Recent Advances in Catalytic Hydrogenation of Furfural

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Abstract: Furfural has been considered as one of the most promising platform molecules directly derived from biomass. The hydrogenation of furfural is one of the most versatile reactions to upgrade furanic components to biofuels. For instance, it can lead to plenty of downstream products, such as (tetrahydro)furfuryl alcohol, 2-methyl(tetrahydro)furan, lactones, levulinates, cyclopentanone(I), or diols, etc. The aim of this review is to discuss recent advances in the catalytic hydrogenation of furfural towards (tetrahydro)furfuryl alcohol and 2-methyl(tetrahydro)furan in terms of different non-noble metal and noble metal catalytic systems. Reaction mechanisms that are related to the different catalytic materials and reaction conditions are properly discussed. Selective hydrogenation of furfural could be modified not only by varying the types of catalyst (nature of metal, support, and preparation method) and reaction conditions, but also by altering the reaction regime, namely from batch to continuous flow. In any case, furfural catalytic hydrogenation is an open research line, which represents an attractive option for biomass valorization towards valuable chemicals and fuels.

Keywords: furfural; catalytic hydrogenation; biomass; heterogeneous catalyst; continuous flow

1. Introduction

The exploration and development of new, non-fossil carbon energy sources are urgently needed due to the increasing energy consumption and the decreasing reserves of fossil resources and global ecological degradation [1]. In this regards, biomass conversion is a promising way to overcome the dependence of society on fossil hydrocarbons (oil, coal, and gas), especially in fuel production and energy areas [2]. Via bio-refinery, lignocellulose can be converted into relevant chemicals, such as furfural [3–10], 5-hydroxymethylfurfural (HMF) [11–15], and alkyl levulinates [16–20], among others. In particular, furfural has been recognized as a crucial bio-based platform molecule, and therefore, its valorization has been attracting researchers’ attention in recent years. As illustrated in Figure 1, several processes, including hydrogenation, oxidation and cyanation, could produce furfural downstream products. Undoubtedly, it can be concluded that the most important and extended application of furfural is focused on its hydrogenation, since ca. 62% of furfural was industrially used for furfuryl alcohol (FA) production [21].
Figure 1. Downstream products of furfural, obtained by hydrogenation (in green), oxidation (in red), cyanation, and other processes (in blue).

FA is a very important monomer for the synthesis of furan resins, which are widely used in thermoset polymer matrix composites, cements, adhesives, coatings, and casting/foundry resins. This molecule is also used as a non-reactive diluent for epoxy resin, a modifier for phenolic and urea resins, an oil well, and a carbon binder. Furthermore, the salt of FA is used in the synthesis of lysine, vitamin C, lubricants, and plasticizers [22,23]. Moreover, it should be highlighted that FA is also an important intermediate for the production of further hydrogenation products (as shown in Scheme 1), such as 2-methylfuran (MF), a potential alternative fuel with better combustion performance and higher Research Octane Number (RON = 103) than that of gasoline (RON = 96.8) [24]. In other applications, MF is used in perfume intermediates, chloroquine lateral chains in medical intermediates, and as a raw material for the production of chrysanthemate pesticides [25].

Moreover, tetrahydrofurfuryl alcohol (THFA) can be used as a green solvent in the pharmaceutical industry and, in addition, it constitutes an outstanding intermediate to produce dihydropyran [26], pyridine [27], tetrahydrofuran, and pentan-1,5-diol [28–30]. Particularly, the latest molecule is an important monomer in the plastics industry. Furthermore, 2-methyltetrahydrofuran (MTHF) is quite engaging for its possible applications in organometallic chemistry, as well as in organic reactions that are related to organocatalysis, biotransformations, and biomass processing [31].
Other downstream products of furfural hydrogenation, such as (tetrahydro)furan [32], tetrahydrofurfural [33], lactones [34–37], levulinates [38,39], cyclopentanone(l) [40–51], or diols [52–55], could also be employed as fuel additives, solvents, and platform molecules. Numerous studies on furfural hydrogenation have been published due to the attractive and broad range of applications of the aforementioned furfural-based compounds. However, to the best of our knowledge, very limited works have been focused on furfural selective hydrogenation [56–58]. The most recent contribution in this regard was addressed by Yan et al. in 2014, through a critical review. Such work focused on furfural hydrogenation towards different products, such as MF, MTHF, FA, THFA, furan, tetrahydrofuran, as well as various cyclo-products [58]. After 2014, there has been a blank period, in which even when the study of furfural hydrogenation has rapidly increased and emerged into a very dynamic research field, no systematical review has been reported to shine a light on the future of furfural hydrogenation.

Therefore, in the present review, recent advances in catalytic hydrogenation of furfural to (tetrahydro)furfuryl alcohol and 2-methyl(tetrahydro)furan in the latest five years will be discussed. This contribution will be mainly focused on catalytic processes while using different kinds of materials, such as non-noble metal (Cu [59–69], Ni [70–80], Co [73,81–83], etc.), and noble metal (Pd [32,33,84–93], Pt [49,55,92,94–99], Ru [84,100–105], etc.) based catalysts. Additionally, special attention will be devoted to the possible reaction mechanisms for the different described reactions.

Although it will not be the focus of our main attention, it should be highlighted that furfural valorization via bio-catalytic and electro-catalytic hydrogenation [21,106–112] has also attracted the interest of the scientific community in recent years, being both, emerging environmentally friendly approaches for the selective reduction of multifunctional chemicals.

2. Non-Noble Metal Catalysts

Over the past few years, non-noble metal catalysts have attracted much attention due to their comparable properties with noble metal catalysts in both homogeneous and heterogeneous catalysis [113–117]. In particular, furfural hydrogenation has been widely tested while using various non-noble metal catalysts, such as Cu, Co, Ni, and Zr, among others. In this section, recent advances in furfural hydrogenation using non-noble metal catalysts will be discussed.

2.1. Cu Based Catalysts

Especially, Cu-based catalysts have been well recognized for its low price, accessibility, and satisfactory hydrogenation selectivity. Therefore, the scientific community has started to move
towards the use of this metal for catalytic hydrogenation processes. Several examples will be addressed below in order to provide a general panorama in this regard.

For instance, Sun et al. have investigated the morphological effect of non-supported copper nanocrystals on furfural hydrogenation [118]. They found out that Cu nanowires exhibited three times higher TOF than Cu nanodisks, suggesting a significant morphology-dependent effect (Figure 2A,B). However, without support, genuine Cu nanowires gave rise to very limited furfural conversion (38%) at 200 °C, even with 30 bar of H2 pressure (Table 1, entry 1).

Moreover, Hu et al. developed novel bifunctional base-metal heterogeneous catalysts (Cu/CaAlO) for the simultaneous furfural hydrogenation and 1,4-butanediol dehydrogenation employing Cu/AC catalyst. Adapted with permission from [119]. Copyright 2016 Elsevier.

Figure 2. Scanning Electron Microscopy (SEM) images of (A) Cu nanodisk and (B) Cu nanowires, Reprinted with permission from [118]. Copyright 2016 Elsevier. (C) Schematic representation of simultaneous furfural hydrogenation and 1,4-butanediol dehydrogenation using Cu/CaAlO based-catalyst, Reprinted with permission from [34]. Copyright 2016 Royal Society of Chemistry. (D) Proposed reaction pathways for transfer hydrogenation of furfural to 2-methylfuran (MF) employing Cu/AC catalyst. Adapted with permission from [119]. Copyright 2016 Elsevier.

Furthermore, Wang et al. studied the effect of the acid and basic features of the support on Cu based catalysts performance [69] with five different supports, namely ZMS-5, Al2O3, SiO2, ZnO, and MgO. The results showed that the total acidity of the copper modified supports followed the order: Cu/ZSM-5 (687.4 μmol/g) > Cu/Al2O3 (268.9 μmol/g) > Cu/SiO2 (200.6 μmol/g) > Cu/ZnO (32.2 μmol/g) > Cu/MgO (0 μmol/g), while the total basicity followed the order: Cu/MgO (312.4 μmol/g) > Cu/Al2O3 (115.2 μmol/g) > Cu/ZnO (17.2 μmol/g) > Cu/SiO2 (9.4 μmol/g) > Cu/ZSM-5 (0 μmol/g). It was found that the acid supported catalyst, such as Cu/ZSM-5, led to a poor mass balance and gave rise to some oligomers as main products. In turn, basic support, such as Cu/MgO, gave a better mass balance and FA as the main product.

Moreover, Hu et al. developed novel bifunctional base-metal heterogeneous catalysts (Cu/CaAlO) for the simultaneous furfural hydrogenation and 1,4-butanediol dehydrogenation under solvent-free conditions and without external H2 supply (Figure 2C) [34]. Inspiringly results of 96% FA and 100% gamma-butyrolactone (GBL) yield was obtained with Cu/CaAlO (Table 1, entry 2), and it was found that furfural hydrogenation accelerated 1,4-butanediol dehydrogenation to GBL. Additionally, FA selectivity greatly decreased due to the formation of MF under H2 conditions. The impressive catalytic performance of the catalyst should be ascribed to the existence of defective Cu NPs, abundant strong Lewis base sites, and Cu+ species on the catalyst surface. Identically, the uniform size and well dispersed Cu nanoparticles on high surface area activated carbon with the suitable proportion of Cu2+, Cu0, and Cu+ was associated with the superior transfer hydrogenation catalytic performance of
Cu/AC catalyst, which offered 92% of MF yield (Table 1, entry 3) [119]. Zhang et al. also proved that Cu⁺/Cu⁰ are both necessary and active species for the furfural reduction reaction, and that depositing a thin Al₂O₃ layer on CuCr₂O₄*CuO increased the catalyst activity while simultaneously decreasing the activation energy of furfural hydrogenation [120].

Furfural hydrogenation to FA under microwave irradiations over Cu/TiO₂ as catalyst has been investigated by Romano et al., being the first contribution using pressurized microwave reactors (Figure 3B) [59]. Microwave irradiations offered an unexpected enhancement in FA selectivity to 99% and a 3–4 fold increase in conversion in comparison to the conventional heating method. Besides, experiments were conducted at relatively mild conditions (125 °C) with CPME as green solvent, and the catalyst could be reused three times without loss of activity (Table 1, entry 19).

Prakruthi et al. found that Al deficient Cu-Al oxide prepared possesses higher surface area and pore volume. By loading Cu (15 wt%) on dealuminated layered double hydroxides, the catalyst could achieve 77% FA yield at 220 °C with 3.6 h⁻¹ LHSV (Table 1 entry 4) [121]. The obtained catalytic performance could be explained by the new term pore occupancy hydrogenation efficiency factor.

![Figure 3](image-url)
In addition, Jiménez-Gómez et al. prepared different kinds of Cu/ZnO and Cu/CeO₂ catalysts, and investigated their catalytic performance under gas-phase hydrogenation of furfural to FA [64,122]. In both cases, best FA yield was around 70%, and the hydrogenation products slightly varied with the time on stream (Table 1, entries 5 and 7). Subsequently, the authors used disordered kerolitic clay formed by kerolite/stevensite mixed layer as catalytic support to disperse Cu-species. In this case, lower selectivity to FA was obtained, and thus the major product was MF [123]. In this regard, the selectivity to FA could be improved by the incorporation of Ce and Zn as promoters (Table 1, entry 8). Yang et al. have improved FA yield to 94% by using Cu/ZnO (Cu/Zn = 0.8) that was prepared via “decrease pH” co-precipitation method (Table 1, entry 6) [65]. The excellent catalyst performance was ascribed to suitable Cu particle size (8 nm) and strong metal-support interactions. Jackson et al. have supported CuO and CeO₂ on γ-Al₂O₃, and then CuO excess on the catalyst surface was stripped with HNO₃ (Table 1, entry 10) [124]. This catalyst could give rise to 85% FA yield at 175 °C in the continuous flow regime, which showed higher intrinsic reactivity than the two control catalysts: Cu/Al₂O₃ and copper chromite.

In 2014, Vargas-Hernández et al. have studied FA production from furfural over Cu/SBA-15 as catalyst, however a limited FA yield of 52% was obtained (Table 1, entry 13) [63]. Afterwards, Srivastava et al. synthesized series Cu–Co bimetallic catalysts supported on SBA-15 for furfural hydrogenation to FA [125]. The aforementioned study attained around 80% yield of FA with 9% of MF and 10% of cyclopentanone. Later on, three different supported bimetallic catalysts (Cu–Co/SiO₂, Cu–Co/H-ZSM-5, and Cu–Co/γ-Al₂O₃) were prepared by an impregnation method, and tested for furfural selective hydrogenation to MF [126]. The results indicated that the strong interaction between Cu and Co has significant influence on the catalytic performance of bi-metallic catalyst. Acid supports, such as H-ZSM-5 and γ-Al₂O₃, are more selective towards MF, which is in accordance with a previous study, where Cu/Al₂O₃ is more effective towards MF production (90%, Table 1 entry 11) than Cu/ZnO and Cu/Al₂O₃ due to the synergistic effect between the metal counterpart and the weak acid site [61]. Srivastava et al. have reported an optimization, kinetics, and reaction mechanism study of furfural conversion to MF over Cu–Co/γ-Al₂O₃ [81]. They suggest that Cu species in the catalyst would dissociate the hydrogen molecule to hydrogen atoms, and then aldehydic oxygen is attracted by the acidic sites of the catalyst, followed by the addition of hydrogen to the carbonyl oxygen atom FA is formed by the further addition of hydrogen to carbonyl carbon atom. It was considered that weak acidic CoOₓ phase facilitates the adsorption of FA on the catalyst surface, and promoted FA further hydrogenolysis to MF. The latest process firstly involved the hydrogen atom addition to hydroxyl oxygen atom, releasing one mole of water, and the final addition of hydrogen atom (H⁺) to positive charged carbon atom, which led to the formation of MF. The experimental data could be explained while using Langmuir-Hinselwood-Hougen-Watson kinetics (see in Scheme 2). Such results indicated that the adsorption of hydrogen and surface reaction were possibly the rate-controlling steps. Dong et al. further improved MF yield to 96% by performing the reaction at 200 °C while using Cu/SiO₂ catalyst, prepared by the ammonia evaporation method [127]. They also developed a kind of Cu-phylllosilicate-like catalyst, which could also furnish 96% MF or 83% FA yield [68]. In the case of the work developed by Srivastava et al, the best MF selectivity (78%) with fully furfural conversion was achieved with Cu–Co/γ-Al₂O₃ at 220 °C and 40 bar of H₂ pressure (Table 1, entry 17). After optimizing with Taguchi method, the authors were able to improve MF yield to 87% [81]. Interestingly, Cu-Co/C-500 bimetallic catalyst gave rise to 49% of cyclopentanone as major product with 36% of FA at 150 °C for 3 h under H₂ pressure (5 bar) [128]. Additionally, highly dispersed Cu-Co/C catalyst (Cu/Co=1/0.4), derived from Co-doped Cu-BTC metal-organic frameworks (MOFs) by thermolysis in nitrogen, has showed highly selectivity to FA, and after calcining the catalyst at 500 °C, a 96% FA yield was achieved at 140 °C with 30 bar H₂ pressure [129].

Moreover, furfural transfer hydrogenation over monometallic and bimetallic Cu-Ni catalysts supported on Al₂O₃ has been investigated by Zhang et al. [130]. It was found that furfuryl ether outcomes as major by-product by using Cu/Al₂O₃ catalyst, and Ni/Al₂O₃ material results
in ring-opening products, while Cu-Ni/Al₂O₃ bimetallic catalysts (especially with Cu/Ni = 1/2) showed improved activity towards the production of MF and MTHF. Under optimal conditions, 65% yield of MF and 18% yield of MTHF were achieved at 230 °C for 4 h. Remarkably, reusability studies displayed that, after the forth reuse cycle of Cu-Ni/Al₂O₃ catalytic system, MF yield only decreased 5%. This report is consistent with the study of Srivastava [131] who reported that the incorporation of Ni with Cu supported on Al₂O₃ increased MF yield from 51% to 82%. Conversely, Pang et al. found that a small amount of Ni addition on Cu/Al₂O₃ indeed improved catalytic activity, but slightly decreased the selectivity to MF [132]. Besides, it was revealed that C18 thiolute-modified Cu-Ni bimetallic catalyst could increase both reaction activity and hydrogenation selectivity. By adding formic acid as co-hydrogen donors, Fu et al. achieved 92% MF yield with 10% Cu-10% Ni alloy, and attained 90% yield towards THFA at mild condition (130 °C and 40 bar H₂ pressure for 10 h) [79].

Scheme 2. Langmuir-Hinshelwood-Hougen-Watson type of reaction mechanism for the hydrogenation of furfural to MF. Adapted from Srivastava et al. [81].

Yang et al. investigated the effect of Al species addition on Cu/ZnO catalytic activity [60]. It was found that the constructed Cu/ZnO-Al₂O₃ catalyst could improve furfural conversion from 85% to 96% at 120 °C with high FA selectivity (96%) in comparison with the Cu/ZnO catalyst. It was confirmed that the role of Al components was to act as both structural and electronic promoter, thus improving the dispersion of copper/zinc species and hindering Cu-ZnO interaction of the aurichalcite derived catalysts (Figure 3C). Similarly, Cu/MgO-Al₂O₃ has been also tested as an efficient catalyst for furfural transfer hydrogenation to FA under near-critical isopropanol (Table 1, entry 29) [62]. Even at milder conditions (150 °C), Cu-Mg-Al catalyst that was prepared by co-precipitation method showed 100% selectivity to FA with fully furfural conversion [66].

Furthermore, Zhang et al. have studied the selective transfer hydrogenation of furfural over hydrotalcite-derived copper catalysts while using methanol as hydrogen donor [135]. The copper catalyst showed excellent transfer hydrogenation selectivity towards FA by giving a FA yield of 94% at 200 °C, while such catalyst activated with H₂ (Cu-Al-A, Table 1, entry 24) notably achieved 94% MF yield at 240 °C. These studies stated that valence of active Cu species, catalyst acidity, and reaction temperature played an important role in product selectivity.
Table 1. Furfural hydrogenation over Cu-based catalysts.

| Entry | Catalyst                  | H Source | Solvent | Temperature (°C) | Time (h) | Pressure (bar) | Yield (%) | Ref.   |
|-------|---------------------------|----------|---------|-----------------|----------|---------------|-----------|--------|
| 1     | Cu nanowire               | H2       | 1,4-dioxane | 200          | 1.5      | 30            | >33       | [118]  |
| 2     | Cu/CaAlO                  | 1,4-BDO  | -       | 210            | 1.8\(^\text{a}\) | 1            | 96       | [34]   |
| 3     | Cu/AC                     | i-PrOH   | i-PrOH  | 200            | 5        | 20            | 8         | [119]  |
| 4     | Cu/CaAlO                  | H2       | -       | 220            | 6\(^\text{a}\) | -            | 77        | [121]  |
| 5     | Cu/ZnO                    | H2       | CPME    | 190            | 1        | -             | 70        | [122]  |
| 6     | Cu/ZrO                    | H2       | -       | 120            | 0.435\(^\text{a}\) | -          | 94        | [65]   |
| 7     | Cu/CoO                    | H2       | CPME    | 190            | 1        | -             | 71        | [64]   |
| 8     | Cu/kerolitic clay         | H2       | -       | 210            | -        | -             | 32        | [123]  |
| 9     | Cu-ClO\text{O}_2/kerolitic clay | H2   | -   | 190            | 5        | -             | 81        | [123]  |
| 10    | CuO-CeO\text{O}_2/g-Al\text{O}_3 | H2   | -       | 175            | 5        | 5             | 85        | [124]  |
| 11    | Cu/SiO\text{O}_2          | H2       | -       | 220            | 5\(^\text{a}\) | 1            | 2         | [61]   |
| 12    | Cu/phyllosilicate         | H2       | -       | 200            | 5\(^\text{a}\) | -            | 2         | [68]   |
| 13    | Cu/SBA-15                 | H2       | CPME    | 170            | 5        | -             | 52        | [63]   |
| 14    | Cu-Co/SBA-15              | H2       | i-PrOH  | 170            | 4        | 20            | 80        | [125]  |
| 15    | Cu-Co/SiO\text{O}_2       | H2       | i-PrOH  | 200            | 4        | 40            | 53        | [81]   |
| 16    | Cu-Co/H-ZSM-5             | H2       | i-PrOH  | 200            | 4        | 40            | 28        | [81]   |
| 17    | Cu-Co/Al\text{O}_3        | H2       | i-PrOH  | 220            | 4        | 40            | 11        | [81]   |
| 18    | Cu-Co/C                    | H2       | EtOH    | 140            | 1        | 30            | 96        | [129]  |
| 19    | Cu/TiO\text{O}_2          | H2       | CPME    | 150            | 3        | 10            | 99        | [59]   |
| 20    | Cu-Ni\text{I}/Al\text{O}_3 | i-PrOH | i-PrOH | 230            | 4        | -             | 0         | [130]  |
| 21    | Cu-Ni\text{I}/Al\text{O}_3 | HCOOH | i-PrOH | 210            | 7        | -             | 2         | [133]  |
| 22    | Cu-Ni/MgAl\text{O}_3      | H2       | EtOH    | 150            | 10       | 40            | 0         | [134]  |
| 23    | Cu-Ni/Al\text{O}_3        | H2       | EtOH    | 130            | 10       | 40            | 0         | [79]   |
| 24    | Cu-Fe                     | H2       | Octane  | 220            | 10       | 90            | 42        | [25]   |
| 25    | Cu-Fe/Al\text{O}_3        | H2       | -       | 175            | 1\(^\text{a}\) | 1            | 92        | [136]  |
| 26    | Cu/ZnO-Al\text{O}_3       | H2       | -       | 120            | 5\(^\text{a}\) | 1            | 92        | [60]   |
| 27    | Cu/MgO-Al\text{O}_3       | i-PrOH   | i-PrOH | 210            | 1        | -             | 89        | [62]   |
| 28    | Cu-Mg-Al                  | i-PrOH   | i-PrOH | 150            | 6        | -             | 0         | [66]   |

\(^{a}\) LHSV in h\(^{-1}\).
A series of non-supported Cu-Fe catalysts were prepared by Yan and Chen and tested for furfural hydrogenation to MF [25]. They got 51% of MF yield at 220 °C for 14 h under 90 bar of H$_2$ pressure (Table 1, entry 26). The promoting effect of Fe on Cu catalyst performance was also studied by Manikandan et al. [136]. Cu-Fe/Al$_2$O$_3$ catalyst, with 10 wt% of Fe, exhibited an excellent activity that led to high furfural conversion (>93%) and FA selectivity (>98%) under mild reaction conditions (Table 1, entry 27). The high activity of Cu-Fe/Al$_2$O$_3$ material could be attributed to the synergy between Cu and Fe, and to the existence of oxygen vacancies in the Fe oxide system. Notably, the bimetallic catalyst showed superior stability after 24 h on stream.

As a short conclusion, Cu-based catalysts could achieve selective hydrogenation of furfural by appropriately choosing supports, solvents, or incorporating other metals. It can be noticed that the acidic and basic sites of the support play the most crucial role in furfural hydrogenation selectivity (acidic sites benefiting to MF production, basic sites resulting to FA), followed by the type of solvent (protic or aprotic) and metal incorporated (Ce, Co, or Ni, etc.).

2.2. Co, Ni Based Catalyst

Co and Ni are also well-recognized low-cost and high activity non-noble metals, which have been widely used for catalysts preparation. As we discussed in the last section, both of the metals have been introduced with Cu forming bimetallic catalytic systems. Most of these materials have showed improved catalytic activities in comparison with mono-metallic catalysts. Previous reports suggest that sole Co based catalysts displayed low activity at low temperature and low selectivity at high temperature [82]. Nonetheless, Audemar et al. have recently demonstrated that monometallic Co/SBA-15 catalyst could reach a FA selectivity of 96% from furfural hydrogenation (Table 2, entry 1), while the catalyst stability analysis revealed that continuous Co leaching occurred, which led to the decrease of the catalytic activity [137].

It is worth mentioning that Lee et al. developed Co/TiO$_2$ catalyst, founding that cobalt particles were covered by a TiO$_x$ layer after high temperature calcination and reduction treatments (Figure 4A) [138]. No leaching or cobalt particles aggregations were observed, even after 105 h time of reaction. The excellent catalytic performance (95% FA yield, Table 2, entry 2) could be possibly associated with the TiO$_x$ overcoat on the cobalt-based material and the relative mild reaction conditions (80 °C). Very recently, Gong and Jiang have synthesized two kinds of Co based catalysts while using N-doped materials as supports [73,82]. In particular, Jiang et al. have synthesized a Co based catalyst using nitrogen-doped porous carbon materials (CPNs) as support (Figure 4B), which gave rise to a comparable FA yield of 98%, albeit with relatively higher reaction temperature (180 °C) [82]. Gong et al. developed a facile one-pot pyrolysis approach using melamine as carbon and nitrogen source to fabricate Co nanoparticles embedded in bamboo-like N-doped carbon nanotubes (named as Co/NCNTs) (Figure 4D–F) [73]. This catalyst showed quite high selectivity to FA at low temperature (100% selectivity at T = 60–100 °C). In turn, by increasing the temperature up to 130 °C, further hydrogenation and rearrangement will occur producing cyclopentanone as the main product. Interestingly, THFA with 100% yield was detected as the final product when using Ni/NCNTs as catalyst at similar reaction conditions (Table 2, entry 5). Therefore, this result suggested that Ni could lead to deeper hydrogenation, in comparison with Co species. The aforementioned data is consistent with the results of Su et al., who prepared carbon-embedded Ni (Ni/C) catalyst by direct thermal decomposition of Ni-MOF (Figure 4C) [70]. Such contribution reports 100% THFA yield at 120 °C in 2 h with 10 bar H$_2$ (Table 2, entry 6). As mentioned above, bimetallic catalyst Cu-Ni/CNTs exhibited good selectivity to THFA (90%, Table 1, entry 23), in fact, Liu et al. also demonstrated that Ni/CNTs catalysts with Ni content ≥10% have similar or even better selectivity to THFA [79].
As it has been shown in Table 2, the reaction performed at 60 °C, employing Ni/AC-SO₃H catalyst, could be considered as the best result, with a 100% of FA yield, while at 100 °C led to THFA formation, in accordance with previous report with Ni/NCNTs catalyst [73]. More importantly, the conversion of transfer hydrogenation of furfural to FA can also reach almost 100% yield under optimal conditions (140 °C, 4 h, Table 2, entries 10 and 12).

Manikandan et al. investigated surface synergistic effect on the performance of Ni-based hydrotalcite derived catalysts with different Ni-Mg-Al ratio, founding that Ni₂/MgAl could give 92% FA yield at 180 °C [77]. Such results have demonstrated that the incorporation of Mg significantly enhances the Ni-support interaction, Ni dispersion, and catalytic performance. Analogously, Sulmonetti et al. synthesized different nickel mixed metal oxides that were derived from layered...

Furthermore, Ni-based catalysts supported on Al₂O₃ modified with various alkaline earth metals (Mg, Ca, Sr, Ba) have been reported by Yang at al. It was found that Ni/Ba-Al₂O₃ was the most efficient catalytic system, with improved THFA selectivity in comparison with the unmodified alumina (from 16% with Ni/Al₂O₃ to 99%) at the same reaction conditions. The presence of alkaline earth metals results in a decrease of NiAl₂O₄ species that lead to the increment of the hydrogenation efficiency [71].

Notably, most of studies has indicated that lower reaction temperature favors FA production, and higher reaction temperature will result in a higher selectivity to THFA. In turn, some works have reported divergent results. For instance, Kotbagi et al. found out that furfural was selectively hydrogenated to FA at 200 °C over Ni supported on N-doped hierarchically porous carbon catalyst (Table 2, entry 8) [74]. Jeong et al. noticed that Ni/SiO₂ and Raney Ni have competitive selectivity...
to FA and THFA at 110 °C under 30 bar H2. Specially, in the aforementioned contribution, the Ni nanoparticles catalysts capped with organic molecules were successfully developed and employed in the selective furfural hydrogenation to FA with a maximum yield of 96% [78]. Xu et al. also noticed that Raney Ni could gave rise to various products by hydrogenation/decarboxylation or rearrangement [75]. Authors also concluded that the additives have great effect on the product distribution. Interestingly, Gong et al. communicated that an enhanced catalytic performance of furfural selective hydrogenation could be accomplished while using sulfonated activated carbon supported Ni catalyst [80]. As it has been shown in Table 2, the reaction performed at 60 °C, employing Ni/AC-SO3H catalyst, could be considered as the best result, with a 100% of FA yield, while at 100 °C led to THFA formation, in accordance with previous report with Ni/NCNTs catalyst [73]. More importantly, the conversion of transfer hydrogenation of furfural to FA can also reach almost 100% yield under optimal conditions (140 °C, 4 h, Table 2, entries 10 and 12).

Manikandan et al. investigated surface synergistic effect on the performance of Ni-based hydrotalcite derived catalysts with different Ni-Mg-Al ratio, founding that Ni2/MgAl could give 92% FA yield at 180 °C [77]. Such results have demonstrated that the incorporation of Mg significantly enhances the Ni-support interaction, Ni dispersion, and catalytic performance. Analogously, Sulmonetti et al. synthesized different nickel mixed metal oxides that were derived from layered double hydroxides containing Ni-Mg-Al and Ni-Co-Al. In this case, a maximum of 70% FA with 10% THFA was yielded [139]. On the other hand, Ni-based catalyst, such as Ni/Cl, could be used to produce MTHF, and Ni-Fe/C bimetallic catalyst, giving rise to MF as the main product with high pressure conditions (Table 2, entries 14 and 15) [140]. In turn, at low pressure (1 bar), the hydrogenation selectivity of Ni/C was quite poor (furan: 18%, MF: 30%, MTHF: 14%, and THFA: 30%), while Ni-Fe/C will retain its hydrogenation selectivity towards MF with 65% yield.

For comparison, our research group recently found that Ni/C was selective to MF at 200 °C with H2 or 260 °C without H2 in batch conditions; however, in continuous flow regime at 150 °C under 50 bar H2, the hydrogenation selectivity was quite poor due to side-reaction between furfural and isopropanol. When altering the solvent with non-protic cyclopentyl methyl ether (CPME), two major products, namely FA and THFA, were obtained [141]. These results gave a clear hint that selective hydrogenation could be achieved by changing the reaction regime and conditions. Moreover, in the aforementioned work, two kinds of bimetallic catalysts, 5%Ni-15%W/C and 10%Ni-15%W/C, were also prepared [142]. Surprisingly, the activities of bimetallic catalysts were relatively lower than that of monometallic catalysts under the same reaction conditions, and poor reaction mass balance was noticed at a higher reaction temperature. Encouragingly, in a continuous flow regime, a better mass balance and a MF yield higher than 70% was observed with bimetallic catalysts. These promising results suggested that side-reactions could be possibly limited in continuous regime, as the reactant experienced a very short residence time in continuous flow (CF).

In terms of the mechanisms for the reduction of furfural and FA to MF, it was found that hydrogen transfer from i-PrOH to furfural mainly occurs through the formation of a complex between furfural, i-PrOH, and Lewis acid sites (Scheme 3a), rather than through the production of H2 from isopropanol on the metal surface (Scheme 3b). Koehle and Lobo showed the role of Lewis acid sites of zeolites in the formation of the corresponding hemiacetal (iPrO-MF) by catalytic hydrogen transfer from alcohols to furfural (Meerwein-Ponndorf-Verley or MPV reduction) [143]. In particular, Gilkey et al. [144] have experimentally demonstrated that FA hydrogenolysis via ring activation (Scheme 3c), which will be discussed later, was predominant over direct metal-mediated hydrogenolysis (Scheme 3d), in good agreement with the work that was developed by our research group.
10–12 indicated furfural hydrogenation selectivity over Ni was obtained as the major product (Table 2, entries 23 and 26) [76]. By supporting Ni and Co on short channeled SBA-15, the catalyst providing 94% FA yield at 180°C could a reactant furfural ring activation and easily separable heterogeneous catalyst for catalytic transfer hydrogenation of furfural to FA, and our previous study also proved that the reaction regimes temperature and H resources; the introduction of Zr instead of Sn into Ni-Zr bimetallic catalysts. Both of the materials showed similar catalytic performance, although reaching very good FA selectivity (92% FA yield) than common SBA-15 and other acid supports, such as MCM-48, MCF-2, and MCF-41 [146]. On the other hand, bimetallic catalyst Ni and Sn, In, etc., were also incorporated with Ni formed bimetallic catalysts (see Table 2, entries 21–23) [76,146,147]. By supporting Ni and Co on short channeled SBA-15, the catalyst showed superior catalytic performance (92% FA yield) than common SBA-15 and other acid supports, such as MCM-48, MCF-2, and MCF-41 [146]. On the other hand, bimetallic catalyst Ni₃Sn₂/Al₂O₃ did not offer a satisfiable FA yield, even in harsh conditions [147]. Rodiansono et al. developed a method for the preparation of a highly dispersed Ni-Sn alloy catalyst supported on aluminum hydroxide, reaching very good FA selectivity (>90%) [148]. Later on, the authors prepared analogous Ni-In and Ni-Zr bimetallic catalysts. Both of the materials showed similar catalytic performance, although it is worth mentioning that, for Ni-Zr/AlOH, a further hydrogenation compound, namely THFA, was obtained as the major product (Table 2, entries 23 and 26) [76].

In general, Co-based catalysts showed good hydrogenation selectivity to FA, despite great differences in supports, H resources, solvent types, and reaction conditions. However, the catalytic activity over Ni-based catalysts varied from all of these parameters. For instance, Table 2, entries 10–12 indicated furfural hydrogenation selectivity over Ni/AC-SO₃H is highly dependent on reaction temperature and H resources; the introduction of Zr instead of Sn into Ni/SO₃H dramatically changed the desired compound from THFA to FA, and our previous study also proved that the reaction regimes could affect furfural hydrogenation selectivity.

**Scheme 3.** (a) Meerwein-Ponndorf-Verley and (b) metal-mediated furfural hydrogenation; (c) FA hydrogenolysis via ring activation; and, (d) direct FA hydrogenolysis.
Table 2. Furfural hydrogenation over Co, Ni-based catalysts.

| Entry | Catalyst            | H Source | Solvent | Temperature (°C) | Time (h) | Pressure (bar) | Yield (%) | Ref. |
|-------|---------------------|----------|---------|------------------|----------|----------------|-----------|------|
| 1     | Co/SBA-15           | H2       | EtOH    | 150              | 1.5      | 20             | 88        | [137]|
| 2     | Co/TiO2             | H2       | -       | 80               | 17.5<sup>a</sup> | 23.4         | 95        | -    | -   | [138]|
| 3     | Co/CPNs             | H2       | i-PrOH  | 110              | 5        | 40             | 92        | -    | -   | [82] |
| 4     | Co/NCNTs            | H2       | H2O     | 100              | 7        | 40             | 0         | 100  | -   | [73] |
| 5     | Ni/NCNTs            | H2       | H2O     | 100              | 4        | 8              | 100       | -    | -   | [73] |
| 6     | Ni/C                | H2       | -       | 120              | 2        | 10             | -         | -    | 100 | [70] |
| 7     | Ni/Ba-Al<sub>2</sub>O<sub>3</sub> | H2       | i-PrOH  | 140              | 4        | 40             | -         | -    | 96  | [71] |
| 8     | Ni/CN               | H2       | i-PrOH  | 200              | 4        | 10             | 91        | 2    | 2   | 1   | [74] |
| 9     | Capped Ni NPs       | H2       | i-PrOH  | 110              | 3        | 30             | 96        | -    | 4   | -   | [77] |
| 10    | Ni/AC-SO<sub>2</sub>H | H2       | i-PrOH  | 60               | 8        | 40             | 100       | -    | -   | -   | [80] |
| 11    | Ni/AC-SO<sub>2</sub>H | H2       | i-PrOH  | 100              | 5        | 40             | -         | -    | 100 | -   | [80] |
| 12    | Ni/AC-SO<sub>2</sub>H | i-PrOH   | i-PrOH  | 140              | 4        | 40<sup>b</sup> | 100       | -    | -   | -   | [80] |
| 13    | Ni<sub>2</sub>MgAl | H2       | -       | 180              | 1.8<sup>a</sup> | 1           | 92        | -    | 4   | -   | [77] |
| 14    | NiCl                | H2       | -       | 180              | 4<sup>a</sup> | 33           | 1         | 1    | 5   | 56  | [140]|
| 15    | NiFe/C              | H2       | -       | 180              | 4<sup>a</sup> | 33           | 4         | 72   | 2   | 6   | [140]|
| 16    | Ni/C                | H2       | i-PrOH  | 200              | 5        | 30             | 6         | 66   | 1   | 2   | [141]|
| 17    | Ni/C                | i-PrOH   | i-PrOH  | 260              | 5        | 1              | 20        | 50   | 1   | 1   | [141]|
| 18    | Ni/C                | H2       | CPME    | 150              | nd       | 50             | 39        | 2    | 32  | 0   | [141]|
| 19    | No-W/C              | i-PrOH   | i-PrOH  | 230              | 1        | 30             | 0         | 70   | 0   | 0   | [142]|
| 20    | NiFeO<sub>4</sub>   | i-PrOH   | i-PrOH  | 180              | 6        | -              | 94        | -    | -   | -   | [145]|
| 21    | Ni-Co/SBA-15        | H2       | EtOH    | 90               | 2        | 50             | 92        | -    | -   | -   | [146]|
| 22    | Ni<sub>2</sub>Sn<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> | H2       | -       | 280              | 0.5<sup>a</sup> | 1           | 41        | -    | -   | -   | [147]|
| 23    | Ni-In/AlOH          | H2       | i-PrOH  | 180              | 3        | 30             | 92        | -    | 4   | -   | [76] |
| 24    | Raney Ni/AlOH       | H2       | i-PrOH  | 180              | 1.25     | 30             | 1         | 99   | -   | -   | [76] |
| 25    | Ni-Sn/AlOH          | H2       | i-PrOH  | 180              | 1.25     | 30             | 91        | -    | 3   | -   | [76] |
| 26    | Ni-Zr/AlOH          | H2       | i-PrOH  | 180              | 1.25     | 30             | 0         | 96   | -   | -   | [76] |

<sup>a</sup>LHSV in h<sup>-1</sup>, <sup>b</sup>N<sub>2</sub>.
2.3. Zr-Based and Other Catalysts

Zr-based compounds have proved to be efficient catalysts for furfural hydrogenation, especially by the Meerwein-Ponndorf-Verley (MPV) reduction. Recently, ZrO$_2$ that was prepared by the microemulsion method showed excellent transfer hydrogenation selectivity to FA (≥98%), although FA yield only rose up to 53% in 120 h, most likely due to relative lower reaction temperature (100 °C) employed for the reaction. In addition, the effect of microwave irradiation was clearly evidenced, accelerating the reaction 15–30 times in comparison with conventional heating method [149]. Zr(OH)$_4$ (might actually existed in the form of ZrO(OH)$_2$·xH$_2$O) also showed almost stoichiometric FA yield when using iso-propanol as hydrogen source and solvent (Table 3, entry 2) [150]. The experimental results indicated that basic centers in Zr(OH)$_4$ displayed a pronounced improvement of furfural transfer hydrogenation, while moderate monoclinic phase content in ZrO$_{2-x}$ could enhance the conversion rate and FA selectivity. Scheme 4 illustrated the proposed mechanism for the transformation of furfural into FA catalyzed by Zr(OH)$_4$ via catalytic transfer hydrogenation with iso-propanol. In detail, iso-propanol was firstly adsorbed on the catalyst surface formed alkoxide, and furfural was then absorbed on the surface forming a six-membered ring transition state with the above-mentioned alkoxide (like the case in Scheme 3a), then hydrogen transfer occurred and released one mole acetone. Finally, another iso-propanol molecule formed the corresponding alkoxide, like in the first step, and give a hydrogen atom to the oxygen atom of furfural generating the final product FA.

![Scheme 4. Proposed mechanism for the transformation of furfural into FA catalyzed by Zr(OH)$_4$ via catalytic transfer hydrogenation with iso-propanol as a hydrogen donor. Adapted from Zhang et al. [150].](image)

Sha et al. developed a super-efficient catalyst Zr-HAs by combining Zr with humic acid. A FA yield of 97% was obtained via MPV reduction at very mild conditions (Table 3, entry 3) [151]. Furthermore, Li et al. synthesized recyclable Hf-phenylphosphonate nanohybrids (PhP-Hf) via the assembly of phenylphosphonate with HfCl$_4$. 98% FA yield, with a formation rate of 9760 µmol /g/h was obtained at 120 °C for 2 h, being, the superior catalytic activity of PhP-Hf, mainly attributed to its moderate acidity and relatively strong basicity [152]. Simultaneously, PhP-Zr showed lower activity than PhP-Hf (Table 3, entries 4 and 5), which is in good agreement with the catalytic activity order that was obtained by theoretical studies: Hf > Zr > Sn [143,153].

It is noteworthy to mention that alumina-carbon composite catalyst (Al$_2$O$_3$-S), synthesized by reaction between Al(NO$_3$)$_3$ with the polyether-based surfactant, showed a comparable FA yield (96%) with Zr-based catalysts though catalytic transfer hydrogenation. The high selectivity observed was attributed to the presence of acid sites on the catalyst [154]. Nonetheless, the gradual deactivation of the catalyst was observed due to Al species leaching.

Recently, Wu et al. presented a rapid and mild-conditions approach for the quantitative production of FA in presence of KF and a liquid H-donorn: polymethylhydrosiloxane (PMHS). It was reported a
97% FA yield in 30 min. of reaction, at room temperature. To the best of our knowledge, this contribution presents the production of FA at the mildest conditions. Although supported Ir on hydrogenated MoOx catalyst could rise a 99% FA at 30 °C, the reaction time was 6 h and the experiments were performed under 20 bar of H2 pressure (Table 3, entry 8) [155]. In the presence of H2, Fe/C combined with K2CO3 achieved 94% of FA yield under harsh conditions (220 °C). Interestingly, when the reaction was performed in the presence of O2, furfural was selectively converted to furan-2-acrolein [156].

In terms of furfural deep hydrogenation, Lee et al. investigated the hydrodeoxygenation of furfural to MF on molybdenum carbide catalyst [157]. The best MF selectivity was around 56%, and the conversion of furfural was less than 10%, which could be possibly associated with the relatively lower reaction temperature (150 °C). Grazia et al. found out that the MgO and Mg/Fe/O catalysts were active for furfural transfer hydrogenation reaction, and MgO was selective for FA formation, whereas Mg/Fe/O showed to be highly active and selective for MF production (Table 3, entries 10 and 11). Further studies, using FeVO4 as catalyst, reported a similar MF yield of 80% under the same system [158].

| Entry | Catalyst | Source | Solvent | Temperature (°C) | Time (h) | Pressure (bar) | Yield (%) | Ref. |
|-------|----------|--------|---------|-----------------|---------|---------------|-----------|-----|
| 1     | ZrO2     | i-ProH | i-ProH  | 100             | 120     | -             | 93        | -   |
| 2     | Zr(OH)4  | i-ProH | i-ProH  | 170             | 2.5     | 10            | 99        | -   |
| 3     | ZrHAs    | i-ProH | i-ProH  | 50              | 15      | -             | 97        | -   |
| 4     | PhP-Zr   | i-ProH | i-ProH  | 120             | 2       | 78            | -         | -   |
| 5     | PhP-Hf   | i-ProH | i-ProH  | 120             | 2       | 78            | -         | -   |
| 6     | Al2O3S   | i-ProH | i-ProH  | 130             | 6       | 96            | -         | -   |
| 7     | KF       | PMHS   | DMF     | 25              | 1.5     | 95            | -         | -   |
| 8     | Ir/H doping MoOx | H2 | H2O | 30               | 6       | 20            | 99        | -   |
| 9     | Fe/C + K2CO3 | H2 | EtOH | 220              | 2       | 20            | 93        | 3   |
| 9     | Fe/C + K2CO3 | H2 | EtOH | 220              | 2       | 20            | 93        | 3   |
| 10    | MgO      | MeOH   | MeOH    | 250             | 1       | 1             | 98        | -   |
| 11    | Mg/Fe/O  | MeOH   | MeOH    | 380             | 1       | 1             | 83        | -   |
| 12    | FeVO4    | MeOH   | MeOH    | 320             | 3 a     | 1             | 80        | -   |

 Table 3. Furfural hydrogenation over Zr-based and other catalysts.

 *a* TOS in h.

Generally, the Zr-based catalysts were used as for furfural transfer hydrogenation, and high selectivity was observed for FA production. The nature of acidic and basic sites of this kind of catalysts played a key role for their activity. For other catalysts (e.g., Mg/Fe/O and FeVO4), relatively harsh reaction temperature should be attributed to furfural hydrogenation selectivity to MF.

3. Noble Metal Catalysts

Noble metals, which were regarded as potential catalysts for hydrogenation, have been extensively studied with promising prospect. When compared with non-noble metal, noble metal catalysts generally gave rise to higher reaction activity and efficiency under a relatively milder condition, especially for the production of deep hydrogenation products, such as MF and THFA, etc. Unlike non-noble metal, studies on noble metal-based materials must be specially directed to the optimization of their performances and recyclability due to their low production in nature.

3.1. Pd Based Catalysts

Taking Pd based catalysts as an example, various Pd supported catalysts were tested for furfural hydrogenation in continuous flow [83, 92, 161]. Continuous processing has been as well contrasted with batch production. In this regard, continuous flow processing has a number of significant and inherent advantages for biomass processing when compared to batch reactor technologies:

- ✔ Continuous flow processing allows a better control of reaction conditions.
- ✔ Flow processing also facilitates scaling up which is an important point taking into consideration that many of the biomass valorization processes are still in the lab scale.
The utilization of flow processing approaches allow the intensification of the chemical processes, thereby significantly contributing to simplify technologies.

Unlike batch processing, fixed-bed flow technologies do not require catalyst separation after reaction and regeneration, if required. It is readily performed over the same catalytic bed.

Safety is increased, as flow operation allows for the continuous removal of gases, which might not interfere in the main catalytic process. However, gases that were generated in batch reactors could lead to increase pressure and potentially result in new and uncontrolled processes.

Multi step reactions can be arranged in a continuous sequence. This can be especially beneficial if intermediate compounds are unstable, toxic, or sensitive to air, since they will only exist momentarily and in small quantities.

The group of Luque has made a great contribution on flow chemistry concerning biomass valorization. For instance, 76% of MF was attained at very mild temperature (90 °C) with Pd/C in continuous flow regime (Table 4, entries 1–3). Interestingly, at a higher temperature (150 °C), the reaction selectivity changed to THFA. The opposite result was obtained with Pd/MAGSNC, which produced THFA when the reaction was performed at 90 °C and FA at 150 °C (Table 4, entries 4 and 5). Herein, it should be noted that selective hydrogenation of furfural could be achieved not only by changing the temperature, but also by varying the flow rate that determines the residence time of reactant in the catalytic system. In these cases, it seems that furfural catalytic valorization over Pd based catalysts led to the formation of FA and THFA. From a mechanistic point of view, these results could be possibly explained, since the most stable adsorption conformation of furfural was with the furan ring lying flat on the Pt (111) surface [162], favoring its hydrogenation. Indeed, catalytic systems that are based on Pd nanoparticles supported on different materials, such as carbon, bio-char, TiO$_2$, and Al$_2$O$_3$, among others, would result in different yields of FA and THFA [87,91,163–166]. Some of them exhibited excellent catalytic performance, for example, Pd supported on hydroxyapatite (HAP) and MIL-101(Cr)-NH$_2$ gave rise to 100% THFA yield [88,89]. Noticeable difference could be found with Pd/Al$_2$O$_3$ as catalyst (see Table 4, entries 13–15).

THFA yield severely decreased by using water rather than iso-propanol as solvent with lower H$_2$ pressure. Interestingly, the side-product was identified as tetrahydrofurfural with 84% yield, which could be understood considering that the catalytic reaction occurred on a double bond of the furan ring rather than in the aldehyde group, under the reaction conditions [33]. Hu et al. suggested that polar solvents facilitate efficient furfural hydrogenation and tended to favor the hydrogenation of the furan ring over that of the carbonyl group [163]. They obtained 6% of tetrahydrofurfural with non-polar diethyl ether as solvent by performing the experiment with Pd/C at 170 °C under 70 bar total pressure (H$_2$ pressure >40 bar). Apart from the effect of the support, solvent, reaction conditions, and different metal reduction methods for the catalysts preparation, also showed significant influence on the catalytic performance. For instance, Pd catalysts that were prepared via chemical reduction method exhibited smaller particle sizes and higher metal dispersions, leading to greater conversions than those that were achieved using catalysts prepared via impregnation followed by the thermal reduction method [90]. Date et al. systematically investigated the effect of different particle size of Pd/C catalysts on furfural hydrogenation [167]. Authors found out that, by using NaBH$_4$ as the reduction agent, the smallest crystallite size (4.8 nm) was obtained, mainly attributed to the incorporation of B into the inner lattices of Pd-Pd. In turn, the use of formaldehyde as reduction agent gave rise to the highest size (22.4 nm). The systematic study of crystallite size and products selectivity revealed that smaller crystallite size enhanced the selectivity of MTHF and THF, which that means ring hydrogenation and decarbonylation reaction were promoted with smaller Pd particle size. This result is in line with the study of Bhogeswararao and Srinivas, who noticed that THFA yield increased and FA yield decreased with Pd particle size decreased from 7.8 nm to 5.8 nm, and furfural conversion decreased at the same time [165]. It seems that the Pd particle size has a negative effect on catalysts activity (in terms of furfural conversion/molPd) [91,165]. Figure 5 shows the catalytic results of Pd based catalysts with different supports.
which means that the particle size of Pt has little effect on catalysts activity (in terms of furfural conversion/mol Pd) [91,165]. Figure 5 shows the catalytic results of Pd based catalysts with different supports. Authors found out that, by employing Pt based catalyst, the reaction preferably occurs on the hydrogenation products productivity. Bimetallic Pd-based catalysts not only improved furfural hydrogenation activity, but also changed reaction selectivity. Moreover, continuous flow showed encouraging improvement on catalyst activity and hydrogenation favor furfural conversion, and a smaller Pd particle size led to deep the hydrogenation of FA to THFA. In terms of Pd-based catalysts, furfural hydrogenation activity and selectivity relied on the supports, Pd nanoparticle size, temperature, reaction regime, and solvent type, etc. Acidic supports favor furfural conversion, and a smaller Pd particle size led to deep the hydrogenation of FA to THFA. Moreover, continuous flow showed encouraging improvement on catalyst activity and hydrogenation products productivity. Bimetallic Pd-based catalysts not only improved furfural hydrogenation activity, but also changed reaction selectivity.

3.2. Pt Based Catalysts

The hydrogenation of furfural with Pt based catalysts differs with the results that were obtained for Pd-modified materials, since, in most of cases, FA and MF or furan were formed rather than THFA. Therefore, it can be understood that, by employing Pt based catalyst, the reaction preferably occurs on the aldehyde group via hydrogenation, hydrodeoxygenation, or decarboxylation. Furthermore, Taylor et al. suggested that the hydrogenation of furfural on Pt (111) depends on the used conditions (Figure 6) [172], since furfural adopts a planar motif at low coverage and a more tilted geometry at higher coverage. The difference of furfural adsorption configurations on the catalyst obviously plays an important role on the hydrogenation selectivity. Even different supports and second metal introduction in Pt-based catalysts also showed a remarkable effect on furfural conversion and products selectivity, no apparent changes were found with Pt nanoparticle size ranged from 1.6 nm to 36.1 nm [97,140,165,173–175], which means that the particle size of Pt has little effect on furfural hydrogenation selectivity.

![Figure 5. Pd based catalyst screening for hydrogenation of furfural with different supports. Adapted from Date et al. [167]. Reaction conditions: Furfural, 5 g; Solvent, Isopropyl alcohol (95 g); Temperature, 220 °C; Pressure, 500 psi; Agitation Speed, 1000 rpm, Catalyst, 4% metal loading; loading, 0.5 g; Reaction time, 5 h.](image-url)
Table 4. Furfural hydrogenation over Pd-based catalysts.

| Entry | Catalyst | H Source | Solvent | Temperature (°C) | Time (h) | Pressure (bar) | Yield (%) | Ref. |
|-------|----------|----------|---------|-----------------|----------|----------------|-----------|-----|
|       |          |          |         |                 |          |                | FA | MF | THFA | MTHF |       |
| 1     | Pd/C     | H₂       | EtAc    | 90              | 20       | 50             | 0 | 76 | -    | -    | [83]  |
| 2     | Pd/PBSAC | H₂       | EtAc    | 90              | 20       | 50             | 72 | 8 | -    | -    | [83]  |
| 3     | Pd/AlSBAred | H₂ | EtAc    | 90              | 20       | 50             | - | - | 91   | -    | [161] |
| 4     | Pd/MAGSNC | H₂   | EtAc    | 150             | 20       | 50             | 74 | - | 26   | -    | [92]  |
| 5     | Pd/MAGSNC | H₂   | EtAc    | 150             | 20       | 50             | 17 | - | 83   | -    | [92]  |
| 6     | Pd/SBA-15 | H₂   | EtAc    | 150             | 20       | 50             | 8  | - | 77   | -    | [92]  |
| 7     | Pd/SBA-15 | H₂   | EtAc    | 150             | 150      | 50             | 22 | - | 58   | -    | [92]  |
| 8     | Pd/C     | H₂       | EtAc    | 150             | 20       | 50             | 0  | - | 74   | -    | [92]  |
| 9     | Pd/C     | H₂       | EtAc    | 150             | 150      | 50             | 0  | - | 80   | -    | [92]  |
| 10    | Pd/BCH   | H₂       | -       | 110             | 265      | 4              | 65 | - | 15   | -    | [164] |
| 11    | Pd/TiO₂  | H₂       | i-PrOH  | 30              | 240      | 3              | - | - | 42   | -    | [91]  |
| 12    | Pd-Pt/TiO₂ | H₂ | i-PrOH  | 30              | 240      | 3              | - | - | 95   | -    | [91]  |
| 13    | Pd/Al₂O₃ | H₂       | i-PrOH  | 25              | 480      | 60             | - | - | 79   | -    | [165] |
| 14    | Pd/Al₂O₃ | H₂       | H₂O     | 30              | 240      | 5              | 0  | - | 16   | -    | [33]  |
| 15    | Pd/Al₂O₃ | H₂       | H₂O     | 90              | 120      | 20             | 28 | - | 72   | -    | [166] |
| 16    | Pd/HAP   | H₂       | i-PrOH  | 40              | 180      | 10             | - | - | 100  | -    | [89]  |
| 17    | Pd/C     | H₂       | H₂O-CO₂ | 40              | 30       | 30             | 62 | - | 9    | -    | [87]  |
| 18    | Pd/MIL-101 (Cr)-NH₂ | H₂ | H₂O     | 40              | 240      | 20             | - | - | 100  | -    | [88]  |
| 19    | Pd/CB    | H₂       | H₂O     | 50              | 30       | 5              | 29 | - | -    | -    | [84]  |
| 20    | Pd/CNT   | H₂       | H₂O     | 50              | 30       | 20             | 39 | - | -    | -    | [84]  |
| 21    | Pd/C     | H₂       | EtOEt   | 170             | 60       | 70             | - | - | 69   | -    | [163] |
| 22    | Pd/C     | H₂       | i-PrOH  | 180             | 300      | 20             | - | 44 | 34   | -    | [90]  |
| 23    | Pd/C     | H₂       | i-PrOH  | 180             | 300      | 20             | - | 18 | 57   | -    | [90]  |
| 24    | Pd-Fe/SiO₂ | H₂ | i-PrOH  | 250             | 4.5      | 1              | - | 83 | 6    | -    | [168] |
| 25    | Pd-Fe/Al₂O₃ | H₂ | i-PrOH  | 250             | 4.5      | 1              | 20 | 5  | 4    | -    | [168] |
| 26    | Pd-Ni/MWNT | H₂ | EtOH    | 130             | 300      | 30             | - | - | 83   | -    | [94]  |
| 27    | Pd-Cu/TiO₂ | H₂ | H₂O    | 110             | 80       | 6              | 98 | - | -    | -    | [169] |
| 28    | Pd-Cu/C  | HCOOH   | 1,4-dioxane | 170             | 180      | -              | 99 | - | -    | -    | [170] |
| 29    | Pd/NPC   | 2-BuOH  | 2-BuOH  | 120             | 600      | -              | 90 | - | -    | -    | [171] |
| 30    | Pd/Al₂O₃ | NaH₂PO₂ | THF-H₂O | 25              | 60       | -              | 68 | - | -    | -    | [93]  |

* TOS in min.  ^ total pressure.  † thermal reduction.  ‡ chemical reduction.  § W/F = catalyst mass/mass flow rate of reactant reduction.
3.2. Pt Based Catalysts

The hydrogenation of furfural with Pt based catalysts differs with the results that were obtained for Pd-modified materials, since, in most cases, FA and MF or furan were formed rather than THFA. Therefore, it can be understood that, by employing Pt based catalyst, the reaction preferably occurs on the aldehyde group via hydrogenation, hydrodeoxygenation, or decarboxylation. Furthermore, Taylor et al. suggested that the hydrogenation of furfural on Pt (111) depends on the used conditions [172], since furfural adopts a planar motif at low coverage and a more tilted geometry at higher coverage. The difference of furfural adsorption configurations on the catalyst obviously plays an important role on the hydrogenation selectivity.

Even different supports and second metal introduction in Pt-based catalysts also showed a remarkable effect on furfural conversion and products selectivity, no apparent changes were found with Pt nanoparticle size ranged from 1.6 nm to 36.1 nm [97,140,165,173–175], which means that the particle size of Pt has little effect on furfural hydrogenation selectivity.

As an example, the use of Pt/SO$_4$-ZrO$_2$ catalyst gave rise to 47% of MF and 33% of furan as the main products at a temperature of 240 °C (Table 5, entry 2). Interestingly, the research of Chatterjee et al. suggested that the formation of THFA could hamper the catalyst robustness [176]. It was, as well, demonstrated that compressed CO$_2$ could have a synergy effect with Pt based catalyst and it could hinder the generation of THFA. Besides, protic solvents, especially methanol, could improve furfural conversion, but simultaneously lead to 74% selectivity to side-product-furfural dimethyl acetal. While using the same catalyst and solvent, Taylor et al. succeed in limiting the formation of this kind of side-products with a selectivity to FA higher than 97%, by decreasing the reaction temperature and H$_2$ pressure (Table 5, entry 3) [177].

One of the methods for improving the catalytic performance, depending on the employed supports, is by modifying their surfaces with different functionalities. For instance Castelbou et al. developed a new methodology for the synthesis of well-defined Pt nanoparticles that were supported on phosphine-functionalized silica [176]. The catalytic performance of the obtained material significantly improved (Table 5, entry 7). Modified carbon materials also showed an improvement on furfural selective hydrogenation [49,176]. For example, Liu et al. prepared porous heteroatom-doped carbon materials, as supports for Pt nanoparticles. They observed more than 99% FA yield at 100 °C, and by

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**Figure 6.** (A) Catalytic hydrogenation and hydrodeoxygenation of furfural over Pt(111); (B) STM image with a single furfural molecule indicated by the blue circle ($T = 145 \text{ K, } V_t = 1.28 \text{ V, } I_t = 0.12 \text{ nA}$). The scale bar (black line) is 2 nm. (C) Expanded area from panel B, indicated by the blue square, overlaid with an atomistic scale model with furfural in a planar geometry. (D) Model of proposed hydrogen-bonded network on the Pt(111). Adapted with permission from [172]. Copyright 2017 American Chemical Society.
performing the experiment at severe conditions, the reaction was selective towards cyclopentane via rearrangement [49]. Indeed, Pt supported on SiO$_2$, without additional modification, only achieved 17% FA yield [99].

Table 5. Furfural hydrogenation over Pt-based catalysts.

| Entry | Catalyst | H Source | Solvent | Temperature (°C) | Time (h) | Pressure (bar) | Yield (%) | Ref. |
|-------|----------|----------|---------|-----------------|----------|---------------|-----------|------|
| 1     | Pt/Al$_2$O$_3$ | H$_2$ | i-PrOH | 120              | 10       | 20            | 91        | -    |
| 2     | Pt/SO$_2$ZrO$_2$ | H$_2$ | i-PrOH | 240              | 8        | 20            | 4         | 47   |
| 3     | Pt/Al$_2$O$_3$ | H$_2$ | CO$_2$ | 80               | 4        | 90$^a$        | 97        | 1    |
| 4     | Pt/Al$_2$O$_3$ | H$_2$ | MeOH    | 50               | 7        | 1             | 80        | -    |
| 5     | Pt(MgO) | H$_2$ | MeOH    | 50               | 7        | 1             | 77        | -    |
| 6     | Pt/SiO$_2$ | H$_2$ | Heptane | 80               | 4        | 40            | 100       | -    |
| 7     | Pt/MWNT | H$_2$ | i-PrOH | 150              | 5        | 20            | 75        | 14   |
| 8     | Pt/NC-BS-500 | H$_2$ | H$_2$O | 100              | 4        | 10            | 99        | -    |
| 9     | PtSiO$_2$ | H$_2$ | Toluene | 100              | 5        | 20            | 17        | -    |
| 10    | Pt/SnSiO$_2$ | H$_2$ | Toluene | 100              | 5        | 20            | 47        | -    |
| 11    | Pt/SnSiO$_2$ | H$_2$ | -       | 160              | nm       | 1             | 97        | -    |
| 12    | Pt-Cu-S-PNPs | H$_2$ | MeOH    | 150              | 12       | 20            | 100       | -    |
| 13    | Pt-Fe/MWNT | H$_2$ | EtOH    | 100              | 5        | 30            | 87        | -    |
| 14    | Pt-Re/TiO$_2$-ZrO$_2$ | H$_2$ | TiOH    | 130              | 8        | 50            | 96        | -    |
| 15    | Pt-CoC | H$_2$ | H$_2$O | 35               | 10       | 1             | 100       | -    |
| 16    | Pt-CoC | H$_2$ | n-PrOH | 180              | 2.5$^b$  | 1             | 0         | 88   |
| 17    | Pt-CoC | H$_2$ | n-PrOH | 180              | 2.5$^b$  | 33            | 0         | 75   |
| 18    | Pt/C | H$_2$ | CPME    | 150              | CF       | 50            | 15        | 78   |

$^a$ 10 bar H$_2$+ 80 bar CO$_2$. $^b$ W/F = catalyst mass/mass flow rate of furfural and H$_2$.

O'Driscoll found out that the incorporation of a second metal could certainly improve furfural conversion while keeping the same FA selectivity [175]. In this regard, the following order has been reported: Sn>Mo>Mg>Ba>Fe>Ni, where the best results were obtained with Pt-Sn/SiO$_2$ catalyst (47% of FA yield). Later on, by changing the Pt/Sn ratio, an improved yield of 63% was obtained [175]. In addition, Maligal-Ganesh et al. synthesized encapsulated intermetallic PtSn@mSiO$_2$ nanoparticle catalysts while using a ship-in-a-bottle strategy [97]. In continuous regime, the catalyst exhibited the best performance with 97% FA yield as compared with its monometallic counterparts Pt@mSiO$_2$ and by using other porous silica as support (Pt-Sn/MCF-17).

In view of the results that were obtained over Pt-based catalysts, we can draw, as a general conclusion, that this kind of catalysts preferred to hydrogenate the aldehyde group of furfural, rather than furan ring, and Pt particle size has not a big effect on the hydrogenation selectivity. The real crux of the matter is the nature of the supports, reaction conditions, as well as the incorporated metals. The continuous flow regime also resulted in a higher reaction activity and a better hydrogenation selectivity to MF.

Bimetallic catalyst Pt-Cu nanoparticles showed poor furfural conversion and FA selectivity due to the formation of furfural dimethyl acetal; however, the Pt-Cu nanoparticles with hollow-core structure exhibited over four-fold increase in catalytic activity with 100% FA selectivity, as compared to Pt-Cu nanoparticles without a hollow structure [96]. The authors proposed that aldehyde group was adsorbed into the hollow cavities (C atoms of C=O group attached to the Pt-rich outside shell and O atoms are proposed to occur toward the Cu-rich inner shell), which prevented the activated C=O bond reacting with methanol. Comparatively, the formation of furfural diethyl acetal seems to be unavoidable when other Pt based bimetallic catalysts on different supports are used [94]. Pt-Fe supported on modified multiwalled carbon nanotubes (MWNT) showed the highest FA yield of 87%, but still with 5% of acetal. Chen et al. reported an improved FA yield of 96% with 3% acetal formation, using Pt-Re/TiO$_2$-ZrO$_2$ as catalyst [95]. Impressively, Pt-Co/C bimetallic catalyst achieved 100% of FA yield at quite mild conditions (Table 5, entry 15), and 86% yield for FA was observed with concentrated furfural (40 wt%) at 50 °C and under 10 bar of H$_2$ pressure [178]. The catalyst characterization revealed that the presence of electron rich Pt and ionic Co species in proximity with each other could be correlated with the catalyst activity. Additionally, this type of catalysts possibly resulted in MF production at a higher
temperature (Table 5, entry 16) [140]. Wang et al. observed a maximum of 88% MF yield at 1 bar of H₂ flow, and a slight decrease to 75% at 33 bar of H₂, due to the formation of over hydrogenated products. For comparison, our research group recently investigated the furfural selective hydrogenation to MF (78% yield) at lower reaction temperature (150 °C vs 180 °C) with monometallic catalyst Pt/C in a continuous flow regime (Table 5, entry 18) [141].

3.3. Ru and Other Noble Metal Based Catalysts

In terms of MF production, non-noble metal catalysts, such as Cu based catalysts, seem to be more efficient than noble catalysts, but relatively harsh reaction conditions are required. Oppositely, noble metal catalysts could achieve the production of MF at mild conditions, especially in a continuous flow regime. Recently, Vlachos et al. have studied the furfural catalytic transfer hydrogenation to MF with Ru catalyst, partially forming oxide species, supported on activated carbon [101, 103]. With iso-propanol as solvent, the authors obtained 61% of MF yield at 180 °C in 10 h, and later they improved the yield to 76% with 2-butanol or 2-pentanol as solvent. Subsequently, the mechanistic study revealed that Lewis acid-catalyzed intermolecular hydride transfer is the dominant pathway for FA formation, and further hydrogenolysis of the C−OH bond in FA to MF mainly occurs via ring-activation involving both metal and Lewis acid sites [144]. Herein, they proved that hydrogen atom was not directly added to the carbon atom after C−OH bond cleavage, but added to the furan ring, and followed by H subtraction while releasing one molecule of H₂O. Finally, a hydrogen atom was added to the above-mentioned carbon atom (Scheme 5). Therefore, the bifunctional nature of a catalyst is critical in the efficient hydrodeoxygenation of furfural to MF. Possibly inspired by these findings, Wang et al. obtained 83% of MF yield with Ru/NiFeO₄ as catalyst, at similar reaction conditions [102]. Unlike the case Vlachos et al. faced, where the catalyst easily deactivated due to the RuOₓ reduction to metallic Ru during the reaction, Ru/NiFeO₄ showed excellent catalytic activity and recycling performance, possibly due to its relatively stable Lewis acid sites. Noticeably, relative bigger Ru particle size (>14.1 nm) than the values that were reported in literatures (ca. 1–4 nm) was observed [105, 179, 180], however, it’s difficult to make a general conclusion on the influence of Ru particle size on furfural hydrogenation selectivity because of the variation of supports, surface area, reaction conditions, and even Ru nature (Ru⁰ or RuOₓ). Interestingly, Aldosari et al. found that ca. 20% of MF could be produced with Pd-Ru/TiO₂ at room temperature in 2 h, and the incorporation of Ru in Pd/TiO₂ decreased the catalytic activity but improved the selectivity towards 2-methylfuran and FA with decreased byproduct formation [105].

![Scheme 5. Reaction mechanism for the hydrogenolysis of FA to MF over Ru/RuOₓ/C catalyst using isotopic labelling. Adapted from Gilkey et al. [144].](image-url)
With Ru based catalysts, more attention was focused on the production of FA at mild conditions. Ru supported on activated carbon, multi-wall carbon nanotubes or carbon black have been proved to be highly efficient candidates for furfural hydrogenation [84,100], but the introduction of bimetallic catalyst or other supports, such as reduced graphite or MOFs-UlO-66 and Al-MIL-53, showed outstanding improvement, and FA yields higher than 90% could be reached at 20 °C (Table 6, entries 8 and 9). Importantly, homogeneous catalyst Ru/PH₂P(CH₂)₃PPh₂ also showed high efficiency, since the reactions could be conducted without solvent, achieving 100% atom economy with a high turnover frequency of 6273 h⁻¹. Besides, the catalyst performance remained stable after twelve consecutive runs, which makes it more competitive with heterogenous catalysts. Recently, Bagnato et al. proposed an innovative ruthenium based catalytic membrane reactor [181]. Under mild conditions and low H₂ loading, they obtained 26% FA yield, however the reaction turnover frequency was 48 000 h⁻¹, two orders of magnitude higher than those obtained so far. Notably, by increasing H₂/furfural molar ratio from 1:1 to 4:1, a >99% selectivity to THFA was obtained under the same process conditions. Hence, Ru based catalysts could be potentially used to reduce C=C bond. Huang et al. concluded that Pd/Al₂O₃ catalyze preferably C=C bond in the furan ring, while Ru/ZrO₂ present higher affinity with C=O bond [33]. By combining these two catalysts physically, an unexpected 100% THFA yield was obtained at 30 °C in 4 h. Detailed kinetics studies suggested that firstly hydrogenation of furfural to tetrahydrofurfural over Pd/Al₂O₃ and then subsequent C=O bond hydrogenation over Ru/ZrO₂ will require lower activation energy, which could be directly associated with the superior activity of the mix-catalyst.

Other noble metals, such as Ir and Au, have been applied for furfural hydrogenation to MF [173,182,183]. Selective TOF over Au/Al₂O₃ (at 150 °C) was obtained, which is significantly higher than the benchmark supported Cu catalysts that operated at higher temperatures (180–220 °C). The higher selective hydrogenation rate can be linked to the greater capacity of nano-sized Au to chemisorb/activate H₂, in comparison with supported Cu [182]. Date et al. prepared various Ir supported catalysts, and reported that Ir/C catalyst with metallic (Ir⁴⁺) and oxide (IrO₂) phases could give rise to 95% of MF yield at very low H₂ pressure of ~6.9 bar (Table 6, entry 13). Consistent with the research of Vlachos and coworkers, who used partially oxidized ruthenium supported on carbon, Date et al. also proposed an acid mediated mechanism from furfural to MF. According to these findings, it can be concluded that acid sites on the catalyst will facilitate furfural hydrogenation to FA, and FA further hydrogenolysis to MF.

### Table 6. Furfural hydrogenation over Ru-based and other catalysts.

| Entry | Catalyst | H Source | Solvent | Temperature °C | Time (h) | Pressure (bar) | Yield (%) | Ref. |
|-------|----------|----------|---------|---------------|---------|---------------|-----------|------|
| 1     | Ru/C     | i-ProH   | i-ProH  | 180           | 10      | 20.4⁴         | 61        | 0    | [103] |
| 2     | Ru-RuO₂/C| 2-ButOH  | 2-ButOH | 180           | 10      | 20.4²         | 7         | 77   | 1    | [101] |
| 3     | Ru/NiFeOₓ| i-ProH   | i-ProH  | 180           | 10      | 21.4           | 1         | 83   | -    | [102] |
| 4     | Pd-Ru/TiO₂| H₂      | octane  | 90            | 5       | 12.5          | 40        | 13   | -    | [105] |
| 5     | Ru/C     | H₂O      | H₂O     | 90            | 5       | 12.5          | 85        | -    | 1    | [100] |
| 6     | Ru/Sn/C  | H₂O      | H₂O     | 20            | 4       | 10            | 91        | -    | -    | [104] |
| 7     | Ru/GO    | H₂O      | H₂O     | 20            | 4       | 5             | 95        | -    | -    | [179] |
| 8     | Ru/UlO-66| H₂O      | H₂O     | 40            | 2       | 5             | 100       | -    | -    | [180] |
| 9     | Ru/Al-MIL-53| H₂O| H₂O     | 20            | 140     | 1.3           | 25        | 100  | -    | [184] |
| 10    | Ru/Pd₂P(CH₂)₃PPh₂| H₂O| - | 70  | CF³         | 7        | 26          | -    | -    | [178] |
| 11    | Ru/PES membrane | H₂O| - | 300 | 4 | 5  | 0          | 100   | -    | [33] |
| 12    | Ru/ZeO₂ + Pd/Al₂O₃| H₂O| - | 300 | 4 | 5  | 0          | 100   | -    | [181] |

⁴ N₂ pressure ³ continuous flow.

As for Ru-based catalysts, mild reaction conditions are better for FA production, and neutral supports seem to be preferable for the production of FA with H₂ as H sources. Lewis acid sites from the supports or Ru oxides and relative higher reaction temperature both contributed to the further hydrodeoxygenation of FA to MF via catalytic transfer hydrogenation.
4. Conclusions and Outlook

Through this contribution, a general vision of the advances and recent investigations in the furfural catalytic hydrogenation has been offered. Specially, we focus our attention in furfural selective hydrogenations over non-noble and noble metal heterogeneous catalysts, a topic that still have a long way to go to fully elucidate the behavior and mechanisms of the reactions, when considering the high amount of variables that determine the final product yield and distribution. Based on the researches that have been performed in the latest five years, it can be concluded that the selectivity to various furfural hydrogenation products can be achieved by (Figure 7): (1) Control the reaction conditions, including a) temperature (>200 °C benefiting to MF formation from furfural with Cu based catalysts); b) H₂ pressure (high H₂ pressure will lead to deep hydrogenation, even ring-opened products); c) time (deeper hydrogenation occurred by prolonging reaction time); and, d) solvents (in certain case, protic solvents leads to side-reactions) etc. (2) Hydrogen resources. It can be noticed that transfer hydrogenation of furfural generally produce FA as product or MF under harsher conditions. Almost no THFA or MTHF is observed. (3) Alternative active metal. For instance, Cu and Ru mainly result in hydrodeoxygenation of furfural to MF, while Co, Ni, and Pd catalysts will lead to furan ring hydrogenation to THFA. (4) Incorporation of different active metals. In many cases, the synergy of bimetallic catalysts showed remarkable improvement of furfural conversion and target product yield, as compared with monometallic catalysts. (5) Alternative supports. The same metal supported on different materials could possibly give rise to different products. Especially, the acidity and basicity of the supports have significant influence on the catalytic performance of the catalyst. (6) Alternative reaction regime. In comparison with batch reaction, continuous flow could result in enhanced productivity and sometimes the type of products varied.

![Diagram](image_url)

Figure 7. Representation of general factors that influence catalytic hydrogenation of furfural.

Furthermore, catalysts preparation approaches and metal reduction methods also have crucial effects on the catalytic performance of the resulting materials. In fact, these factors could complicate the analysis, which makes comparison of different catalysts not an easy task. Therefore, further efforts
should be performed in order to find more efficient and greener methods for furfural selective transfer hydrogenation, involving non-noble metal catalysts and continuous flow regime. Although lab-scale studies employing continuous flow methodologies have been broadly described, more endeavors should be accomplished to scale-up furfural valorization through catalytic hydrogenation processes. In this regard, challenges for continuous flow technologies should be recognized, for example:

(i) Dedicated equipment is needed for precise continuous dosing (e.g., pumps), connections, etc.
(ii) Start up and shut down procedures have to be established.
(iii) Scale up of micro effects, such as the high area to volume ratio, is not possible.
(iv) Safety issues for the storage of reactive material still need to be solve.

Despite all of the progress that has been achieved so far in this area, the remarkable potential of furfural for the preparation of added-value chemicals and the possible optimization of catalytic systems and reactions conditions still lead to a broad range of possibilities. We hope that this contribution becomes an useful tool for the scientific community and that, at the same time, it can inspire researchers to keep working in this area, allowing the development of greener and more efficient process for furfural and biomass valorization.

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