processes

MDPI

Review

Progress of Reactions between Furfural and Aliphatic Alcohols via Catalytic Oxidation Processes: Reaction Routes, Catalysts, and Perspectives

Junying Tian [1,2,*], Xiaowei Cheng [1,2], Yingying Fan [1,2], Weiguo Fang [1,2], Peng Dong [1,2], Guixian Li [1,2] and Yongle Guo [1,2,*]

[1] School of Petrochemical Engineering, Lanzhou University of Technology, Lanzhou 730050, China
[2] Key Laboratory of Low Carbon Energy and Chemical Engineering of Gansu Province, Lanzhou 730050, China
* Correspondence: jytian@lut.edu.cn (J.T.); ylguo@lut.edu.cn (Y.G.)

Abstract: Furfural is one of the most important biomass platform compounds and can be used to prepare various high-value-added chemicals. The reactions of furfural with aliphatic alcohols via an oxidative esterification reaction or oxidative condensation reaction can bond two carbon molecules together and produce longer hydrocarbon chains chemicals, including methylfuroate and some low-volatility liquid biomass fuels. Thus, these reactions are considered significant utilization routes of furfural, and many inspiring catalytic systems have been designed to promoted these reactions. In this work, the reported catalytic systems for the oxidative esterification and oxidative condensation reactions are reviewed separately. The catalysts for the oxidative esterification reaction are reviewed for the classification of noble metal catalysts and non-noble metal catalysts, according to the active metals in the catalysts. For the oxidative condensation reactions, the studies using oxygen as the oxidant are reviewed firstly, and then the studies conducted using the hydrogen transfer process are analyzed subsequently. Furthermore, suggestions for future research directions for the oxidative esterification and oxidative condensation reactions are put forward.

Keywords: furfural; oxidative esterification; oxidative condensation

check for updates

Citation: Tian, J.; Cheng, X.; Fan, Y.; Fang, W.; Dong, P.; Li, G.; Guo, Y. Progress of Reactions between Furfural and Aliphatic Alcohols via Catalytic Oxidation Processes: Reaction Routes, Catalysts, and Perspectives. *Processes* **2023**, *11*, 640. https://doi.org/10.3390/pr11020640

Academic Editors: Jacek Grams and Agnieszka Ruppert

Received: 14 January 2023
Revised: 9 February 2023
Accepted: 11 February 2023
Published: 20 February 2023

1. Introduction

Furfural is one of the most important biomass platform compounds, which can be prepared from widespread, abundant and inexpensive renewable biomass resources [1–5]. Meanwhile, because of its active aldehyde and furan ring groups, furfural can convert to various high-value-added chemicals via oxidation, hydrogenation, reductive amination, isomerization and so on [6–10]. Among them, reactions of furfural with aliphatic alcohols via oxidation processes, including an oxidative esterification reaction and oxidative condensation reaction, could bond two molecules together and produce longer hydrocarbon chains and chemicals. As shown in Figure 1, through the oxidative esterification reaction, furfural can react with the methanol to prepare methylfuroate (MF), which is a significant synthetic perfume and chemical intermediate [11–13]. Through the oxidative condensation reaction, furfural can react with various short-chain aliphatic alcohols to prepare low volatile liquid biomass fuels [14–16]. These reactions of furfural are considered significant utilization routes of furfural, and many inspiring catalytic systems have been designed to promoted these reactions. Thus, a summary of these previous studies is important to facilitate an understanding of the reactions and provide a reference for the design of novel catalytic systems.

Hence, reactions of furfural with aliphatic alcohols via oxidation processes, including oxidative esterification and oxidative condensation, are reviewed. The catalysts used in the reactions are summarized and the reaction routes are presented. Moreover, the future research directions of the reactions are prospected. This review has the potential to provide knowledge and insights on the utilization of furfural by catalytic oxidation.

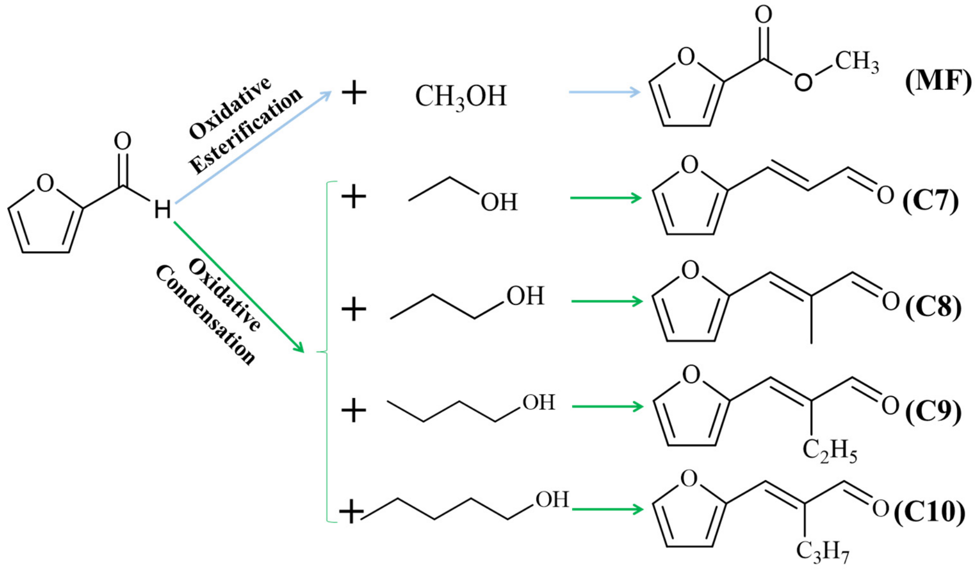

Figure 1. Schematic diagram reactions of furfural with aliphatic alcohols via oxidation processes.

2. Oxidative Esterification of Furfural

Generally, the oxidative esterification of furfural with aliphatic alcohols is accomplished in two steps, as shown in Figure 2 [11]. In the first step, a condensation reaction is conducted between furfural and alcohol to produce the intermediate hemiacetal. In the second step, the hemiacetal is oxidized to furoic acid esters. Theoretically, furfural can react with various aliphatic alcohols to produce furoic acid esters via the oxidative esterification reaction. However, only methylfuroate (MF) can be obtained efficiently via the oxidative esterification reaction between furfural and methanol. The reason is that the steric effects and electronic structure of the other aliphatic alcohols limit their activity in terms of oxidative esterification with furfural. MF is a significant synthetic perfume with broad application prospects. Therefore, many researchers have focused on the oxidative esterification of furfural with methanol. In the oxidative esterification process, the oxidation of the hemiacetal is the rate-determining step and is usually promoted by catalysts. Various catalysts have been used for the oxidative esterification reaction, and have exhibited good performance. Herein, these studies are reviewed for the classification of noble metal catalysts and non-noble metal catalysts, according to the active metals in the catalysts.

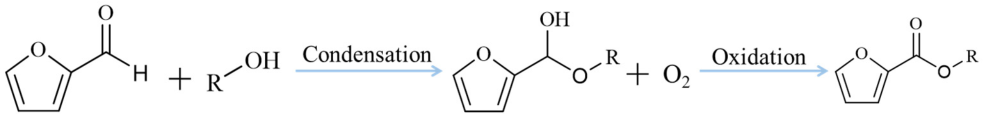

Figure 2. Mechanism diagram of the oxidative esterification of furfural with aliphatic alcohols.

2.1. Noble Metal Catalysts

Noble metal catalysts are one class of important catalytic materials with good properties in terms of their high activity, high temperature resistance, oxidation resistance, and corrosion resistance. Au has been widely used as active metal in the catalytic oxidative esterification of furfural, and exhibits excellent activity. Meanwhile, it was discovered that the composition and particle size of the active components and the properties of the supports affect the performance of the catalysts significantly.

Xu et al. [17] reported a general oxidative esterification process of aldehydes with methanol to produce methyl esters over metallic gold nanoparticles. Various aldehydes, including formaldehyde, acetaldehyde, benzaldehyde, and benzeneacetaldehyde, were converted to relative methyl esters with high selectivity. The schematic mechanism for this process conducted on the surface of Au (111) was revealed by the authors. Atomic oxygen ($O_{(a)}$) and methoxy ($CH_3O_{(a)}$) were formed when O_2 and CH_3OH were introduced onto the Au (111) surface. The methoxy could react with aldehydes rapidly via nucleophilic attack to form the intermediate hemiacetal, whereas the atom oxygen promoted the oxidation of the intermediate hemiacetal to form the methyl esters.

Nielsen et al. [12] stated that the Au/TiO_2 catalyst exhibited excellent performance in the aerobic oxidation of primary alcohols to methyl esters with the CH_3ONa additive. The selected substrates, including 1-hexanol, benzyl alcohol, cinnamyl alcohol, and 2-(hydroxymethyl) pyridine, were converted to corresponding methyl esters with yields over 88%. Then, the catalyst was used in the oxidative esterification of furfural by the authors [13]. As shown in Table 1, the furfural was full oxidized to MF under mild reaction conditions within 10–12 h with the addition of CH_3ONa.

Table 1. Studies on the oxidative esterification of furfural to MF over noble metal catalysts.

Entry	Condition	Catalyst	Furfural Conversion (%)	MF Selectivity (%)	Ref.
1	Catalyst (0.25 g), furfural (4 mmol), methanol (12.65 mL), molar ratio Au/furfural/methanol = 1/300/23,500, 8% CH_3ONa relative to furfural, 22 °C, 0.1 MPa O_2 (bubbling conditions), 10–12 h.	Au/TiO_2 + CH_3ONa	~100	~100	[13]
2 [a]	Catalyst (0.1 g), furfural (3.6 mmol), methanol (150 mL), molar ratio Au/furfural/methanol = 1/500/5 × 10^5, 120 °C, 0.6 MPa O_2, 3 h.	AZ150 AZ300 AZ500 AZ600 AZ650	99 98 100 57 24	94 94 98 76 60	[18]
3	Catalyst (0.1 g), furfural (3.6 mmol), methanol (150 mL), molar ratio Au/furfural/methanol = 1/500/5 × 10^5, 120 °C, 0.6 MPa O_2, 90 min.	Au/ZrO_2 Au/CeO_2 Au/TiO_2	82 66 20	92 ~70 ~90	[19]
4 [b]	Catalyst (0.1 g), furfural (3.6 mmol), methanol (150 mL), molar ratio Au/furfural/methanol = 1/500/5 × 10^5, 120 °C, 0.6 MPa O_2, 90 min.	Ce90Au300 Ce110Au300 Ce300Au300 Ce90Au500 Ce110Au500 Ce500Au500	29 29 54 6 28 74	100 100 100 100 100 100	[20]
5	Catalyst (0.05 g), furfural (2.1 mmol), K_2CO_3 (0.05 g), methanol (15 mL), molar ratio Au/furfural/methanol = 1/160/29,000, 140 °C, 0.3 MPa O_2, 4 h.	Au/FH + K_2CO_3	93	99	[14]
6	Catalyst (0.05 g), furfural (3.6 mmol), methanol (20 mL), molar ratio Au/furfural/methanol = 1/300/38,900, 120 °C, 1.5 MPa O_2, 3 h.	5%Au/CMK-3	99.7	99.6	[21]

[a] AZ150, AZ300, AZ500, AZ600, and AZ650 were the Au/ZrO_2 catalysts calcined in air for 1 h at 150 °C, 300 °C, 500 °C, 600 °C, and 650 °C, respectively. [b] Here, Ce90 means the synthesis temperature of the CeO_2 support was 90 °C without calcination. Ce110, Ce300, and Ce300 mean the CeO_2 supports without calcination and calcined at 300 °C and 500 °C, respectively. Au300 and Au500 mean the calcination temperatures of catalysts after loading Au were 300 °C and 500 °C, respectively.

Signoretto's team [18] performed several inspiring studies on the oxidative esterification of furfural catalyzed by Au nanoparticles supported on the metal oxides. They found that the Au/ZrO_2 catalyst could promote the oxidative esterification of furfural to MF efficiently without any base additive. The effect of the calcination temperature of the catalysts on their catalytic performance was investigated, and the catalyst obtained at 500 °C (AZ500) showed the best performance among the tested catalysts (Table 1, entry 2). Depending on the experiment results, the authors suggested that the calcination at 500 °C allowed the modulation of the size of the gold nanoparticles (below 3 nm) and stabilized the gold clusters, which could dissociate the O_2 molecules. The furfural conversion and

MF selectivity could reach 100% and 98%, respectively, over the AZ500 catalyst under optimal conditions.

Afterwards, Menegazzo et al. of Signoretto's team [19] investigated the catalytic performance of Au-based catalysts supported on different supports in the oxidative esterification of furfural. It was found that the catalytic performance followed the trend of $Au/ZrO_2 > Au/CeO_2 >> Au/TiO_2$ (Table 1, entry 3). Depending on the study of the properties and performance of the catalysts, it was declared that the surface area of the catalysts influenced the conversion of furfural, while the surface sites affected the selectivity of MF. Meanwhile, the Au/ZrO_2 was proven to be the ideal catalyst for the oxidative esterification of furfural due to its active, selective, recyclable, and applicable properties in this work.

Furthermore, Manzoli et al. of Signoretto's team [20] studied the effects of the calcination temperatures of supports and catalysts on the catalytic performance of Au/CeO_2 for furfural oxidative esterification (Table 1, entry 4). It was discovered that the calcination temperature could affect the structure properties of the catalysts, especially the particle size of Au, which affected the activity of the catalysts. It is noteworthy that the catalytic activity of the catalysts increased with the particle size, which was contrary to the conclusion obtained over Au/ZrO_2 catalysts in the authors' previous work [18]. The roles of CeO_2 and Au nanoparticles in the reaction were investigated and are shown in Figure 3. Depending on the experiment results, it was proposed that the Au cluster was not needed to activate O_2 over the Au/CeO_2 catalysts, which was different to the catalytic mechanism over the Au/ZrO_2 catalysts. As shown in Figure 3, the activated oxygen atoms were provided by the CeO_2 support and then spilled over from the support to the Au at the perimeter of the nanoparticles over the Au/CeO_2 catalysts. Meanwhile, the methanol molecules were activated at the perimeter of the Au nanoparticles.

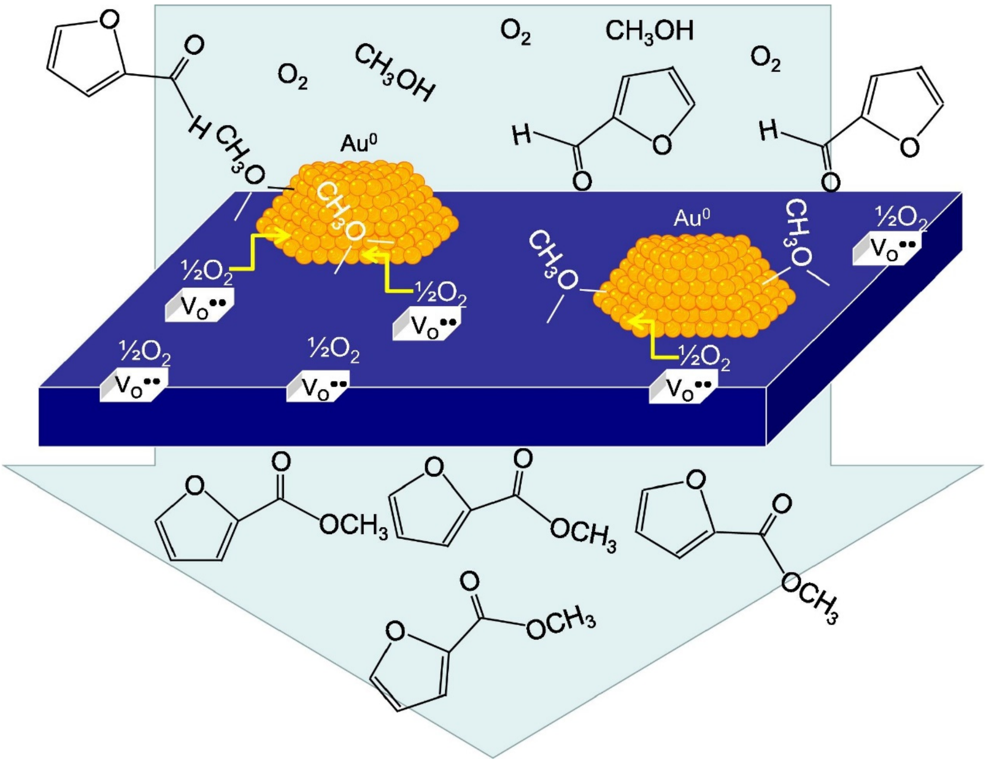

Figure 3. Proposed roles of CeO_2 and Au nanoparticles in the furfural oxidative esterification reaction. Reproduced with permission from [20]. Copyright: Elsevier 2015.

Tong et al. [14] applied a Au catalyst supported on FeO_x-modified hydroxyapatite (Au/FH) in the furfural oxidative esterification 93% conversion of furfural and 99% selectivity of MF were obtained with the addition of K_2CO_3 (Table 1, entry 5). It was considered that the special properties of the Au/FH catalyst, including the large surface area and pore volume, small and average Au nanoparticles, and numerous weak acid sites, led to its excellent catalytic performance. Moreover, it was declared that the basic FH support and K_2CO_3 promoted the semi-acetalization of furfural with methanol to generate the semi-acetal intermediate, and the Au/FH catalyst promoted the oxidation of the intermediate to produce MF.

Radhakrishnan et al. [21] prepared a Au catalyst supported on the ordered mesoporous carbon CMK-3, and compared its catalytic performance with the Au catalysts supported on SBA-15, graphite, graphene, MWCNT, activated carbon, and TiO_2 for furfural oxidative esterification. The Au/CMK-3 catalyst showed better activity than the other tested catalysts. The authors presumed the reason for the better performance of Au/CMK-3 was the excellent dispersion of smaller Au particles onto the pore channels of CMK-3. Excellent furfural conversion (99.7%) and MF selectivity (99.6%) were obtained under optimized conditions without any base additive (Table 1, entry 6).

In the above studies, Au was used as the active component for the oxidative esterification of furfural and exhibited good performance. The good dispersion of the Au could increase the performance of the Au catalysts, which were revealed in some studies. Meanwhile, the properties of the supports also had an obvious influence on the performance of the catalysts. On the one hand, the properties of supports could affect the dispersion of the Au particles, thereby affecting the performance of the catalysts. On the other hand, some special properties of the supports could also promote the catalytic activity of the catalysts. For example, the CeO_2 support activated the O_2 to produce activated oxygen atoms, and then the activated oxygen atoms spilled over to the Au particles to promoted the oxidative esterification reaction. In addition, homogeneous alkali additives were not needed when ZrO_2, TiO_2, CeO_2, and CMK-3 Au supports were used as catalysts. This was an advantage of these catalysis systems, because an extra separation process was necessary and additional by-products were usually generated if the homogeneous alkali additives were used.

2.2. Non-Noble Metal Catalysts

The current studies of non-noble metal catalytic systems for furfural oxidative esterification mainly focus on Co catalysts supported on the N-doped C materials. Beller's group [22] firstly prepared Co_3O_4-N@C catalysts by impregnating in-situ-generated amino-ligated cobalt(II) acetate complexes on Vulcan XC72R carbon powder with subsequent pyrolysis at 800 °C for 2 h (Figure 4), and applied the obtained catalysts in the oxidative esterification of alcohols. The catalysts exhibited good performance in the oxidative esterification of various alcohols such as aromatic alcohols, heterocyclic alcohols, and aliphatic alcohols. Inspired by this excellent work, Studies on furfural oxidative esterification over modified Co_xO_y-N/C catalytic systems were conducted to increase the activity of catalysts and reveal the catalytic mechanism in recent years.

Deng et al. [23] prepared a Co_xO_y catalyst supported on N-doped active carbon using a similar method to that reported by Beller's group, and studied the effect of ligands on the catalytic performance in the furfural oxidative esterification reaction. As shown in entry 1 of Table 2, the Co_xO_y-N@C catalyst prepared with the 1,10-phen ligand (Co_xO_y-N@C-1,10-phen) demonstrated good activity, with 100% conversion of furfural and 95% selectivity of MF. The activity was much better than the Co_xO_y-N@C catalyst prepared with the 2,2-diPy ligand (Co_xO_y-N@C-2,2-diPy), with 58% conversion of furfural and 46% selectivity of MF. The XPS results of the two catalysts indicated higher amounts of the pyridine-type nitrogen and grapheme-type nitrogen in the Co_xO_y-N@C-1,10-phen catalyst, which were the main active components of the metal–N@C catalysts. Moreover, the content of oxidized cobalt was higher in the Co_xO_y-N@C-1,10-phen catalyst than that in the Co_xO_y-N@C-2,2-diPy catalyst, which should be another reason for the better catalytic performance of the Co_xO_y-N@C-1,10-phen catalyst.

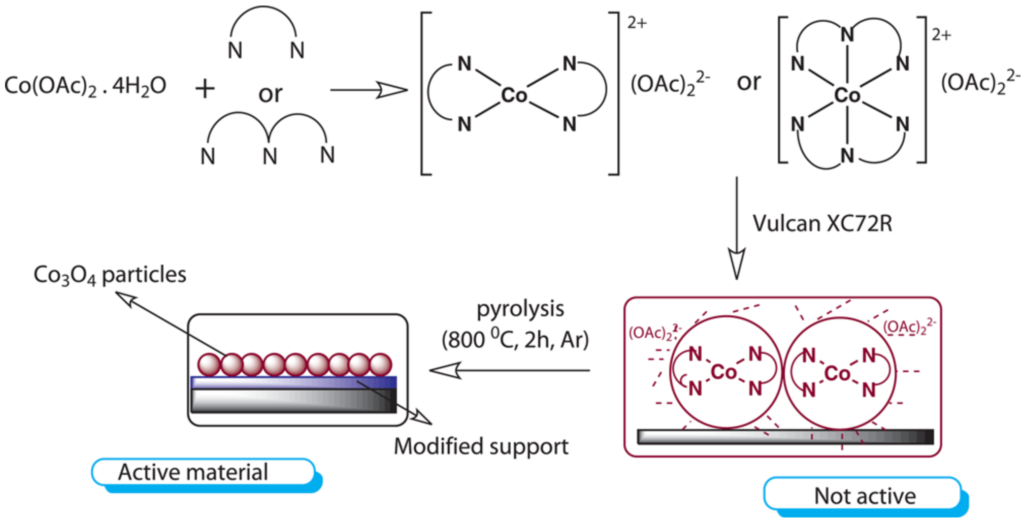

Figure 4. Preparation of Co_3O_4-N/C catalysts with different ligands. Reproduced with permission from [22]. Copyright: American Chemical Society 2013.

Table 2. Studies of oxidative esterification of furfural to MF over non-noble metal catalysts.

Entry	Condition	Catalyst	Furfural Conversion (%)	MF Selectivity (%)	Ref.
1	25 mg catalyst, 0.5 mmol furfural, 4 mL methanol, 0.2 equiv K_2CO_3, 0.1 MPa O_2, 60 °C, 12 h.	Co_xO_y-N@C	100	95	[23]
		Co_xO_y-2,2-diPy/C	58	46	
2	80 mg catalyst, 0.5 mmol furfural, 5 mL methanol, 0.5 MPa O_2, 100 °C, 6 h.	Co-N-C/MgO	89.3	90.1	[11]
		Co-N-C/MgO [a]	93.0	98.5	
		CoO_x-N/C	67.2	84.4	
		CoNC/CaO	22.0	38.8	
		CoNC/NaX	40.1	83.6	
		CoNC/NaY	64.0	85.4	
3	60 mg catalyst, 1 mmol furfural, 5 mL of methanol, 0.5 MPa O_2, 100 °C, 6 h.	CoO_x@N-C(g)	95.0	97.1	[24]

Note: [a] reaction time was 12 h.

Huo et al. [11] prepared A Co-N-C/MgO catalyst BY impregnating and pyrolyzing a cobalt(II) phenanthroline complex on MgO at 800 °C in N_2, and investigated its catalytic performance in the furfural oxidative esterification reaction. As shown in entry 2 of Table 2, the Co-N-C/MgO catalyst exhibited better activity than the Co-N-C catalysts supported on activated carbon, NaX, NaY, and CaO supports, and achieved 93.0% conversion of furfural and 98.5% selectivity of MF in the optimized condition without any base additive. Based on the comparative experiments, it was inferred that the MgO support might play a similar role with an alkaline additive such as K_2CO_3 to promote the reaction. Moreover, it was discovered that the Cl^- exhibited a negative influence on the reaction, and the oxygen pressure (0.3–1.0 MPa) had a negligible effect on the reaction by using the Co-N-C/MgO catalyst.

Wang et al. [24] synthesized a nitrogen-doped, carbon-encapsulated cobalt nanoparticles catalyst CoO_x@N-C(g) with an ultra-high N content of 14.0% via the impregnation and pyrolysis of a cobalt (II) phenanthroline complex, as shown in Figure 5. Significantly, g-C_3N_4 nanosheets were used as nitrogen sources and self-sacrificing templates in the preparation of the catalyst. The catalyst achieved excellent activity in the furfural oxidative esterification reaction, with 95.0% conversion of furfural and 97.1% selectivity of MF under a base-free condition (Table 2, entry 3). Depending on the structural analysis, it was found that an ultra-high N content of the catalyst with higher amounts of basic sites and pyridinic-N could be induced by the exfoliated g-C_3N_4 nanosheets. Meanwhile, it was revealed that the CoO_x@N-C(g) had the capacity for activating dioxygen and that the pyridinic-N might play a base role like K_2CO_3, which promoted the superior performance of the catalysts.

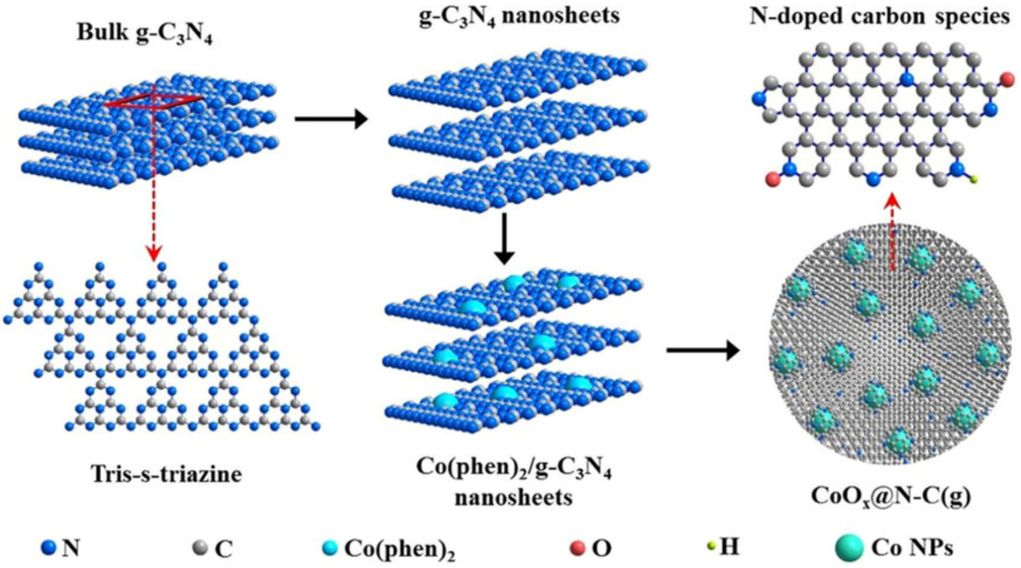

Figure 5. Schematic diagram of the synthesis process of the CoO_x@N-C(g) catalyst. Reproduced with permission from [24]. Copyright: Wiley 2019.

The above three studies all used similar N-modified Co in the active sites to catalyze the oxidative esterification of furfural. The catalytic performance of these catalysts was equivalent to that of the Au catalysts. However, the exact active sites of these catalysts were still unclear, and further studies are needed to reveal the active sites and reaction mechanism over the catalysts.

3. Oxidative Condensation of Furfural

The oxidative condensation of furfural with short-chain alcohols is also a significant utilization route of furfural. As shown in Figure 1, various renewable liquid biomass fuels can be prepared via this process. Meanwhile, the short-chain alcohols, such as ethanol, propanol, and butanol, can also be produced from renewable biomass resources through biological fermentation or chemical catalysis. Therefore, the oxidative condensation reaction is considered a promising route to develop renewable biomass fuels instead of fossil fuels. In recent years, many studies have focused on this reaction, and two different routes have been presented. In the one route, oxygen is used in the reaction to oxidize alcohols or generate furfuryl alcohol. In the other route, oxygen is not needed in the reaction and the oxidation process is conducted via hydrogen transfer between the furfural and alcohols. Herein, the studies using oxygen as the oxidant were reviewed first, and then the studies conducted using the hydrogen transfer process were reviewed subsequently.

3.1. Studies Using Oxygen as the Oxidant

Tong's team presented many inspirational studies for the oxidative condensation of furfural with aliphatic alcohols. Their studies mainly focused on the route using oxygen as oxidant. Both noble metal catalysts and non-noble metal catalysts were presented for the oxidative condensation of furfural.

Tong et al. [14] found that the Au catalyst supported on FeO_x modified hydroxyapatite (Au/FH) also showed good catalytic performance in the oxidative condensation reaction of furfural with n-propanol to produce C8, except its good activity in the oxidative esterification reaction of furfural as mentioned above. As shown in entry 1 of Table 3, the conversion of furfural and selectivity of C8 could reach 93% and 97%, respectively, when Au/FH was used as the catalyst and K_2CO_3 was used as the promoter. Moreover, it was proposed that the oxidation of propanol to propanal was the rate-controlling step, and the Au/FH catalyst and K_2CO_3 contributed to the oxidation of propanol and condensation between furfural and propanal, respectively.

Table 3. Studies of oxidative condensation of furfural with alcohols presented by Tong' group.

Entry	Condition	Catalyst	Aliphatic Alcohols	Furfural Conversion (%)	Product Seletivity (%)	Ref.
1	0.2 g furfural, 0.05 g catalyst, 0.05 g K_2CO_3, 15 mL n-propanol, 0.3 MPa O_2, 140 °C, 4 h.	Au/FH + K_2CO_3	n-propanol	94	97	[14]
2	0.2 g furfural, 0.05 g catalyst, 0.05 g K_2CO_3, 15 mL ethanol or n-propanol, 0.3 MPa O_2, 140 °C, 4 h.	Pt/FH + K_2CO_3	n-propanol	90.1	90.0	[25]
		Pt/H + K_2CO_3	n-propanol	73.0	90.1	
		Pt/HTc + K_2CO_3	n-propanol	87.8	88.5	
		Pt/Fe_3O_4 + K_2CO_3	n-propanol	80.6	91.1	
		Pt/Al_2O_3 + K_2CO_3	n-propanol	81.4	90.4	
		Pt/ZrO_2 + K_2CO_3	n-propanol	31.9	90.0	
		Pt/FH + K_2CO_3	ethanol	93.9	67.9	
3	0.2 g furfural, 0.05 g catalyst, 0.05 g additive, 15 mL n-propanol, 0.3 MPa O_2, 140 °C, 4 h.	Pt/FH + Cs_2CO_3	n-propanol	75.1	92.8	[26]
		Pt/FH + K_2CO_3		36.4	91.2	
		Pt/FH + Na_2CO_3		12.5	2.1	
		Pt/FH + Li_2CO_3		3.8	4.3	
		Pt/FH + $CaCO_3$		25.0	1.0	
		Pt/FH + KOH		82.3	93.2	
		Pt/FH + NaOH		75.9	53.4	
		Pt/FH + H_3PO_4		49.3	2.1	
4	0.2 g furfural, 0.05 g catalyst, 0.05 g K_2CO_3, 15 mL n-propanol, 0.3 MPa O_2, 140 °C, 4 h.	CuO-CeO_2 + K_2CO_3	n-propanol	85.4	95.3	[16]
			ethanol	83.2	92.1	
5	0.1 g furfural, 0.025 g catalyst, 0.025 g Cs_2CO_3, 15 mL ethanol or n-propanol, 0.3 MPa O_2, 140 °C, 4 h.	ACS-I + Cs_2CO_3	n-propanol	63.4	99	[27]
		ACS-II + Cs_2CO_3	n-propanol	84.9	99.7	
		ACS-I + Cs_2CO_3	ethanol	74.9	93.9	
		ACS-II + Cs_2CO_3	ethanol	83.3	83.2	
6	0.2 g furfural, 0.05 g catalyst, 0.05 g K_2CO_3, 15 mL aliphatic alcohol, 0.3 MPa O_2, 140 °C, 4 h.	Fe@C + K_2CO_3	ethanol	84.2	82.7	[28]
			n-propanol	86.7	96.2	
			i-propanol	50.7	78.1	
			n-butanol	55.6	53.3	
			n-pentanol	34.9	47.9	
			n-hexanol	26.8	36.4	
7	0.1 g furfural, 0.025 g catalyst, 0.025 g K_2CO_3, 15 mL ethanol, 0.3 MPa O_2, 140 °C, 4 h.	Au@UiO-66-COOH + K_2CO_3	ethanol	66.7	84.1	[29]
8	0.1 g furfural, 0.025 g catalyst, 0.025 g K_2CO_3, 15 mL ethanol, 0.3 MPa O_2, 140 °C, 4 h.	Pt@MOF-5 + K_2CO_3	ethanol	84.1	90.1	[30]
9	0.2 g furfural, 0.05 g catalyst, 0.05 g K_2CO_3, 15 mL ethanol or n-propanol, 0.3 MPa O_2, 140 °C, 4 h.	PdO@TiO_2 + K_2CO_3	n-propanol	77.8	89.2	[31]
			Ethanol	88.4	85.7	
10	0.2 g furfural, the initial ratio of azo dicarboxylates and K_2CO_3 is 7.5:10, 7.25% mol CuI, 7.25% mol Phen, 17.4mol% DBAD, 15 mL ethanol, 0.3 MPa O_2, 160 °C, 4 h.	CuI and o-phenanthroline + K_2CO_3	Ethanol	82.5	87.7	[32]
11	0.2 g furfural, 0.1 g catalyst, 15 mL ethanol, 0.3 MPa O_2, 140 °C, 4 h.	Au@CaO	Ethanol	85.9	81.8	[15]

Liu et al. [25] prepared various Pt catalysts supported on FeO_x–hydroxyapatite (FH), hydroxyapatite (H), calcined hydrotalcite (HTc), Fe_3O_4, Al_2O_3, and ZrO_2, and investigated their catalytic performance in the oxidative condensation reaction of furfural and aliphatic alcohols with the addition of K_2CO_3. The Pt/FH catalyst showed higher activity than the other catalysts in the oxidative condensation reaction of furfural and n-propanol, with 90.1% conversion of furfural and 90.0% selectivity of C8 (Table 3, entry 2). The large surface area and pore volume, small- and average-sized Pt nanoparticles, and numerous weak acid sites of the catalysts were considered the main factors for the superior catalytic performance of the catalysts. Moreover, the Pt/FH catalyst also showed good activity in the oxidative condensation reaction of furfural and ethanol, with 93.9% conversion of furfural and 69.7% selectivity of C7.

Yu et al. [26] synthesized a Co_xO_y-N@K-10 catalyst by impregnating and pyrolyzing a cobalt (II) phenanthroline complex on montmorillonite K-10 at 800 °C in N_2, and applied it for the oxidative condensation of furfural with aliphatic alcohols with the addition of $CsCO_3$, whereby 75.1% conversion of furfural and 92.8% selectivity of C8 were obtained in the oxidative condensation of furfural with n-propanol (Table 3, entry 3). The effects of additives on the catalytic performance were studied and the results were are shown in entry 3 of Table 2. The catalytic systems with strong base additives such as NaOH and KOH exhibited higher furfural conversion rates than with the other additives, which revealed that the strong bases were effective and essential in this reaction. Furthermore, the oxidative condensation of furfural with various aliphatic alcohols using the Co_xO_y-N@K-10+ Cs_2CO_3 system was further investigated, and the results are reprinted in Figure 6. As can be seen, the oxidative condensation process became more difficult with the growth of the carbon chains in the alcohol molecules. The reaction mechanism for the reaction was further studied and the proposed reaction mechanism is reprinted in Figure 7. As shown in Figure 7, firstly slight n-propanol was oxidized by O_2 to produce slight molecular propanal, and then the in-situ-generated propanal reacted with furfural rapidly via an aldol condensation process to produce the C8. Meanwhile, another route was presumed to occur simultaneously in the reaction system, as shown in Figure 7. In this route, the hydrogen transfer process occurred firstly between furfural and n-propanol, and certain amounts of propanal and furfuryl alcohol were generated. Afterwards, the condensation was conducted between the remaining furfural and the generated propanal, while the furfuryl alcohol was oxidized to furfural by O_2.

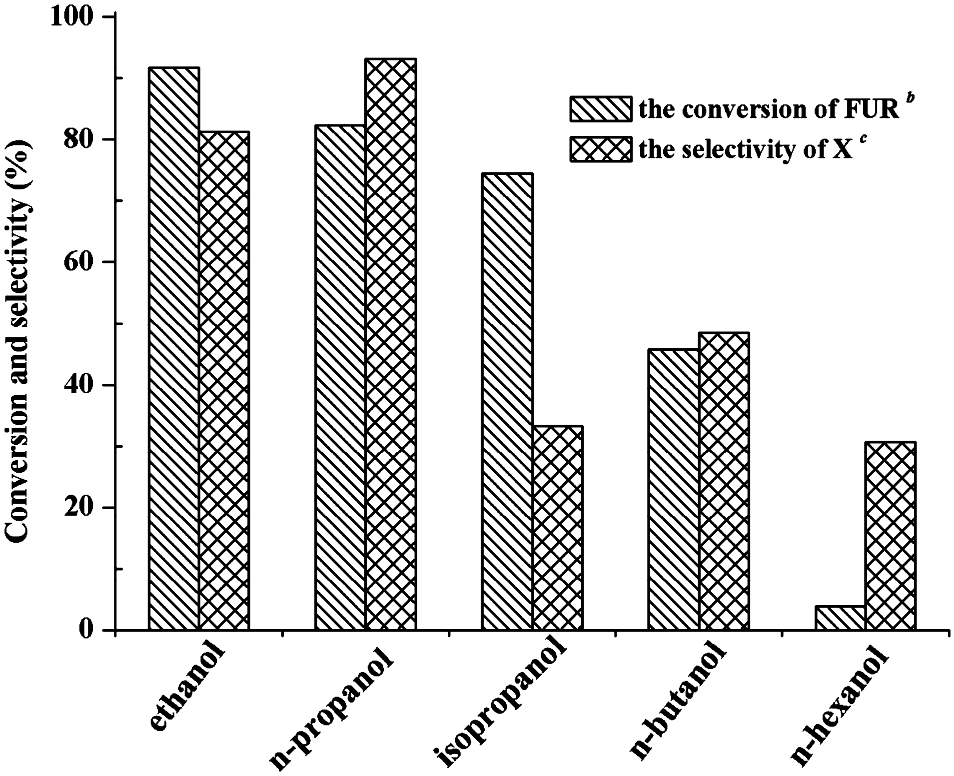

Figure 6. Oxidative condensation of furfural with various alcohols. Reaction conditions: 0.2 g of furfural, 0.05 g Co_xO_y-N/K-10 catalyst (2 wt% loading) and 0.05 g Cs_2CO_3, 15 mL n-propanol, 0.3 MPa O_2, 140 °C, 4 h. ^{b} The conversion of furfural. ^{c} The selectivity of oxidative condensation products. Reproduced with permission from [26]. Copyright: American Chemical Society 2016.

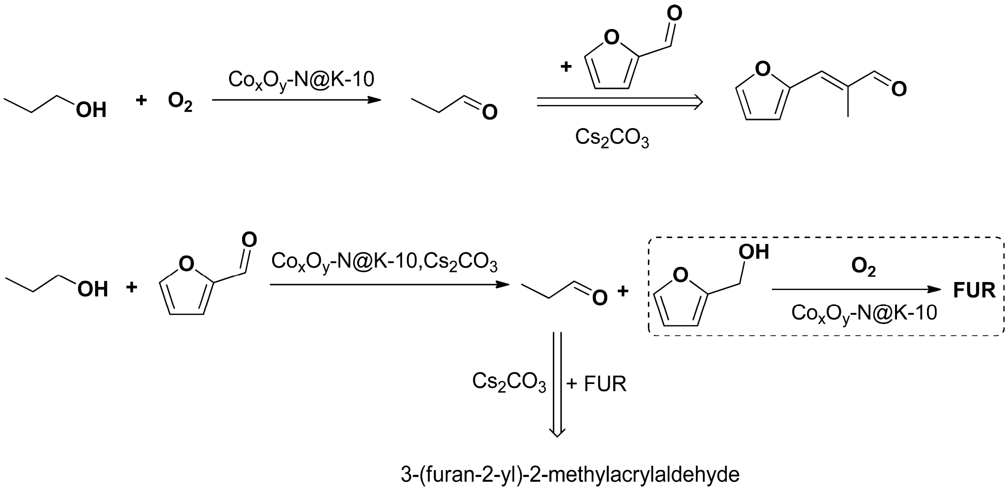

Figure 7. Proposed catalytic routes for the oxidative condensation of furfural with n-propanol. Reproduced with permission from [26]. Copyright: American Chemical Society 2016.

Tong et al. [16] applied simple and low-cost mixed Cu-Ce oxides as the catalysts to catalyze the oxidative condensation of furfural with aliphatic alcohols. The conversion of furfural and selectivity of C8 reached 85.4% and 95.3%, respectively, in the furfural-n-propanol-O_2 system with the addition of K_2CO_3 (Table 3, entry 4). Depending on the experiment results, it was concluded that the component of the catalyst promoted the conversion of furfural, while the surface area and weak acid sites of the catalyst were responsible for the good selectivity of C8. Moreover, the CuO-CeO_2 catalyst also exhibited high activity in the oxidative condensation reaction of furfural and ethanol, with 93.9% conversion of furfural and 69.7% selectivity of C7.

Ning et al. [27] prepared two types of Co-based catalysts denominated as ACS-I and ACS-II using 2D Co-based MOFs ($[Co(tia)(H_2O)_2]_n$) as precursors. The ACS-I catalyst was produced by removing coordinated water molecules of the precursor under Ar atmosphere at 300 °C, while the ACS-II catalyst was obtained by pyrolyzing the precursor at 700 °C. Both the catalysts showed good performance in the oxidative condensation of furfural with aliphatic alcohols. In the furfural-n-propanol-O_2 system, 63.4% conversion of furfural and 99% selectivity of C8 were obtained for the ACS-I catalyst, while the furfural conversion and selectivity of C8 were increased by up to 84.9% and 99.7%, respectively, for the ACS-II catalyst (Table 3, entry 5). Based on the experiment results, it was concluded that active sites of the ACS-I catalyst were generated from the unsaturated coordinated open Co centers in the 2D layers, while the active sites of the ACS-II catalyst were the well-defined multi-elementary nanocomposites. Meanwhile, the real active sites were proved to be metal Co in both the ACS-I and ACS-II catalysts by comparing them with the catalytic performance of Ni-based catalysts prepared form Ni-based MOFs in similar process.

Zhang et al. [28] prepared a Fe@C catalyst via the thermal decomposition of an Fe-EDTA complex under H_2 atmosphere at 450 °C, and applied it in the oxidative condensation of furfural with aliphatic alcohols. The conversion of furfural and selectivity of C7 reached 84.2% and 82.7%, respectively, in the furfural-ethanol-O_2 system (Table 3, entry 6). The catalyst also showed good performance in the oxidative condensation of furfural with other low chain alcohols, as shown in Table 2. The oxidative condensation process also became more difficult with the growth of the carbon chains in the alcohol molecules, which was consistent with the previously reported results. In the reaction with n-propanol, furfural conversion of 86.7% and C8 selectivity of 96.2% were achieved.

Ning et al. [29] prepared a Au catalyst supported on functionalized MOFs of UiO-66 (Au@UiO-66-COOH), and investigated its performance in the oxidative condensation of furfural with ethanol, whereby 66.7% conversion of furfural and 84.1% selectivity of C7 were achieved in the furfural-ethanol-O_2 system with the addition of K_2CO_3 (Table 3, entry 7). Depending on the experimental results, it was considered that the oxidative condensation of furfural with ethanol in this system followed a route similar to the route shown in Figure 7. In the first step, a hydrogen transfer process between furfural and ethanol was conducted and small amounts of acetaldehyde and furfuryl alcohol were generated. Then, the condensation reaction happened immediately between furfural and the in-situ-generated acetaldehyde, and the generated furfuryl alcohol was oxidized to furfural by O_2. In this process, the hydrogen transfer and condensation reaction were mainly attributed to the synergetic effect between UiO-66-COOH and K_2CO_3, and the oxidation of furfuryl alcohol was promoted by the UiO-66-COOH.

Ning et al. [30] designed a Pt@MOF-5 catalyst, in which the Pt nanoparticles were confined in the pores of MOF-5 to improve the dispersion and stability of the Pt nanoparticles. The Pt@MOF-5 catalyst was applied in the oxidative condensation of furfural with ethanol, and 84.1% conversion of furfural and 90.1% selectivity of C7 were achieved with the addition of K_2CO_3 (Table 3, entry 8). The good performance of the catalyst was attributed to the synergistic effect among the Pt nanoparticles, MOFs, and additives. More importantly, the Pt@MOF-5 catalysts were very stable under the reaction condition and exhibited excellent recycling performance in the reused experiments.

Tong et al. [31] fabricated a TiO_2-nanosheet-anchored PdO catalyst (PdO@TiO_2) for the oxidative condensation of furfural with aliphatic alcohols, with the addition of K_2CO_3, whereby 77.8% conversion of furfural and 89.2% selectivity of C8 were achieved in the furfural-n-propanol-O_2 system. Meanwhile, the catalyst also exhibited notable performance in the oxidative condensation of furfural with ethanol, and achieved 88.4% conversion of furfural and 85.7% selectivity of C7 (Table 3, entry 9). It was declared that the good catalytic activity was attributed to the uniform distribution of PdO and large surface area of the TiO_2 support.

Cui et al. [32] applied a homogeneous catalytic system for the oxidative condensation of furfural with ethanol, in which the reaction was conducted in two steps. In the first step, the hydrogen transfer between furfural and ethanol was proceeded under the N_2 atmosphere by combining the azodicarboxylate and K_2CO_3 to produce furfuryl alcohol and C7. In the second step, the CuI and O_2 were supplemented into the reaction system to increase the yield of C7. Under the catalyzation by CuI and o-phenanthroline, 82.5% conversion of furfural with 87.7% selectivity of C7 could be achieved with the assistance of diethylazodicarboxylate (DEAD) and K_2CO_3 (Table 3, entry 10).

Gao et al. [15] presented a novel catalytic system for the oxidative condensation of furfural with ethanol, in which base additives were not needed for the reaction. In the study, CaO-supported Au catalysts (Au@CaO) were prepared using the colloid immobilization method and applied in the oxidative condensation of furfural with ethanol, whereby 85.9% conversion of furfural and 81.8% selectivity of C7 were achieved without any base additives (Table 3, entry 11). Based on further investigations, it was declared that the synergistic effect between the Au nanoparticles and basic CaO support was responsible for the production of C7.

As summarized above, Tong's group presented various catalytic systems for the oxidative condensation of furfural with aliphatic alcohols. Both noble metal catalysts and non-noble metal catalysts exhibited excellent activity in the oxidative condensation of furfural with aliphatic alcohols, especially in the reaction with the n-propanol and ethanol. The reaction routes were considered to be the same in all studies and are shown in Figure 7. The homogeneous alkali additives were used in most of the catalytic systems, except for the catalytic system using Au/CaO as the catalyst, because the condensation process was considered to be promoted by the base, as shown in the Figure 7. The usage of basic supports or basic heterogeneous catalysts may be a good method to avoid the use of homogeneous alkali additives.

3.2. Studies Conducted via Hydrogen Transfer Process

Li et al. [33] demonstrated a new route for the oxidative condensation of furfural with ethanol to prepare C7 by combining Meerwein–Ponndorf–Verley (MPV) reduction with in situ cross-aldol condensation. As shown in Figure 8, oxygen was not needed in this system, and the oxidation of ethanol was conducted through a transfer hydrogenation process of the MPV reduction catalyzed by Lewis acid (Zr-β zeolite). Simultaneously, the condensation reaction was conducted between the left furfural and the in-situ-generated aldehyde under the catalysis of K_2CO_3. Two valuable chemicals, furfuryl alcohol and C7, with similar yields (∼40.0%) simultaneously produced from furfural in this reaction.

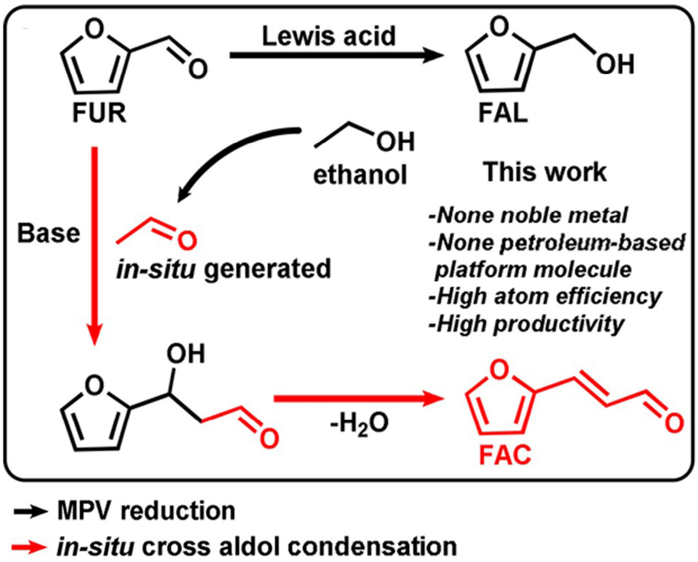

Figure 8. An integrated process combining MPV reduction with in situ cross-aldol condensation for the upgrading of furfural in ethanol to FAL and C7. Reproduced with permission from [33]. Copyright: American Chemical Society 2018.

Yang et al. [34] presented a new catalytic system for the oxidative condensation reactions of furfural with alcohols in the absence of any homogeneous base additives. Similar to Li's work, the oxidation reaction of the alcohols was also conducted through a transfer hydrogenation process between furfural and alcohols, as shown in Figure 9. The authors prepared an Fe/FeOx@LDH (layered double hydroxides) catalyst via the reduction of pre-synthesized complex anion tris(oxalato)ferrate(III)-intercalated LDH, and investigated its catalytic performance in the reaction of furfural with n-propanol under oxidative, inert, and reductive reaction atmospheres by filling the reactor with 0.5 MPa of O_2, Ar, or a mixture gas of Ar (95%) and H_2 (5%), respectively. As shown in Table 4, the conversion rate of furfural under O_2 was only 20.8%, which was significantly lower than the conversion rates (71.3% and 71.4%, respectively) with the Ar and H_2/Ar mixed gases. The reason was supposed to be that Fe/FeO_x could be oxidized easily in the O_2 atmosphere and lost its catalytic activity for the transfer hydrogenation. Under optimal reaction conditions, furfural conversion of 71.3% and C8 selectivity of 87.1% were achieved without any base additive under the atmosphere of Ar. Based on the results of the control experiments, it was revealed that the catalytic active components for the transfer hydrogenation were the composite Fe/FeO_x@LDH rather than the sole Fe/FeO_x and LDH. The catalyst also exhibited good activity in the reaction of furfural with ethanol, and furfural conversion of 89.3% and C7 selectivity of about 99% were achieved under the atmosphere of 0.65 MPa Ar. However, the Fe/FeO_x in the used catalyst was easily oxidized during the drying process of the cycle experiments, leading to the deactivation of the catalyst. Although the cyclic stability of the catalyst could be effectively improved by soaking it in the $Ni(NO_3)_2$ solution, the conversion rate of furfural (48.4%) in the first cycle was much lower than that (71.3%) before the treatment.

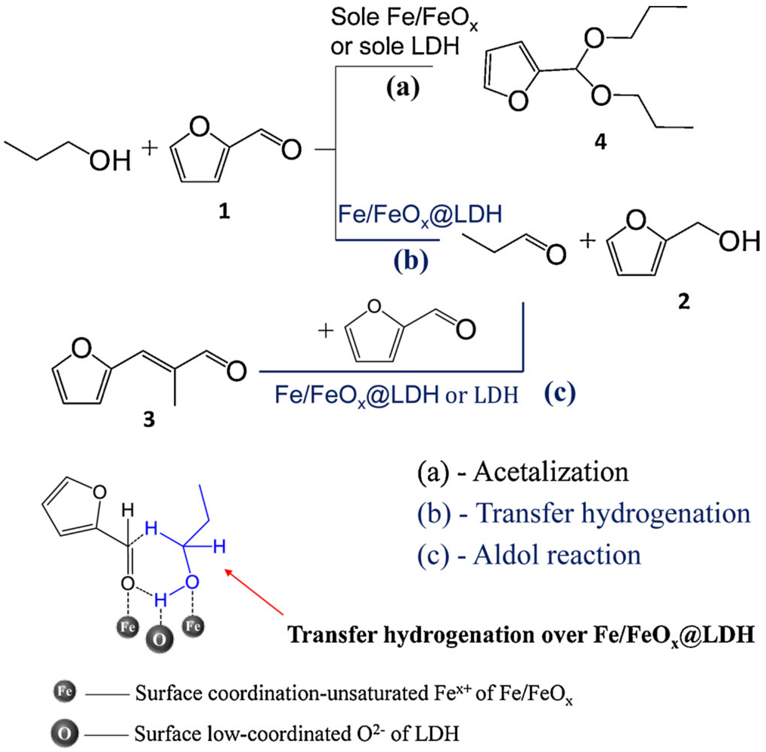

Figure 9. Possible reaction routes using Fe/FeOx@LDH, Fe/FeOx@LDH, and LDH as catalysts. Reproduced with permission from [34]. Copyright: Elsevier 2020.

Table 4. Studies of oxidative condensation of furfural with n-propanol in different gas atmospheres [a] [34].

Entry	Gas Atmosphere	Furfural Conversion (%)	Product Seletivity (%)
1	O_2	20.8	~99
2	Ar	71.3	87.1
3	mixture gas of Ar (95%) and H_2 (5%)	71.4	~99

[a] Reaction conditions: 50 mg Fe/FeO$_x$@LDH catalyst, 1 mmol furfural, 5 mL n-propanol, 45 µL o-xylene (internal standard), gas pressure: 0.5 MPa, 140 °C, 4 h.

4. Summary and Prospect

The oxidative esterification and oxidative condensation of furfural with aliphatic alcohols are two significant utilization routes of furfural. MF can be obtained through the oxidative esterification reaction, while various renewable liquid biomass fuels can be prepared via the oxidative condensation reaction. For the oxidative esterification reaction, supported Au catalysts were designed for the reaction and showed good activity. Among them, the ZrO_2-, CeO_2-, TiO_2-, and CMK-3-supported catalysts could catalyze the oxidative esterification reaction with high furfural conversion and MF selectivity rates in the condition, without homogeneous base additives. In addition, N-doped C materials supported Co_xO_y also exhibited good performance in the oxidative esterification reaction. For the oxidative condensation reaction, Tong's team presented many inspirational studies for the reaction by using oxygen as the oxidant. The reported catalysts showed excellent performance in the oxidative condensation of furfural with n-propanol or ethanol. The homogeneous base additives were used in most of the reported catalytic systems, except the catalytic system with Au@CaO as the catalyst. Furthermore, several studies have presented a new route for the oxidative condensation reaction, in which the oxidation reaction of the alcohols is conducted through a transfer hydrogenation process between furfural and alcohols.

In order to promote the commercial application of the oxidative esterification and oxidative condensation reactions of furfural, some factors should be focused on in the future studies. Firstly, usage of the homogeneous base additives should be avoided as much as possible to decrease the product separation cost. Secondly, catalysts with low dosages of noble metals and excellent performance should be prepared. The design of noble metal and non-noble metal composite catalysts to utilize the synergistic effect between the two metals may be a feasible method. Moreover, the concentration of furfural in the alcohols should be increased to make the process more economical and efficient.

Author Contributions: Writing—original draft preparation, J.T. and X.C.; writing—review and editing, Y.F., W.F., P.D., G.L. and Y.G. All authors have read and agreed to the published version of the manuscript.

Funding: This work was funded by Young Science and Technology Fund in Gansu Province of China (grant no. 21JR7RA251) and National Natural Science Foundation of China (grant no. 21902164).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the first author.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Delidovich, I.; Leonhard, K.; Palkovits, R. Cellulose and hemicellulose valorisation: An integrated challenge of catalysis and reaction engineering. *Energy Environ. Sci.* **2014**, *7*, 2803–2830. [CrossRef]
2. Zhang, T.; Li, W.; Xiao, H.; Jin, Y.; Wu, S. Recent progress in direct production of furfural from lignocellulosic residues and hemicellulose. *Bioresour. Technol.* **2022**, *354*, 127126. [CrossRef] [PubMed]
3. Lee, Y.; Kwon, E.E.; Lee, J. Polymers derived from hemicellulosic parts of lignocellulosic biomass. *Rev. Environ. Sci. Biol.* **2019**, *18*, 317–334. [CrossRef]
4. Cousin, E.; Namhaed, K.; Peres, Y.; Cognet, P.; Delmas, M.; Hermansyah, H.; Gozan, M.; Alaba, P.A.; Aroua, M.K. Towards efficient and greener processes for furfural production from biomass: A review of the recent trends. *Sci. Total Environ.* **2022**, *847*, 157599. [CrossRef]
5. Jiang, Z.; Hu, D.; Zhao, Z.; Yi, Z.; Chen, Z.; Yan, K. Mini-review on the synthesis of furfural and levulinic acid from lignocellulosic biomass. *Processes* **2021**, *9*, 1234. [CrossRef]
6. Mariscal, R.; Maireles-Torres, P.; Ojeda, M.; Sádaba, I.; López Granados, M. Furfural: A renewable and versatile platform molecule for the synthesis of chemicals and fuels. *Energy Environ. Sci.* **2016**, *9*, 1144–1189. [CrossRef]
7. Sun, Y.; Wang, Z.; Liu, Y.N.; Meng, X.H.; Qu, J.B.; Liu, C.Y.; Qu, B. A review on the transformation of furfural residue for value-added products. *Energies* **2020**, *13*, 21. [CrossRef]
8. Zhu, J.; Yin, G. Catalytic transformation of the furfural platform into bifunctionalized monomers for polymer synthesis. *ACS Catal.* **2021**, *11*, 10058–10083. [CrossRef]
9. Yan, K.; Wu, G.; Lafleur, T.; Jarvis, C. Production, properties and catalytic hydrogenation of furfural to fuel additives and value−added chemicals. *Renew. Sustain. Energy Rev.* **2014**, *38*, 663–676. [CrossRef]
10. Zhang, Z.; Du, B.; Quan, Z.; Da, Y.; Wang, X. Dehydration of biomass to furfural catalyzed by reusable polymer bound sulfonic acid (PEG-OSO$_3$H) in ionic liquid. *Catal. Sci. Technol.* **2014**, *4*, 633–638. [CrossRef]
11. Huo, N.; Ma, H.; Wang, X.; Wang, T.; Wang, G.; Wang, T.; Houa, L.; Gao, J.; Xu, J. High-efficiency oxidative esterification of furfural to methylfuroate with a non-precious metal Co-N-C/MgO catalyst. *Chin. J. Catal.* **2017**, *38*, 1148–1154. [CrossRef]
12. Taarning, E.; Nielsen, I.S.; Egeblad, K.; Madsen, R.; Christensen, C.H. Chemicals from renewables: Aerobic oxidation of furfural and hydroxymethylfurfural over gold catalysts. *ChemSusChem* **2008**, *1*, 75–78. [CrossRef] [PubMed]
13. Nielsen, I.S.; Taarning, E.; Egeblad, K.; Madsen, R.; Christensen, C.H. Direct aerobic oxidation of primary alcohols to methyl esters catalyzed by a heterogeneous gold catalyst. *Catal. Lett.* **2007**, *116*, 35–40. [CrossRef]
14. Tong, X.; Liu, Z.; Yu, L.; Li, Y. A tunable process: Catalytic transformation of renewable furfural with aliphatic alcohols in the presence of molecular oxygen. *Chem. Commun.* **2015**, *51*, 3674–3677. [CrossRef] [PubMed]
15. Gao, Y.; Tong, X.; Zhang, H. A selective oxidative valorization of biomass-derived furfural and ethanol with the supported gold catalysts. *Catal. Today* **2020**, *355*, 238–245. [CrossRef]
16. Tong, X.; Yu, L.; Luo, X.; Zhuang, X.; Liao, S.; Xue, S. Efficient and selective transformation of biomass-derived furfural with aliphatic alcohols catalyzed by a binary Cu-Ce oxide. *Catal. Today* **2017**, *298*, 175–180. [CrossRef]
17. Xu, B.; Liu, X.; Haubrich, J.; Friend, C.M. Vapour-phase gold-surface-mediated coupling of aldehydes with methanol. *Nat. Chem.* **2010**, *2*, 61–65. [CrossRef] [PubMed]

18. Signoretto, M.; Menegazzo, F.; Contessotto, L.; Pinna, F.; Manzoli, M.; Boccuzzi, F. Au/ZrO_2: An efficient and reusable catalyst for the oxidative esterification of renewable furfural. *Appl. Catal. B Environ.* **2013**, *129*, 287–293. [CrossRef]
19. Menegazzo, F.; Signoretto, M.; Pinna, F.; Manzoli, M.; Aina, V.; Cerrato, G.; Boccuzzi, F. Oxidative esterification of renewable furfural on gold-based catalysts: Which is the best support? *J. Catal.* **2014**, *309*, 241–247. [CrossRef]
20. Manzoli, M.; Menegazzo, F.; Signoretto, M.; Cruciani, G.; Pinna, F. Effects of synthetic parameters on the catalytic performance of Au/CeO_2 for furfural oxidative esterification. *J. Catal.* **2015**, *330*, 465–473. [CrossRef]
21. Radhakrishnan, R.; Thiripuranthagan, S.; Devarajan, A.; Kumaravel, S.; Erusappan, E.; Kannan, K. Oxidative esterification of furfural by Au nanoparticles supported CMK-3 mesoporous catalysts. *Appl. Catal. A Gen.* **2017**, *545*, 33–43. [CrossRef]
22. Jagadeesh, R.V.; Junge, H.; Pohl, M.; Radnik, J.; Brückner, A.; Beller, M. Selective oxidation of alcohols to esters using heterogeneous Co_3O_4-N@C catalysts under mild conditions. *J. Am. Chem. Soc.* **2013**, *135*, 10776–10782. [CrossRef] [PubMed]
23. Deng, J.; Song, H.; Cui, M.; Du, Y.; Fu, Y. Aerobic oxidation of hydroxymethylfurfural and furfural by using heterogeneous Co_xO_y-N@C catalysts. *ChemSusChem* **2014**, *7*, 3334–3340. [CrossRef] [PubMed]
24. Wang, T.; Ma, H.; Liu, X.; Luo, Y.; Zhang, S.; Sun, Y.; Wang, X.; Gao, J.; Xu, J. Ultrahigh-content nitrogen-doped carbon encapsulating cobalt NPs as catalyst for oxidative esterification of furfural. *Chem. Asian J.* **2019**, *14*, 1515–1522. [CrossRef]
25. Liu, Z.; Tong, X.; Liu, J.; Xue, S. A smart catalyst system for the valorization of renewable furfural in aliphatic alcohols. *Catal. Sci. Technol.* **2016**, *6*, 1214–1221. [CrossRef]
26. Yu, L.; Liao, S.; Ning, L.; Xue, S.; Liu, Z.; Tong, X. Sustainable and cost-effective protocol for cascade oxidative condensation of furfural with aliphatic alcohols. *ACS Sustain. Chem. Eng.* **2016**, *4*, 1894–1898. [CrossRef]
27. Ning, L.; Liao, S.; Liu, X.; Yu, L.; Zhuang, X.; Tong, X. Selective transformation of renewable furfural catalyzed by diverse active species derived from 2D Co-based metal-organic frameworks. *J. Catal.* **2017**, *352*, 480–490. [CrossRef]
28. Zhang, Z.; Tong, X.; Zhang, H.; Li, Y. Versatile catalysis of iron: Tunable and selective transformation of biomass-derived furfural in aliphatic alcohol. *Green Chem.* **2018**, *20*, 3092–3100. [CrossRef]
29. Ning, L.; Liao, S.; Liu, X.; Guo, P.; Zhang, Z.; Zhang, H.; Tong, X. A regulatable oxidative valorization of furfural with aliphatic alcohols catalyzed by functionalized metal-organic frameworks-supported Au nanoparticles. *J. Catal.* **2018**, *364*, 1–13. [CrossRef]
30. Ning, L.; Liao, S.; Cui, H.; Yu, L.; Tong, X. Selective conversion of renewable furfural with ethanol to produce furan-2-acrolein mediated by Pt@MOF-5. *ACS Sustain. Chem. Eng.* **2018**, *6*, 135–142. [CrossRef]
31. Tong, X.; Zhang, Z.; Gao, Y.; Zhang, Y.; Yu, L.; Li, Y. Selective carbon-chain increasing of renewable furfural utilizing oxidative condensation reaction catalyzed by mono-dispersed palladium oxide. *Mol. Catal.* **2019**, *477*, 110545. [CrossRef]
32. Cui, H.; Tong, X.; Yu, L.; Zhang, M.; Yan, Y.; Zhuang, X. A catalytic oxidative valorization of biomass-derived furfural with ethanol by copper/azodicarboxylate system. *Catal. Today* **2019**, *319*, 100–104. [CrossRef]
33. Li, G.; Jiao, W.; Sun, Z.; Zhao, Y.; Shi, Z.; Yan, Y.; Feng, L.; Zhang, Y.; Tang, Y. A scalable upgrading of concentrated furfural in ethanol: Combining Meerwein–Ponndorf–Verley reduction with in situ cross aldol condensation. *ACS Sustain. Chem. Eng.* **2018**, *6*, 4316–4320. [CrossRef]
34. Zhong, Y.; Zhou, B.; Wang, L. Fe/FeO_x embedded in LDH catalyzing C-C bond forming reactions of furfural with alcohols in the absence of a homogeneous base. *Mol. Catal.* **2020**, *493*, 111056. [CrossRef]