared to that at the C_2 position. Ru_3Sn_7 selectively produces 1,2-PDO via both THFA and FOL pathways.

Date and coworkers reported that the Pd/MMT-K10 catalyst could transform FA to 1,2-PD with a 66% yield [38]. By adding HCl and 2,6-lutidine (the quencher of Brønsted sites), respectively, they found acidic sites, especially Brønsted sites, which have a great influence on the 1,2-PD yield. The mechanism of H^+ from Brønsted sites directly attacked the furan ring after the form of partially hydrogenated species to produce 1-hydroxy-2-pentanone (HPO), which is hydrogenated to produce 1,2-PD.

Zhang et al. studied the aqueous-phase hydrogenolysis of FOL over a Ru/MnO_x catalyst with a 42.1% yield to 1,2-PD. This was attributed to the fact that MnO_x existed in the form of $Mn(OH)_x$ species. $Mn(OH)_x$ not only inhibited the polymerization of FOL but also promoted the ring-opening reaction by changing the adsorption configuration. 1,2-PD was produced via partially hydrogenated intermediates rather than dihydrofurans and tetrahydrofurans. The partially hydrogenated intermediates exhibit p-π conjugation between the p-orbital of the O_1 atom and π orbital of the C_2=C_3 bond, which effectively weakens the C_5-O_1 bond, potentially facilitating the hydrogenolysis of the C_5-O_1 bond. Consequently, they display more desired reactive activity than tetrahydrofurfuryl alcohol (THFA) when used as a reactant [37]. Kaneda [42] used a hydrotalcite-supported Pt nanoparticle catalyst, achieving a 73% yield of 1,2-PD by transforming FA. A similar route occurs but with the formation of alcoholate species between the substrates and basic sites of the catalyst surface to further elucidate the adsorption configuration.

He's group synthesized a series of $Pt/Mg(Al)O@Al_2O_3$ (MgAl-LDHs were synthesized in situ on the surface of γ-Al_2O_3 [43]) catalysts with an 86% yield of 1,2-PD from FOL [44]. By screening the loading of Pt and utilizing various thermal treatment methods, Pt particles with different sizes and morphology were produced, named atomic Pt, 2D cluster (one-atom-thick dispersion), and 3D cluster (multi-atom-thick dispersion), which led to different selective products (Scheme 2). The atomic Pt catalyst showed more positive states on the active metal surface, resulting in the best selectivity of 2-MF. The presence of the positive metal is favorable for adsorbing O-terminal groups, which results in the cracking of C-O bonds to generate 2-MF. As the Pt loading increases, the percentage of 2D/3D Pt clusters also rises. The selectivity towards THFA results in the hydrogenation of the C=C ring increasing with an increasing percentage of Pt 2D clusters. Regarding the 3D cluster, the large particle size possesses more terrace sites, which facilitate the production of more THFA [45]. The formation of 1,2-PD requires 3D Pt clusters, especially at corners/edges, rather than terrace Pt-Pt sites. The C_1=C_2 bond of FOL can be hydrogenated to form 4,5-dihydrofuran-2-yl)methanol (1,2-DHFA). In 1, 2-DHFA, the C_1-O bond is in close proximity to the newly formed C_1-C_2 bond, making it more likely to be adsorbed at 3D Pt-Pt sites through unsaturated coordination. In addition, the C_1-O bond is weakened due to p-π conjugation of the O-C_4=C_3 bond, facilitating the cleavage of C_1-O and subsequent ring opening. The species resulting from the cleavage of C_1-O is quickly converted into HPO, and 1,2-PD is produced through the hydrogenation of C=O in HPO.



Scheme 2. Proposed reaction paths for the hydrogenation of furfuryl alcohol over engineered Pt sites from Reference [44]. Copyright 2020 American Chemical Society.

Fan's group reported a Pt/Mg_xAlO_y catalyst, achieving a 64.9% yield of 1,2-PD from FOL [46]. Tuning the Mg/Al molar ratio can effectively adjust the metal-support interaction and oxygen vacancy. A positive correlation has been observed between FOL conversion and the ratio of Pt^0, indicating that Pt^0 species serve as active sites in the FOL hydrogenation reaction, which facilitates the C-O bond cracking. The oxygen vacancy, as the absorption sites, interacts with substrates, leading to an angled configuration. Furthermore, this angled configuration distorts, polarizing C_4=C_5-O groups, resulting in the high selectivity of the targeted product, 1,2-PD.

2.1.2. Non-Noble-Metal Catalyst

Liang's group synthesized a Cu-Mg-Al hydrotalcite catalyst for the hydrogenation of FA, yielding both 1,2-PD (55.2%) and 1,5-PD (28.5%), along with some byproducts of 2-MF [47]. The formation of 2-MF is attributed to insufficient hydrogen supply. The ring saturation reaction has a faster reaction rate than the acid-catalyzed ring-opening process under conditions of excess hydrogen concentration. During the ring-opening process, the acidic sites can promote both C_5-O and C_2-O bond cracking, and the basic sites can effectively suppress the isomerization and polymerization. Moreover, the Cu^+ sites are the major parts in charge of activating hydrogen.

Zhang's group synthesized an $Al(OH)_3$/Cu catalyst by adding Cu-Al alloy powder in NaOH solution for the hydrogenation of FA [48]. $Al(OH)_3$ changed the adsorption configurations of FA on the catalyst surface. The titled adsorption model favors the production of ring-opening products, whereas FA prefers to adsorb $Al(OH)_3$ (111) in a parallel-ring model, which exhibits a lower ring-opening barrier compared to a vertical configuration on the Cu_2O surface. The presence of basic metal oxides and hydroxides on the surface of Cu catalysts significantly enhanced the selectivity of 1,2-PD from furfural, presenting a nearly fourfold increase in the 1,2-PD:2-MF ratio.

Liu and coworkers reported a Cu-LDH (Mg_3Al) catalyst with a 51.8% yield of 1,2-PD from FOL [49]. The strong dispersion of Cu played a critical role in the ring-opening process. The catalytic activity and Cu particle size exhibited a volcanic variation, indicating that the FOL hydrogenolysis is a structure-sensitive natural reaction for the Cu-LDH catalyst. A weak adsorption strength between the substrates and products on the Cu surface, coupled with large particle sizes, leads to undesired steric hindrance, preventing the C=C bond of the furan ring from the catalyst surface. In the same year, they designed a series of Cu/Al_2O_3 catalysts using the precipitation-gel method for the transformation of FOL [50].

The number of acidic sites decreased, and the particle size of the Cu also increased with increasing Cu contents. For the effect of the particle size of Cu/Al_2O_3, it displayed an analogous trend to that observed in the Cu-LDH (Mg_3Al) catalyst. To clarify the effect of acidic sites, they introduced the W species to increase the number of acidic sites. The presence of acidic sites enhanced the overall selectivity of pentadiols but detrimentally affected the conversion efficiency, leading to the production of increased byproducts.

Zhao's group prepared a Cu@MgO-La_2O_3 catalyst to transform FOL to 1,2-PD, with a 63.7% yield [51]. In comparison to MgO or La_2O_3 supports, the MgO-La_2O_3 composite support exhibited more alkaline sites and suitable particle sizes. FOL adsorbed on the alkaline sites of the La_2O_3 support through interactions involving the O atoms of the furan ring and CH_2OH, triggering the ring-opening reaction and facilitating the formation of enol intermediates, subsequently further hydrogenating to 1,2-PD and 1,5-PD over the Cu^0 nanoparticles. The presence of C=C bonds is essential for the ring-opening process. 2-MF obtains a similar yield of 1-pentanol and 2-pentanol, which can be attributed to the reduced steric hindrance in its structure. From the point of the reaction kinetics, moderate particle sizes of the catalyst exhibit the highest TOF. Conversely, small Cu particles possess a strong adsorption capacity for FOL and PD, leading to a scarcity of available Cu active sites for the reaction. Meanwhile, the large Cu particles have lower catalyst activity for the steric hindrance effect between the C=C bond of the furan ring.

Table 1. The results of converting from furfural (FA) and furfuryl alcohol (FOL) into 1,2-pentadiol (1,2-PD) as the dominant product.

Entry	Catalyst	Reactant	Solvent	H_2 (MPa)	T (°C)	Time (h)	Conv. (%)	Sel. to 1,2-PD (%)	Sel. to 1,5-PD (%)	Ref.
1	Pt-Fe/MT	FA	H_2O	0.1	140	10	>99	81	15	[5]
2	Pt/CeO_2	FA	IPA	2	165	2	>99	59.9	3.1	[39]
3	Pt/HT	FA	IPA	3	150	8	>99	73	8	[42]
4	Pt/Al_2O_3	FA	Water/IPA	2	240	5	>99	17.3	-	[52]
5	Ru-Sn/ZnO	FA	IPA	3.6	140	6	>99	84.5	9.1	[27]
6	Ru/PVP + HDA	FA	1-propanol	2	125	48	>99	36	-	[53]
7	Rh/OMS-2	FA	methanol	3	160	8	>99	87	-	[41]
8	Pd/MMT-K10	FA	IPA	3.4	220	5	>99	66	-	[38]
9	Cu-Mg-Al	FA	ethanol	6	150	6	84.1	55.2	28.5	[47]
10	$Al(OH)_3$/Cu	FA	IPA	4.5	170	6	>99	34.1	-	[50]
11	Ru/MnO_x	FOL	H_2O	1.5	150	4	>99	42.1	-	[37]
12	Ru/Al_2O_3	FOL	H_2O	10	200	1	>99	32	-	[54]
13	Ru-Mn/CNTs	FOL	H_2O	1.5	150	4	81.8	16.5	-	[55]
14	Ru/MgO	FOL	H_2O	3	190	1	>99	42	2.9	[56]
15	Pt/CeO_2	FOL	ethanol	2	165	24	>99	77	7	[40]
16	Pt/Mg(Al)O@Al_2O_3	FOL	ethanol	3	200	-	>99	86	5	[44]
17	Pt/Mg_7AlO	FOL	ethanol	2	160	2	>99	64.9	-	[46]
18	Pt/MgO	FOL	H_2O	1	160	10	>99	59.4	16.2	[57]
19	Pt/CeO_2	FOL	H_2O	1	170	1.5	>99	65	8	[58]
20	$CoWO_4$	FOL	IPA	-	160	7	91	67	-	[36]
21	Cu-$Mg_3AlO_{4.5}$	FOL	ethanol	6	140	24	>99	51.2	28.8	[49]
22	Cu-Al_2O_3	FOL	ethanol	8	140	8	85.8	48.1	22.2	[50]
23	Cu/MgO-La_2O_3	FOL	IPA	6	140	8	94.9	67.1	17.8	[51]

Qurbayni and coworkers [36] synthesized a $CoWO_4$ catalyst to produce 1,2-PD, with a 67% yield from FOL. Heat treatment under different temperatures resulted in synthesized $CoWO_4$ with different degrees of crystallinity. The low-crystalline $CoWO_4$ showed remarkable catalytic activity of 1,2-PD. This high activity can be attributed to the amorphous structure of the low-crystalline catalyst, which possesses a shorter nearest-neighbor distance between different Co^{2+} species. This proximity of active sites facilitates the breaking of the C-O bond. Furthermore, ^1H NMR was used to detect signatures of unsaturated diol, providing evidence to support the proposed catalytic mechanism of the direct ring-opening process.

In summary, the conversion of FA or FOL to 1,2-PD is intricately influenced by some parameters. Notably, noble metal catalysts operate under milder conditions than their non-noble-metal counterparts, owing to their superior hydrogen activation capability. Moreover, the particle size of metal sites plays a pivotal role. Larger sizes favor full saturation products via furan ring adsorption, whereas smaller sizes promote dehydration reactions due to strong hydroxyl group adsorption. The absorption configuration also determines the reaction pathways. Establishing this configuration involves catalyst design featuring acidic and/or base sites, along with exploring the synergistic effects between metal sites and metal oxides and the role of oxygen vacancies. High hydrogen pressure, a crucial parameter in reactions, tends to promote the formation of fully saturated compounds and excessive hydrogenation byproducts. Conversely, a restricted supply of hydrogen pressure can lead to alternative reactions, such as hydration. Additionally, elevated temperatures can trigger excessive reactions, including dehydration and even carbonization.

2.2. The Production of 1,4-PD

The production of 1,4-butanediol(1,4-PD) from levulinic acid or γ-valerolactone, despite their biomass origins, often necessitates harsh reaction conditions. Consequently, there has been a surge of interest in developing milder pathways for converting FA or FAL into 1,4-PD. Up to now, three distinct routes have been proposed: (1) the hydrogenolysis of FOL to 3-carbon-but-1-ol (3-AP) followed by hydrogenation to 1,4-PD [59]; (2) the etherification of FOL to 2-ethoxymethylfuran, ring opening to ethyl levulinate, and subsequent hydrogenation to 1,4-PD [60]; (3) the hydrogenolysis of FOL to 2-methylfuran (2-MF) and further hydrogenolysis to 1,4-PD in the aqueous phase [61]. The results of converting FA, FOL, and 2-MF into 1,4-PD as the dominant product are listed in Table 2.

Zhang's group prepared a Ru/CMK-3 catalyst for the hydrogenation of FA [62]. FA directly cracked the C-O bond in the H_2-CO_2 atmosphere without going through the LA or GVL hydrogenation pathway. 1,4-PD with a 90% yield was obtained via 3-AP intermediates. Acidic sites are usually provided by a support or metallic oxide. In this catalytic system, the acidic sites mainly come from the electron-deficient Ru species, rather than being contributed by the support. A low reduction temperature was chosen for keeping a portion of Ru in its positive valence state, ensuring the presence of enough acidic sites for the reaction. This showed that THFA tended to form in the absence of an acidic environment. To address this, the introduction of CO_2 was employed, which could form carbonic acid in situ, benefitting the formation of 1,4-PD. By controlling the reaction parameters, neither LA nor GVL intermediates were detected, indicating that weak acidic sites could induce the occurrence of the Piancatelli rearrangement [63]. In a hydrogen atmosphere, the rearrangement process was effectively suppressed, allowing the pentadienyl cation intermediate to quickly transform into 3-carbo-but-1-ol and, ultimately, to 1,4-PD. To address the challenges of the aggregation and deactivation of a Ru/CMK-3 catalyst in water, Zhang et al. used a solid acidic support, Amberlyst-15, to replace the carbon dioxide (carbonic acid formed in situ), which can obtain an 86% yield of 1,4-PD from FA [64]. Furthermore, the strategic introduction of an appropriate amount of FeO_x played a dual role, effectively improving the dispersion of metal and decreasing the surface acidic sites. Too small an amount of FeO_x may not be sufficient to significantly decrease the number of acidic sites on the catalyst surface, leading to undesired side reaction products such as LA or GVL. However, too high an FeO_x content makes the particle size of Ru larger, which decreases the hydrogen activation ability, resulting in the formation of a large amount of 3-carbo-but-1-ol. Connecting metallic sites with acidic sites, excessive metal acidic sites lead to the absence of detectable ring-opening products. A low ratio indicated that the 3-AP intermediate can be transformed into 1,4-PD through hydrogenation, indicating that a suitable ratio of metal-acid sites is of paramount importance for the yield of the target product.

Shimazu's group synthesized a NiSn alloy catalyst for the selective conversion of C_5-furan compounds (FA, FOL, and 2-MF) to 1,4-PD [65]. The synergistic effects between the Ni-Sn alloy, H_2, and the hydroxylated solvents are pivotal in facilitating catalytic reactions. The

Ni-Sn alloy catalyst has demonstrated remarkable performance, achieving yields of 1,4-PD as high as 92% from FA, 71% from FOL, and 48% from 2-MF, all in an ethanol/H_2O solvent system. By using different reactants as substrates, a novel pathway that circumvents the Piancatelli rearrangement was proposed: FA was hydrogenated to FOL, which subsequently adsorbed and was protonated on the Sn^{2+} surface, and then the hydrogenolysis of FOL led to the formation of 2-MF, serving as a precursor for partially hydrogenated species. Water preferentially attacked the C_2 atom of 2-methyl-4,5-dihydrofuran, resulting in the production of a hemiketal intermediate. It could be transformed into 3-AP assisted by H^+.

Hou's group developed a Ru/(sulfated)SBA-15 catalyst using FA as a substrate to obtain 1,4-PD with an 87% yield [66]. The electron exchange between Ru and -SO_3H leads to a more electron-rich Ru species, enabling it to efficiently activate hydrogen and, thus, promote the hydrogenation reaction. By comparing the catalytic performance of Ru/AC, it was found that the weak acid site may not contribute significantly to the system, while the introduced -SO_3H group played a crucial role. The influence of varying the amount of -SO_3H at the surface was also investigated. Too many -SO_3H groups cause some undesired performances as follows (1) hydrolysis, polymerization, and many other side reactions occur; (2) the pore structure of the catalyst collapses or clogs; (3) the strong nucleophilicity of -SO_3H makes the substrate competitive with the solvent for adsorption.

Wang's group used a Cu/SiO_2 catalyst with an 86.2% yield to 1,4-PD from FA [60]. They discovered that the composition of the solvent had a profound impact on the dispersion of the product. When ethanol was employed as the solvent, ether species was formed, which protected the hydroxyl group of FA from polymerization, contrary to the widely held belief that 2-methyltetrahydrofuran (2-MTHF) underwent ring opening to produce 1,4-PD. Moreover, 2-MTHF was derived from the dehydration of 1,4-PD in water-scarce conditions. Based on catalytic performance evaluations, the mixed solvent of ethanol and H_2O was found to effectively enhance the catalytic activity.

Wu and coworkers developed a PtNi alloy catalyst that was capable of opening the ring of 2-MF to produce 1,4-PD with a yield of 69% [67]. The electron migration from Ni to Pt resulted in the formation of oxidized Ni species. The synergistic effect between Pt and Ni facilitated the hydrogenation of the furan ring. The reaction route includes the semi-hydrogenation of furan rings, which are initially protonated by acidic sites. Subsequently, the product was attacked by H_2O, leading to the introduction of the hydroxyl group at the -CH_3 position. This is facilitated by the presence of C-C bonds adjacent to the -CH_3 group, which make the site more reactive for hydroxylation. The resulting hemiketal intermediates are generated through a proton transfer process to produce 3-AP, following the formation of 1,4-PD via hydrogenation.

In summary, the conversion of FA and furfuryl alcohol FOL to 1,4-PD requires water (H_2O) as a nucleophile to attack the furan ring, as direct ring opening cannot generate the tertiary hydroxyl groups. Consequently, utilizing water as a solvent or a reactant is a relatively effective strategy to facilitate this transformation. Beyond direct ring-opening mechanisms, levulinic acid or levulinate esters present a well-established pathway for producing 1,4-PD.

Table 2. The results of converting from furfural (FA), furfuryl alcohol (FOL) and 2-methylfuran (2-MF) into 1,4-pentadiol (1,4-PD) as the dominant product.

Entry	Catalyst	Reactant	Solvent	H_2 (MPa)	T (°C)	Time (h)	Conv. (%)	Sel. to 1,4-PD (%)	Ref.
1	Ru/CMK-3	FA	H_2O	1	80	20	>99	90	[62]
2	Ru-6.3FeOx/AC + Amberlyst-15	FA	H_2O	0.2	80	20	>99	86	[64]
3	Ru/SC-SBA-15	FA	H_2O	1.5	140	4	>99	87	[66]
4	Cu/SiO_2	FA	ethanol/H_2O	4	180	8	>99	86.2	[60]
5	Ni-Sn	FA	ethanol/H_2O	3	160	12	>99	92	[65]
6	Ni_3Sn_2	FA	ethanol/H_2O	3	160	10	>99	87	[68]
7	Ni–Sn(x)/AlOH	FA	ethanol/H_2O	3	160	12	>99	78	[69]
8	Ni-Sn	FOL	ethanol/H_2O	3	180	12	>99	71	[65]
9	Ni-Sn	2-MF	ethanol/H_2O	3	160	12	>99	48	[65]
10	Pt-Ni	2-MF	ethanol/H_2O	2	120	3	>99	69	[67]

2.3. The Production of 1,5-PD

To produce 1,5-pentanediol (1,5-PD) from FA and its furan derivatives, two primary routes were explored. The first route involves directly breaking the furan ring to produce penta-1,3-diene-1,5-diol, which is subsequently hydrogenated to form 1,5-PD. Another route is the full hydrogenation of the furan ring to form the tetrahydrofurfuryl alcohol (THFA) intermediate. The C_2-O bond in THFA is cleaved to produce 1,5-PD. The results of converting FA and FOL into 1,5-PD as the dominant product are listed in Table 3.

2.3.1. Furan Ring Cracking and Hydrogenation

Xu and coworkers reported the use of a Pt/Co_2AlO_4 catalyst to achieve a 34.9% yield of 1,5-PD from FA [70]. In this catalyst system, Pt demonstrated a remarkable ability to activate hydrogen but showed a relatively low level of adsorption for C=C bonds. However, the incorporation of CoO_x, especially Co^{3+}, effectively enhanced the adsorption of the C=C bond, making the ring-opening process feasible [71]. Following the C_2-O cracking and hydrogenation process, 1,5-PD was obtained through the hydrogenation of the penta-1,3-diene-1,5-diol intermediate.

Álvarez et al. found that Co-Al nanoparticles, a non-noble-metal catalyst, could produce a 30% yield of 1,5-PD from FA [72]. Co^0 activated hydrogen, while Co^{3+} and Al^{3+} provided adsorption sites for the furan ring. A higher reduction temperature results in a stronger surface acidity, which is beneficial for C=C bond adsorption. The reaction followed Markovnikov's rule. Based on this rule, a route is proposed. The hydroxyl group of 2-propanol polarizes the O of the furan ring by activating the C_2-O bond. With the assistance of Lewis acid, the C_2-O bond is cleaved to produce a carbocation intermediate, which is stabilized because of resonance within the furan ring.

Kim's group studied the transformation of FA to 1,5-PD (47.5% yield) using a Ni-Co-Al catalyst [73]. The number of ultra-small Ni^0 domains exposed on the surface was sufficient to promote the dissociative adsorption of H_2 molecules and suppress a ring-saturated reaction. Meanwhile, hydrogen spillover occurred from Ni^0 to oxygen-vacant CoO_x (O_v-CoO_x) sites. The $Co^{\delta+}$ sites near the O_v sites had stronger adsorption strength in terms of hydroxyl O atoms of FOL, which made the hydrolysis energy barrier of the C_2-O bond lower than other side reactions. It also proved that the directly open process is more depleted than the partially hydrogenated route. Similarly, Peng [74] and coworkers synthesized a Ni-Co-Al hydrotalcite-derived catalyst. A low ratio of Ni and Co showed the highest yield of 1,5-PD (42.5%) from FOL. A low content of Ni decreased the particle size, which prevented excess hydrogenation. Additionally, due to the presence of hydrogen transfer, the catalyst was able to provide enough hydrogenation sites with a relatively low number of Ni sites. Furthermore, the Co^{2+} inhibited C=C adsorption, changing the adsorption configuration from a flat to a tilted structure, which is beneficial for producing 1,5-PD.

Zeng's group synthesized the ZnCo(LDH) catalyst using $Co(NO_3)_2$ to etch the template of ZIF-8 for the hydrogenation of FA [75]. The introduction of Co^{2+} species not only induced a tilted configuration but also increased the amount of Brønsted and Lewis acidic sites, resulting from the electron transfer from $Zn^{\delta+}$ to $Co^{\delta+}$, which are beneficial to ring opening, with a 46.9% yield of 1,5-PD from FA.

Liu's group prepared Cu-modified cobalt-based catalysts supported on cerium dioxide catalysts (Cu-Co/CeO_2) [76]. Adding an alkali solution into a metal salt solution resulted in a higher precipitation rate for Co compared to Cu. This process was beneficial for the reduction of both cerium oxide and cobalt oxide, significantly promoting the formation of oxygen vacancies and activated substances to effectively improve the hydrogenolysis of FA. With the assistance of Lewis acidic sites and oxygen vacancy, the C-O bond was activated, weakening its strength, which subsequently facilitated its cleavage during the further hydrogenation of penta-1,3-diene-1,5-diol to 1,5-PeD, with a 53.4% yield.

Huang's group synthesized the Co-Pt-La catalyst for the hydrogenation of FA [77]. The introduction of Co improved the conversion of FOL and changed the major product from 1,5-PD to 1,2-PD. The presence of the CoO_x-PtO_x interface, which promotes the dispersion of Co and Pt particles and strengthens the electronic interactions between them, could accelerate the rate of hydrogen transfer in the spillover process. This benefited the overall reaction activity, resulting in a yield of 40.3% for 1,5-PD and 11.1% for 1,2-PD, respectively.

A kind of Cu/MFI catalyst was synthesized by Liu's group [78]. They found that the ratio of $Cu^0/(Cu^0 + Cu^+)$ has a linear correlation with the selectivity towards 1,5-PD (69.2% yield) and 1,2-PD (16.0% yield) from FOL. Additionally, the Brønsted acidic sites in the catalyst provide H^+, which facilitates the cleavage of the C-O bond in the furan ring. The incorporation of Cu shifts the p-band of the catalyst away from the Fermi level, resulting in a decrease in surface energy, thereby favoring the absorption of substrates. There is an electron transfer from MFI to Cu, resulting in metallic sites being more electron rich, while oxygen atoms coordinated with metallic sites exhibit increased electron vacancies. The electron-rich methoxy group of FOL preferentially absorbs at Cu^+ sites due to the low adsorption energy, forming alkoxide species that facilitate the ring-opening process. One year later, Liu et al. adopted an ammonia evaporation method to synthesize the Cu/MFI-AEM catalyst, achieving better catalytic activity with a 76.4% yield of 1,5-PDO from FOL [79]. In precursor solution, NH_3 chelates with metal ions, allowing for the exchange of hydroxyl groups on the support for anchoring the metal ions during the impregnation process. After a series of heat treatment processes, the anchoring effect provided uniform distribution of the metal particles and an excellent anti-coking performance, resulting in high stability and activity.

2.3.2. Hydrogenation and Ring Cracking

Tomishige's group synthesized a Pd-Ir-ReO_x/SiO_2 catalyst that achieved a 71.4% yield of 1,5-PD from FA using a two-step temperature process in a one-pot reaction [80]. In the low-temperature reaction step, the Pd-ReO_x species catalyzed the saturated hydrogenation, transforming FA into THFA. Subsequently, the Ir-ReO_x species promoted the conversion of THFA to 1,5-PD via hydrogenolysis at high temperature [81]. A similar temperature control method was employed in the Rh-Ir-ReO_x/SiO_2 catalytic system [82]. In comparison to Ir-ReOx species, the Ir-Rh alloy modified with ReO_x enhanced the hydrogenation rate of FA to THFA during the low-temperature step. The same Ir-Rh alloy modified by ReO_x catalyzed the hydrogenolysis of THFA into 1,5-PD during the high-temperature step.

Wu's group designed a $Pt@Al_2O_3$ catalyst and used $NaBH_4$ as a hydrogen source to produce 1,5-PD from FA [83]. The presence of pentacoordinate Al^{3+} was detected, and these unsaturated coordinate structures not only strongly anchored and dispersed Pt NPs but were also the source of Brønsted acidic sites. As we know, Brønsted acid sites are beneficial for hydrogen spillover on the catalyst surface, which plays an essential role in the formation of Pt-H active sites in the hydrolysis of $NaBH_4$. H_2O may either directly participate in the reaction or a hydroxyl exchange phenomenon may occur. The intermediates produced by C_2-O or C_5-O bond cracking are unstable and can react rapidly with water for the formation of a more stable structure. Due to the reversibility of this process, it is influenced slightly and conforms with the isotope labeling results. When hydrogen is selected as a hydrogen source, 1,2-PD is the dominant product. However, when only $NaBO_2$ is added, 1,5-PD becomes the major product. It is agreed that the O from $NaBO_2$ interacts with Pt, which decreases the energy barrier for C_2-O bond cracking.

Table 3. The results of converting from furfural (FA) and furfuryl alcohol (FOL) into 1,5-pentadiol (1,5-PD) as the dominant product.

Entry	Catalyst	Reactant	Solvent	H_2 (MPa)	T (°C)	Time (h)	Conv. (%)	Sel. to 1,2-PD (%)	Sel. of 1,5-PD (%)	Ref.
1	Pt/Co_2AlO_4	FA	ethanol	1.5	140	24	>99	16.2	34.9	[70]
2	$Pt@Al_2O_3$	FA	H_2O	$NaBH_4$	45	8	>99	-	75.4	[83]
3	Pd-Ir-ReO_x/SiO_2	FA	H_2O	6	40/100	8/72	>99	1.4	71.4	[80]
4	Rh-Ir-ReO_x/SiO_2	FA	H_2O	6	40/100	8/32	>99	1.2	78.2	[82]
5	Co-Al	FA	IPA	3	150	8	>99	-	30	[72]
6	Ni-Co-Al	FA	H_2O	3	160	6	>99	19.2	47.5	[73]
7	ZnCo	FA	ethanol	4	160	4	>99	8.1	46.9	[75]
8	Cu-Co/CeO_2	FA	ethanol	3	150	4	>99	12.8	53.4	[76]
9	Ni-Y/HT	FA	IPA	2	150	72	>99	1.9	46.0	[84]
10	Ni-La/HT	FA	IPA	2	150	72	>99	2.8	55.8	[84]
11	Pt/Co-La	FOL	IPA	3	160	10	>99	11.1	40.3	[77]
12	Ni-Co-Al	FOL	IPA	4	150	4	>99	12.2	42.5	[74]
13	Cu/MFI *	FOL	ethanol	2.5	160	--	>99	16.0	69.2	[78]
14	Cu/MFI-AEM *	FOL	-	2.5	180	--	>99	14.3	76.4	[79]
15	Cu-$LaCoO_3$	FOL	ethanol	6	140	2	>99	15.2	40.3	[85]
16	Cu-Co-Al	FOL	ethanol	4	160	2	97.8	18.9	44.7	[86]

* Continuous reaction.

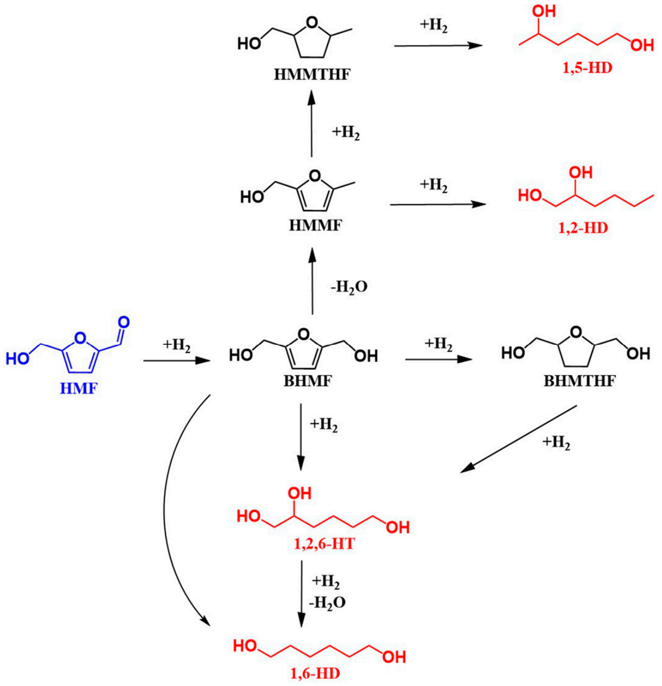
In summary, the direct reaction routes can effectively convert FA or FOL into 1,5-PD, which has a similar process to 1,2-PD. Therefore, its production alongside 1,2-PD is desirable. The boiling point of 1,2-PD is 30 °C lower than that of 1,5-PD. Separation can be achieved through distillation and rectification. However, the fundamental difference lies in the specific bond cleavage required: 1,5-PD necessitates the breaking of a C_2-O bond, whereas 1,2-PD involves the cleavage of a C_5-O bond. From what we know, Ni based catalysts should form 1,5-PD, Ru based catalysts could form 1,2-PD, Cu based catalysts can produce both products. Others, like Pd, Pt, and Rh, can produce 1,2-PD and 1,5-PD by using different methods to adjust the electronic state and/or spatial structure. Moreover, acidic and/or basic sites, as well as the synergistic interaction between metal sites and metal oxides, and the creation of oxygen vacancies, have been devised to achieve excellent catalytic performance. Notably, Co has been extensively employed as a second component due to its exceptional properties. Co can contribute Lewis acidic sites, generate oxygen vacancies, effectively disperse metal components, and promote ring opening within various catalytic systems.

2.4. The Production of 1,2,5-Pentanetriol

Tong and coworkers [87] adopted different precursors and methods to synthesize CoP, Co_2P, and NiP catalysts with different space groups. The variation in the adsorption configurations of the feed molecules on the catalyst surface has a profound impact on the product's distribution and selectivity. As a result, different products were obtained with distinct yields: 80.2% for 1,2,5-pentanetriol and 62.8% for cyclopentanol. Interestingly, the vertical adsorption configuration on the Co_2P and NiP catalysts favored the production of the ring rearrangement products. According to past works, the partially hydrogenated species typically form with a tilted adsorption configuration, while the ring-opening product preferentially forms through a flat configuration. Moreover, isotopic labeling experiments confirmed that the 2^o hydroxyl group originated from the H_2O solvent. When methanol was used as a solvent, no ring-opening product was detected, suggesting that only H_2O provided sufficient force to break the furan ring.

3. The Ring Opening of 5-Hydroxymethylfurfural and Its Furanic Derivatives

The routes for the synthesis of polyols from 5-hydroxymethylfurfural (HMF) are proposed in Scheme 3. To produce 1,2,6-hexanetriol (1,2,6-HT), HMF is initially converted to 2,5-dihydroxymethylfuran (BHMF). Two methods have been reported for the ring opening of BHMF, one directly breaking the unsaturated furan ring [88] and the other involving full hydrogenation to produce 2,5-bishydroxymethyltetrahydrofuran (BHMTHF), followed by hydrolysis of the C-O to form 1,2,6-HT [89]. Furthermore, BHMF can be transformed into 1,6-hexanediol (1,6-HD) through selective hydration [90]. Alternatively, 1,6-HD can also be formed directly from BHMF via hydrolysis, involving a hexan-1,3,5-triene-1,6-diol intermediate [91]. A few reports have indicated that 1,2-hexanediol (1,2-HD) can be obtained through the hydrolysis of 5-methylfurfuryl alcohol (HMMF) [92]. Additionally, the fully saturated structure of 5-methyl tetrahydrofurfuryl alcohol (HMMTHF) can be converted to 1,5-HD [93].



Scheme 3. The ring-opening route from 5-hydroxymethylfurfural (HMF) and its derivatives to Polyols.

Zhang's group devised a strategy to divide active metal sites into two parts (Pd/SiO_2 and Ir-ReO_x/SiO_2) within a fixed-bed reactor with a high 1,6-HD yield from HMF [90]. HMF was first transformed into 2,5-bishydroxymethyltetrahydrofuran (BHMTHF) on the surface of Pd/SiO_2, and then BHMTHF underwent ring opening at the Ir-ReO_x/SiO_2 catalyst, which facilitated the hydration reaction to produce 1,6-HD. Water and ReO_x can form hydroxyl species that increase the number of acidic sites [94,95]. THF, as a non-protonic solvent, has been proved to facilitate stronger alcohol adsorption compared to water in the Ir-ReO_x/SiO_2 catalytic system [96]. Also, it is important to note that too many acidic sites and excessively strong absorption abilities can lead to the generation of undesirable byproducts. A suitable ratio of H_2O and THF in the reaction mixture is crucial to improve the yield of the target product.

Tuteja and coworkers prepared a Pd/ZrP catalyst for the hydrogenation of HMF using HCOOH as a hydrogen source, with a 43% yield of 1,6-HD [91]. HMF adopts a tilted configuration due to electrostatic interactions with the metal and acidic ZrP support. The ZrP support provides acidic sites that facilitate the ring-opening process and the elimination of the epoxy group while also positioning the furan ring in a favorable orientation for the formation of hexan-1,3,5-triene-1,6-diol. Meanwhile, the dissociation of HCOOH at Pd sites generates H^+ and H^-, which are essential for achieving the hydrogenation reaction.

Yao and coworkers found that the Cu-Co/Al_2O_3 catalyst displayed the desired catalytic activity to transform HMF to 1,2,6-HT [97]. A 64.5% yield of the target product was achieved at 120 °C, 4 MPa H_2, 12 h. The ring-opening process in this system effectively breaks the unsaturated bond, as evidenced by the lack of reactivity observed for BHMTHF.

Kataoka and coworkers synthesized a Pt-Co/CeO_2 catalyst for the hydrogenation of HMF [88]. In their study, they used methanol as a model compound to screen various supports and found the presence of methoxy species with different coordination modes according to IR measurements. Conspicuously, only the monodentate mode shows selectivity to 1,2,6-HT. However, there are some exceptions, such as deriving from a few basic sites, with the cyclopentanone derivatives (rearrangement) as the major product. Additionally, the method of synthesis used to form the Pt-Co alloy can also impact the catalytic performance, with different methods resulting in undesired product dispersion.

Matsagar and coworkers synthesized a Pt@Al_2O_3 catalyst precursor including a series of heat treatments for the hydrogenolysis of HMF to 1,2,6-HT with a 63% yield [98]. Compared with Pt/Al_2O_3 synthesized via impregnation, the Pt-Co/CeO_2 catalyst exhibits a higher proportion of pentacoordinate Al^{3+} , which can anchor metal sites through the metal-support interaction. The lower binding energy of O_{1s} orbitals has proved this hypothesis.

Likozar's group successfully synthesized a Ni-Ce/Al_2O_3 catalyst for the hydrogenation of HMF, achieving a yield of 1,2,6-HT with 64.5% [99]. The introduction of Ce into the Ni/Al_2O_3 catalyst leads to a change in the number of both acidic and basic sites. Additionally, when Ni/Al_2O_3 and Co/Al_2O_3 are physically mixed to create a bimetallic catalyst, the performance is inferior. From the perspective of isoelectric points, Dumesic's hypothesis suggests that supports with a high isoelectric point tend to favor the formation of unsaturated BHMTHF, without the desired ring-opening product [100]. Interestingly, they found that when metallic oxides were used as additives, the major product obtained from HMF hydrogenation was 1,2,6-HT. These results suggest that the ring-opening process does not exclusively occur on metal NP but can also happen primarily at separate active sites that are not necessarily located near metal NP and/or the support. Additionally, after the catalytic reaction, the spent catalyst exhibits an increase in the number of basic sites compared to its pre-reaction state. This is attributed to the migration of O^{2-} from the bulk phase to the surface, which causes a decrease in the isoelectric point, producing an abundance of negative charge. This negative charge has a repulsive effect on the furan ring, resulting in the preferential adsorption of C=O at the surface to produce the BHMF. Two years later, a similar system was explored in another direction [4]. Researchers discovered, from the reaction kinetics, that adding water as a solvent could not only suppress dehydration reactions but also have varying, and even opposite, effects depending on the catalyst used. Specifically, water effectively eliminates unnecessary dehydration reactions by blocking plenty of acidic and basic sites, especially strong acidic sites. The incorporation of Ce introduces abundant O vacancies, which significantly enhances dehydration reactions without the presence of H_2O. After adding H_2O, it adsorbed at the O vacancies, particularly at strong acidic sites, effectively suppressing the dehydration effect.

Hu's group prepared a Cu-Mg-Al catalyst for the transformation of HMF to 1,2-HD [92]. With the Mg/Cu ratio increased, there was a linear growth in the number of basic sites, accompanied by a decrease in the particle size of Cu. This suggests that the presence of Mg contributes to the generation of additional basic sites, which inhibits the agglomeration of Cu particles. The critical intermediate, HMMF, can be formed via two distinct routes. One route is the hydrogenation of HMF to yield BHMF and further hydration to produce HMMF. Another route is the direct hydrogenolysis of HMF to the 5-methylfurfural intermediate and then further hydrogenation to produce 5-methylfurfuryl alcohol. Finally, 5-methylfurfuryl alcohol opens its unsaturated furan ring to form the target product, 1,2-HD.

4. The Effect of Reaction Conditions on the Transformation of Furan Compounds

4.1. Solvent

Except for the nature of the reactant and catalyst, some external factors should be considered. The solvent not only dispersing but even polarizing the reactant is an unavoidable factor in the catalytic system. Currently, the modes of action include the following:

(1) Participating in the reaction directly. Gong's group found that water directly participates in the ring-opening process of FA [58]. Generally, C_2-O cracking leads to the production of 1,5-PD, while 1,2-PD is produced via C_5-O cracking. This means that all the oxygen atoms in the products originated from FA. Interestingly, a $H_2{}^{18}O$ isotopic tracing experiment revealed the presence of ^{18}O at 2°-OH. Combined with DFT calculations, they concluded that 1,2-PD was produced by C_2-O cracking rather than C_5-O cracking. Because the additional reaction happened between $H_2{}^{18}O$ and C_2=C_3, ^{18}O was detected at 2°-OH. Additionally, the dehydration reaction occurs at 5°-OH with hydrogen transfer. Wang et al. found that when ethanol is used as the solvent, the produced ether species protect the hydroxyl group of FA from undesired polymerization [60]. Meanwhile, it also facilitates the conversion of the intermediate from an alcohol to an ester. The solvent can also act as the hydrogen source in catalytic systems. For instance, in the $CoWO_4$ catalytic system [36], 2-propanol (IPA) serves as both the solvent and hydrogen source, participating directly in the transfer of hydrogenation to transform FOL to 1,2-PD. The transfer mechanism was not elaborated in depth. Compared with ethanol, IPA exhibited a low dissociation energy barrier by producing the hydrogen route.

(2) Changing the surface states of catalysts. Wang et al. found that alkaline sites of Mn-OH groups were formed through the rehydration of Mn species in a water environment, while the high-oxidation-state Mn_3O_4 species was generated in a n-propanol environment [55]. Jones's group found that the addition of H_2O led to a decrease in selectivity towards PDs. They proposed two plausible hypotheses to explain this phenomenon. One hypothesis is that H_2O may act as an oxidant, causing the oxidation of the active metal site on the catalyst surface. Another hypothesis is that the presence of H_2O may promote the reversion of the catalyst structure towards layered double hydroxides (LDHs) [86]. The change in catalyst structure may lead to a reduction in the surface area or the formation of hydroxyl species [101]. The presence of water and ReO_x has been reported to facilitate the generation of hydroxyl species, which enhances the number of acidic sites on the catalyst surface [94,95]. In addition, the use of non-protonic solvents, such as THF in the $ReOx/SiO_2$ catalytic system, has been shown to promote stronger adsorption of alcohols compared to water [96]. Also, too many acidic sites and too strong an absorption ability result in the generation of byproducts. A suitable ratio of H_2O and THF improves the yield of the target product dramatically.

(3) Influence of the solubility of hydrogen and the speed of hydrogen spillover. Bretzler's group selected THF and IPA as solvents in the $Ni\text{-}W_xC/SiO_2$ catalytic system, respectively [102]. The dehydration reaction acts favorably in aprotic solvents such as THF. The use of IPA as a solvent resulted in a faster reaction rate and the stabilization of the intermediate to produce 1,2-PD [5].

(4) Inducing substrate polarization and/or stabilizing intermediates. In the Ru/OMS-2 catalytic system, methanol achieved the best yield with the highest dielectric constant [41].

In various catalysis systems, the same solvent may lead to different results. Indeed, there is no universally optimal solvent, but a suitable solvent may offer excellent solubility for substrates, stabilize intermediates, and positively influence polarization, thereby decreasing the energy barriers in target routes. For furan compounds, water and alcohols exhibit a desirable performance. Water acts as a nucleophile, attacking the furan ring to lower the energy barrier for ring opening and suppressing the side reaction of dehydration. However, water also promotes a rearrangement reaction. Conversely, alcohols tend to suppress the rearrangement reaction but often lead to dehydration.

4.2. Temperature, Hydrogen Pressure and Other Parameters

Temperature and hydrogen pressure are paramount among various reaction parameters, with the underlying mechanism being relatively well understood. Temperature, commonly regarded as an energy donor, ensures that the reactants are in the desired active state.

Similar absorption and reaction processes are confirmed for some ring-opening reactions, meaning that similar kinetics and thermodynamics should be followed. Thermodynamic analysis of the ring-opening process has confirmed that high temperature could accelerate the reaction rate but likely decrease the selectivity of the target product [103]. It means that it possesses a kinetic advantage, incurring a thermodynamics disadvantage. Thus, a low temperature is beneficial to chemical equilibrium. Since the hydrogenolysis of the C-OH bond is enhanced at higher reaction temperatures compared to the hydrogenation of the double bonds, lower temperature favors the formation of THFA. Although the production of ring-opening products results in greater heat release than fully saturated products, high temperatures are vital conditions for the ring-opening process [54]. It means that a complex system needs to not only consider global Gibbs free energy but also satisfy the necessary activation energy. Furthermore, kinetic factors are often pivotal in determining product selectivity in most instances.

Hydrogen pressure for reactants that influence thermodynamics is minimal. In non-noble-metallic systems, elevating the hydrogen pressure can positively contribute by furnishing an abundance of hydrogen ions, thereby enhancing the reaction rate. Nevertheless, this increase in pressure can alter the reducibility structure of the catalyst, leading to different catalytic performances. A limited supply of hydrogen pressure can result in hydration, whereas excessively high hydrogen pressure tends to favor the formation of fully saturated species [38] and excessive hydrogenation products [80]. Additionally, the transformation of biomass-derived furan compounds at high temperature and H_2 pressure can lead to the occurrence of oligomers [41]. Therefore, maintaining an appropriate temperature and hydrogen supply is crucial for the effectiveness of the reaction.

A few researchers have delved into the effects of furan loading. In different catalysis systems, distinct phenomena may be observed. Usually, for higher furan loading, the conversion of furan significantly decreases, and the selectivity of the target product decreases with other side reactions occurring in a specific loading range [41,57]. In addition, the catalytic activity increased when increasing the furan loading within a certain range [5].

Different types of reactors may have advantages. The fixed-bed reactor can achieve a tandem reaction by using two and even more types of catalysts, enabling the production of a target product [90]. The bath reactor is easy to operate, so it has been widely applied in the laboratory.

4.3. Catalytic Stability

When examining solely the nature of the metal, noble metals emerge as superior catalysts for the transformation of furan compounds into polyols, demonstrating enhanced stability against deactivation mechanisms compared to other metals. As the run time progresses, deactivation processes inevitably arise due to phenomena, such as leaching, carbon deposition, reconfiguration, sintering, and catalyst poisoning. These phenomena are influenced by some parameters, such as the nature of the metal and the reaction conditions [104]. The leaching process, in particular, is governed by the interplay of the metal's properties, the solvent used, the reactant involved, and the reaction conditions. When examining solely the nature of the metal, noble metals emerge as superior catalysts for the transformation of furan compounds into polyols, demonstrating enhanced stability against deactivation mechanisms compared to other metals.

5. Conclusions and Outlook

This review summarizes the transformation of biomass-derived furan compounds into polyols, which have been widely used in the fields of humectants, drug intermediates, polymerization feeds, and so on. The most promising routes involve transforming FA and HMF into target alcohols (1,5-PD and 1,6-HD). It is meaningful to replace toxic, non-renewable traditional chemical industry processes in the context of sustainable development. The most critical step is the ring-opening process, where suppressing the side reactions and achieving C-O cracking selectively determine the yield of the target product. Consequently, extensive research has focused on optimizing various reaction parameters to achieve this goal. Designing an effective catalytic system and a series of reaction conditions, especially the temperature and solvent, has been considered. A suitable temperature and H_2 pressure provide the right force to facilitate ring opening. Additionally, solvents play a crucial role by participating in the reaction, polarizing and/or stabilizing reactants and reconstructing the catalyst. The catalyst is at the core of catalytic systems. Achieving targeted chemical bond cleavage necessitates highly selective absorption and polarization capabilities, which can be tailored through catalyst design and synthesis. A single functional catalyst hardly undergoes both the hydrogenation and ring-opening process, emphasizing the need for bifunctional and multifunctional catalysts that show more desired catalytic activity. Also, the relatively expensive feeds, the certain self-polymerization at high concentrations, and the wastage of catalyst and solvent usage all contribute to the immaturity of biomass-derived routes. To solve these problems, the development of more efficient catalytic systems with high conversion and selectivity is imperative. In the production of 1,2-PD, both Pt-Fe/MT and Rh/OMS-2 catalysts could achieve relatively high product yields. Pt-Fe/MT stands out for its ability to operate under ambient pressure and relatively low temperatures, making it a favorable choice. Regarding the production of 1,4-PD, the Ni-Sn catalyst represents a cost-effective option due to the low-cost metal composition and high yield of 1,4-PD. Although Ru/CMK-3 also displays a desired yield, its complex synthesis process and the expense associated with noble metals render it less attractive for commercial applications. For the synthesis of 1,5-PD, Cu/MFI-AEM may be the most desirable catalyst, offering the highest product yield and acceptable reaction conditions. Furthermore, the adoption of a high-pressure fixed-bed reactor enhances the feasibility of large-scale application.

From the perspective of catalysis, we provide a comprehensive summary of the ring-opening process of biomass-derived furan compounds. To gain the desired selectivity and conversion, a catalyst should be designed to satisfy the right amount of absorption that could create a suitable surface reaction environment. In general, Ni-based catalysts favor the formation of 1,5-PD, whereas Ru-based catalysts preferentially yield 1,2-PD. Cu-based catalysts exhibit versatility, capable of producing both products. Meanwhile, catalysts including noble metals, such as Pd, Pt, and Rh, can selectively produce 1,2-PD or 1,5-PD through changes in their geometrical configuration and electronic states. Hydrogenation and hydrogenolysis, two inescapable steps in the ring-opening process, pose challenges for single-metal catalysts in achieving high selectivity on a single active site. Addressing this, the development of bi- or multi-metallic catalysts emerges as an effective solution. In particular, metals, metal oxides, metal phosphides, and alloys that construct multi-site synergistic effects significantly enhance selectivity. The prevailing theory postulates that hydrogen activation occurs at metallic sites, while acidic and/or basic sites facilitate reactant absorption and polarization, promoting reaction occurrence.

The above processes can be illuminated through various methodologies, including isotope labeling experiments for tracing atomic migration processes and in situ or operando characterizations for capturing dynamic processes. The widespread acceptance of self-consistent mechanisms offers invaluable guidance for future research endeavors. However, limitations in the current research methodologies obscure details about catalyst dynamic reconstruction during operando conditions and render certain transition states elusive. Researchers, thus, rely on indirect approaches, such as intermediate detection and density functional theory (DFT) simulations, to unravel these processes, resulting in mechanisms that may appear divergent or even contradictory. This underscores the need for more innovative design strategies and advanced characterization techniques to overcome these challenges. Despite there being some challenges in achieving large-scale applications, the route of converting biomass furan compounds has significance and potential to replace traditional fossil industries.

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Abbreviations

HMF	5-hydroxymethylfurfural
FA	furfural
FOL	furfuryl alcohol
1,2-PD	1,2-pentadiol
1,4-PD	1,4-pentadiol
1,5-PD	1,5-pentadiol
1,2-HD	1,2-hexanediol
1,6-HD	1,6-hexanediol
1,2,6-HT	1,2,6-hexanetriol
3--AP	3-carbon-but-1-ol
BHMF	2,5-dihydroxymethylfuran
BHMTHF	2,5-bishydroxymethyltetrahydrofuran
HMMTHF	5-methyl tetrahydrofurfuryl alcohol
HMMF	5-methylfurfuryl alcohol
THFA	tetrahydrofurfuryl alcohol
2-MF	2-methylfuran

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