



Conversion of Biomass-Derived Molecules into Alkyl Levulinates Using Heterogeneous Catalysts

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Abstract: Alkyl levulinates are promising and versatile biomass-derived chemicals, which are utilized as fuel additives, flavoring agents, fragrances, solvents, and precursors for synthesizing valuable γ -valerolactone. A method for synthesizing alkyl levulinates involves the esterification of levulinic acid with the corresponding alkyl alcohols in the presence of solid acid catalysts that have abundant Brønsted acid sites. Alkyl levulinates can also be synthesized from other biomass-derived molecules such as furfuryl alcohol and furfural via alcoholysis and one-pot conversion, respectively. Thus far, various heterogeneous catalysts have been developed for the conversion of the biomass-derived molecules (levulinic acid, furfuryl alcohol, and furfural) into alkyl levulinates. To obtain the target products in high yields, numerous strategies have been employed including increasing Brønsted acidity, dispersing and incorporating Brønsted acid sites, inducing the formation of mesopores, and inducing a synergistic effect of metal–Brønsted acid sites that are present on a catalyst surface. Here, we summarily reviewed the performances of the heterogeneous catalysts in the conversions, describing the design and development of the heterogeneous catalysts that ensured the excellent yield of alkyl levulinates.

Keywords: biomass-derived molecules; levulinic acid; furfuryl alcohol; furfural; alkyl levulinates; esterification; alcoholysis; one-pot conversion; heterogeneous catalysts

1. Introduction

The conversion of renewable biomass resources into chemicals and fuels has recently attracted considerable attention as a strategy for reducing the overdependence on nonrenewable resources [1–3]. Lignocellulose, which is the most abundant biomass source, is mainly composed of cellulose (30-50 wt%), hemicellulose (20-35 wt%), and lignin (15–30 wt%) [4,5]. Cellulose, a linear polymer composed of glucose, undergoes hydrolysis to produce glucose, which undergoes isomerization to form fructose (Figure 1) [4–8]. Fructose can undergo dehydration to form 5-hydroxymethylfurfural, which can be decomposed to form levulinic acid (Figure 1) [5,8,9]. Levulinic acid is a versatile building block for the synthesis of value-added chemicals with extensive applications, and this is attributable to the presence of different functional groups of a ketone carbonyl group and a carboxyl group [10-12]. Among the various levulinic acid derivatives, alkyl levulinates are particularly fascinating because of their numerous potential industrial applications as flavoring agents, fragrances, green solvents, and precursors for synthesizing valuable γ -valerolactone [3,13,14]. Alkyl levulinates exhibit similar physicochemical properties to those of biodiesel composed of fatty acid methyl esters; however, they do not exhibit the principal drawbacks of biodiesel, namely cold flow properties and gum formation [3]. The addition of alkyl levulinates to biodiesel can address these drawbacks because of their properties such as low toxicity, high lubricity, flash point stability, and moderate flow properties under low-temperature conditions [3,11,15].



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Figure 1. Synthetic pathways of alkyl levulinates from cellulose and hemicellulose. Adapted from reference [8] with permission from Multidisciplinary Digital Publishing Institute, copyright 2021.

Alkyl levulinates can be synthesized directly from carbohydrates such as cellulose, glucose, and fructose [16,17]. However, this method has frequently given target products in relatively low yields and selectivities due to the formation of multiple products [18]. It is known that the esterification of levulinic acid is the simplest and most sustainable pathway for the synthesis of alkyl levulinates because only water is formed as a side product [18]. Conventionally, the esterification of levulinic acid into alkyl levulinates was carried out using the corresponding alkyl alcohols in the presence of mineral acids such as HCl, H_2SO_4 , and H_3PO_4 [1,13]. These acids are cost-effective homogeneous catalysts for the esterification reaction. However, they exhibit several drawbacks that are associated with catalyst removal, product separation, and environmental issues [13]. These issues of homogeneous catalysts can be overcome by using heterogeneous catalysts. Furfuryl alcohol was recently identified as a good starting material for the synthesis of alkyl levulinates owing to its inexpensiveness and high alcoholysis reactivity. Therefore, various solid acid catalysts with abundant Brønsted acid sites have been developed for the alcoholysis of furfuryl alcohol to alkyl levulinates [19,20]. Furfuryl alcohol is synthesized by the metal-catalyzed hydrogenation of furfural, which is produced via the hydrolysis of hemicellulose (a branched heteropolymer composed of various pentoses and hexoses, with the pentose xylose being the major component) into xylose, followed by dehydration (Figure 1) [4,7,8,21–24]. Based on this, several research groups have performed the one-pot synthesis of alkyl levulinates directly from furfural using metal-acid bifunctional catalytic systems. Regarding sustainability and energy efficiency, the one-pot conversion of furfural into alkyl levulinates is preferred to the process starting from furfuryl alcohol [21]. Lignin is a cross-linked polymer composed of three main phenolic monomers: *p*-coumaryl, coniferyl, and sinapyl alcohols [25,26]. To the best of our knowledge, there are no reports of the synthesis of alkyl levulinates from lignin or its derivatives.

Only a few available reviews described the catalytic synthesis of alkyl levulinates from levulinic acid, furfuryl alcohol, and furfural. Thus, in this microreview, we summarized the performance of heterogeneous catalysts in the conversion of the biomass-derived molecules into alkyl levulinates and described the design and development of the heterogeneous catalysts that facilitated excellent yields of the target products. We believe that this microreview will furnish subsequent studies with valuable information on the rational design and development of highly active and selective catalysts for the synthesis of alkyl levulinates from biomass-derived molecules.

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2. Heterogeneous Catalyst-Driven Conversion of Biomass-Derived Molecules into Alkyl Levulinates

The catalytic syntheses of alkyl levulinates described in this section are classified into three categories based on the utilized starting materials, namely levulinic acid, furfuryl alcohol, and furfural. The esterification of levulinic acid and the alcoholysis of furfuryl alcohol have been achieved by using solid acid catalysts with abundant Brønsted acid sites [4,8]. To achieve the one-pot conversion of furfural, metal catalysts that hydrogenate the carbonyl group more preferentially than the olefin group are also desired [7].

2.1. Levulinic Acid

J. Hamdi et al. demonstrated that halloysite, a natural 1:1 aluminosilicate clay mineral exhibiting a multilayer tubular structure, can facilitate the quantitative conversion of levulinic acid into alkyl levulinates (Table 1, entry 1) [27]. This is attributed to the presence of surface hydroxyl groups acting as Brønsted acid sites. Clay minerals have also been utilized as supports to develop solid acid catalysts that are effective for the esterification reaction. W. Zhao et al. developed a sulfonic acid-functionalized lignin-montmorillonite complex (LMT-SO₃H) for the esterification of levulinic acid into *n*-butyl levulinate [1]. Montmorillonite is also a natural aluminosilicate clay mineral, although its structure and composition are totally different from those of halloysite. Montmorillonite exhibits a multilayer platy structure composed of two Si-O tetrahedral sheets and one Al-O octahedral sheet [3]. The research group developed LMT-SO₃H by exploiting the unique property of montmorillonite, namely the adsorption of hydroxyl-containing compounds such as lignin. LMT-SO₃H quantitatively produced the target product, *n*-butyl levulinate (Table 1, entry 2). By changing the utilized alcohols, the yield of the corresponding alkyl levulinates decreased as the steric hindrance increased, exhibiting the following trend: primary > secondary > tertiary alcohols. They proposed a reaction mechanism for the esterification of levulinic acid into *n*-butyl levulinate (Figure 2). The esterification reaction proceeded through the enol form of levulinic acid, which was converted into α -angelica lactone via intramolecular lactonization. The subsequent protonation and nucleophilic addition via *n*-butanol facilitated the conversion of α -angelica lactone into *pseudo*-butyl levulinate. Following a similar process, *pseudo*-butyl levulinate was converted into an intermediate, I; the literature has reported the formation of *pseudo*-butyl levulinate [11]. Thereafter, I undergoes ring opening to produce another intermediate, II. Finally, the target product was formed by the elimination of *n*-butanol. Montmorillonite K10 (K10), an acid-treated montmorillonite, exhibits a higher specific surface area and higher surface acidity than montmorillonite. S. Dharne and V. V. Bokade supported dodecatungstophosphoric acid (DTPA), a heteropolyacid, on K10 to improve the low specific surface area and mitigate the separation issues from the reaction mixture [12]. The obtained DTPA/K10 exhibited better catalytic activity than the parent K10 for the esterification of levulinic acid into *n*-butyl levulinate; furthermore, it exhibited high stability, with 97% levulinic acid conversion and 100% *n*-butyl levulinate selectivity for two reuses without requiring any additional active treatments (Table 1, entry 3).

To prevent the leaching of heteropolyacids, G. Pasquale et al. incorporated a Wells– Dawson-type heteropolyacid during the synthesis of silica [10]. The resulting silicacontaining heteropolyacid was employed as an active and selective catalyst for the esterification of levulinic acid into ethyl levulinate (the yield and selectivity were 76% and 100%, respectively) and maintained its Wells–Dawson structure for up to four reaction cycles (Table 1, entry 4). F. Su et al. developed a heteropolyacid-based reusable catalyst, H₃PW₁₂O₄₀/ZrO₂-Si(Ph)Si, as a hybrid catalyst for the esterification of levulinic acid into methyl levulinate [28]. The high catalytic stability stemmed from a strong Keggin unit-ZrO₂ support interaction. The catalyst showed excellent activity toward the esterification reaction under mild conditions and is mainly attributed to the surface hydrophobicity caused by the introduction of phenyl groups, facilitating the adsorption of levulinic acid and the desorption of water formed during the reaction (Table 1, entry 5).

Table 1. Synthesis of alkyl levulinates from levulinic acid.

Entry	Catalyst	Temp. (°C)	Time (h)	Alkyl Group	Yield (%)	Ref.
1	Halloysite	170	24	Me to <i>n</i> -Bu	97–99	[27]
2	LMT-SO ₃ H	120	4	<i>n</i> -Pr to <i>n</i> -Hep	9.5-99.3	[1]
3	DTPA/K10	120	4	<i>n</i> -Bu	97	[12]
4	40WD-S	78	10	Et	76	[10]
5	H ₃ PW ₁₂ O ₄₀ /ZrO ₂ -Si(Ph)Si	65	3	Me	99.9	[28]
6	TiO ₂	120	8	<i>n</i> -Bu	87.5	[11]
7	DTPA/DH-ZSM-5	78	4	Et	94	[29]
8	GC400	100	4	<i>n</i> -Bu	90.5	[15]



Figure 2. Proposed mechanism of the esterification of levulinic acid (LA) with *n*-butanol (BuOH) into *n*-butyl levulinate (BL). Adapted from reference [1] with permission from Elsevier, copyright 2020.

To increase the rate of the esterification of levulinic acid with *n*-butanol over commercial TiO₂, S. Zhou et al. added a small amount of water into the reaction system (Table 1, entry 6) [11]. The increased yield of *n*-butyl levulinate might be due to the conversion of the surface Lewis acid sites into Brønsted acid sites. Other strategies for increasing the rate of the esterification of levulinic acid with alcohols include the desilication of H-ZSM-5 to form mesopores while sacrificing the micropores [29]. Regarding the esterification of levulinic acid with ethanol, the desilicated H-ZSM-5 (DH-ZSM-5) exhibited higher catalytic activity than the parent H-ZSM-5. In addition to inducing the mesoporosity, increasing the Brønsted acid sites, total acidity, and specific surface area contributed to enhancing the catalytic activity. Nevertheless, DH-ZSM-5 achieved 28% conversion and 100% selectivity after 4 h. The efficiency of synthesizing ethyl levulinate was improved by loading DTPA onto DH-ZSM-5 (DTPA/DH-ZSM-5; Table 1, entry 7). J. Yang et al. observed that sulfonated glucose-derived amorphous carbon (GC400) exhibited good swelling capability toward increasing the accessibility of the $-SO_3H$ sites in the bulk structure, while sulfonated active carbon, AC400, exhibited poor swelling due to the decreased flexibility of the carbon sheets generated by a higher graphitization [15]. The good swelling capability of GC400 contributed to the high catalytic performance in *n*-butyl levulinate synthesis (Table 1, entry 8). GC400 exhibited a much higher turnover frequency (TOF) value compared with other typical solid acid catalysts, including Nafion-212 which exhibited stronger Hammett acidity and higher $-SO_3H$ density. They attributed the higher esterification rate to the increased interaction with the hydrophilic reactants by the oxygen-containing functional groups such as the -OH and -COOH groups on the GC400 surface, improving the access to the -SO₃H sites.

To elucidate the effect of the γ -keto group of levulinic acid on catalysis, I. Ogino et al. applied synthesized sulfonated carbon catalysts to two kinds of esterification reactions [30].

In the esterification of acetic acid with ethanol, all of the catalysts exhibited almost the same apparent TOF per -SO₃H group despite their completely different physicochemical properties. Conversely, various apparent TOF values were obtained in the esterification of levulinic acid with ethanol. The apparent TOF values correlated positively with the combined concentration of the -COOH and -OH groups, indicating that the neighboring functional groups enhanced the catalytic performance of the -SO₃H groups for the esterification of levulinic acid with ethanol. They proposed the hydrogen-bonding interaction between the γ -keto group of levulinic acid and the surface functional groups (Scheme 1).



Scheme 1. A proposed mechanism for the rate enhancement by proximity effect enabled by interaction of γ -keto group of levulinic acid with the surface functional groups. Adapted from reference [30] with permission from Elsevier, copyright 2018.

2.2. Furfuryl Alcohol

D. Zhao et al. applied commercially available zeolites (H-ZSM-5-30, H-ZSM-5-50, H-Y-5.2, and H-Y-60) to the alcoholysis of furfuryl alcohol in methanol [31]. Compared with the H-Y zeolites, H-ZSM-5 obtained higher yields of methyl levulinate (H-ZSM-5: 54–60% yield; H-Y: 30–37% yield) (Table 2, entry 1). Based on the reaction results, they concluded that the catalytic performances of the zeolites proceeded mainly from their acidities. However, regarding H-ZSM-5, the more acidic H-ZSM-5-30 catalyzed a slightly lower yield than H-ZSM-5-50 in the synthesis of methyl levulinate. This difference in the yields may be attributed to other characteristics such as the specific surface area, pore size, and hydrophobicity of the materials. Other commercially available materials such as Amberlyst-15 and Purolite CT151 demonstrated effectiveness in the synthesis of ethyl levulinate, although large amounts of catalysts were required (>50 wt%) (based on the mass of furfuryl alcohol) [8]. The latter catalyst gave various alkyl levulinates in moderate to good yields of up to 71% (Table 2, entry 2). D. Ren et al. reported that commercially available α -Fe₂O₃ is effective for the alcoholysis of furfuryl alcohol in methanol, ethanol, and *n*-butanol (Table 2, entry 3) [32].

To date, various solid acid catalysts have been developed for the alcoholysis of furfuryl alcohol into alkyl levulinates. A glucose-derived carbonaceous catalyst bearing sulfo groups facilitated the conversion of furfuryl alcohol into ethyl levulinate, with a lower catalytic loading of 20 wt% (based on the mass of furfuryl alcohol); the highest yield was 67.1% (Table 2, entry 4) [33]. With the increasing reaction cycles, the carbon content increased from 52.2% to 60.6%, whereas the sulfur content decreased from 1.5% to 0.9%. These results reflected the deposition of humins on the catalyst surface as well as the leaching of the sulfo group. It is well known that furfuryl alcohol polymerizes readily to form insoluble substances such as humins in the presence of acid catalysts [34]. When utilizing solid acid catalysts, the obtained oligomeric/polymeric products are deposited on the surfaces, thereby decreasing the accessibility of the active sites for the alcoholysis of furfuryl alcohol into alkyl levulinates [31,34]. E. S. Sankar et al. also reported such catalyst deactivation [20]. A significantly high n-butyl levulinate yield (97%) was obtained over an SBA-16-supported tungstophosphoric acid catalyst (Table 2, entry 5) [20]. However, this yield decreased to 84% after the fourth cycle. G. Wang et al. developed a highly efficient and reusable SO_3H -functionalized ionic liquid for the synthesis of a series of alkyl levulinates [35]. In the synthesis of ethyl levulinate, the catalytic performances of ionic liquids were strongly

related to their Brønsted acidities, as determined using the Hammett method. An ionic acid bearing two alkyl sulfonic acid groups exhibited the highest efficiency as a catalyst for the conversion, maintaining its catalytic activity after six runs. The catalyst facilitated the synthesis of various alkyl levulinates in the corresponding alkyl alcohols, with good to excellent yields of up to 95% (Table 2, entry 6). The reaction result revealed that the yields were attributable to the carbon lengths, boiling points, and molecular volumes of the alkyl alcohols. The effects of the carbon lengths and molecular volumes on the catalytic alcoholysis of furfuryl alcohol were also noted by A. M. Hengne et al. (Table 2, entry 7) [36].

Entry	Catalyst	Temp. (°C)	Time (h)	Alkyl Group	Yield (%)	Ref.
1	H-ZSM-5-50	150	5 min	Me	60	[31]
2	Purolite CT151	80-120	5	Me to sec-Bu	30-71	[8]
3	α -Fe ₂ O ₃	250	40 min–80 min	Me to <i>n</i> -Bu	73–86	[32]
4	GCC	150	1	Et	67.1	[33]
5	TPA/SBA-16	110	3	Me to <i>n</i> -Bu	8–97	[20]
6	[(HSO ₃ -p) ₂ im][HSO ₄]	110	2	Me to <i>n</i> -Pe	80–95	[35]
7	[BMIm-SH][HSO ₄]	130	2	Me to <i>n</i> -Bu	68–99	[36]
8	Al-TUD-1	140	24	Et	80	[37]
9	SBA-15-SO ₃ H	110	4	<i>n-</i> Bu	96	[38]
10	MMS(0.3)-0.15	160	2	Et	83.8	[39]
11	Graphene oxide	120	6	Me to <i>n</i> -Hex	78.2–95.5	[40]
12	γ -Fe ₃ O ₄ /H-ZSM5	130	8	sec-Bu	Not available	[41]

Table 2. Synthesis of alkyl levulinates from furfuryl alcohol.

P. Neves et al. tested various aluminosilicate acids exhibiting different acidities and porosities in the alcoholysis of furfuryl alcohol with ethanol [37]. Among them, Al-TUD-1 obtained the highest ethyl levulinate yield despite its relatively lower acidity (Table 2, entry 8). As the aluminosilicate exhibited the highest specific surface area, it was proposed that the accessibility of the active sites to the reactants played a dominant role in the efficiency of the catalyst in the formation of ethyl levulinate. In the development of sulfonic acid-functionalized SBA-15, P. D. Carà et al. used a template agent to enhance the accessibility of the active sites to reactants [38]. In the alcoholysis of furfuryl alcohol with *n*-butanol, the catalyst exhibited 96% selectivity toward *n*-butyl levulinate at complete conversion (Table 2, entry 9) [38]. X. Liu et al. developed mesoporous metal-organic frameworks (MOFs) because of the limited diffusion and mass transfer of reactants in most microporous MOFs (Figure 3) [39]. The walls of the mesoporous materials, MIL-101(Cr)- SO_3H (MMSs), were composed of crystalline microporous frameworks. When utilizing a series of MMSs for the alcoholysis of furfuryl alcohol with ethanol, MMS(0.3)-0.15 with a moderate pore size and Brønsted acid density of -SO₃H displayed the highest catalytic performance (83.8% ethyl levulinate yield at full conversion; Table 2, entry 10).

A promotional effect of the oxygen-containing functional groups has also been reported in the alcoholysis of furfuryl alcohol. S. Zhu et al. revealed that the -COOH groups, but not the -OH groups, on the surface of graphene oxide facilitated the adsorption of furfuryl alcohol [40]. Thus, graphene oxide showed a higher yield of ethyl levulinate than H_2SO_4 and *p*-toluenesulfonic acid contained many more -SO₃H groups (Table 2, entry 11).

From the above, various solid acid catalysts have been developed to obtain alkyl levulinates in high yields. T. M. Lima et al. developed an H-ZSM-5 catalyst that can be readily recovered from the reaction mixture using an external magnet [41]. The catalyst was designed by encapsulating Fe_3O_4 in H-ZSM-5. The magnetic nanocomposite catalyst exhibited excellent selectivity toward *sec*-butyl levulinate at full conversion, although the selectivity and yield were not adequately described (Table 2, entry 12).



Figure 3. Hierarchically micro- and mesoporous structure-functionalized MOFs for the alcoholysis of furfuryl alcohol to ethyl levulinate. Reprinted from reference [39] with permission from American Chemical Society, copyright 2019.

The molecular-level elucidation of a reaction mechanism is crucial to the design of more effective catalysts for the reaction. In the synthesis of ethyl levulinate from furfuryl alcohol and ethanol, X. Liu et al. unveiled the formation of 2-ethoxymethylfuran, 4,5diethoxy-5-hydroxypentan-2-one, and 4,5,5-triethoxypentan-2-one via gas chromatographymass spectroscopy [39]. The yields of the three compounds exhibited volcano trends, indicating that they were the intermediates. Based on these results, the research group proposed two reaction pathways for the conversion of furfuryl alcohol into ethyl levulinate (Scheme 2). Path 1 is initiated by the protonation of the oxygen atom of the furan ring, after which the protonated furfuryl alcohol is attacked by one ethanol molecule to form 2-ethoxymethylfuran. The following acidification converts the intermediate into the target product. The first step of Path 2 is also the protonation of furfuryl alcohol, although the protonated position is totally different: the oxygen atom of the hydroxyl group. Thereafter, the protonated furfuryl alcohol is attacked by two and three ethanol molecules to form 4,5-diethoxy-5-hydroxypentan-2-one and 4,5,5-triethoxypentan-2-one, respectively. Path 2 involves the formation of 4,5,5-triethoxypentan-2-one via the condensation reaction of 4,5-diethoxy-5-hydroxypentan-2-one with one ethanol molecule. Thereafter, 4,5-diethoxy-5hydroxypentan-2-one and 4,5,5-triethoxypentan-2-one are converted into the target product, following the elimination of one ethanol and diethyl ether molecules, respectively. As the formation of a large amount of 2-ethoxymethylfuran has also been reported by the research group, Path 1 is likely the main pathway for the conversion of furfuryl alcohol into ethyl levulinate.

G. Wang et al.'s group agreed with Path 1 proposed by X. Liu et al. [35]. However, they proposed a slightly different path, Path 2 (Scheme 3) [35]. The protonated furfuryl alcohol is attacked by three ethanol molecules to form 4,5,5-triethoxypentan-2-one. The condensation of the intermediate with one water molecule results in the formation of 4,5-diethoxy-5-hydroxypentan-2-one. H. G. Bernal et al.'s group has also proposed this pathway [19].



Scheme 2. Possible reaction pathways for the alcoholysis of furfuryl alcohol to ethyl levulinate in ethanol over MMS(0.3)-0.15. Reprinted from reference [39] with permission from American Chemical Society, copyright 2019.



4,5-Diethoxy-5-hydroxypentan-2-one

Scheme 3. G. Wang et al.'s [35] reaction pathway for the alcoholysis of furfuryl alcohol into ethyl levulinate.

2.3. Furfural

H. G. Bernal et al. synthesized *iso*-propyl levulinate directly from furfural via the consecutive addition of CuO_x/Fe_3O_4 and Amberlyst-70 to the reaction system [19]. First, the former catalyst (CuO_x/Fe_3O_4) transformed furfural into furfuryl alcohol using *iso*-propanol as the reducing agent. Thereafter, the latter (Amberlyst-70) was added into the reaction system for the alcoholysis of the in situ-formed furfuryl alcohol into *iso*-propyl levulinate. Although the target product was obtained in a high yield (84%), the one-pot, two-step process can still be improved (Table 3, entry 1). CuO_x/Fe_3O_4 delivered a furfural conversion of <80% before the addition of Amberlyst-70 for the subsequent alcoholysis reaction. Therefore, the remaining furfural interacted with the Brønsted acid catalyst, resulting in a lower *iso*-propyl levulinate yield with respect to the use of neat furfuryl alcohol. Additionally, Amberlyst-70 catalyzed the condensation of the remaining furfural and acetone generated from *iso*-propanol, generating small amounts of furfurylideneacetone as an unwanted byproduct. In 2022, our group reported a novel catalytic system comprising Ni₃Sn₂ alloy nanoparticles and montmorillonite K10. It catalyzed the one-pot, two-step synthesis of various alkyl levulinates [3]. Regardless of the utilized alkyl alcohols,

the Ni₃Sn₂ alloy nanoparticles facilitated the quantitative transformation of furfural into furfuryl alcohol using molecular hydrogen as the reducing agent. Afterward, the addition of montmorillonite K10 into each reaction system facilitated the smooth alcoholysis of the in situ-formed furfuryl alcohol, generating the corresponding alkyl levulinates in moderate to high yields of up to 71% (Table 3, entry 2).

Entry	Catalyst	Temp. (°C)	Time (h)	Alkyl Group	Yield (%)	Ref.
1	Cu-Fe ₃ O ₄ Amberlyst-70	185 120	4	<i>iso</i> -Pr	84	[19]
2	Ni ₃ Sn ₂ Montmorillonite K10	180 120	16–42	Me to <i>n</i> -Bu	37–71	[3]
3	Zr-MCM-41 + Amberlyst-15	130	24	Me to iso-Bu	85.3 (<i>iso-</i> Pr)	[42]
4	Zr-SBA-15 + ZSM-5	180	18	Et	55	[43]
5	Pt/ZrNbO ₄	130	6	Et to tert-Bu	75.67 (Et)	[44]
6	Au-H ₄ SiW ₁₂ O ₄₀ /ZrO ₂	120	24	Et to sec-Bu	50.2-80.2	[21]

Table 3. Synthesis of alkyl levulinates from furfural.

The one-pot (single reactor), one-step (catalysts and reagents are mixed in a single reactor at the same time) processes have also been developed for the conversion of furfural into alkyl levulinates. L. Peng et al. obtained a high yield (85.3%) of iso-propyl levulinate by combining Zr-MCM-41 and Amberlyst-15 catalysts (Table 3, entry 3) [42]. The utilization of iso-butanol as a secondary alcohol generated the corresponding alkyl levulinate in a moderate yield (59.2%), while that of primary alcohols such as methanol, ethanol, and *n*propanol obtained low yields of the corresponding alkyl levulinates. These reaction results revealed that the reduction potential of the alcohols accounted for the transfer hydrogenation of furfural into furfuryl alcohol in the presence of Zr-MCM-41. They investigated the reusability of the catalytic system for the one-pot conversion of furfural into *iso*-propyl levulinate. Considerable catalyst deactivation was observed from the subsequent run. The color of the spent Zr-MCM-41 surface turned black. They presumed that the catalyst deactivation was due to the deposited polymer impurities from the Amberlyst-15-catalyzed polymerization of furfural at the active sites. Furfural is also susceptible to polymerization [43]. Unfortunately, the total acidity of the spent Amberlyst-15 decreased significantly after the first run. The reason for the catalyst deactivation may be the partial shielding of the acid sites and/or cation exchange. To realize the successive runs, the spent catalysts were subjected to sufficient regeneration treatments, namely calcination and soaking in HCl solution, respectively. K. Tang et al. applied Lewis acidic Zr-SBA-15 to the transfer hydrogenation of furfural in ethanol [43]. Interestingly, when conducting the reaction at 180 °C, ethyl levulinate was obtained in a 41.8% yield after 18 h and was accompanied by the formation of a solid residue (10 wt%). They investigated whether the solid residue was formed from furfural (FUR) or from furfuryl alcohol. In the reaction system, ethanol acted as the hydrogen donor and was subsequently converted into acetaldehyde diethyl acetal (DEA) via acetalization with ethanol. The ratio of [DEA]/[FUR]₀ was >98% under the above-mentioned reaction conditions. This result indicates the Zr-SBA-15-catalyzed complete conversion of furfural into furfural alcohol, also indicating that the undesired polymerization/resinification to form the solid residue may be predominantly promoted by furfuryl alcohol. The yield of ethyl levulinate increased to 55% when the conversion of furfural was performed in the co-presence of ZSM-5, exhibiting Brønsted acidity under identical reaction conditions (Table 3, entry 4).

A metal–acid bifunctional catalyst of Pt nanoparticles supported on a ZrNb binary phosphate solid acid was developed by B. Chen et al. to catalyze the conversion of furfural into ethyl levulinate via a one-pot process [44]. The ZrNb binary phosphate has strong Brønsted acid sites and flexible Lewis acid sites, and by adjusting the ratio of Zr to Nb, they controlled the degree of the hydrogenation and the selectivity for the target product.

Pt/ZrNbPO₄ (Zr/Nb = 1:1) displayed the best ethyl levulinate selectivity (75.67%) at the furfural conversion of 92.28% (Table 3, entry 5). Concurrently, tetrahydrofurfuryl alcohol and 5.5-diethoxylpentan-2-one were formed as undesired byproducts, although the formation of the acetal and oligomers of furfural was completely suppressed. S. Zhu et al. observed a synergistic effect of metal and acid species on the integrated conversion of furfural [21]. A bifunctional catalyst, Au-H₄SiW₁₂O₄₀/ZrO₂, accounted for a much higher *iso*-propyl levulinate yield (80.2%) than a physically mixed catalyst comprising Au/ZrO₂ and H₄SiW₁₂O₄₀/ZrO₂ (47.6% yield) (Table 3, entry 6). Unexpectedly, when using primary alcohols (ethanol, *n*-propanol, and *n*-butanol), the transfer hydrogenation of furfural by the Au nanoparticles proceeded effectively, producing the corresponding alkyl levulinates in moderate to good yields of up to 77.6%. They used various Au-heteropolyacid bifunctional catalysts supported on ZrO₂ in the one-pot conversion of furfural with *iso*-propanol to reveal the relationship between their *iso*-propyl levulinate yields and the total acidities. A significant linear relationship was observed between them, indicating that the acidity played a crucial role in the one-pot conversion.

3. Conclusions and Outlook

Based on the existing contributions, we performed a general overview of the catalytic synthesis of alkyl levulinates from the biomass-derived molecules (levulinic acid, furfuryl alcohol, and furfural). Levulinic acid and furfuryl alcohol were converted into alkyl levulinates in the presence of solid acid catalysts with abundant Brønsted acid sites. When furfural was employed as the starting material for the synthesis, metal catalysts that recognize and reduce the carbonyl group more preferentially than the olefin group were also required. To date, numerous strategies have been employed for the development of effective heterogeneous catalysts for the conversions; they include increasing Brønsted acidity, dispersing and incorporating Brønsted acid sites, inducing the formation of mesopores, and inducing the synergistic effect of metal–Brønsted acid sites that are present on a catalyst surface. Despite the tremendous research efforts, only a few heterogeneous catalysts can facilitate the excellent yields of alkyl levulinates using furfuryl alcohol and furfural as the substrates. This is because of the undesired polymerization of the two compounds due to the utilized solid acid catalysts. To suppress this side reaction, numerous studies performed the conversions of furfuryl alcohol and furfural into alkyl levulinates at moderate reaction temperatures, although relatively long reaction times were needed, particularly when using furfural as the starting material. Therefore, it is strongly demanded to develop highly active and selective heterogeneous catalysts for the one-pot conversion of furfural to alkyl levulinates.

Here, we proposed the design of high-activity and high-selectivity heterogeneous catalysts that can drive the synthesis of alkyl levulinates from furfural via furfuryl alcohol. By spatially restricting the reaction fields around Brønsted acid sites in the nanometer range, the furfural and furfuryl alcohol polymerizations might be significantly suppressed without tediously controlling the reaction temperature. Furthermore, loading metal nanomaterials onto the restricted spaces would make the metal–acid bifunctional nanocomposites highly active for the one-pot conversion of furfural into alkyl levulinates, which is attributed to the synergistic effect of the metal and acid species that are present on the surface. Zeolites exhibit such spatially restricted reaction fields, although the Brønsted acid sites are also present on the external surface, and this can induce the undesired polymerization of furfural and furfuryl alcohol. Based on the surveys in the literature, we identified several materials with Brønsted acid sites in nanospaces only and are evaluating their catalytic performances for the alcoholysis of furfuryl alcohol with alkyl alcohols to develop highly active and selective metal–acid bifunctional catalysts for the one-pot conversion of furfural to alkyl levulinates.

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