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COMMUNICATION

Synthesis of Medium-Chain Acids or α, ω-Dicarboxylic Acids from Cellulose-Derived Platform Chemicals

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Medium-chain fatty acids and their derivatives have important applications in the energy and chemical industries. Thus, we have prepared a series of medium-chain fatty acids by selective hydrodeoxygenation of the aldol condensation products derived from cellulose using a metal triflate and Pd/C catalyst system. The selective retention of the carboxyl group is a notable feature of this catalytic system.

The escalating depletion of fossil resources and deterioration of the environment necessitate the employment of renewable biomass resources as raw materials for the production of liquid fuels and chemicals. [1, 2] Since cellulose-based carbohydrates are the largest components of biomass raw materials, catalytic processes that effect their conversion to chemicals and fuels are of immense interest. [3-5]

Medium-chain acids and α,ω-dicarboxylic acids are widely used in the manufacturing of various chemicals and intermediates, such as detergents, surfactants, drugs, lubricants, plasticizers, greases, perfumes, nylons, and some polymers. [6-8] Decanoic acid and sebacic acid (1, 10-decanedioic acid), as important medium-chain fatty acids, can be used for the synthesis of all-purpose esters and alcohols. For instance, tens of thousands of tons of sebacic acid are consumed annually in the production of nylon-6,10. [9]

Medium-chain carboxylic and α, ω-dicarboxylic acids are predominantly synthesised either by hydrocarboxylation of olefins (e.g., Reppe chemistry) or by oxidation of hydrocarbons, both of which are petrochemical processes. [10, 11] Hydrocarboxylation of olefins (Koch process) is industrially used to manufacture highly branched tert-monocarboxylic acids, such as versatic acid (Hexion, formerly Shell), neo decanoic acid (ExxonMobil), ceKanoic acid (ExxonMobil, formerly Kuhlmann), The hydroformylation or oxo process, practiced by Oxea (incl. Celanese technology), BASF and others, as well as caustic fusion to produce iso-tridecanoic acid from tridecanol (Clariant) have been industrially employed. However, petrochemical raw materials, in fact, have little significance in the field of monocarboxylic fatty acids. The overwhelming majority is based on natural fats and oils, which in case of milk fats supply all kind of carboxylic acids with chain length between C_4 and $C_{20/22}$, whereas the lauric oils (coconut and palm kernel oil) supply fatty acids in the range of C_6 to C_{20}. The same applies to industrial dicarboxylic acids. Sebacic acid, azelaic acid, dimer fatty acids are based on renewable raw materials. [12-16] However, the oxidation of such acids usually requires harsh conditions, including high temperatures and pressures, the use of strong acids (H_2SO_4, HNO_3) and toxic substances, which cause environmental concerns and lead to equipment failure. [13, 14] Enzymatic degradation of unsaturated long-chain fatty acids to a mixture of medium-chain carboxylic acids and ω-hydroxycarboxylic acids has been reported, [9, 17-20] but the difficulties associated with product separation, enzyme inactivation, and the relatively low lipid content in biological crops preclude practical industrialisation of this process. [21]

Alternatively, medium-chain carboxylic acids can be prepared from the cellulose-based compounds, which are abundant in nature. However, only carboxylic acids with less than six carbon atoms (i.e., C6 chains) can be obtained due to the limited number of carbon atoms in sugars. [22-24] Thus, various condensation processes, including aldol, [25-28] hydroxyalkylation/alkylation, [29-31] benzoin, [32-34] and dimerization, [35-37] have been systematically employed to increase the carbon chain length, with aldol condensation being a particularly common method. However, no selectivity was observed in the subsequent hydrodeoxygenation process because of the non-selective removal of all oxygen groups. [38-43] Pioneering works concerning selective hydrodeoxygenation include the reaction protocols reported by Leitner *et al.* [44] and Wang *et al.* [45] In these cases, the primary hydroxyl groups were retained, and 1-octanol and dioctyl ether were subsequently obtained as the products. Nonetheless, reports

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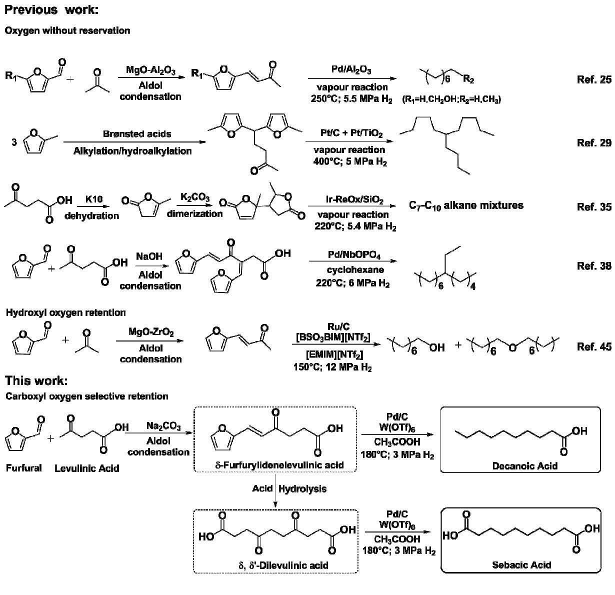
of medium-chain carboxylic acids prepared from biomass platform molecules are still rare.

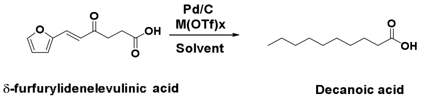
Herein, we would like to report the synthesis of medium-chain carboxylic and α, ω-dicarboxylic acids via selective hydrodeoxygenation from cellulose-derived aldol condensation products. For this purpose, we note that δ-furfurylidenelevulinic acid, which is synthesised by aldol condensation of furfural (viz. the hydrolysis of pentose [46]) and levulinic acid (viz. the hydrolysis of hexose [47, 48]), has three types of oxygen-containing groups: a furan ring oxygen (converted into tetrahydrofuran ether upon hydrogenation); a ketone carbonyl oxygen (converted to a secondary alcohol hydroxyl group by hydrogenation); and carboxylic acid oxygen atoms. Regarding to the preparation of decanoic acid, a key challenge is to promote the selective hydrogenolysis of the first two types of oxygen moieties while preserving the last type of oxygen (i.e., the carboxylic groups). To the best of our knowledge, how to selectively remove the specific oxygen atoms in biomass platform molecules continues to be a challenging work. To this end, we recently found that the hydrogenolysis using a high-valent metal triflate (i.e., $M(OTf)_n$) as the catalyst could selectively retain the carboxylic oxygen and remove all the other oxygen atoms (i.e., those in both the ether and hydroxyl groups) under mild reaction conditions. Given this, decanoic and sebacic acids can be efficiently prepared through this strategy from the easily accessible furfural and levulinic acid, which are important biomass platform molecules. (Scheme 1).



Scheme 1. Conversion of condensation products to value-added

To determine the optimal reaction conditions, different metal triflates were initially tested (Table 1, Entries 1–7). As seen, the yield of decanoic acid gradually increased with an increasing effective charge density on the metal cation.[49, 50] In our method, the exocyclic C-C double bond and the furan ring were first saturated to afford intermediate 1. Subsequent hydrogenation of the ketone carbonyl group and the following cyclisation gave intermediate 2, which contains a lactone moiety and a THF ring (see the 'Catalyst and Substrate Production' section in the ESI). Starting from intermediate 2, the following steps involve a polymerisation process. In particular, it is known that metal triflates can promote polymerisation [51] and depolymerisation. [52] With the metal triflate acting as the catalyst, the lactone and tetrahydrofuran rings underwent ring opening process to afford a mixture of unbranched polyesters. Unsaturated carboxylic acids, which originate from the depolymerisation of polyester mixtures, can be further hydrogenated to give the corresponding saturated acids. The highest yield of decanoic acid can reach 98.2 % when $W(OTf)_6$ was used as the catalyst (Table 1, Entry 7).

Table 1. Acid and solvent screening for the preparation of decanoic acid from δ-furfurylidenelevulinic acid.[a]



Entry	Acid catalyst	Solvent	Conversion/%	Yield/% [b, c]
1	$Sn(OTf)_2$	acetic acid	>99	0.5 [d]
2	$La(OTf)_3$	acetic acid	>99	25.6 [d]
3	$Fe(OTf)_3$	acetic acid	>99	54.8
4	$Al(OTf)_3$	acetic acid	>99	82.1
5	$Hf(OTf)_4$	acetic acid	>99	86.4
6	$Zr(OTf)_4$	acetic acid	>99	92.3
7	$W(OTf)_6$	acetic acid	>99	94.0 (98.2 [e])
8	$W(OTf)_6$	water	>99	6.2 [d]
9	$W(OTf)_6$	MeOH	>99	2.7 (15.3 [f])
10	$W(OTf)_6$	n-octane	>99	15.9 [d]
11	$W(OTf)_6$	THF	>99	25.5 [d]

[a] Reaction conditions: 0.5 mmol substrate, 2 mol% 10% Pd/C, 6 mol% acid co-catalyst, 180 °C, 2 MPa H_2, 8 h, 5 mL solvent. [b] The yield of decanoic acid was measured by GC analysis, with dimethyl phthalate as the internal standard. [c] Carbon balance is not conserved due to the presence of intermediates **1** and **2** and oligomers that cannot be detected by GC analysis. [d] The main products were the furan-ring saturated products, intermediate **1** and intermediate **2**. [e] 3 MPa H_2, 10 h. [f] Yield of methyl decanoate.

For the solvent effect, we observe that the solubility of the reactant, as well as the dielectric constant (ε) of the solvents, has a close correlation with the product yield (Table 1, Entries 7–11). Cleavage of ester C-O bond is known to proceed particularly well in solvents with a moderate dielectric constant. [49] Only a trace amount of product was obtained when water (ε = 79.7) was used as the solvent (Table 1, Entry 8). In fact, water molecules (more specifically, the oxygen of H_2O) can irreversibly interact with the metal triflate and compete with the substrate. Similarly, only a small amount of methyl decanoate and decanoic acid were detected using methanol (ε = 32.6) as the solvent (Table 1, Entry 9). The low product yield can now be rationalized as the catalyst deactivation. [50] More specifically, the metal triflate, which is a Lewis acid, is deactivated by the interaction with a solvent bearing Lewis basic oxygen atoms. Negative results were also observed for solvents with low/moderate dielectric constants like n-octane (ε = 1.9) or tetrahydrofuran (ε = 7.6) (Table 1,

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Entries 10–11), despite a slight increase of the yield compared to that of methanol and water. These results can be understood in terms of the ineffectiveness of these two solvents to dissolve the formed oligomers. Moreover, tetrahydrofuran could also undergo ring-opening reactions in such a system to produce butane and oligomers, which is detrimental to the reaction progress. [41]

Notably, a good yield of decanoic acid was obtained if acetic acid is employed as the solvent (Table 1, Entry 7). Acetic acid can dissolve the starting materials, intermediate oligomers, and products more effectively than the other solvents tested. Moreover, acetic acid was also involved in the formation of intermediates (Figure 2.b, Figure 2.d and Figure S5 in ESI). The esterification promoted by acetic could restrict the increase of the carbon chain during the oligomerization process, as the reactive hydroxyl group is now blocked. It is therefore beneficial to the subsequent depolymerisation process.

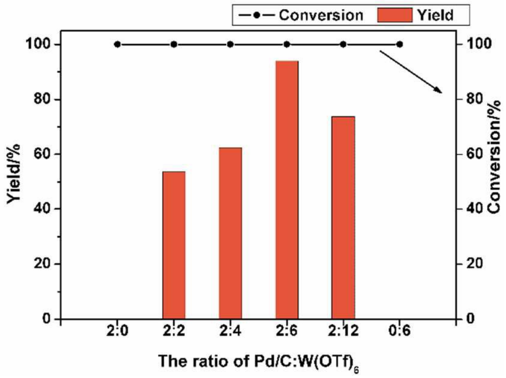

Figure 1. The effect of catalyst mole ratio on product distribution. Reaction conditions: 0.5 mmol substrate, 10% Pd/C, W(OTf)$_6$, 5 mL acetic acid, 180 °C, 2 MPa H_2, 8 h.

It is very important to choose the appropriate mol ratio of Pd/C and W(OTf)$_6$ to improve the selectivity and yield of decanoic acid. We first experimented with only Pd/C catalyst and W(OTf)$_6$ catalyst (the mol ratio of 2: 0 and 0: 6, respectively), and found that no product of decanoic acid was obtained. This further illustrated that the hydrogenation catalyst and Lewis acid catalyst were indispensable. In the presence of Pd/C catalyst alone, the main product resulting from the reaction was intermediate **2** and almost no ring-opened product were obtained. In the presence of W(OTf)$_6$ catalyst alone, no obvious products and raw materials were observed, probably due to the self oligomerization of substrate catalyzed by metal triflate. The reaction solution became a black turbid liquid with a clear coke attached to the autoclave wall could support this assumption. With the addition of W(OTf)$_6$ catalyst, we found that the yield of decanoic acid increased. It was shown that the W(OTf)$_6$ catalyst, along with acetic acid, had a significant catalytic effect on the ring-opening of lactone ring and tetrahydrofuran ring, the fracture of straight chain esters, the formation and depolymerization of polymers. The highest yield of decanoic acid was 94% as the mol ratio of Pd/C and W(OTf)$_6$ was 2:6. The yield of decanoic acid decreased along with further increased the ratio of W(OTf)$_6$ (2:12). The reduced product selectivity and undesirable byproducts might be the main reason for the decreased product yield. Therefore, the preparation of decanoic acid by hydrodeoxygenation process required a suitable ratio of the hydrogenation catalyst and Lewis acid catalyst.

Other factors of the reaction conditions were also optimised, and the results of which are provided in the ESI (‘Further Screening of Reaction Conditions’). In summary, the optimal reaction conditions were located as: 0.5 mmol substrate, 2 mol% 10% Pd/C, 6 mol% W(OTf)$_6$, 5 mL acetic acid, 180 °C, 3 MPa H_2, and 10 h of reaction time.

In addition, mechanistic studies were performed to provide further insights into this reaction protocol. At the first instance, the correlation of the decanoic acid yield with reaction time was investigated. It took approximately 30 minutes to increase the reaction temperature from room temperature to 180 °C (i.e., known as the pre-heating procedure), which is the optimal reaction temperature. After 20 minutes at this temperature, the reaction was terminated and the products were measured. It was found that decanoic acid was obtained in 54.4 % yield (Figure 2.a). The results show that the raw materials was converted over a short time period, which may be due to the relatively high initial concentration of reactants. However, we also found that the solvent-free reaction is not practical because the substrate is in the solid state and the formed polyester intermediate is a sticky paste. The selection of a suitable concentration of substrate is therefore necessary. Considering the solvent effect, acetic acid was found to facilitate the ring-opening process of tetrahydrofuran by the forming of acetate esters. [53] When acetic acid is used as the solvent, a medium level of yield can be obtained even at a lower hydrogen pressure (0.6 MPa) [Figure S1, ESI]. In contrast to previous reports, [54] the intermediate 1 and intermediate 2, in which the furan ring is saturated by hydrogenation, were obtained. No further reaction regarding to the ring-opening of tetrahydrofuran was noticed, which is different from the case with water as the solvent.

The product yield increased with extended reaction time, but the formation rate of the product decreased. A lower degree of polymerisation were observed in the ESI-MS spectra (Figure 2.b). Previous investigations on the rate of ester bond cleavage found that highly stabilised carbocations formed during the reaction make it easier to cleave the C_{alkyl}–O bond. [55, 56] Marks and co-workers found that the activity order of the C_{alkyl}–O bond in an ester is 3° > 2° > 1° (with respect to the alcohol). [49] Gordon et al. showed that it is difficult to break the C_{alkyl}–O bonds in 1° esters, since more than 10 % of the acetic ester products retained at 200 °C under 200 psi H_2 for 14 h. [57] In contrast, the reaction conditions employed herein are more moderate than these, and the yield of decanoic acid was higher due to the stronger Lewis acidity of W(OTf)$_6$ than that of La(OTf)$_3$. The straight chain ester mixtures obtained in the reaction were 1° esters (Figure 2.b). Cleavage of 1° esters requires relatively harsh conditions, and it takes a long time to reach the complete conversion of intermediates. To this end,

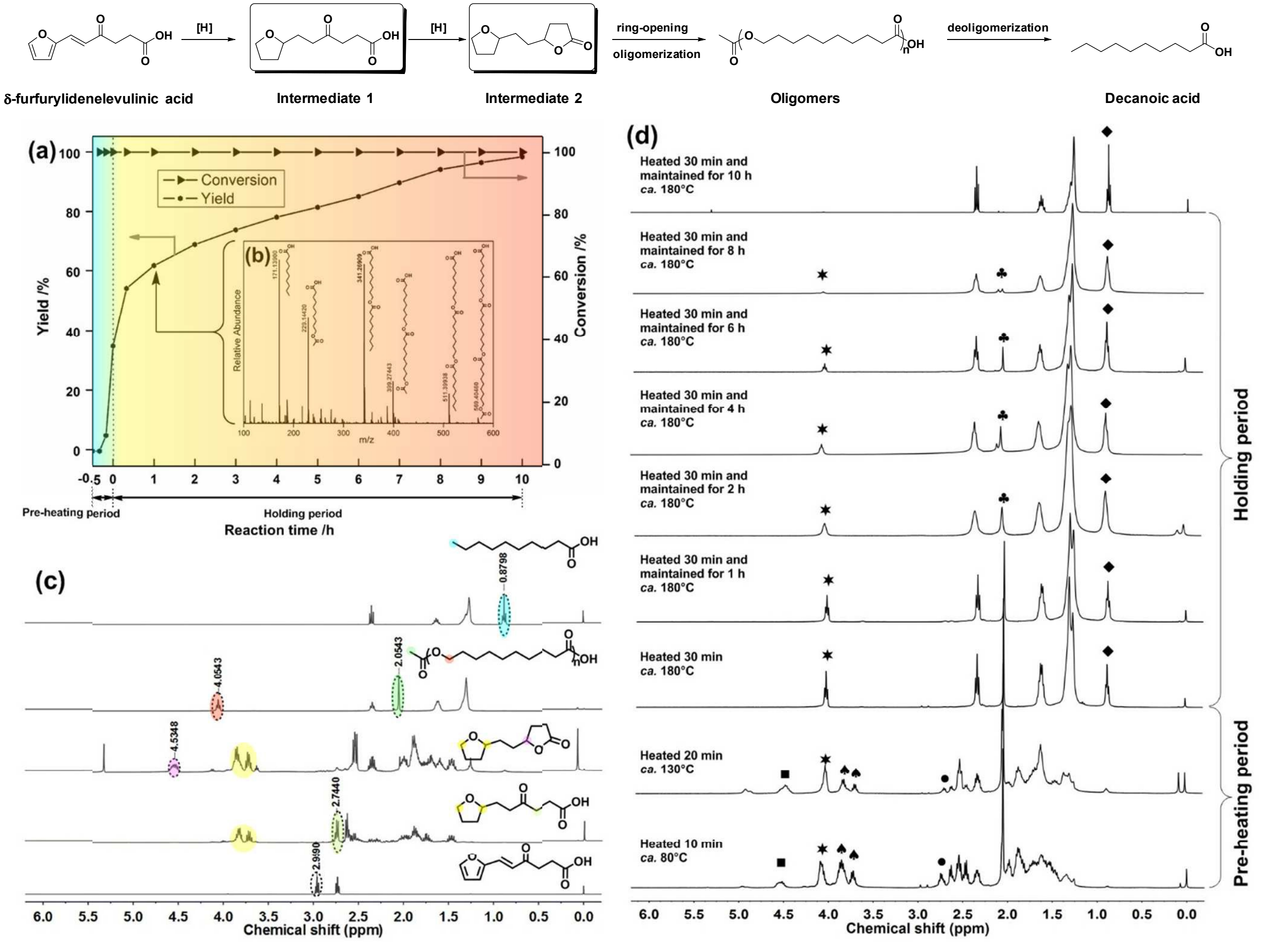

Figure 2. (a) Effect of reaction time on the yield of decanoic acid; (b) ESI-MS spectrum of reaction solution after 1 h; (c) Comparison of ^{1}H-NMR characteristic peaks of the substrate, intermediates, and products; (d) Comparison of ^{1}H-NMR spectra with different reaction times. [●]: Characteristic peaks belonging to intermediate **1**; [■]: characteristic peaks belonging to intermediate **2**; [♠]: characteristic peaks belonging to the tetrahydrofuran ring of intermediates **1** and **2**; [♦]: characteristic peaks belonging to decanoic acid; [✶]: characteristic peaks (~4.05 ppm) belonging to the hydrogen on the *α*-carbon of O atoms on the ester bond (-CO-O-C**H**$_2$-); [♣]: characteristic peak (~2.05 ppm) corresponding to the hydrogen atoms of the methyl groups on acetate (**CH$_3$**CO-).

decanoic acid can be obtained in nearly quantitative yield if the reaction time is extended to 10 h (Figure 2.a). The reaction solution was also analysed by ^{1}H-NMR spectroscopy (Figure 2.d). First, we compared the characteristic ^{1}H-NMR peaks of the reaction solution at different reaction times (Figure 2.c). It was found that the peaks at ~2.96 ppm, ~2.74 ppm, ~4.53 ppm, and ~0.88 ppm correspond to the starting material, intermediate 1, intermediate 2, and decanoic acid, respectively. We found that the exocyclic C-C double bond and the furan ring belonging to δ-furfurylidenelevulinic acid became saturated quickly (10 min) via hydrogenation during the pre-heating period. Meanwhile, intermediates 1 and 2 were the main products formed in this time interval, and no decanoic acid was observed. However, oligomeric straight chain esters were observed in small amounts. For the oligomers, the characteristic peak at ~4.05 ppm corresponds to the hydrogen atoms on the α-carbon adjacent to the alkyl O atom (-CO-O-C***H***$_2$-), and the characteristic peak at ~2.05 ppm belongs to the hydrogen atoms of the acetyl group (C***H***$_3$CO-). The results show that an enrichment of key intermediates occurred at this stage. After extending the pre-heating time to 20 min, the peaks of intermediate 1 were lowered, whereas the peaks of intermediate 2, oligomers, and a small amount of decanoic acid emerged. After heating for 30 min, the peaks of intermediates 1 and 2 completely disappeared and only those belonging to decanoic acid (~0.88 ppm) and polyesters (i.e., oligomers) were observed. Overall, as the reaction temperature and time increased, the intermediates gradually transformed into oligomer mixtures with different carbon-chain lengths (Figure 2.b).

As mentioned previously, acetic acid was found to block the growth of the polymer carbon chains and also facilitate mass and heat transfer processes. Termination of the polyester carbon chain occurred either when acetic acid was

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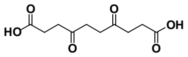
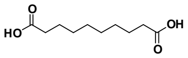
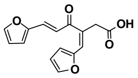
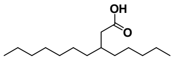
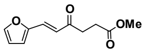
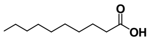
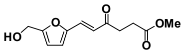
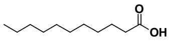
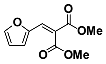
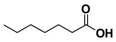
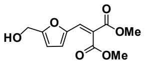
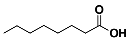
involved in the reaction or when the C–O bond of the terminal hydroxyl group of 10-hydroxydecanoic acid was cleaved. When the heating time was extended, the characteristic peaks (~4.05 ppm) corresponding to the hydrogen atoms on the α-carbon adjacent to the alkyl O atom (-CO-O-C***H***$_2$-) and the characteristic peaks (~2.05 ppm) belonging to the hydrogen atoms of the acetyl group (C***H***$_3$CO-) gradually disappeared. Concomitantly, the intensity of the characteristic peaks (~0.88 ppm) corresponding to the hydrogen atoms of the terminal methyl groups on decanoic acid gradually increased. After 10 h of heating, only the characteristic peaks of decanoic acid were observed.

Table 2. Substrate extension of other aldol condensation products using the Pd/C and W(OTf)$_6$ co-catalyst system.

Entry	Substrate	Product	Yield/%
1			88
2			72
3			94
4			90
5			85
6			80

Reaction conditions: 0.5 mmol substrate, 2 mol% 10% Pd/C, 6 mol% W(OTf)$_6$, 5 mL acetic acid, 180 °C, 3 MPa H$_2$, 10 h.

As noted, the industrial significance of sebacic acid encouraged us to prepare it from biomass-based feedstock. The starting material (i.e., δ, δ'-dilevulinic acid) can be prepared through the acid-promoted hydrolysis of δ-furfurylidenelevulinic acid (please refer to the ESI for a plausible mechanism).[58] Gratifyingly, it was found that δ, δ'-dilevulinic acid could be efficiently converted to sebacic acid at an improved yield of 88 % using our catalytic protocol (Table 2, Entry 1). Meanwhile, attempts were made to expand the substrate scope using this protocol (Table 2, Entry 2). In addition to the hydrolysis of biomass feedstock, alcoholysis of biomass raw material is an alternative method utilized in industry, though such a process generates levulinic esters rather than levulinic acid. Thus, reactions using esters as the starting material were conducted (Table 2, Entries 3–4). However, the results show that the methyl ester cannot survive in this procedure, which may be due to a transesterification reaction occurring in the acetic acid solvent. The synthesis of heptylic acid and caprylic acid were also studied by introducing methylmalonate in the aldol condensation reaction. The corresponding products were obtained by decarboxylation, transesterification, and hydrodeoxygenation (Table 2, Entries 5–6). Overall, a satisfactory yield of all saturated acid products was obtained, and good substrate compatibility was established.

Finally, given the excellent catalytic ability of metal triflate in esterification reactions,[59, 60] as well as the importance of medium-chain carboxylic acid esters in numerous applications, a one-pot two-step process has been established for synthesising medium-chain fatty acid esters from biomass substrates [ESI, 'The Reaction Application'].

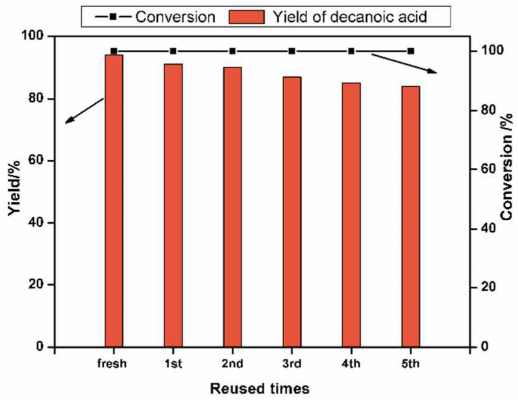


Figure 3. The catalyst circulation experiment of Pd/C catalyst. Reaction conditions: 1 mmol δ-Furfurylidenelevulinic acid, 2 mol% 10% Pd/C, 6 mol% W(OTf)$_6$, 5 mL acetic acid, 180 °C, 2 MPa H$_2$, 8 h.

The catalyst circulation experiment of Pd/C was carried out and the results were listed in the Figure 3. The experimental operation for the recycling of Pd/C catalyst was listed in the SI ('Further Screening of Reaction Conditions'). The catalyst yield was declined slightly after five cycles. This indicated that the catalytic effect of Pd/C catalyst appeared partially decreased. We carried out transmission electron microscopy (TEM) (**SI, Figure S4, Figure S5**) test to investigate the loss of catalyst activity during catalyst circulation process. The TEM graphs showed that the Pd/C catalyst was partial reunion after recycling. The decreased yield may be due to the partial reunion of Pd/C catalyst and the loss of catalyst in the operation process. Hydrogenation of the double bonds in the substrates and intermediates by Pd/C catalyst can prevent the occurrence of undesired polymerization reactions. This may be the reason that the product yield decreases gradually with the recycling.

Conclusions

In summary, an efficient strategy for the preparation of medium-chain carboxylic acids and their derivatives from biomass-based feedstock has been developed. Different from previous reports on the hydrogenation of condensation intermediates, a carboxylic acid product rather than an alkane or alcohol was successfully obtained using our metal triflate and Pd/C co-catalytic system. Notably, the carboxylic acid structure can be retained with our catalytic protocol, while all the other oxygen atoms are selectively removed.

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Acetic acid and metal triflate were found to significantly promote the ring opening of tetrahydrofuran and the subsequent depolymerisation of the oligomer intermediates. Meanwhile, the substrate scope was expanded to prepare other biomass-based medium-chain carboxylic acids. Overall, this study demonstrates a novel and general route for the preparation of medium-chain aliphatic carboxylic acids using cellulose-derived platform molecules.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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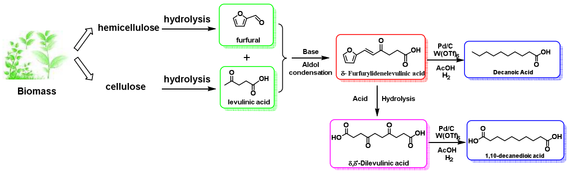
Synthesis of Medium-Chain Acids or α, ω-Dicarboxylic Acids from Cellulose-Derived Platform Chemicals



Applying $M(OTf)_n$ + Pd/C co-catalyst for production of medium-chain carboxylic acids from carbohydrate derivatives by means of selective hydrodeoxygenation.