Tetrahedron Green Chem 3 (2024) 100037

Contents lists available at ScienceDirect

Tetrahedron Green Chem

journal homepage: www.journals.elsevier.com/tetrahedron-green-chem

Valorization of biomass platform molecules through one-pot cascade processes using heterogeneous catalysts

Karen S. Arias, Alexandra Velty, Maria J. Climent **, Sara Iborra *

Instituto de Tecnología Química (Universitat Politècnica de València- Agencia Estatal Consejo Superior de Investigaciones Científicas).Avda Dels Tarongers s/n, 46022, Valencia, Spain

A B S T R A C T

The transformation of biomass derived platform molecules is an interesting approach to produce valuable chemicals from biomass. In addition, process intensification by reducing the number of steps for final chemicals production by performing cascade-type catalytic reactions in one-pot mode is largely desirable in a biorefinery facility. In this review the possibilities of valorization of representative platform molecules such as sugars, itaconic and levulinic acids and furanic aldehydes through one-pot cascade processes using mono and multifunctional heterogeneous catalysts are illustrated through selected examples.

1. Introduction

Fossil feedstocks are traditionally the source of the chemical building blocks required for organic synthesis. However, the limited reserves of fossil fuels along with the environmental concerns associated to their use [1], have prompted to researchers to look for alternative sources of renewable energy and chemicals. In this sense, biomass represents an abundant source of renewable carbon that can constitute the basis for sustainable fuels and chemicals [2–4]. As occurs in a petroleum refinery, in a biorefinery the transformation of biomass feedstocks into valuable products can be achieved through transformation of a range of molecules derived from biomass, commonly referred to as platform molecules. The identification of these platform molecules was initially conducted by the US Department of Energy (DOE) in 2004 [5], and later revised in 2010 [6]. These molecules include sugars (glucose, xylose), polyols (sorbitol, xylitol, glycerol), furans (furfural, 5-hydroxymethylfurfural), and acids (itaconic, succinic, levulinic, and lactic acid acids). These platform chemicals can be further processed through biological, chemical or thermochemical methods to produce a range of valuable compounds that are conventionally produced from fossil resources or have similar properties to petroleum-derived compounds [7]. In this context, the development of new catalytic processes to competitively and efficiently produce biomass-derived chemicals through process intensification is largely needed. In these new eco-friendly processes, the number of steps for final fuels and chemicals production must be reduced by performing consecutive or cascade-type catalytic reactions in one-pot mode [8]. These cascade processes, where several catalytic events occur in the same reaction vessel, offer a variety of advantages over the conventional step-by-step approach. Thus, allow the decrease of energy consuming steps such as separation and purification of intermediates, reducing therefore the operating time, waste and cost of the process. Solid catalysts are promising candidates to perform these multi-step processes since they allow creating robust site-isolated and well-defined multisite catalysts in where the active sites (including incompatible sites) can act both in a cooperative way (for instance acid-base and also redox) and in different steps of a given cascade process [9–12].

In this mini-review, selected examples of one-pot processes for converting biomass derived sugars, acids, such as itaconic and levulinic acids, and furanic aldehydes into valuable compounds which are carried out on solid catalysts are reported.

2. Conversion of biomass-derived sugars to value-added products

Carbohydrates represent the major fraction of the biomass, being D-glucose the most abundant carbohydrate. D-glucose can be converted into valuable chemicals through different reactions as isomerization, dehydration, hydrogenation and oxidation [13]. An important sugar alcohol derived from glucose hydrogenation is sorbitol that can be further converted into isosorbide through an acid catalyzed dehydration, being D-sorbitol and isosorbide among the 15 target molecules of special interest for biorefinery development [5].

The selective synthesis of isosorbide (**5**) directly from glucose (**1**) by

* Corresponding author.
** Corresponding author.
E-mail addresses: mjclio@qim.upv.es (M.J. Climent), siborra@itq.upv.es (S. Iborra).

https://doi.org/10.1016/j.tgchem.2024.100037
Received 20 December 2023; Received in revised form 24 January 2024; Accepted 5 February 2024
Available online 9 February 2024

coupling hydrogenation and dehydration steps in one-pot (Scheme 1) has been performed over a heterogeneous bifunctional catalyst bearing metal and Brønsted and acid sites (Ru@Dowex-H) [14]. The reaction is performed in water at 190 °C, 30 bar H_2 achieving 85% isosorbide yield after 48 h of reaction time. The hydrogenation selectivity of the resin supported-metal catalyst was attributed to the positive combination of the microporous structure of the resin support with the narrow size distribution of immobilized Ru nanoparticles, while selectivity in dehydration can be attributed to the proper balance of density and strength of Brønsted acid sites. More recently, a MW-assisted one-pot two step isosorbide catalytic synthesis from glucose was investigated in the presence of a physical mixture of Ru/TiO_2 catalyst and H-Beta zeolite [15]. The hydrogenation step was first performed at 155 °C, 40 bar H_2 pressure and 1 h of reaction followed by dehydration step at 190 °C, 30 min, 20 bar N_2, achieving 47% yield of isosorbide. Interestingly, similar results were achieved in the one-pot conversion of cellulose into isosorbide, which is a more challenging process. In this case, a bifunctional Ni doped $NbOPO_4$ catalyst containing both Lewis and Brønsted acid sites, was used to perform the cascade process in water which involves cellulose hydrolysis into glucose followed by hydrogenation and subsequent dehydration [16]. Working at 200 °C and 30 bar H_2 pressure, a 47% isosorbide yield was reached after 24 h of reaction. The catalytic performance of the bifunctional catalysts was attributed to an appropriate total acid sites and high Brønsted/Lewis acid sites ratio. Moreover, a study of catalyst stability showed that catalytic performance of the $Ni/NbOPO_4$ remained practically constant during five consecutive runs.

Fatty acid isosorbide esters constitute a class of non-ionic sugar biobased surfactants that are widely used in cosmetic, household and other industrial applications [17]. The production of isosorbide esters is usually performed starting from pure isosorbide under homogeneous acid catalysis [18]. Therefore, the direct conversion of sorbitol (**2**) to isosorbide ester is highly attractive. However, due to the polyhydroxylated structure of sorbitol, the direct conversion is challenging due to the existence of several side reactions such as isomerization and humins formation. A simple and efficient cascade process for the direct conversion of sorbitol and fatty acids to isosorbide esters (**8,9**) on H-beta zeolite in the presence of methyl isobutyl ketone (MIBK) has recently been reported (Scheme 2) [19]. The key to this tandem reaction is the formation of sorbitol ketals with MIBK (that acts as co-solvent and protecting group), preferentially forming the 1,3-dioxolane structure with terminal vicinal-dihydroxyl groups of sorbitol (compound **6**) and with 1,4-sorbitan (compound **7**), that control the reaction pathway and minimize the side reactions. Similar strategy was previously described in a two-step cascade process for the synthesis of sorbitol fatty acid esters using acid zeolites and acetone as protecting group [20]. The ketal protection of hydroxyl groups allowed a controlled cascade sequence of sorbitol dehydration into isosorbide (**5**) followed by esterification with the fatty acid preventing side reactions of sorbitol and limiting the formation of 1,4-sorbitan (**3**) and humins. The direct dehydration-esterification of sorbitol with various C2–C8 fatty acids was successfully performed over H-beta (Si/Al = 20), achieving 79–84% yield of isosorbide esters (**8,9**) containing 59–65% of diesters (**9**), at 190 °C within 4 h.

A two-steps one-pot sequential process was also performed using different sulfonic resins as acid catalysts for the dehydration of sorbitol under solvent free conditions at 130 °C under vacuum for 24 h, followed by the esterification of isosorbide with acetic or octanoic acids at 130 °C or 160 °C for 24 h [21]. Isosorbide yield up to 80% and 70–80% diacetate yield and up to 57% dioctanoate yield were obtained in the presence of DOWEX-50 or SAC-13 catalysts.

3. Conversion of biomass-derived carboxylic acids to high value-added products

Among renewable chemicals, biomass-derived carboxylic acids with bifunctional groups such as itaconic, levulinic and succinic acids play a key role in the production of valuable biobased chemicals such as tetrahydrofuran derivatives, pyrrolidones and esters [22–24]. Particularly pyrrolidones, are high value products with a wide range of applications, serving as solvents, surfactants, chelating agents, agrochemical components, or pharmaceuticals [25,26].

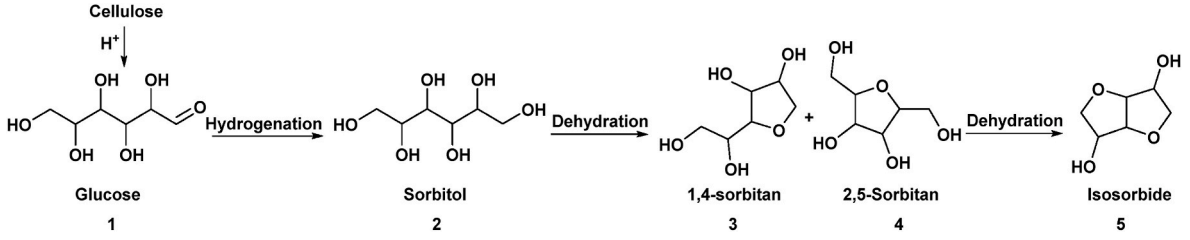
The tandem one-pot reductive amidation/amination of biogenic carboxylic acids with ammonia or primary amines offers a promising approach for 2-pyrrolidones synthesis. In this section, recent examples of the preparation of methyl 2-pyrrolidones through one-pot cascade processes starting from itaconic and levulinic acids are presented.

3.1. Synthesis of 2-pyrrolidones from itaconic acid

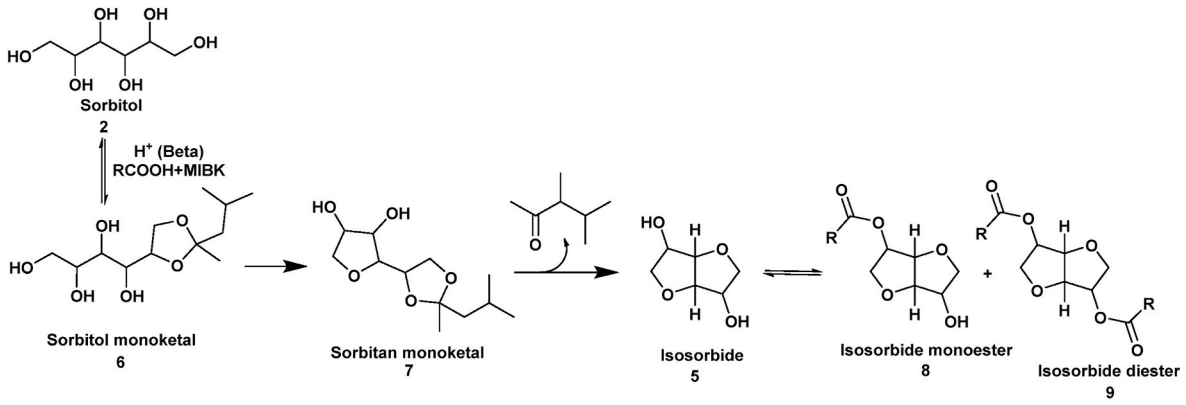
Itaconic acid (**10**) is a monounsaturated diacid widely used in the food, plastics, textile, paint and pharmaceutical industries. Itaconic acid is produced via glucose fermentation, being the global itaconic acid market size USD 97.9 million in 2022 and is expected to grow at a compound annual growth rate (CAGR) of 4.4% from 2023 to 2030 [27].

The reductive amidation of itaconic acid with ammonia has been recently performed on a commercial Ru/C as catalyst, using a low amount of water as a solvent and hydrogen as reducing agent [28]. The proposed reaction pathway (Scheme 3) involves as a first step the double bond hydrogenation of itaconic acid (**10**) into 2-methyl succinic acid (**11**), followed by amidation (compounds **12a-c**) and cyclisation (thermally driven steps), leading to 3-methylsuccinimide (**13**) that is finally hydrogenated into 3- and 4- methylpyrrolidones isomers (**14a-b**), being this last step the rate-determining reaction step. 3- and 4-Methylpyrrolidones (**14a-b**) were obtained in 83% yield, while the recycling study of the catalyst showed good stability over five consecutive cycles. Additionally, the catalytic system could be applied to other biogenic acids such as levulinic and succinic acids with 45–47% yield. Interestingly, under optimized reaction conditions, the catalytic system was applied to the reductive amidation of itaconic and succinic acids with ethanolamine yielding N-(2-hydroxyethyl)-2-pyrrolidones, which are precursors of N-vinyl-2-pyrrolidones of interests as valuable monomers. The authors performed the dehydration of N-(2-hydroxyethyl)-2-pyrrolidones into N-vinyl-2-pyrrolidones in a continuous gas phase dehydration process over sodium-doped silica, achieving N-vinyl pyrrolidone with a total yield of ≥72% over two process steps [22].

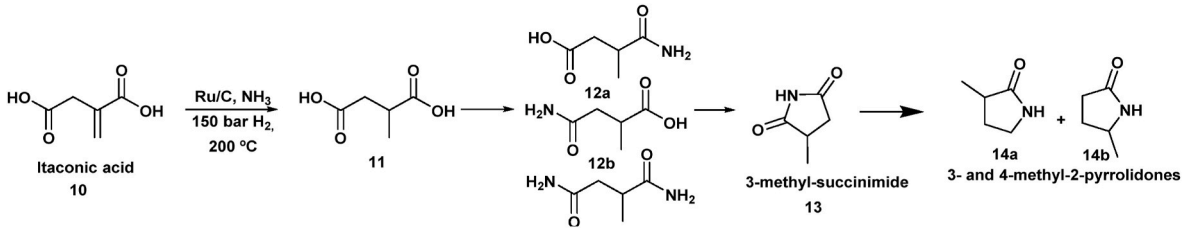
The catalytic system for itaconic acid amidation with ammonia was further improved by using a Pd catalyst based on Pd nanoparticles



Scheme 1. Reaction pathway for the direct conversion of glucose (or cellulose) to isosorbide.



Scheme 2. Selective one-pot dehydration-esterification of sorbitol to isosorbide esters over H-beta catalyst.



Scheme 3. One-pot reductive amidation reaction pathway of itaconic acid with ammonia to 3- and 4-methyl-2-pyrrolidones.

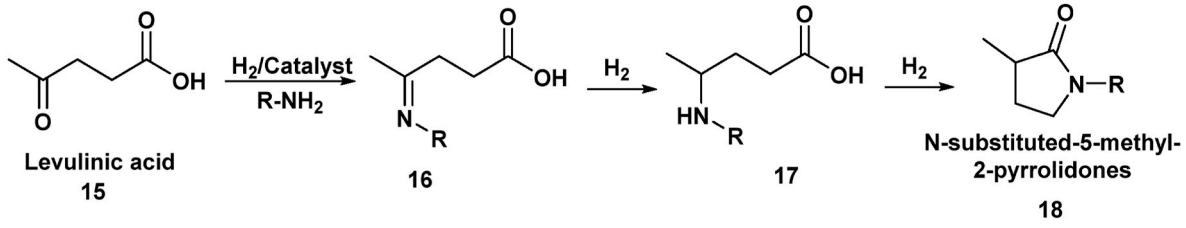
supported on an oxidized carbon (Pd/C_{ox}) [29]. Optimization of the nanoparticle size showed that the reaction was sensitive to the structure of the metal, achieving optimal results with Pd nanoparticles with average size between 1.8 and 2.2 nm, yielding 3- and 4-methyl-2-pyrrolidones (**14a-b**) up to 95% yield. Subsequently, the authors performed the vinylation of the synthesized methyl-2-pyrrolidones with acetylene under standard industrial conditions (10–18 bar acetylene, 150 °C, KOH catalyst, solvent-free), obtaining up to 80% N-vinyl--methyl-2-pyrrolidone. Furthermore, Pd/C_{ox} catalyst displayed high activity in the reductive amination of levulinic acid, successfully producing 5-methyl-2-pyrrolidone. These findings hold significant promise for industrial-scale applications. However, a challenge remains in the recycling of the catalyst, as the oxidized carbon material undergoes degradation under reaction conditions, resulting in a significant reduction in surface area and pore volume.

3.2. Synthesis of 2-pyrrolidones from levulinic acid

Levulinic acid (LA) (4-oxopentanoic acid) is a bifunctional γ-ketocarboxylic acid with rich chemistry that can be converted into a wide range of fuel additives and commodity chemicals [30]. LA can be produced from carbohydrates present in agricultural wastes, wheat straw, and residues from agrochemical industries. On an industrial scale, levulinic acid is usually produced by synthetic, biological and extraction routes. Synthetic processes use sulphuric acid, hydrochloric acid, hydrogen peroxide and phosphoric acid as catalysts. The global levulinic acid market was valued at USD 27.38 Billion in 2021 and is expected to grow at a CAGR of 14% from 2022 to 2030 [31].

The one-pot reductive amination of LA (or esters) (**15**) with primary amines (Scheme 4) yields 5-methyl-N-(alkyl/aryl) substituted-2-pyrrolidones (**18**). The reaction usually proceeds through of the acid-catalyzed formation of an imine intermediate (**16**), which is the rate-determining step [32] followed by its hydrogenation into amine (**17**) and spontaneous cyclisation to the 2-pyrrolidone derivative (**18**). For this process, noble metal-based catalysts such as Pt, Ru, Ir, Pd, Rh and Au have been the most used [33–38], while different reducing agents such formic acid, hydrosylanes and ammonia borane have also been reported [39,40], being gaseous H_2, especially green H_2, the preferred due to its industrial, economic and environmental advantages. This emerging approach has received a great attention for both research and industrial perspectives [41] and several reviews on the reductive amination of levulinic acid (or esters) with amines or N-containing precursor compounds have been recently reported [26,42–44].

In Table 1 are summarized some of the more relevant results on reductive amination of LA (or esters) with primary amines and H_2. In general, noble metal-based catalysts are the most active for the reductive amination of LA. Among them, Pt and Pd supported on acidic supports, as well bimetallic catalysts such as AuPd represent efficient bifunctional acid-metal catalysts for performing the one-pot cascade process, while more sophisticated Ru based catalysts, recently reported, also showed good performances. Additionally, the reductive amination of levulinic acid (esters) starting from nitroarenes instead of anilines is a more direct



Scheme 4. One-pot reductive amination of levulinic acid with primary amines into N-substituted-5-methyl-2-pyrrolidones.

Table 1
Reductive amination of levulinic acid (or esters) with alkylamines with different metal-based solid catalyst and H_2 as reductant.

Entry	Catalyst (mmol%)	H_2 (bar)	T (°C)	Time (h)	Substrate	Amine	Yield (%)	Ref
1	Pt-MoO_x/TiO_2 (0.001)	3	100	20	LA	octyl	95	[47]
2	Pt/TiO_2 (0.05)	10	120	2	EL	octyl	98	[48]
3	Pt/P–TiO_2 (0.1)	1	RT	3	LA	octyl	97	[49]
4	Pt/P–TiO_2 (0.1)	1	RT	10	EL	octyl	94	[49]
5	Pd/ZrO_2 (0.1)	5	90	12	LA	octyl	98.7	[37]
6	C–$Au_{66}Pd_{34}$ (0.3)	1	85	12	LA	octyl	93	[38]
7	C–$Au_{66}Pd_{34}$ (0.3)	1	85	12	EL	octyl	99	[38]
8	Ru@GOIL	15	130	5	LA	heptyl	81	[39]
9	Ru-PP/CNTs	3	120	24	EL	octyl	89	[50]
10	10% Ni@CeO_x	20	140		LA	methyl	96.8	[51]
11	$Cu_{15}Pr_3/Al_2O_3$ (5)	50	175	20	LA	octyl	94.2	[52]
12	CNF_{30}@Ni@CNTs	30	130	4	LA	benzyl	99	[53]
13	CoNi@NC	30	130	6	LA	benzyl	99	[54]

LA: Levulinic acid; EL: Ethyl levulinate; P–TiO_2: porous TiO_2 nanosheets; C–$Au_{66}Pd_{34}$: $Au_{66}Pd_{34}$ alloy nanoparticles loaded onto C; Ru@GOIL: Ru supported on ionic liquid immobilized into graphene oxide; Ru-PP/CNTs: Polymeric ruthenium porphyrin-functionalized carbon nanotubes; CoNi@CN: CoNi alloy nanoparticles confined in N-doped porous carbon.

and atom-economical process than has been comparatively less investigated. Efficient catalytic systems for the reductive amination of LA with nitroarenes such as Pt supported on TiO_2 nanotubes [45] Pt/Nb_2O_5 [46] and Ir supported on polyvinylpyrrolidone (Ir/PVP) [36] have been recently reported, being Pt/Nb_2O_5 and Ir/PVP of remarkable activity able to perform the process under very mild reaction conditions.

Comparatively, the reductive amination of LA on non-noble metal-based catalysts has been much less studied due to they suffer of poor stability and are prone to deactivation by metal aggregation and leaching, while harsh reaction conditions are usually required to achieve satisfactory performances. Recently, monometallic catalytic systems based on Co [55,56], Ni [51,53,57] and Fe [58] have been found to be effective in the reductive amination of levulinic acid. An operative strategy to increase catalyst stability is by encapsulating metal nanoparticles within a protective shell that prevents metal aggregation and leaching. For instance, porous-carbon-coated Ni catalysts supported on carbon nanotubes (CNF_{30}@Ni@CNTs) performed the reductive amination of LA with benzyl amine in excellent yield, while exhibited higher stability than Ni@CNTs and Ni/C catalysts. Interestingly, an unconventional reaction pathway with amide formation first, followed by tandem cyclisation, intramolecular dehydration and hydrogenation to pyrrolidone was observed [53]. An strategy to increase the catalytic activity has been the introduction of a second metal to form a multicomponent alloy or bimetallic catalyst, providing more active sites, while improving metal dispersion [59,54]. The development of cost-effective non-noble metal catalysts for reductive amination is economically appealing and it remains a challenge to develop a large-scale industrial process using an efficient and robust non-noble metal-based catalyst able to operate under mild reaction conditions.

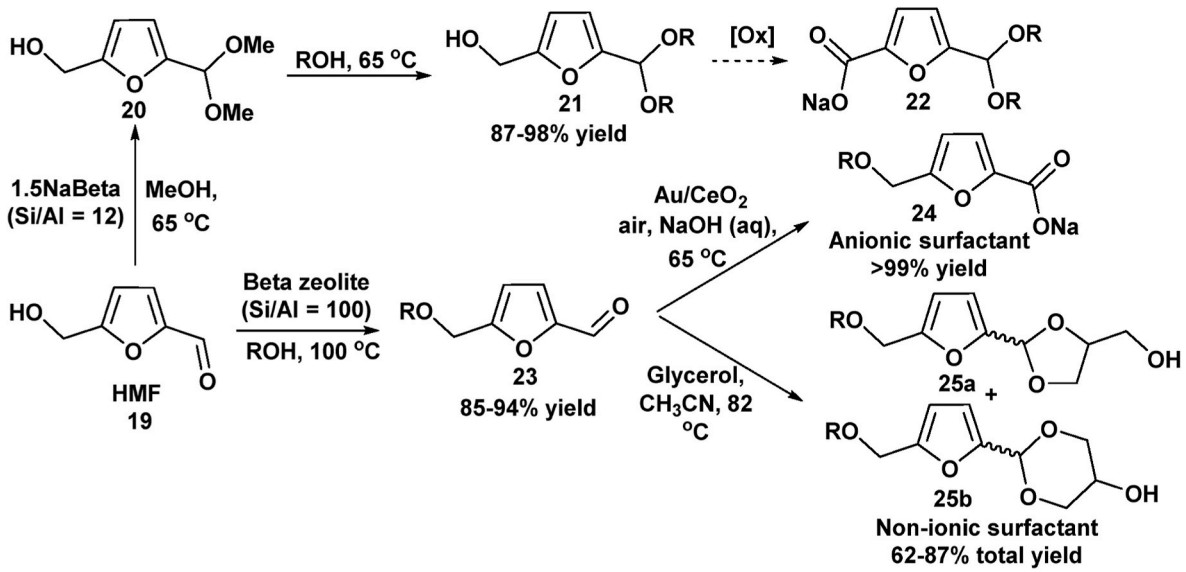
4. Conversion of furanic aldehydes to high value-added products

Furfural and 5-Hydroxymethylfurfural (HMF) are two important biomass derived platform molecules with high potential to serve as building blocks for high value-added chemicals and materials due their chemical versatility associated to the presence of different functions in their structure [60–63]. These compounds can be prepared by the acid-catalyzed dehydration of pentoses and hexoses respectively. Furfural is produced on a large scale from lignocellulosic biomass, with annual global production being approximately 652 kilotons [64]. The global furfural market valued USD 595.14 million in 2023, and is expected to reach USD 954.36 million by 2030 [65] while the global market size of 5-hydroxymethylfurfural reached USD 61 million in 2022, and it is expected the market to reach USD 68.2 million by 2028 [66].

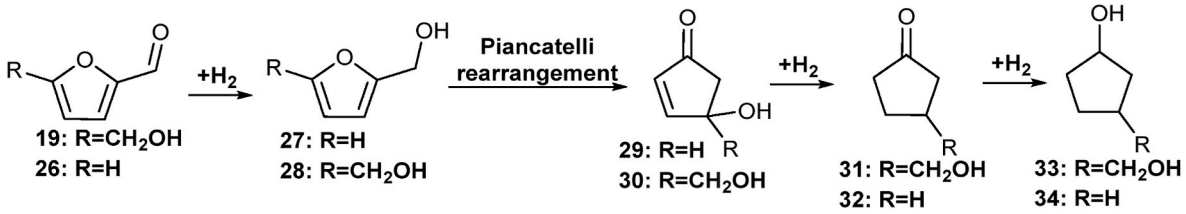
In this section, we focused on the preparation of two types of important compounds such as surfactants and amine derivatives starting from furfural and HMF by one-pot cascade processes through selected examples.

4.1. Synthesis of biobased surfactants from HMF

Surfactants, which contain a polar head groups and a hydrophobic counterpart in their structure are found in many commonly used products. In the last years, HMF has been considered as a valuable starting material for biobased surfactants due to its renewability and improved biodegradability [67,68]. Surfactants (or surfactant precursors) derived from HMF (**19**) were prepared in one-pot mode, by reacting in a first step the HMF with fatty alcohols to introduce the lipophilic moiety using H-beta zeolite as acid catalyst (Scheme 5). The selective acetalization of the aldehyde group or etherification of the hydroxymethyl group with the fatty alcohol could be controlled by optimizing the acidity and adsorption properties of the beta zeolite and reaction conditions [69–71]. Thus, by controlling the acidity of H-beta zeolites by partial exchange of H^+ with Na^+ the synthesis of dialkyl acetals of HMF (**21**) was selectively achieved by transacetalization with a fatty alcohol of a in situ preformed dimethyl acetal (**20**) in excellent yields (87–98%) while the undesirable side reaction of etherification was avoided. The dialkylacetal derivative (**21**) could be further converted in a carboxylate derived surfactant (**22**) by subsequent oxidation of the hydroxymethyl group. In addition, by controlling the adsorption properties of hydrophobic H-beta zeolites synthesized in fluoride media and free of connectivity defects, the etherification of the hydroxymethyl group of HMF with fatty alcohols was selectively achieved yielding 5-alkoxymethylfurfural derivatives (**23**) in high yields (98 % yield). In a second step, the introduction of the polar moiety was achieved by two different strategies. One of them involves the oxidation of the formyl group of 5-alkoxymethylfurfural derivative intermediate (**23**) into carboxylate function using gold nanoparticles supported on CeO_2 and air as oxidant in aqueous alkaline media, leading to 5-alkoxymethyl-2-furoates surfactants (**24**). The other one, involves the acetalization of the formyl group with glycerol catalyzed the same H-beta catalyst yielding a dioxolan and dioxan isomers mixture (**25a-b**).



Scheme 5. Valorization of HMF into anionic and non-ionic biobased surfactants.



Scheme 6. Transformation of HMF and furfural to cyclopentanone and cyclopentanol derivatives.

4.2. Synthesis of cyclopentanone and cyclopentanol derivatives from furanic aldehydes

Cyclopentanone and cyclopentanol derivatives are important intermediates in organic synthesis used to produce a variety of compounds, such as fragrances, cosmetics, solvents and agrochemicals [72–74]. Cyclopentanone derivatives can be obtained from furfural (**26**) and HMF (**19**) through a cascade reaction (Scheme 6) that and includes metal catalyzed hydrogenation and rearrangement reactions. The hydrogenative ring rearrangement usually occurs in pure water that acts as a solvent and reactant [75], while temperatures higher than 120 °C are commonly required to promote the ring rearrangement reactions. In the process, first, furfural (**26**) or HMF (**19**) are hydrogenated on the metal sites into furfuryl alcohol (**27**) and 2,5-bis(hydroxymethyl)furan (**28**), respectively, followed by the rearrangement of (**27**) to 4-hydroxy-2-cyclopentenone (**29**) or **28** to 4-hydroxy-4-hydroxymethyl-2-cyclopentenone (**30**) through the acid catalyzed Piancatelli rearrangement. Finally, hydrogenation of the Piancatelli rearrangement products (**29** and **30**) produces the final cyclopentanones or cyclopentanols (**33** and **34**) (Scheme 6) [74,76–79]. Important aspects of the reaction are that the metal sites should have a high activity for aldehyde group hydrogenation into alcohols while simultaneously exhibit low activity for the furan ring hydrogenation and hydrogenolysis of the C–O bond, since when the later reactions occur the generated products cannot undergo isomerization to cyclopentanone derivatives. In addition, an important drawback of the reaction is the possible polymerization of the furfuryl alcohol intermediates (**27** and **28**) in a hot acidic aqueous solution. Therefore, weak acidity is required for the formation cyclopentanone derivatives, and most active catalytic systems are based on metal supported on medium-weakly Lewis acid supports [80,81], while on Brønsted acid supports the polymerization of active intermediates was observed [82]. On the other hand, when non-acidic supports are involved, the slightly acidic conditions generated by the water dissociation at elevated temperature are enough to promote the ring-rearrangement [83–85].

Since the pioneering work of Hronec et al. [86] for the transformation of furfural into cyclopentanone, several catalytic systems based on supported noble metals such as Pd, Pt, Ru, and Au [81,82,87–91] and non-noble metals such as Ni, Co and Cu [92–98] have been reported for furanic aldehydes rearrangement into cyclopentanones. However, sintering of monometallic species in aqueous media as well as over-hydrogenation reaction of the furan ring and C–O hydrogenolysis are the main drawbacks associated to the monometallic catalysts [98–102]. Therefore, the introduction of a second metal has been a widely adopted strategy to modulate the hydrogenating activity and increasing the stability of the metal catalyst through a synergistic effect. For instance, highly selective bimetallic catalysts such as PdCu [103], PdCo [104], CuCo [105], CuNi [106–108], CuZn [109] and NiMo [110] have been recently reported for the conversion of furfural into cyclopentanone. Conversion of furanic aldehydes into cyclopentanone and cyclopentanol derivatives has been recently reviewed [111–113]. Therefore, in Table 2 are collected several representative catalytic

Table 2
Catalytic systems for the conversion of furfural and HMF into cyclopentanones and cyclopentanols.

Entry	Catalyst (mmol%)	H_2 (bar)	T (°C)	Time (h)	Substrate	Product	Conv. (%)	Yield (%)	Ref.
1	Ni_1Co_1@C	20	140	7	HMF	**31**	99	92.0	[84]
2	$(Sr_2P_2O_7)_{0.40}/Ni_2P$	1	150	12	HMF	**31**	>99	72.1	[114]
3	PdZn/ZnO	40	120	12	HMF	**31**	99.9	95.8	[115]
4	Co@C	20	140	6	HMF	**33**	100	95.0	[84]
5	$Pd/NiMoO_4$	40	150	12	HMF	**33**	99.9	65.4	[116]
6	Ni/Nb_2O_5	20	130	5	Furfural	**32**	>98	>92	[117]
7	Ni_3Sn_2-ReO_x/TiO_2	30	140	5	Furfural	**32**	100	92.5	[118]
8	Ni@NP-C	15	130	2	Furfural	**32**	100	86.7	[119]
9	$(Sr_2P_2O_7)_{0.40}/Ni_2P$	30	150	4	Furfural	**32**	>99	91.6	[114]
10	$Pd/CeO_2/SiO_2$	20	150	3	Furfural	**32**	93	78.1	[120]
11	Ni@HCS	20	150	12	Furfural	**32**	100	99.1	[121]
12	Ni_5Cu_5/m-SiO_2	30	140	4	Furfural	**32**	99.9	89.6	[122]
13	$NiCu/SiO_2$	20	150	6	Furfural	**32**	100	95.4	[123]
14	Co@Co–NC	40	150	6	Furfural	**32**	100	95.1	[124]
15	$Pd/NiMoO_4$-AC	40	150	6	Furfural	**34**	100	85.2	[116]

systems recently reported for the transformation of furfural and HMF into cyclopentanone and cyclopentanol derivatives.

3-hydroxymethyl cyclopentanone (31), cyclopentanone (32), 3-hydroxymethyl cyclopentanol (33), cyclopentanol (34). Co1Ni1@C and Co@C: Co–Ni alloy and Co nanoparticles covered by a carbon shell; NP-C: P and N co-doped carbon; Ni@HCS: nickel hollow carbon spheres catalyst; Co@Co–NC: N-doped carbon-encapsulated Co nanoparticles.

4.3. Synthesis of biobased linear ketones from HMF

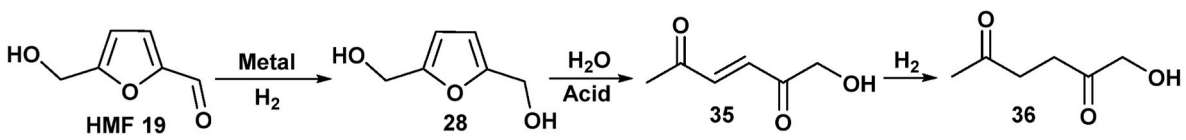
Besides cyclic ketones, linear diketones can also be obtained through the tandem conversion of C6 furanic aldehydes. For instance, 1-hydroxy-2,5-hexanedione have gained increased attention as novel starting compound for synthesizing high-value chemicals from biomass with applications ranging from energy and food to pharmaceuticals and beyond [85,125–136]. 1-Hydroxy-2,5-hexanedione (**36**) is typically obtained from HMF in aqueous phase through a cascade sequence that involves as the first step the hydrogenation of HMF into 2,5-bis-(dihydroxymethyl)furan (**28**) followed by ring opening promoted by acid sites, giving the intermediate 1-hydroxy-3-hexene-2,5-dione (**35**) which is subsequently hydrogenated into **36** (Scheme 7) [137–139]. Moreover, the reaction temperature is usually maintained below 130 °C to avoid competitive reactions such as ring rearrangement into cyclopentanone derivatives [134].

It has been showed that the nature and size (or dispersion) of the metal catalyst have a notable impact on the conversion of HMF. For instance, Rosseinsky et al. [128] reported the conversion of HMF to linear ketones using beta zeolite loaded with various metal species (Co, Ni, Cu, Ru, Pd), being Pd nanoparticles the most efficient metal. Indeed, the suitability Pd-based catalysts for the synthesis of the linear diketone from HMF has been showed by other authors [139–141]. Moreover, the hydrogenation activity and selectivity to the diketone have been associated to smaller Pd nanoparticle size (entries 1 and 2, Table 3) [128,133,142]. Interestingly, the influence of the bimetallic synergy between Pd–Au catalysts on the HMF conversion was reported by Cao et al. [143] where it was showed that Pd decorated Au/TiO_2 catalyst exhibited higher catalytic activity than the non-decorated one (entry 3, Table 3). This effect was attributed to the increase of hydrogen dissociation activity on the modified Pd surface species.

On the other hand, and concerning to the acidity required for the process, it is generally considered that Brønsted acid sites promote the ring opening of the furan ring to diketones [128,145], while Lewis acid sites are prone to induce ring closing reaction through an intramolecular aldol condensation of diketone **36** giving cyclopentanone derivatives [80]. However, recently it has been demonstrated that Lewis acids are also selective promoting the formation of 1-hydroxy-2,5-hexanedione, although their efficiency is lower than Brønsted acids. For instance, it has been demonstrated that Lewis acid sites on the TiO_2 support [143] and Cr^{+3} species in the bifunctional Pd/MIL-101(Cr) [144] catalyst promote the formation of linear ketones with selectivities higher than 80 % (entries 3 and 6, Table 3). More recently, the combination of Brønsted and Lewis acids has been investigated in transforming C6 furan compounds into linear diketones. For instance, Ru/AH_{Sw} (AH_{Sw}, biochar derived from hazelnut shells) showed increased HMF conversion and diketone selectivity than the commercial Ru/C, which was mainly attributed to the synergy between Lewis acid (from the oxidized Ru species) and the Brønsted acid sites from the biochar support [142]. Interestingly, it was recently reported that the metal–support interaction not only affects the catalyst activity, but also has an important influence on the selectivity towards the ring opening [127,129]. For instance, Deng et al. [129] have recently reported that using a bifunctional Pd-loaded MAX (Pd/Ti_3AlC_2) catalyst, 91 % selectivity to the diketone **36** (at practically total conversion of HMF) was obtained (entry 7, Table 3). Mechanistic studies showed that the exceptional activity and selectivity of the catalyst can be attributed to the generation of additional acid sites for the furan ring opening, associated to frustrated Lewis $H^{+-}H^-$ pairs ((H–Pd/Ti–O(H^+)–Al) which are produced in situ by H_2O-assisted hydrogen spillover. In Table 3 are summarized the results of some relevant catalytic systems here discussed.

4.4. Synthesis of amine derivatives from furanic aldehydes

Amines are important chemicals widely used in the synthesis of a variety of pharmaceuticals, insecticides, surfactants, polymers, pigments and food additives [146–148]. The one-pot reductive amination of aldehydes and ketones is a remarkable approach for the synthesis of amines which allows the direct conversion of carbonyl compounds into amines using simple operations. The direct reductive amination of carbonyl compounds with ammonia or amines involves the in-situ hydrogenation of a pre-formed imine intermediate on acid sites, into amine. The one-pot reductive amination of furfural and HMF with ammonia and primary (or secondary amines) yielding furfuryl amine,



Scheme 7. Conversion of HMF into 1-hydroxy-2,5-hexanedione.

Table 3
Catalytic systems for the conversion of HMF into linear diketones.

Entry	Catalyst	H_2 (bar)	T (°C)	Time (h)	Conv. (%)	Product	Yield (%)	Ref.
1	Pd/Beta (d_M = 16.2 nm)	20	110	6	56	**36**	22	[128]
2	Pd/Beta (d_M = 3.5 nm)	20	110	6	96	**36**	54	
3	$Pd_{0.02}$Au/TiO_2	10	120	1	73	**36**	64	[143]
4	Commercial Ru/C	30	100	1	81	**36**	0	[142]
						28	81	
5	Ru/A_{HSw}	30	100	1	97	**36**	72	
						28	21	
6	Pd/MIL-101(Cr)	40	140	6	64	**36**	52	[144]
7	Pd/Ti_3AlC_2	40	90	6	99.1	**36**	91	[129]

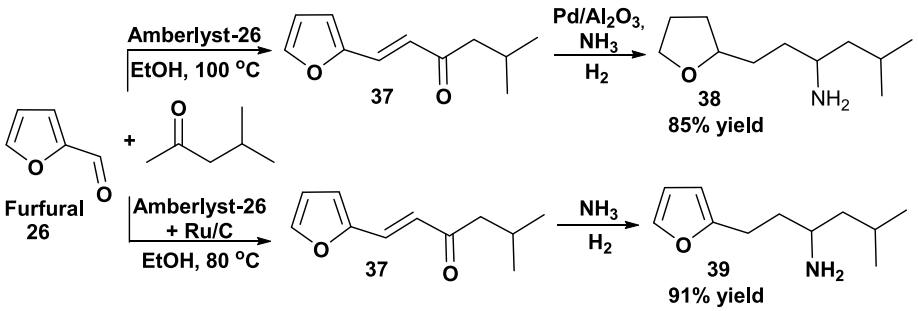
5-hydroxymethylfurfuryl amine and 2,5-bis(aminomethyl)furan and derivatives has attracted great attention in recent years due to its wide application in the production of pesticides, pharmaceuticals and monomers [149–152], and the subject has been extensively reviewed recently [153–155]. Therefore, in this section we have selected different examples of one-pot cascade processes leading to valuable amine compounds starting from furanic aldehydes and where reductive amination is involved.

For instance, a new family of tetrahydrofuran-derived amines has been prepared by a two-step one-pot process by combining C–C bond formation and reductive amination [156]. THF-derived amines (**38**) have high potential for the synthesis of biosolvents or biosurfactants, while the presence of the THF moiety is of high importance for the solvent properties and production of polymers [24,157,158]. The one-pot cascade process to synthetize this type of amines involves as the first step the aldol condensation of furfural with MIBK to the corresponding α,β-unsaturated ketone intermediate (**37**) using Amberlyst 26 as basic catalyst, followed by the reductive amination of the ketone intermediate with ammonia, and the hydrogenation of the furan ring catalyzed by Pd/Al_2O_3 (Scheme 8) [156]. The authors showed that a physical mixture of both catalysts gave low yield of the target compound, while a complex mixture of hydrogenated products and amines was formed. This was overcome by adding the Pd/Al_2O_3 in the reductive amination step, and under optimized reaction conditions, the THF-derived amine (**38**) could be obtained into in a yield of up to 85%. Using similar strategy, the authors also performed the synthesis of furan-derived amines (**39**) [159] but in this case using a Ru/C catalyst instead of Pd/Al_2O_3. Interestingly, in this case the physical mixture of Amberlyst 26 and Ru/C was compatible and could be used from the beginning of the reaction, although better results were achieved when the ammonia and hydrogen were inserted in a second step. Notably, a high yield of the furan-amine derivative **39** was obtained directly from furfural following this two-step process and the catalytic system was also successfully applied to other ketones such as 2-pentanone and 2-heptanone.

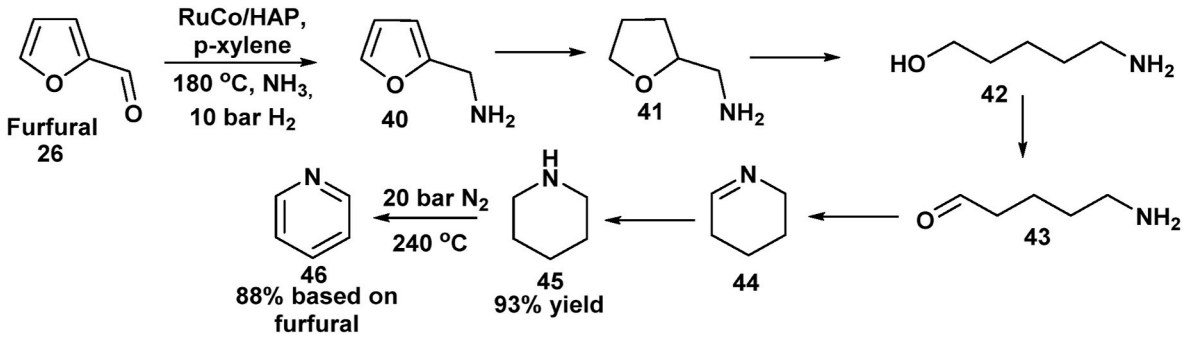
Biobased piperidines have been recently prepared by Beller et al. [160] through a one-pot cascade process starting from furfural, ammonia and H_2 in presence of a bimetallic Ru–Co supported on hydroxyapatite (Ru_1CoNP/HAP) catalyst. The cascade process starts with the reductive amination of furfural into tetrahydrofurfurylamine (**41**) followed by hydrogenative ring cleavage into 5-amino-1-pentanol (**42**) that is quickly converted into piperidine (**45**) through ring closure following alcohol dehydrogenation (**43**), intramolecular reductive amination (**44**), and final hydrogenation sequence (Scheme 9). Optimization of the Co/Ru ratio was key and allowed obtaining 97 % yield of piperidine. Catalyst characterization coupled with theoretical studies showed that the high catalytic activity is due to the formation of atomically dispersed Ru species on the surface of Co nanoparticles, forming a surface single-atom alloy structure, which is only achieved at Co/Ru ≥ 10 on the HAP support. These surface species play a key role in the hydrogenative ring opening of the intermediate tetrahydrofurfurylamine (**41**) into piperidine. The strategy was also extended to the synthesis of 2-substituted piperidines. Interestingly, pyridine (**46**) could be also obtained in excellent yield (88 %) in one pot from the pre-formed piperidine by increasing the temperature at 240 °C and by simply switching the H_2 gas to N_2.

Another recent example involves the transformation of HMF in 3-hydroxymethylcyclopentylamine (**48**) of interests as intermediate in the preparation of several pharmaceuticals [161]. The process is performed in one-pot mode in aqueous phase and using a non-noble metal as catalyst. The strategy involves as the first step the hydrogenative ring rearrangement of HMF in 3-hydroxymethyl cyclopentanone (**31**) (>90% yield) catalyzed by a NiCo catalyst (Ni/Co molar ratio = 1) partially covered with a thin carbon layer, that is subsequently aminated with ammonia in aqueous phase [84]. The high performance of the catalyst was attributed to the formation of NiCo alloy structures as hydrogenating sites, which prevented competitive reactions such as hydrogenation of the furan ring and over-reduction of the formed cyclopentanone, while are highly active in the hydrogenation of the intermediate imine (**47**) (Scheme 10). Thus, the formation of the alloy as well the cover of carbon plays a key role in the catalytic activity, selectivity and stability of the catalyst, being possible their recycling over six consecutive runs without loss of activity and selectivity.

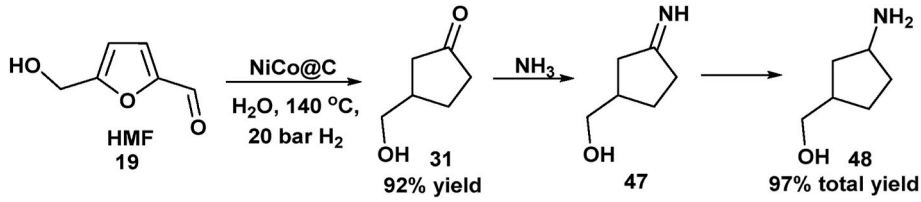
A final example recently reported, involves the synthesis of isoindolinones (**51**) starting from furfural derivatives through an intramolecular cycloaromatization strategy based on the selective formation of exo- Diels Alder adducts followed by aromatization (Scheme 11) [162]. The one-pot tandem intramolecular Diels Alder



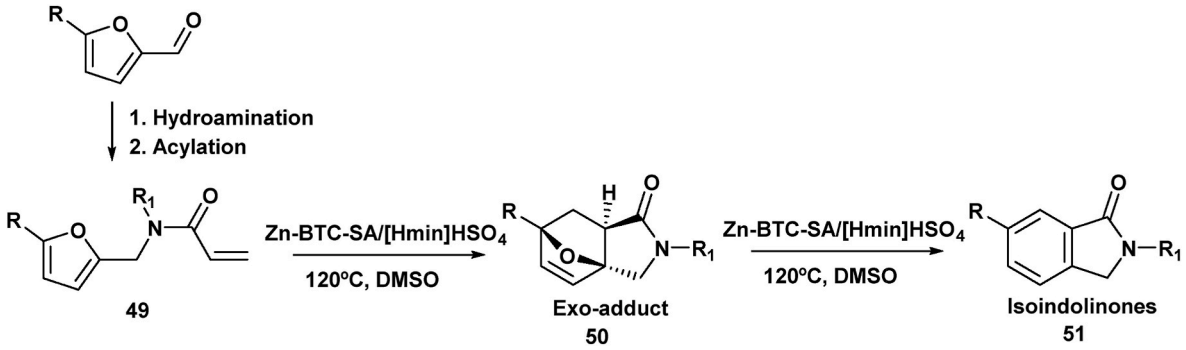
Scheme 8. Synthesis of furan and tetrahydrofuran derived amines from furfural.



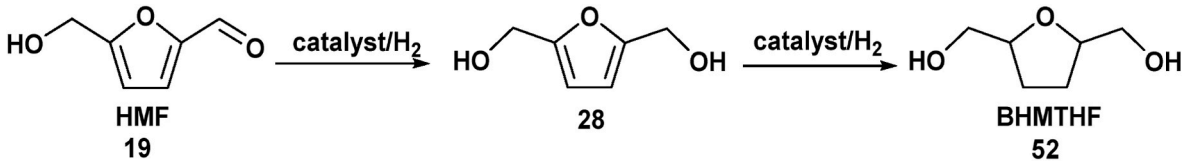
Scheme 9. One-pot synthesis of piperidine and pyridine from furfural.



Scheme 10. Cascade process to produce 3-hydroxymethyl cyclopentylamine from HMF.



Scheme 11. One-pot tandem intramolecular Diels Alder cycloaddition-aromatization for the synthesis of isoindolinones from renewable furfural derivatives. [Hmim]HSO_4: N-methylimidazolium hydrogen sulfate; Zn-BTC-SA: Stearic acid grafted Zn-BTC.



Scheme 12. Total hydrogenation of HMF into BHMTHF.

cycloaddition-aromatization was successfully performed in the presence of heterogeneous bifunctional catalyst prepared by impregnation of Brønsted acidic ionic liquid [Hmim]HSO_4 on Zn-BTC-SA (MOF) (Zn-BTC-SA/[Hmim]HSO_4). Zn-BTC-SA catalyst promoted the targeted regioselective exo-Diels Alder cycloaddition while [Hmim]HSO_4 catalyzed the dehydration-aromatization. Thus, the catalytic system showed a broad substrate scope for producing isoindolinones with excellent yields (89–94%).

4.5. *Synthesis of diols derivatives from HMF*

2,5-bis (hydroxymethyl)tetrahydrofuran (BHMTHF) constitutes a valuable furan diol for the production of biodegradable plastics and fine chemicals [163,164]. BHMTHF (**52**) is produced through the total hydrogenation of furan ring and aldehyde group of HMF(Scheme 12). Extensive efforts have been dedicated to developing diverse metal catalytic systems involving Ni, Co, Ru, Pd, Pt and their composites in conjunction with operating conditions for the selective hydrogenation of HMF to BHMTHF [165–167]. Among the noble metal-based catalysts, Ru catalysts are the most active. For instance, a commercial Ru/C catalyst, exhibits notable efficiency with a 88.6% BHMTHF yield at 50 bar and 100 °C within 4 h [168], however their industrial applicability is limited by high costs and low availability. Among non-noble metal catalysts, Ni-based catalysts usually offer high activity [169–171], although their main drawback is associated to the leaching of Ni species under harsh reaction conditions. In addition, bimetallic catalysts can offer an enhancement in catalytic performance, stability, and product selectivity. For instance, NiPd/SiO2 [172], PdIr/SiO2 [173], RuPd/-graphene oxide [174], NiRe/TiO2 [175] and carbon encapsulated CoNi alloy [176] exhibited very good performances. In Table 4 are summarized some relevant examples of catalytic systems used in the total hydrogenation of HMF. Additionally, although processes in continuous

Table 4
Catalytic systems for the total HMF hydrogenation into BHMTHF.

Entry	Catalyst	Reaction conditions	Residence time (min)	HMF conv. (%)	52 yield (%)	Ref.
1	5 wt% Ru/C	100 °C, 70 bar, 1 h, 2-propanol	Batch	100	88.6	[168]
2	$Ru/MnCo_2O_4$	100 °C, 82 bar, 16 h, MeOH	Batch	98.7	97.3	[166]
3	1 wt% Pd-HAP	40 °C, 10 bar, 3 h, 2-propanol	Batch	100	100	[167]
4	Ni Raney	100 °C, 50 bar, 4 h, MeOH	Batch	100	99	[169]
5	NiAl-450	60 °C, 60 bar, 6 h, dioxane	Batch	100	96.2	[170]
6	Ni1.5Al-LDO-700	140 °C, 30 bar, 1 h, THF	Batch	100	99	[171]
7	Ru–Pd/graphene oxide	RT, 10 bar H_2, 8 h, H_2O	Batch	100	93	[174]
	$NiRe/TiO_2$	90 °C, 50 bar H2, 8 h, water	Batch	100	>75	[175]
8	Raney® Cu-Raney-Ni	0.05 mL min^{-1}, 90 °C, 90 bar H_2, 1.0 wt% HMF in H_2O	FB, 280	–	76.0	[177]
9	5 wt% Ru/C	1 mL min^{-1}, 100 °C, 50 bar H_2, H_2O	FB, 300	100	93.7	[179]
10	5 wt% Pd-5 wt% ReO_x/SiO_2	100 °C, 30 bar H_2, H_2O/THF (2:3, v/v)	FB, 1000	100	72.9	[178]
11	Pd/SiO_2(0.6) + Ir-ReO_x/SiO_2(5-5 wt%)	100 °C, 30 bar H_2, H_2O/THF (2:3, v/v)	FB, 1000	100	73.8	[178]
12	0.6 wt% Pd/SiO_2	100 °C, 30 bar H_2, 1.0 wt% HMF in H_2O	FB, 1000	100	100	[178]
13	Co_1Ni_1@C	0.1 mL min^{-1},160 °C, 20 bar H_2, 1.25 wt% HMF in H_2O	FB, 238	100	91	[176]

HAP: Hydroxyapatite; LDO: layered double oxides; FB: fixed bed.

flow are preferred for industrial applications, up to now there are limited examples of the continuous hydrogenation of HMF into BHMTHF [176–179] in fixed bed reactors.

5. Conclusions and perspectives

In this Mini-review, we have briefly highlighted the utility of one-pot cascade processes for the valorization of various selected biomass derived platform molecules through several representative examples of transformations carried out with mono- and multifunctional solid catalysts that have been recently reported. Thus, one pot cascades on the same active sites such as acidic sites on H-beta zeolites have been showed for instance in the conversion of sorbitol into isosorbide esters and in the synthesis of surfactants by combining HMF, fatty acids and glycerol. Single atom bifunctional metal active sites able to catalyze hydrogenation, dehydrogenation and reductive amination steps have showed remarkable activity, for instance, in the transformation of furfural into piperidine, while cascades processes that requires bifunctional catalysts such as acid-metal active sites have been performed by employing a single bifunctional catalyst, containing both metal and acid sites (case of reductive aminations, HMF conversion into ketones or conversion of glucose into sorbitol) or by combining different catalysts containing acid (or basic) and metal sites, as the case of the synthesis of 5-alkoxymethyl furoates biosurfactants and THF-amines. As showed, some of them occurs in the same vessel and under the same reaction conditions, while in other examples, the one-pot reactions have to be carried out in two or more stages under different optimized reaction conditions. Although the one-pot methodology is highly promising for designing multi-synthetic sequences for valorizing biomass into chemicals, this strategy is still poorly exploited. Future developments for process intensification not only will require a more systematic design and deep understanding of a multifunctional catalyst but also a deep knowledge of the mechanism of the reactions involved. Additionally, the combination of versatile heterogeneous catalysis with the highly selective enzymatic catalysis offers a vast potential for transforming biomass into valuable compounds through one pot chemo-enzymatic processes.

CRediT authorship contribution statement

Karen S. Arias: Writing – original draft, Conceptualization. **Alexandra Velty:** Writing – original draft, Conceptualization. **Maria J. Climent:** Writing – review & editing, Supervision, Conceptualization. **Sara Iborra:** Supervision, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been funded by the Spanish Ministry of Science and Innovation through the “Severo Ochoa Program” (CEX-2021-001230-S) and the PID2021-125897OB-I00 (MCIU/AEI/) 10.13039/501100011033 by “ERDF A way of making Europe project.

References

[1] A.R. Ravishankara, Y. Rudich, J.A. Pyle, Role of chemistry in earth’s climate, Chem. Rev. 115 (2015) 3679–3681.
[2] G.W. Huber, S. Iborra, A. Corma, Synthesis of transportation fuels from biomass: chemistry, catalysts, and engineering, Chem. Rev. 106 (2006) 4044–4098.
[3] A. Corma, S. Iborra, A. Velty, Chemical routes for the transformation of biomass into chemicals, Chem. Rev. 107 (2007) 2411–2502.
[4] M.J. Climent, A. Corma, S. Iborra, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, Green Chem 16 (2014) 516–547.
[5] T. Werpy, G. Petersen, Top Value Added Chemicals from Biomass: Volume I – Results of Screening for Potential Candidates from Sugars and Synthesis Gas, 2004.
[6] J.J. Bozell, G.R. Petersen, Technology development for the production of biobased products from biorefinery carbohydrates—the US Department of Energy’s “Top 10” revisited, Green Chem 12 (2010) 539–554.
[7] G. Fiorentino, M. Ripa, S. Ulgiati, Chemicals from biomass: technological versus environmental feasibility. A review,, Biofuel, Bioprod. Bioref. 11 (2017) 195–214.
[8] X. Ma, W. Zhang, Recent developments in one-pot stepwise synthesis (OPSS) of small molecules, IScience 25 (2022) 105005.
[9] M.J. Climent, A. Corma, S. Iborra, Heterogeneous catalysts for the one-pot synthesis of chemicals and fine chemicals, Chem. Rev. 111 (2011) 1072–1133.
[10] M.J. Climent, A. Corma, S. Iborra, M.J. Sabater, Heterogeneous catalysis for tandem reactions, ACS Catal 4 (2014) 870–891.
[11] S. De, S. Dutta, B. Saha, Critical design of heterogeneous catalysts for biomass valorization: current thrust and emerging prospects, Catal. Sci. Technol. 6 (2016) 7364–7385.
[12] P. Sudarsanam, R. Zhong, S. Van Den Bosch, S.M. Coman, V.I. Parvulescu, B. F. Sels, Functionalised heterogeneous catalysts for sustainable biomass valorisation, Chem Soc Rev 47 (2018) 8349–8402.
[13] J. Moreno, J. Iglesias, J. Blanco, M. Montero, G. Morales, J.A. Melero, Life-cycle sustainability of biomass-derived sorbitol: proposing technological alternatives for improving the environmental profile of a bio-refinery platform molecule, J. Clean Prod. 250 (2020) 119568.
[14] P. Barbaro, F. Liguori, C. Moreno-Marrodan, Selective direct conversion of C5 and C6 sugars to high added-value chemicals by a bifunctional, single catalytic body, Green Chem 18 (2016) 2935–2940.
[15] M. Belluati, S. Tabasso, F. Bucciol, T. Tabanelli, F. Cavani, G. Cravotto, M. Manzoli, Sustainable isosorbide production by a neat one-pot MW-assisted catalytic glucose conversion, Catal Today 418 (2023) 114086.

[16] M. He, J. Guo, X. Wang, Y. Song, S. Liu, H. Wang, C. Li, Direct conversion of cellulose into isosorbide over Ni doped NbOPO4 catalysts in water, New J. Chem. 44 (2020) 10292–10299.

[17] A.B. Moldes, L. Rodríguez-López, M. Rincón-Fontán, A. López-Prieto, X. Vecino, J. M. Cruz, Synthetic and bio-derived surfactants versus microbial biosurfactants in the cosmetic industry: an overview, Int. J. Mol. Sci. 22 (2021) 2371.

[18] S. Dutta, N.S. Bhat, Chemocatalytic value addition of glucose without carbon–carbon bond cleavage/formation reactions: an overview, RSC Adv 12 (2022) 4891–4912.

[19] P. Che, H. Ma, X. Nie, W. Yu, J. Xu, Methyl isobutyl ketone-enabled selective dehydration–esterification of sorbitol to isosorbide esters over the H-beta catalyst, Green Chem 24 (2022) 7545–7555.

[20] A. Corma, S.B.A. Hamid, S. Iborra, A. Velty, Surfactants from biomass: a two-step cascade reaction for the synthesis of sorbitol fatty acid esters using solid acid catalysts, ChemSusChem 1 (2008) 85–90.

[21] J.M. Fraile, C.J. Saavedra, Synthesis of isosorbide esters from sorbitol with heterogeneous catalysts, ChemistrySelect 2 (2017) 1013–1018.

[22] M. Otto Haus, Y. Louven, R. Palkovits, Extending the chemical product tree: a novel value chain for the production of N-vinyl-2-pyrrolidones from biogenic acids Extending the chemical product tree: a novel value chain for the production of N-vinyl-2-pyrrolidones from biogenic acids, Green Chem 21 (2019) 6225–6516.

[23] J. Becker, A. Lange, J. Fabarius, C. Wittmann, Top value platform chemicals: bio-based production of organic acids, Curr. Opin. Biotechnol. 36 (2015) 168–175.

[24] F.M.A. Geilen, B. Engendahl, A. Harwardt, W. Marquardt, J. Klankermayer, W. Leitner, Selective and flexible transformation of biomass-derived platform chemicals by a multifunctional catalytic system, Angew. Chem. Int. Ed. 49 (2010) 5510–5514.

[25] S. Shorvon, Pyrrolidone derivatives, The Lancet 358 (2001) 1885–1892.

[26] Y. Jiang, Z. Li, Y. Li, L. Chen, H. Zhang, H. Li, S. Yang, Recent advances in sustainable catalytic production of 5-methyl-2-pyrrolidones from bio-derived levulinate, Fuel 334 (2023) 126629.

[27] Itaconic Acid Market Size Was USD 97.9 Million in, 2022 n.d.), https://www.cognitivemarketresearch.com/itaconic-acid-market-report?gad_source=5&gclid=EAIaIQobChMIl6in-bDmggMVqwUGAB1o1QdREAAYAiAAEgKDHvD_BwE. (Accessed 28 November 2023).

[28] Y. Louven, K. Schute, R. Palkovits, Ruthenium catalyzed reductive transformation of itaconic acid and ammonia into 3- and 4-Methyl-pyrrolidone, ChemCatChem 11 (2019) 439–442.

[29] Y. Louven, M.O. Haus, M. Konrad, J.P. Hofmann, R. Palkovits, Efficient palladium catalysis for the upgrading of itaconic and levulinic acid to 2-pyrrolidones followed by their vinylation into value-added monomers, Green Chem 22 (2020) 4532–4540.

[30] K. Yan, C. Jarvis, J. Gu, Y. Yan, Production and catalytic transformation of levulinic acid: a platform for speciality chemicals and fuels, Renew. Sust. Energ. Rev. 51 (2015) 986–997.

[31] Global Levulinic Acid Market Size Report, 2022, 2030, (n.d.), https://www.polarismarketresearch.com/industry-analysis/levulinic-acid-market. (Accessed 28 November 2023).

[32] X.L. Du, L. He, S. Zhao, Y.M. Liu, Y. Cao, H.Y. He, K.N. Fan, Hydrogen-independent reductive transformation of carbohydrate biomass into γ-valerolactone and pyrrolidone derivatives with supported gold catalysts, Angew. Chem. Int. Ed. 50 (2011) 7815–7819.

[33] E. Calcio Gaudino, M. Manzoli, M.L. Testa, V. La Parola, G. Grillo, G. Cravotto, E. Acciardo, S. Tabasso, Batch and flow green microwave-assisted catalytic conversion of levulinic acid to pyrrolidones, ChemSusChem (2023) e202301200.

[34] K. Saini, S. Kumar, R. Kaur, S.A. Babu, S. Saravanamurugan, Accelerated H2 activation over Pt/M-ZrO2 for the reductive amination of levulinic acid esters under benign conditions, Catal. Sci. Technol. 13 (2023) 1666–1676.

[35] A.K. Kar, A. Chauhan, R. Srivastava, A CoPd nanoalloy embedded N-doped porous carbon catalyst for the selective reduction and reductive amination of levulinic acid using formic acid in water, Sustain. Energy Fuels 7 (2023) 1855–1869.

[36] C. Chaudhari, M. Shiraishi, Y. Nishida, K. Sato, K. Nagaoka, One-pot synthesis of pyrrolidones from levulinic acid and amines/nitroarenes/nitriles over the Ir-PVP catalyst, Green Chem 22 (2020) 7760–7764.

[37] J. Zhang, B. Xie, L. Wang, X. Yi, C. Wang, G. Wang, Z. Dai, A. Zheng, F.S. Xiao, Zirconium oxide supported palladium nanoparticles as a highly efficient catalyst in the hydrogenation–amination of levulinic acid to pyrrolidones, ChemCatChem 9 (2017) 2661–2667.

[38] M. Muzzio, C. Yu, H. Lin, T. Yom, D.A. Boga, Z. Xi, N. Li, Z. Yin, J. Li, J.A. Dunn, S. Sun, Reductive amination of ethyl levulinate to pyrrolidones over AuPd nanoparticles at ambient hydrogen pressure, Green Chem 21 (2019) 1895–1899.

[39] A.B. Raut, V.S. Shende, T. Sasaki, B.M. Bhanage, Reductive amination of levulinic acid to N-substituted pyrrolidones over RuCl3 metal ion anchored in ionic liquid immobilized on graphene oxide, J. Catal. 383 (2020) 206–214.

[40] V. Boosa, S. Varimalla, M. Dumpalapally, N. Gutta, V.K. Velisoju, N. Nama, V. Akula, Influence of Brønsted acid sites on chemoselective synthesis of pyrrolidones over H-ZSM-5 supported copper catalyst, Appl. Catal. B 292 (2021) 120177.

[41] L.E. Manzer, Process for Converting α-angelica Lactone to 5-Methyl-N-Alkyl-2-Pyrrolidone Using Alkyl Amines, US6743819B1, 2004.

[42] M.V. Bukhtiyarova, G.A. Bukhtiyarova, Reductive amination of levulinic acid or its derivatives to pyrrolidones over heterogeneous catalysts in the batch and continuous flow reactors: a review, Renew. Sust. Energ. Rev. 143 (2021) 110876.

[43] Z. Xue, D. Yu, X. Zhao, T. Mu, Upgrading of levulinic acid into diverse N-containing functional chemicals, Green Chem 21 (2019) 5449–5468.

[44] J. Wang, X. Lu, M. Guo, R. Zhang, J. Xiong, Y. Qiao, Z. Yu, Reductive amination of levulinic acid to pyrrolidones: key step in biomass valorization towards nitrogen-containing chemicals, ChemSusChem 16 (2023) e202301091.

[45] J.D. Vidal, M.J. Climent, A. Corma, D.P. Concepcion, S. Iborra, One-pot selective catalytic synthesis of pyrrolidone derivatives from ethyl levulinate and nitro compounds, ChemSusChem 10 (2017) 119–128.

[46] S. Li, X. Liu, Y. Guo, Y. Wang, Room temperature synthesis of N-substituted pyrrolidone from levulinic acid and nitrobenzene via a tandem hydrogenation and reductive amination process, J. Catal. 429 (2024) 115191.

[47] A.S. Touchy, S.M.A. Hakim Siddiki, K. Kon, K. Shimizu, Heterogeneous Pt catalysts for reductive amination of levulinic acid to pyrrolidones, ACS Catal 4 (2014) 3045–3050.

[48] J.D. Vidal, M.J. Climent, P. Concepcion, A. Corma, S. Iborra, M.J. Sabater, Chemicals from biomass: chemoselective reductive amination of ethyl levulinate with amines, ACS Catal 5 (2015) 5812–5821.

[49] C. Xie, J. Song, H. Wu, Y. Hu, H. Liu, Z. Zhang, P. Zhang, B. Chen, B. Han, Ambient reductive amination of levulinic acid to pyrrolidones over Pt nanocatalysts on porous TiO2 nanosheets, J. Am. Chem. Soc. 141 (2019) 4002–4009.

[50] T. Zhang, Y. Ge, X. Wang, J. Chen, X. Huang, Y. Liao, Polymeric ruthenium porphyrin-functionalized carbon nanotubes and graphene for levulinic ester transformations into γ-valerolactone and pyrrolidone derivatives, ACS Omega 2 (2017) 3228–3240.

[51] J. Guo, F. Li, Y. Chu, P. Zou, C. Li, Conversion of levulinic acid and its esters to 1,5-dimethyl-2-Pyrrolidone over a nonnoble metallic Ni@CeOx catalyst, ChemSusChem 16 (2023) e202300754.

[52] P. Cao, T. Ma, H.-Y. Zhang, G. Yin, J. Zhao, Y. Zhang, Conversion of levulinic acid to N-substituted pyrrolidinones over a nonnoble bimetallic catalyst Cu15Pr3/Al2O3, Catal. Commun. 116 (2018) 85–90.

[53] G. Gao, P. Sun, Y. Li, F. Wang, Z. Zhao, Y. Qin, F. Li, Highly stable porous-carbon-coated Ni catalysts for the reductive amination of levulinic acid via an unconventional pathway, ACS Catal 7 (2017) 4927–4935.

[54] Y. Wang, M. Chen, K. Zhang, H. Wu, J. Wang, Y. Cheng, Y. Liu, Z. Wei, CoNi alloy nanoparticles confined in N-doped porous carbon as an efficient and versatile catalyst for reductive amination of levulinic acid/esters to N-substituted pyrrolidones, ACS Catal 13 (2023) 12601–12616.

[55] P.-D. Wu, H. Li, Z. Fang, P.-D. Wu, H. Li, Z. Fang, Synergistic catalysis of Co-Zr/CNx bimetallic nanoparticles enables reductive amination of biobased levulinic acid, Adv. Sustain. Syst. 6 (2022) 2100321.

[56] J. Gao, L. Feng, R. Ma, B.J. Su, A.M. Alenad, Y. Liu, M. Beller, R.V. Jagadeesh, Cobalt single-atom catalysts for domino reductive amination and amidation of levulinic acid and related molecules to N-heterocycles, Chem. Catalysis 2 (2022) 178–194.

[57] A.S. Amarasekara, Y.M. Lawrence, Raney-Ni catalyzed conversion of levulinic acid to 5-methyl-2-pyrrolidone using ammonium formate as the H and N source, Tetrahedron Lett 59 (2018) 1832–1835.

[58] G. Metzker, R.M.P. Dias, A.C.B. Burtoloso, Iron-catalyzed reductive amination from levulinic and formic acid aqueous solutions: an approach for the selective production of pyrrolidones in biorefinery facilities, ChemistrySelect 3 (2018) 368–372.

[59] G. Chieffi, M. Braun, D. Esposito, Continuous reductive amination of biomass-derived molecules over carbonized filter paper-supported FeNi alloy, ChemSusChem 8 (2015) 3590–3594.

[60] J.C. Serrano-Ruiz, R. Luque, A. Sepúlveda-Escribano, Transformations of biomass-derived platform molecules: from high added-value chemicals to fuels via aqueous-phase processing, Chem. Soc. Rev. 40 (2011) 5266–5281.

[61] R. Gérardy, D.P. Debecker, J. Estager, P. Luis, J.C.M. Monbaliu, Continuous flow upgrading of selected C2-C6 platform chemicals derived from biomass, Chem. Rev. 120 (2020) 7219–7347.

[62] R.J. Van Putten, J.C. Van Der Waal, E. De Jong, C.B. Rasrendra, H.J. Heeres, J. G. De Vries, Hydroxymethylfurfural, a versatile platform chemical made from renewable resources, Chem. Rev. 113 (2013) 1499–1597.

[63] C. Xu, E. Paone, D. Rodríguez-Padrón, R. Luque, F. Mauriello, Recent catalytic routes for the preparation and the upgrading of biomass derived furfural and 5-hydroxymethylfurfural, Chem. Soc. Rev. 49 (2020) 4273–4306.

[64] M. Crnomarković, Y. Panchaksharam, J. Spekreijse, C. Vom Berg, Á. Puente, R. Chinthapalli, Business Cases Case Studies on Potentially Attractive Opportunities for Bio-Based Chemicals in Europe Consortium, 2020.

[65] https://www.grandviewresearch.com/press-release/global-furfural-market,n.d.. https://www.grandviewresearch.com/press-release/global-furfural-market (accessed December 12, 2023).

[66] https://www.imarcgroup.com/5-hydroxymethylfurfural-market,n.d.. https://www.imarcgroup.com/5-hydroxymethylfurfural-market (accessed December 12, 2023).

[67] X. Yue, Y. Queneau, 5-Hydroxymethylfurfural and furfural chemistry toward biobased surfactants, ChemSusChem 15 (2022) e202102660.

[68] A. Velty, S. Iborra, A. Corma, Synthetic routes for designing furanic and non furanic biobased surfactants from 5-hydroxymethylfurfural, ChemSusChem 15 (2022) e202200181.

[69] K.S. Arias, S.I. Al-Resayes, M.J. Climent, A. Corma, S. Iborra, From biomass to chemicals: synthesis of precursors of biodegradable surfactants from 5-hydroxymethylfurfural, ChemSusChem 6 (2013) 123–131.

[70] A. Garcia-Ortiz, K.S. Arias, M.J. Climent, A. Corma, S. Iborra, One-pot synthesis of biomass-derived surfactants by reacting hydroxymethylfurfural, glycerol, and fatty alcohols on solid acid catalysts, ChemSusChem 11 (2018) 2870–2880.

[71] K.S. Arias, M.J. Climent, A. Corma, S. Iborra, Biomass-derived chemicals: synthesis of biodegradable surfactant ether molecules from hydroxymethylfurfural, ChemSusChem 7 (2014) 210–220.

[72] P. Marcé, Y. Díaz, M.I. Matheu, S. Castillón, Synthesis of D- and L-carbocyclic nucleosides via rhodium-catalyzed asymmetric hydroacylation as the key step, Org Lett 10 (2008) 4735–4738.

[73] J. Scognamiglio, L. Jones, C.S. Letizia, A.M. Api, Fragrance material review on cyclopentanone, Food Chem. Toxicol. 50 (2012) S608–S612.

[74] Y. Duan, Y. Cheng, Z. Hu, C. Wang, D. Sui, Y. Yang, T. Lu, A comprehensive review on metal catalysts for the production of cyclopentanone derivatives from furfural and HMF, Molecules 28 (2023) 5397.

[75] R. Weng, X. Lu, N. Ji, A. Fukuoka, A. Shrotri, X. Li, R. Zhang, M. Zhang, J. Xiong, Z. Yu, Taming the butterfly effect: modulating catalyst nanostructures for better selectivity control of the catalytic hydrogenation of biomass-derived furan platform chemicals, Catal. Sci. Technol. 11 (2021) 7785–7806.

[76] A. Piancatelli, G. Scettri, A simple conversion of 4-substituted 5-Hydroxy-3-oxocyclopentenes into the 2-substituted analogs, Synthesis 1977 (1977) 116–117.

[77] C. Piutti, F. Quartieri, The Piancatelli rearrangement: new applications for an intriguing reaction, Molecules 18 (2013) 12290–12312.

[78] C. Verrier, S. Moebs-Sanchez, Y. Queneau, F. Popowycz, The Piancatelli reaction and its variants: recent applications to high added-value chemicals and biomass valorization, Org. Biomol. Chem. 16 (2018) 676–687.

[79] S. Zhong, S. Zhong Lei Xu, C. Author Yunfei Cai, Recent advances on Piancatelli reactions and related cascade processes, Synthesis 54 (2022) 589–599.

[80] J. Ohyama, R. Kanao, Y. Ohira, A. Satsuma, The effect of heterogeneous acid–base catalysis on conversion of 5-hydroxymethylfurfural into a cyclopentanone derivative, Green Chem 18 (2016) 676–680.

[81] J. Ohyama, Y. Ohira, A. Satsuma, Hydrogenative ring-rearrangement of biomass derived 5-(hydroxymethyl)furfural to 3-(hydroxymethyl)cyclopentanol using combination catalyst systems of Pt/SiO2 and lanthanoid oxides, Catal. Sci. Technol. 7 (2017) 2947–2953.

[82] Q. Deng, R. Gao, X. Li, J. Wang, Z. Zeng, J.J. Zou, S. Deng, Hydrogenative ring-rearrangement of biobased furanic aldehydes to cyclopentanone compounds over Pd/pyrochlore by introducing oxygen vacancies, ACS Catal 10 (2020) 7355–7366.

[83] M.V. Morales, J.M. Conesa, A. Guerrero-Ruiz, I. Rodríguez-Ramos, Tunable selectivity of Ni catalysts in the hydrogenation reaction of 5-hydroxymethylfurfural in aqueous media: role of the carbon supports, Carbon 182 (2021) 265–275.

[84] B. Hurtado, K.S. Arias, M.J. Climent, P. Concepción, A. Corma, S. Iborra, Selective conversion of HMF into 3-hydroxymethylcyclopentylamine through a one-pot cascade process in aqueous phase over bimetallic NiCo nanoparticles as catalyst, ChemSusChem 15 (2022) e202200194.

[85] S. Zhang, H. Ma, Y. Sun, Y. Luo, X. Liu, M. Zhang, J. Gao, J. Xu, Catalytic selective hydrogenation and rearrangement of 5-hydroxymethylfurfural to 3-hydroxy-methyl-cyclopentone over a bimetallic nickel–copper catalyst in water, Green Chem 21 (2019) 1702–1709.

[86] M. Hronec, K. Fulajtarová, Selective transformation of furfural to cyclopentanone, Catal. Commun. 24 (2012) 100–104.

[87] J. Lee, J. Woo, C. Nguyen-Huy, M.S. Lee, S.H. Joo, K. An, Highly dispersed Pd catalysts supported on various carbons for furfural hydrogenation, Catal Today 350 (2020) 71–79.

[88] R. Fang, H. Liu, R. Luque, Y. Li, Efficient and selective hydrogenation of biomass-derived furfural to cyclopentanone using Ru catalysts, Green Chem 17 (2015) 4183–4188.

[89] G.S. Zhang, M.M. Zhu, Q. Zhang, Y.M. Liu, H.Y. He, Y. Cao, Towards quantitative and scalable transformation of furfural to cyclopentanone with supported gold catalysts, Green Chem 18 (2016) 2155–2164.

[90] X. Li, Q. Deng, L. Zhang, J. Wang, R. Wang, Z. Zeng, S. Deng, Highly efficient hydrogenative ring-rearrangement of furanic aldehydes to cyclopentanone compounds catalyzed by noble metals/MIL-MOFs, Appl. Catal. A: Gen. 575 (2019) 152–158.

[91] X. Li, Q. Deng, S. Zhou, J. Zou, J. Wang, R. Wang, Z. Zeng, S. Deng, Double-metal cyanide-supported Pd catalysts for highly efficient hydrogenative ring-rearrangement of biomass-derived furanic aldehydes to cyclopentanone compounds, J. Catal. 378 (2019) 201–208.

[92] S. Chen, T.T. Qian, L.L. Ling, W. Zhang, B.B. Gong, H. Jiang, Hydrogenation of furfural to cyclopentanone under mild conditions by a structure-optimized Ni-NiO/TiO2 heterojunction catalyst, ChemSusChem 13 (2020) 5507–5515.

[93] Z. Yu, H. Tian, K. Sun, Y. Shao, L. Zhang, S. Zhang, P. Duan, Q. Liu, S. Niu, D. Dong, X. Hu, Impacts of externally added Brønsted and Lewis acid on conversion of furfural to cyclopentanone over Ni/SiC catalyst, Mol. Catal 496 (2020) 111187.

[94] X. Zhou, Z. Feng, W. Guo, J. Liu, R. Li, R. Chen, J. Huang, Hydrogenation and hydrolysis of furfural to furfuryl alcohol, cyclopentanone, and cyclopentanol with a heterogeneous copper catalyst in water, Ind. Eng. Chem. Res. 58 (2019) 3988–3993.

[95] P. Pan, W.Y. Xu, T.J. Pu, X. Wang, X.J. Pei, F. Tang, Y. Feng, Selective conversion of furfural to cyclopentanone and cyclopentanol by magnetic Cu-Fe3O4 NPs catalyst, ChemistrySelect 4 (2019) 5845–5852.

[96] V. Ranaware, R.G. Kurniawan, D. Verma, S.K. Kwak, B.C. Ryu, J.W. Kang, J. Kim, Solvent-mediated selectivity control of furfural hydrogenation over a N-doped carbon-nanotube-supported Co/CoOx catalyst, Appl. Catal. B 318 (2022) 121838.

[97] Y. Shao, K. Sun, M. Fan, G. Gao, J. Wang, L. Zhang, S. Zhang, X. Hu, Synthesis of a thermally and hydrothermally stable copper-based catalyst via alloying of Cu with Ni and Zn for catalyzing conversion of furfural into cyclopentanone, ACS Sustain. Chem. Eng. 10 (2022) 8763–8777.

[98] H. Li, J. Liu, C. Cai, H. Wang, Y. Huang, C. Wang, L. Ma, Selectivity catalytic transfer hydrogenation of biomass-based furfural to cyclopentanone, Fuel 332 (2023) 126057.

[99] Y. Su, C. Chen, X. Zhu, Y. Zhang, W. Gong, H. Zhang, H. Zhao, G. Wang, Carbon-embedded Ni nanocatalysts derived from MOFs by a sacrificial template method for efficient hydrogenation of furfural to tetrahydrofurfuryl alcohol, Dalton Trans 46 (2017) 6358–6365.

[100] M. Zhou, H. Zhu, L. Niu, G. Xiao, R. Xiao, Catalytic hydroprocessing of furfural to cyclopentanol over Ni/CNTs catalysts: model reaction for upgrading of bio-oil, Catal. Letters 144 (2014) 235–241.

[101] Y. Wang, M. Zhou, T. Wang, G. Xiao, Conversion of furfural to cyclopentanol on Cu/Zn/Al catalysts derived from hydrotalcite-like materials, Catal Letters 145 (2015) 1557–1565.

[102] M.V. Twigg, M.S. Spencer, Deactivation of supported copper metal catalysts for hydrogenation reactions, Appl. Catal. A: Gen. 212 (2001) 161–174.

[103] M. Hronec, K. Fulajtárová, I. Vávra, T. Soták, E. Dobročka, M. Mičušík, Carbon supported Pd-Cu catalysts for highly selective rearrangement of furfural to cyclopentanone, Appl. Catal. B 181 (2016) 210–219.

[104] Y. Wang, C. Liu, X. Zhang, One-step encapsulation of bimetallic Pd–Co nanoparticles within UiO-66 for selective conversion of furfural to cyclopentanone, Catal. Letters 150 (2020) 2158–2166.

[105] X.L. Li, J. Deng, J. Shi, T. Pan, C.G. Yu, H.J. Xu, Y. Fu, Selective conversion of furfural to cyclopentanone or cyclopentanol using different preparation methods of Cu-Co catalysts, Chin. Chem. Lett. 17 (2015) 1038–1046.

[106] Y. Yang, Z. Du, Y. Huang, F. Lu, F. Wang, J. Gao, J. Xu, Conversion of furfural into cyclopentanone over Ni-Cu bimetallic catalysts, Green Chem 15 (2013) 1932–1940.

[107] S. Zhang, H. Ma, Y. Sun, X. Liu, M. Zhang, Y. Luo, J. Gao, J. Xu, Selective tandem hydrogenation and rearrangement of furfural to cyclopentanone over CuNi bimetallic catalyst in water, Chinese J. Catal. 42 (2021) 2216–2224.

[108] V.M. Kadam, G.D. Yadav, Development of a green process for the synthesis of cyclopentanone using selective aqueous phase hydrogenation of furfural over Ni–Cu@MOF-5 catalyst, Ind. Eng. Chem. Res. 62 (2023) 17408–17427.

[109] M. Zhou, J. Li, K. Wang, H. Xia, J. Xu, J. Jiang, Selective conversion of furfural to cyclopentanone over CNT-supported Cu based catalysts: model reaction for upgrading of bio-oil, Fuel 202 (2017) 1–11.

[110] C. Chen, M. Zhou, J. Jiang, Selective aqueous-phase hydrogenation of furfural to cyclopentanol over Ni-based catalyst under mild conditions, J. Chin. Chem. Soc. 68 (2021) 1177–1180.

[111] Y. Duan, Y. Cheng, Z. Hu, C. Wang, D. Sui, Y. Yang, T. Lu, A comprehensive review on metal catalysts for the production of cyclopentanone derivatives from furfural and HMF, Molecules 28 (2023) 5397.

[112] X. Li, Q. Deng, Review on metal–acid tandem catalysis for hydrogenative rearrangement of furfurals to C5 cyclic compounds, Trans. Tianjin Univ. 29 (2023) 347–359.

[113] S. Dutta, N.S. Bhat, Catalytic transformation of biomass-derived furfurals to cyclopentanones and their derivatives: a review, ACS Omega 6 (2021) 35145–35172.

[114] C. Cheng, C. shan Zhao, D. Zhao, S. min Ding, C. Chen, The importance of constructing Triple-functional Sr2P2O7/Ni2P catalysts for smoothing hydrogenation Ring-rearrangement of Biomass-derived Furfural compounds in water, J. Catal. 421 (2023) 117–133.

[115] L. Zhang, Y. Zhong, J. Wang, Z. Zeng, S. Deng, J.J. Zou, Q. Deng, Intermetallic palladium-zinc nanoparticles for the ultraselective hydrogenative rearrangement of furan compounds, ACS Catal 13 (2023) 13205–13214.

[116] X. Li, Z. Tong, S. Zhu, Q. Deng, S. Chen, J. Wang, Z. Zeng, Y. Zhang, J.J. Zou, S. Deng, Water-mediated hydrogen spillover accelerates hydrogenative ring-rearrangement of furfurals to cyclic compounds, J. Catal. 405 (2022) 363–372.

[117] W. Cai, Y. Li, Q. Zheng, M. Song, P. Ma, W. Fang, W. Song, W. Lai, Hydrogenative rearrangement of bioderived furfurals to cyclopentanones over Ni/Nb2O5 catalysts: promotion effect of reducible NbOx and water, Fuel 338 (2023) 127345.

[118] W. Lin, Y. Zhang, Z. Ma, Z. Sun, X. Liu, C.C. Xu, R. Nie, Synergy between Ni3Sn2 alloy and Lewis acidic ReOx enables selectivity control of furfural hydrogenation to cyclopentanone, Appl. Catal. B 340 (2024).

[119] Z. Hu, A. Xie, C. Chen, Z. Zou, Y. Shen, Z. Fu, Y. Zhang, H. Zhang, H. Zhao, G. Wang, Facile synthesis of N, P co-doped carbon encapsulated Ni catalyst for green production of cyclopentanone from biomass derivative furfural, Fuel 319 (2022).

[120] E. Yuan, C. Wang, C. Wu, G. Shi, P. Jian, X. Hou, Constructing hierarchical structures of Pd catalysts to realize reaction pathway regulation of furfural hydroconversion, J. Catal. 421 (2023) 30–44.

[121] Z. Hu, M. Han, C. Chen, Z. Zou, Y. Shen, Z. Fu, X. Zhu, Y. Zhang, H. Zhang, H. Zhao, G. Wang, Hollow carbon sphere encapsulated nickel nanoreactor for aqueous-phase hydrogenation-rearrangement tandem reaction with enhanced catalytic performance, Appl. Catal. B 306 (2022) 121140.

[122] R. Balaga, P. Balla, X. Zhang, K. Ramineni, H. Du, S. Lingalwar, V. Perupogu, Z. C. Zhang, Enhanced cyclopentanone yield from furfural hydrogenation: promotional effect of surface silanols on Ni-Cu/m-Silica catalyst, Catalysts 13 (2023) 580.

[123] Z. Fan, J. Zhang, D. Wu, Highly efficient NiCu/SiO2 catalyst induced by Ni(Cu)-Silica interaction for aqueous-phase furfural hydrogenation, Catal. Letters 153 (2023) 1543–1555.
[124] X. Li, L. Zhang, R. Zhou, S. Chen, J. Wang, Z. Zeng, J.J. Zou, S. Deng, Q. Deng, Bifunctional role of hydrogen in aqueous hydrogenative ring rearrangement of furfurals over Co@Co-nc, ACS Sustain. Chem. Eng. 10 (2022) 7321–7329.
[125] B. Wozniak, S. Tin, J.G. De Vries, Bio-based building blocks from 5-hydroxymethylfurfural via 1-hydroxyhexane-2,5-dione as intermediate, Chem. Sci. 10 (2019) 6024–6034.
[126] D. Ren, Z. Song, L. Li, Y. Liu, F. Jin, Z. Huo, Production of 2,5-hexanedione and 3-methyl-2-cyclopenten-1-one from 5-hydroxymethylfurfural, Green Chem 18 (2016) 3075–3081.
[127] Z. Tong, X. Li, J. Zhu, S. Chen, G. Dai, Q. Deng, J. Wang, W. Yang, Z. Zeng, J. J. Zou, Iodine-modified Pd catalysts promote the bifunctional catalytic synthesis of 2,5-hexanedione from C6 furan aldehydes, ChemSusChem 15 (2022) e202102444.
[128] R. Ramos, A. Grigoropoulos, B.L. Griffiths, A.P. Katsoulidis, M. Zanella, T. D. Manning, F. Blanc, J.B. Claridge, M.J. Rosseinsky, Selective conversion of 5-hydroxymethylfurfural to diketone derivatives over Beta zeolite-supported Pd catalysts in water, J. Catal. 375 (2019) 224–233.
[129] Q. Deng, R. Zhou, Y.C. Zhang, X. Li, J. Li, S. Tu, G. Sheng, J. Wang, Z. Zeng, T. Yoskamtorn, S.C. Edman Tsang, H+−H− pairs in partially oxidized MAX phases for bifunctional catalytic conversion of furfurals into linear ketones, Angew. Chem. Int. Ed. 62 (2023) e202211461.
[130] K. Gupta, D. Tyagi, A.D. Dwivedi, S.M. Mobin, S.K. Singh, Catalytic transformation of bio-derived furans to valuable ketoacids and diketones by water-soluble ruthenium catalysts, Green Chem 17 (2015) 4618–4627.
[131] A.D. Dwivedi, K. Gupta, D. Tyagi, R.K. Rai, S.M. Mobin, S.K. Singh, Ruthenium and formic acid based tandem catalytic transformation of bioderived furans to levulinic acid and diketones in water, ChemCatChem 7 (2015) 4050–4058.
[132] S. Panigrahy, R. Mishra, P. Panda, M. Kempasiddaiah, S. Barman, Carbon-supported Ag nanoparticle aerogel for electrocatalytic hydrogenation of 5-(hydroxymethyl)furfural to 2,5-hexanedione under acidic conditions, ACS Appl. Nano Mater. 5 (2022) 8314–8323.
[133] Y. Duan, M. Zheng, D. Li, D. Deng, L.F. Ma, Y. Yang, Conversion of HMF to methyl cyclopentenolone using Pd/Nb2O5 and Ca–Al catalysts via a two-step procedure, Green Chem 19 (2017) 5103–5113.
[134] Y. Duan, R. Wang, Q. Liu, X. Qin, Z. Li, Tungsten promoted Ni/Al2O3 as a noble-metal-free catalyst for the conversion of 5-hydroxymethylfurfural to 1-hydroxy-2,5-hexanedione, Front. Chem. 10 (2022) 857199.
[135] M. Hua, J. Song, X. Huang, M. Hou, H. Fan, Z. Zhang, T. Wu, B. Han, Support effect of Ru catalysts for efficient conversion of biomass-derived 2,5-hexanedione to different products, ACS Catal 11 (2021) 7685–7693.
[136] J.D. Woodroffe, B.G. Harvey, Synthesis of bio-based methylcyclopentadiene from 2,5-hexanedione: a sustainable route to high energy density jet fuels, ChemSusChem 14 (2021) 339–343.
[137] T. Buntara, S. Noel, P.H. Phua, I. Melián-Cabrera, J.G. De Vries, H.J. Heeres, Caprolactam from renewable resources: catalytic conversion of 5-hydroxymethylfurfural into caprolactone, Angew. Chem. Int. Ed. 50 (2011) 7083–7087.
[138] F. Liu, M. Audemar, K. De Oliveira Vigier, J.M. Clacens, F. De Campo, F. Jérôme, Combination of Pd/C and Amberlyst-15 in a single reactor for the acid/hydrogenating catalytic conversion of carbohydrates to 5-hydroxy-2,5-hexanedione, Green Chem 16 (2014) 4110–4114.
[139] F. Liu, M. Audemar, K. De Oliveira Vigier, J.M. Clacens, F. De Campo, F. Jérôme, Palladium/carbon dioxide cooperative catalysis for the production of diketone derivatives from carbohydrates, ChemSusChem 7 (2014) 2089–2093.
[140] Y. Liu, G. Li, Y. Cong, N. Li, T. Zhang, Integrated conversion of cellulose to high-density aviation fuel, Joule 3 (2019) 1028–1036.
[141] Y. Yang, D. Yang, C. Zhang, M. Zheng, Y. Duan, Preparation of 1-Hydroxy-2,5-hexanedione from HMF by the combination of commercial Pd/C and acetic acid, Molecules 25 (2020) 2475.
[142] L. Longo, S. Taghavi, E. Ghedini, F. Menegazzo, A. Di Michele, G. Cruciani, M. Signoretto, Selective hydrogenation of 5-hydroxymethylfurfural to 1-Hydroxy-2,5-hexanedione by biochar-supported Ru catalysts, ChemSusChem 15 (2022) e202200437.
[143] M.M. Zhu, X.L. Du, Y. Zhao, B.B. Mei, Q. Zhang, F.F. Sun, Z. Jiang, Y.M. Liu, H. Y. He, Y. Cao, Ring-opening transformation of 5-hydroxymethylfurfural using a golden single-atomic-site palladium catalyst, ACS Catal 9 (2019) 6212–6222.
[144] Y. Yang, Y. Xie, D. Deng, D. Li, M. Zheng, Y. Duan, Highly selective conversion of HMF to 1-hydroxy- 2,5-hexanedione on Pd/MIL-101(Cr), ChemistrySelect 4 (2019) 11165–11171.
[145] G. Nie, C. Shi, Y. Dai, Y. Liu, Y. Liu, C. Ma, Q. Liu, L. Pan, X. Zhang, J.J. Zou, Producing methylcyclopentadiene dimer and trimer based high-performance jet fuels using 5-methyl furfural, Green Chem 22 (2020) 7765–7768.
[146] X. Chen, Y. Liu, J. Wang, Lignocellulosic biomass upgrading into valuable nitrogen-containing compounds by heterogeneous catalysts, Ind. Eng. Chem. Res. 59 (2020) 17008–17025.
[147] R.V. Jagadeesh, K. Murugesan, A.S. Alshammari, H. Neumann, M.M. Pohl, J. Radnik, M. Beller, MOF-derived cobalt nanoparticles catalyze a general synthesis of amines, Science 358 (2017) 326–332, 1979.
[148] V.G. Chandrashekhar, W. Baumann, M. Beller, R.V. Jagadeesh, Nickel-catalyzed hydrogenative coupling of nitriles and amines for general amine synthesis, Science 376 (2022) 1433–1441, 1979.
[149] Le Gou, L. Xie, Y. Wang, L. Dai, Efficient conversion of furfural to furfural amine over 4Ru1Co/AC catalyst, Appl. Catal. A: Gen. 647 (2022) 118902.
[150] X. Zhang, S. Xu, Q. Li, G. Zhou, H. Xia, Recent advances in the conversion of furfural into bio-chemicals through chemo- and bio-catalysis, RSC Adv 11 (2021) 27042–27058.
[151] J.A.T. Caetano, A.C. Fernandes, One-pot synthesis of amines from biomass resources catalyzed by HReO4, Green Chem 20 (2018) 2494–2498.
[152] J. Zhang, J. Yang, X. Li, H. Liu, A. Wang, C. Xia, J. Chen, Z. Huang, Efficient synthesis of pharmaceutical intermediates from biomass-derived aldehydes and ketones over robust NixAl nanocatalysts, ACS Sustain. Chem. Eng. 10 (2022) 5526–5537.
[153] C.C. Truong, D.K. Mishra, Y.W. Suh, Recent catalytic advances on the sustainable production of primary furanic amines from the one-pot reductive amination of 5-hydroxymethylfurfural, ChemSusChem 16 (2023) e202201846.
[154] J. He, L. Chen, S. Liu, K. Song, S. Yang, A. Riisager, Sustainable access to renewable N-containing chemicals from reductive amination of biomass-derived platform compounds, Green Chem 22 (2020) 6714–6747.
[155] M.K. Saini, S. Kumar, H. Li, S.A. Babu, S. Saravanamurugan, Advances in the catalytic reductive amination of furfural to furfural amine: the momentous role of active metal sites, ChemSusChem 15 (2022) e202200107.
[156] S. Jiang, C. Ma, E. Muller, M. Pera-Titus, F. Jérôme, K. De Oliveira Vigier, Selective synthesis of THF-derived amines from biomass-derived carbonyl compounds, ACS Catal 9 (2019) 8893–8902.
[157] X. He, A.H. Conner, J.A. Koutsky, Evaluation of furfurylamines as curing agents for epoxy resins, J. Polym. Sci., Part A: Polym. Chem. 30 (1992) 533–542.
[158] Y. Liu, K. Zhou, H. Shu, H. Liu, J. Lou, D. Guo, Z. Wei, X. Li, Switchable synthesis of furfurylamine and tetrahydrofurfurylamine from furfuryl alcohol over RANEY® nickel, Catal. Sci. Technol. 7 (2017) 4129–4135.
[159] S. Jiang, W. Ramdani, E. Muller, C. Ma, M. Pera-Titus, F. Jerôme, K. De Oliveira Vigiera, Direct catalytic conversion of furfural to furan-derived amines in the presence of Ru-based catalyst, ChemSusChem 13 (2020) 1699–1704.
[160] H. Qi, Y. Li, Z. Zhou, Y. Cao, F. Liu, W. Guan, L. Zhang, X. Liu, L. Li, Y. Su, K. Junge, X. Duan, M. Beller, A. Wang, T. Zhang, Synthesis of piperidines and pyridine from furfural over a surface single-atom alloy Ru1CoNP catalyst, Nat. Commun. 14 (2023) 1–10.
[161] H. Rapoport, Y. Chen, R.M. Mohareb, J.H. Ahn, T.B. Sim, J.Z. Ho, An efficient procedure for the preparation of (1S,3R)- and (1S,3S)-1-Amino-3-(hydroxymethyl)cyclopentanes, Chem. Pharm. Bull. 51 (2003) 1153–1156.
[162] F. Xu, Z. Li, L.L. Zhang, S. Liu, H. Li, Y. Liao, S. Yang, Synthesis of renewable isoindolines from bio-based furfurals, Green Chem 25 (2023) 3297–3305.
[163] Q. Wang, J. Feng, L. Zheng, B. Wang, R. Bi, Y. He, H. Liu, D. Li, Interfacial structure-determined reaction pathway and selectivity for 5-(hydroxymethyl) furfural hydrogenation over Cu-based catalysts, ACS Catal 10 (2020) 1353–1365.
[164] M. Chatterjee, T. Ishizaka, H. Kawanami, Selective hydrogenation of 5-hydroxymethylfurfural to 2,5-bis-(hydroxymethyl)furan using Pt/MCM-41 in an aqueous medium: a simple approach, Green Chem 16 (2014) 4734–4739.
[165] C. Chien Truong, D. Kumar Mishra, S. Hyeok Ko, Y. Jin Kim, Y.W. Suh, Sustainable catalytic transformation of biomass-derived 5-hydroxymethylfurfural to 2,5-Bis(hydroxymethyl)tetrahydrofuran, ChemSusChem 15 (2022) e202200178.
[166] D.K. Mishra, H.J. Lee, C.C. Truong, J. Kim, Y.-W. Suh, J. Baek, Y.J. Kim, Ru/MnCo2O4 as a catalyst for tunable synthesis of 2,5-bis(hydroxymethyl)furan or 2,5-bis(hydroxymethyl)tetrahydrofuran from hydrogenation of 5-hydroxymethylfurfural, Mol. Catal. 484 (2020) 110722.
[167] C. Li, G. Xu, X. Liu, Y. Zhang, Y. Fu, Hydrogenation of biomass-derived furfural to tetrahydrofurfuryl alcohol over hydroxyapatite-supported Pd catalyst under mild conditions, Ind. Eng. Chem. Res. 56 (2017) 8843–8849.
[168] S. Fulignati, C. Antonetti, D. Licursi, M. Pieraccioni, E. Wilbers, H.J. Heeres, A. M. Raspolli Galletti, Insight into the hydrogenation of pure and crude HMF to furan diols using Ru/C as catalyst, Appl. Catal. A Gen 578 (2019) 122–133.
[169] J.G. De Vries, Teddy, in: Preparation of caprolactone, caprolactam, 2,5-tetrahydrofuran-dimethanol, 1,6-hexanediol or 1,2,6-hexanetriol from 5-Hydroxymethyl-2-Furfuraldehyde, EP2390247A1, 2011.
[170] X. Kong, R. Zheng, Y. Zhu, G. Ding, Y. Zhu, Y.W. Li, Rational design of Ni-based catalysts derived from hydrotalcite for selective hydrogenation of 5-hydroxymethylfurfural, Green Chem 17 (2015) 2504–2514.
[171] Y. Zhang, A. Rezayan, K. Wang, J. Wang, C.C. Xu, R. Nie, On-demand, highly tunable, and selective 5-hydroxymethylfurfural hydrogenation to furan diols enabled by Ni and Ni3Ga alloy catalysts, ACS Catal 13 (2023) 803–814.
[172] Y. Nakagawa, K. Tomishige, Total hydrogenation of furan derivatives over silica-supported Ni–Pd alloy catalyst, Catal. Commun. 12 (2010) 154–156.
[173] Y. Nakagawa, K. Takada, M. Tamura, K. Tomishige, Total hydrogenation of furfural and 5-hydroxymethylfurfural over supported Pd-Ir alloy catalyst, ACS Catal 4 (2014) 2718–2726.
[174] J. Tan, J. Cui, Y. Zhu, X. Cui, Y. Shi, W. Yan, Y. Zhao, Complete aqueous hydrogenation of 5-hydroxymethylfurfural at room temperature over bimetallic RuPd/graphene catalyst, ACS Sustain. Chem. Eng. 7 (2019) 10670–10678.

[175] J.J. Wiesfeld, M. Kim, K. Nakajima, E.J.M. Hensen, Selective hydrogenation of 5-hydroxymethylfurfural and its acetal with 1,3-propanediol to 2,5-bis(hydroxymethyl)furan using supported rhenium-promoted nickel catalysts in water, Green Chem 22 (2020) 1229–1238.
[176] K. Arias, B. Hurtado, M.J. Climent, S. Iborra, A. Corma, Noble metal free carbon encapsulated CoNi alloy catalyst for total hydrogenation of 5-hydroxymethylfurfural to tetrahydrofurandiol in aqueous media, ChemPlusChem (2024) e202300643.
[177] S. Lima, D. Chadwick, K. Hellgardt, Towards sustainable hydrogenation of 5-(hydroxymethyl)furfural: a two-stage continuous process in aqueous media over RANEY® catalysts, RSC Adv 7 (2017) 31401–31407.
[178] B. Xiao, M. Zheng, X. Li, J. Pang, R. Sun, H. Wang, X. Pang, A. Wang, X. Wang, T. Zhang, Synthesis of 1,6-hexanediol from HMF over double-layered catalysts of Pd/SiO2 + Ir–ReOx/SiO2 in a fixed-bed reactor, Green Chem 18 (2016) 2175–2184.
[179] S. Fulignati, C. Antonetti, E. Wilbers, D. Licursi, H.J. Heeres, A.M. Raspolli Galletti, Tunable HMF hydrogenation to furan diols in a flow reactor using Ru/C as catalyst, J. Ind. Eng. Chem. 100 (2021), 390.e1-390.e9.