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Deoxygenation of biobased molecules by decarboxylation and decarbonylation – a review on the role of heterogeneous, homogeneous and bio-catalysis

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Use of biomass is crucial for a sustainable supply of chemicals and fuels for future generations. Compared to fossil feedstocks, biomass is more functionalized and requires defunctionalisation to make it suitable for use. Deoxygenation is an important method of defunctionalisation. While thermal deoxygenation is possible, high energy input and lower reaction selectivity makes it less suitable for producing the desired chemicals and fuels. Catalytic deoxygenation is more successful by lowering the activation energy of the reaction, and when designed correctly, is more selective. Catalytic deoxygenation can be performed in various ways. Here we focus on decarboxylation and decarbonylation. There are several classes of catalysts: heterogeneous, homogeneous, bio- and organocatalysts and all have limitations. Homogeneous catalysts generally have superior selectivity and specificity but separation from the reaction is cumbersome. Heterogeneous catalysts are more readily isolated and can be utilised at high temperatures, however they have lower selectivity in complex reaction mixtures. While bio-catalysts can operate at ambient temperatures, the volumetric productivity is lower. Therefore it is not always apparent in advance which catalyst is the most suitable in terms of conversion and selectivity under optimal process conditions. Here we compare classes of catalysts for the decarboxylation and decarbonylation of biobased molecules and discuss their limitations and advantages. We mainly focus on the activity of the catalysts and find there is a strong correlation between specific activity (turn over frequency) and temperature for metal based catalysts (homogeneous or heterogeneous). Thus one is not more active than the other at the same temperature. Alternatively, enzymes have a higher turnover frequency but drawbacks (low volumetric productivity) should be overcome.

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1. Introduction

In order to ensure our planet remains habitable for future generations and to satisfy our needs for chemicals, fuels and energy, the use of renewable resources has become essential. This has motivated the European Commission to strive for the use of 20% by usage of renewable energy sources, 20% reduction in CO_2 emission compared to 1990, and 20% increase in energy efficiency, by 2020.[1] In order to achieve these ambitions alternative energy and fuel sources have been developed, such as solar,[2] geothermal,[3] hydropower[4] and biofuel production from biomass.[5] While a number of such developments are promising for energy supplies, only biomass feedstocks satisfy our need for the production of chemicals and materials.

Biomass is extremely diverse in its composition, which necessitates the development of a biorefinery. A biorefinery is defined as "*a facility that integrates biomass conversion processes and equipment to produce fuels, power, and chemicals from biomass. The biorefinery concept is analogous to today's petroleum refineries, which produce multiple fuels and products from petroleum*".[6] One example of this in practice can be seen by looking into current-technology for bioethanol production, where a single plant[7] produces not only ethanol, but also electricity and dried distillers grains and solubles (DDGS), which is sold as animal feed.

The development of chemical production from biomass using fermentation is already becoming economically and industrially viable. Products such as 3-hydroxypropionic acid and lactic acid (for the production of acrylic acid) are currently emerging onto the market,[8] and even hydrocarbon-based fuels

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are being produced fermentatively.[9] The feedstock of choice for fermentation is glucose or glucose containing substrates such as starch or, more recently, cellulose.[10] Recent research has focused on deriving these from sustainable secondary material streams *e.g.* second generation lignocellulosic fermentation,[11] utilising cornstover or wood from otherwise unproductive land[12–14] or chemical and thermal reclamation from waste such as slaughterhouse effluents or household garbage.[15,16]

So far, a significant focus has been on fermentative techniques for bio-based chemical production due to low temperature selective conversions and the ability for molecules to undergo various transformations in one processing step. However, fermentation processes can have low substrate/product concentrations in water which requires isolation. Another means of inducing chemical transformation is by using (bio)chemical transformation. Enzymes have also been successfully applied in industry for bulk chemical production. The use of nitrile hydratase[17] for acrylamide production from acrylonitrile has been employed industrially since the 1990's and is preferred to the chemical conversion as it leads to lower side product formation. Amino acids can be produced enzymatically, *e.g.* alanine from fumaric acid using aspartase.[18] Hydrolysis reactions in general are very important in industrial applications of enzymes, for example peptidases[19] and lipases[20] used in biological washing powders, and α-amylase[21] and cellulase[10] are being investigated for their application in the production of glucose for fermentation. The high selectivity and retention of chirality of enzymatic conversions is of particular interest for medicines, where single enantiomers are required.[22,23] For example, ketoreductases can be used to selectively produce single enantiomeric products from racemic starting materials. However, the high selectivity of enzymes can be problematic when using racemic feedstocks, as up to 50% of the starting material may not be transformed.[24] The use of enzymes is considered one of the most expensive components of biomass conversion.[10,25]

Chemo-catalytic conversion can be used to produce chemicals with high volumetric turnovers and are widely used in current chemical synthesis techniques. For the conversion of biomass current examples include high intensity techniques like gasification of biomass to form bio-syngas.[26–28] This can be fed into Fischer–Tropsch reactors to produce waxes and paraffins for fuels.[29–31] Pyrolysis of biomass such as woodchips allows for the production of bio-oil,[32] lignin depolymerisation in supercritical carbon dioxide allows for the production of BTX-like aromatics for the chemicals industry.[33] Lower temperature chemical conversions are also common, such as the production of isosorbide, a monomer and plasticising agent,[34] from glucose[35] or cellulose.[36] Ethanol dehydration to green ethylene is a large and growing area.[37] Furandicarboxylic acid, a novel plastic monomer[38] can be produced from fructose *via* hydroxymethylfurfural.[39] Fatty acid transesterification is also chemocatalysed[40] and the byproduct, glycerol, is industrially converted into epichlorohydrin,[41,42] a monomer used for resin production.[43]

An important trend in the conversion technologies used in combination with biomass is that they tend towards defunctionalisation, including deoxygenation. An example of this is the fermentation of ethanol from glucose, where the mass percentage of oxygen drops from 53% to 34%. This is due to the desire to supply 'drop-in' replacements (identical to current chemicals and products) to maintain the current market requirements, and crude oil-derived end products have comparatively low functionality compared to biomass. Decarboxylation offers opportunities to produce existing products from bio-based molecules to make products of a similar Gibbs free energy in a simple transformation. Decarboxylase enzymes comprise of 80 members, mostly amino acid decarboxylases. Examples of using these enzymes have been investigated[44–46]

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in significant detail on the transformation of biomass,[25,47] but reviews on chemocatalytic defunctionalisation are less prolific. Defunctionalisation by removing oxygen can be performed using hydrodeoxygenation, decarboxylation and decarbonylation. Hydrodeoxygenation has been reviewed previously for biobased feedstocks and will be left out of the current review.[48] In our review we will focus on the decarboxylation and decarbonylation transformations of bio-based molecules such as a variety of aromatic and aliphatic molecules, including amino acids, into industrially relevant compounds using hetero-, homo- and bio- catalysis. It will attempt to draw parallels between the use of a specific catalytic systems on various substrates, and also between types of conversion, showing the resulting activity, selectivity's, and where appropriate, mechanistic details. Based on this review of the literature, we show the relation of activity for decarboxylation and decarbonylation as a function of the type of catalyst under various operating conditions.

2. Homogeneous catalysis

2.1. Silver/copper decarboxylation/decarbonylation

In the presence of catalytic quantities of silver(I) salts, it was originally shown that fatty acids are able to undergo decarboxylation to alkanes. Fatty acids are commonly found in nature as components of oils, such as those derived from plants (*e.g.* soybean oil, palm oil), algae, and animal sources (*e.g.* tallow, lard). They are typically pressed out of seeds as an oil, which usually consists of triacylglycerides, where three long chain fatty acids are attached to glycerol by ester linkages, and must be hydrolysed to form free fatty acids and glycerol. There are two broad classes of fatty acid: saturated fatty acids such as stearic acid ($C_{18}H_{36}O_2$) and palmitic acid ($C_{16}H_{32}O_2$) which typically come from animal fats, and unsaturated fatty acids such as oleic acid ($C_{18}H_{34}O_2$) and linoleic acid ($C_{18}H_{32}O_2$) which typically come from plant sources, and typically have lower melting points due to their more bulky structures. The distribution of these molecules from different sources is covered in other works.[40] As these molecules are very rich in carbon and hydrogen and otherwise poor in functional groups, they are attractive for the formation of fuels and oils. Global production scale is around 6.5 billion litres, as per 2006.[49] Current transformation methods for fatty acids involve the production of fatty acid methyl esters (FAMEs) by transesterification from glycerol, in order to produce bio-diesel, a fuel product that can supplement diesel fuels.[50] Diesel typically comprises of aliphatic hydrocarbons of between 9 and 28 carbon constituents, with an aim to contain as little aromatic residues as possible in order to prevent carcinogenic effects.[51] FAMEs from plant origin are between 9 and 21 carbons in content and do not contain aromatic moieties by default, therefore are an excellent replacement. As of 2011, the United States has a production capacity of 2.1 billion litres per year of biodiesel,[52] and in Europe, the EU2020 directive promotes replacement of 10% transportation fuel by biofuel by the year 2020.[1] However, FAMEs suffer a reduction in lower heating value from 43 MJ kg^{-1} to 37 MJ kg^{-1}, and are considered to be only 91% as effective in a combustion engine when compared to conventional diesel.[53] They also suffer from an increase of cloud point by 10 to 15 °C, decreasing the ability for this fuel to be effective in colder climates.[54] Thus, current research has been focused on converting plant oils into a drop-in substitute for diesel fuel in order to maintain the desired properties. Thus, a decarboxylation reaction to remove oxygen is required to form alkanes or alkenes which can be used as fuel.

Heavy metals have been known to allow the decarboxylation of fatty acids for many years, such as by the use of lead tetraacetate.[55] However, as this reaction requires stoichiometric amounts of lead, it is not catalytic and will not be covered any further. The use of silver(I) salts and sodium peroxydisulphate to produce alkenes by oxidative decarboxylation has been

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observed previously.[56,57] In these reactions the driving force comes from the peroxydisulphate ion, which produces silver(II) ions in solution. These ions are able to selectively decarboxylate fatty acids.[58] The peroxydisulphate ion is a strong oxidising agent itself that can be used to oxidise several organic species such as formic acid and small alcohols in water, but is unselective.[59] The mechanism for this reaction has been expanded upon in further work.[60] Drawing together these references, we see that this reaction proceeds *via* the formation of a silver(II) ion in solution after reaction with the peroxydisulphate as shown in Fig. 1.

This reaction proceeds *via* the formation of a silver–carboxylate complex **B**, then radical initiation to form an unstable carboxyl radical. This subsequently degrades into an alkyl group **E**. It was initially unclear whether the *in situ* formation of silver(II) ions proceeded *via* single electron oxidation to directly oxidise silver(I), or a two electron process to form silver (III) followed by disproportionation with silver(I) to form silver (II). Initially these were kinetically inseparable, but silver(III) ion disproportionation was confirmed as the correct mechanism in a later work.[61] This is advantageous: silver(III) ions are capable of oxidizing water to oxygen at room temperature,[58] and a low concentration of these should be maintained in order to keep efficiency high.[62] As the reaction was shown to be proportional to pH, the reaction to form molecule **B** was stated to be the rate determining step. Normally, the formation of **C**, **D** and **E** proceed rapidly from there. With the addition of copper(II) salts to this reaction, additional coordination of the alkyl radical occurs to form **F** in Fig. 1, stabilising it and allowing oxidative elimination to occur. This enables the pathway to instead effectively decarbonylate, and produce alkenes **G**,[63] or primary alcohols **H**, where X = OH. As the copper(II) ion is itself reduced by these actions, it must be regenerated, using more peroxydisulphate. In terms of a Green Chemistry approach, the use of further use of reagents is considered less attractive.

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Harry Bitter is Professor of the group Biobased Chemistry and Technology at Wageningen University. His group focuses on the sustainable production of bulk chemicals and fuels from biomass by an integrated approach. The group motto is TIPTOP chemistry and technology: Turning variable InPut into Tailored OutPut, one of the great challenges in biomass conversion. He studied chemistry at the Radboud University and obtained his PhD at the University of Twente. He continued working in the field of heterogeneous catalysis at Utrecht University, focusing on the use of spectroscopy in catalysis. During the last years he has focused on the application of catalysis in biomass conversions and the use of carbon-based catalysts.

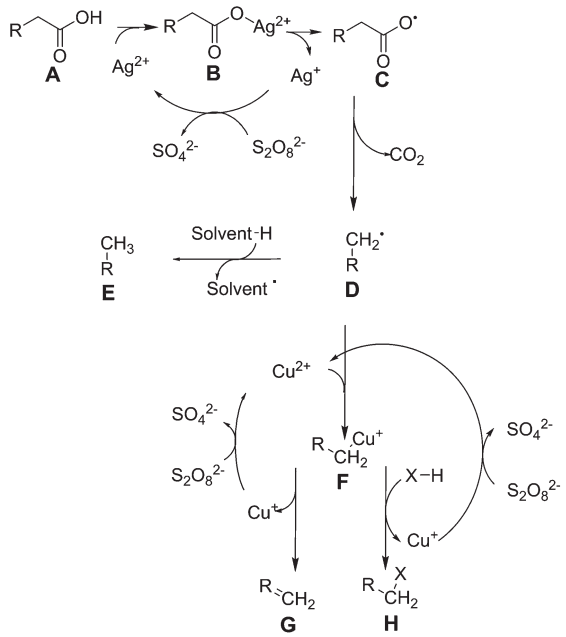

Fig. 1 Reactions controlling silver(II) and copper(II) mediated fatty acid oxidative decarboxylation.

Recently, silver nitrate was used as a catalyst for decarboxylation of several saturated (stearic and palmitic acid) and unsaturated (oleic, ricinoleic, eliadic, linoleic, linolenic) fatty acids.[64] In the case of saturated fatty acids, it was shown that a selectivity for alkanes of max. 50 mol% at complete conversion when using palmitic acid as a substrate. This reaction was performed at 78 °C for 20 min, in water–acetonitrile 5 : 9 in the presence of silver nitrate and sodium peroxydisulphate. The details and yields can be seen in Table 1. The other side products for this reaction are not characterised, but a small fraction of 1-pentadecenol and pentadecene were observed in the reaction mixture. By using thermogravimetric analysis, as much as 35 mol% of the material is noticed at 200–500 °C, and up to 10 mol% from 500–800 °C, implying that a significant amount of polymerisation is occurring in the radical-based reaction. With the addition of copper(II) sulphate, 37 mol% 1-alkene and 22 mol% 1-alkanol was produced from

Table 1 Decarboxylation of palmitic acid by silver and copper salts with sodium peroxydisulphate[a]

$AgNO_3$	$CuSO_4$	$Na_2S_2O_8$	Conversion %	A	B	C
1	—	0.5	80	<1	19.6	<1
1	—	2.5	97	<1	49.9	<1
1	1	0.5	93	12.3	<1	7.4
1	1	2.5	99	35.4	2.2	16.5

[a] Reaction conditions: Acetonitrile : H_2O, 9 : 5, 20 min, 78 °C A: pentadecane, B: 1-pentadecene, C: 1-pentadecanol.

palmitic acid. The authors note that the terminal alkene is not the only product of this reaction. As the copper(II) salt can coordinate with alkenes, at the reaction temperature of 78 °C it allows for an isomerisation to occur, moving the double bond along the molecule, and thus affecting the purity of the final product, however the overall selectivity for monomeric products was increased. When using unsaturated fatty acids the problem of incomplete mass balance becomes more significant due to the presence of reactive double bonds in the molecule, increasing the probability of polymerisation, however 10–35% of the desired alkane or alkene was obtained. Other authors have further investigated and reviewed the mechanistic pathways in the deoxygenation of vegetable oils.[65]

Aromatic molecules are produced in plants and animals on a regular basis (such as products of the shikimic acid pathway[66]), and some aromatic chemicals can be made from the resultant biomass components. For example, plant oils derived from terpenes can be rich in benzoic acid, for example benzoin resin. The latter can be derived from the bark of the *Styrax* species of tree where up to 40% is benzoic acid, and 40% cinnamic acid can be present.[67] Another source could be citrus peel oil, where *p*-cymene can be found, which can be subsequently converted into other compounds.[68] However, no method of producing aromatic compounds from biomass is yet adopted by the market, largely due to plant oils being either in very low concentrations, or the plants very slow growing and thus have a low productivity. Alternatively, a substantial source of biomass-derived aryl rings could be lignin. Lignin is described in more detail later in this review, but briefly, depolymerised lignin can contain oxygenated aromatic structures such as vanillic acid and syringic acid and phenol.[33,69] Silver(I) has been shown to act as an efficient decarboxylating agent of aryl carboxylates such as *ortho*-anisic acid, producing 98 mol% anisole in the presence of 10 mol% silver(I) acetate and 15 mol% potassium carbonate in *N*-methylpyrrolidone (NMP) at 120 °C for 16 hours, as shown in Table 2. They also showed that silver(I) can decrease the activation energy for the decarboxylation of 2-fluorobenzoic acid to as little as 29 kcal mol^{-1} when NMP is used as a solvent.[70,71]

Besides silver salts, copper(I) has also been shown to act as a catalyst for the decarboxylation of compounds such as cinnamic acid.[72] Here, 20 mol% of copper(I) bromide was used, in addition to 240 °C and 2 equivalents of 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU) for a 30 minute period to produce styrene at 75% yield.

Silver(II) and peroxydisulphate mixtures can also be used to decarboxylate amino acids.[73] Amino acids could be an interesting feedstock for the formation of chemicals, as several are structurally similar to current industrial chemicals.[74] With the use of decarboxylation reactions a number of relevant products could be obtained. At catalytic concentrations of silver(II) in water they successfully showed that a radical mechanism occurs, shown in Fig. 2. Interestingly, they show that at higher concentrations a cyclic structure is formed, where the silver atom bridges between the amine and carboxyl groups, potentially directing towards alpha decarboxylation. The main product of this reaction is an imine, which is not a commonly found intermediate in industrial applications. If this reaction were to be performed in a more selective approach it would produce an amine.

Butanone, which can be produced from levulinic acid by decarboxylation, is used as an industrial solvent, and has a

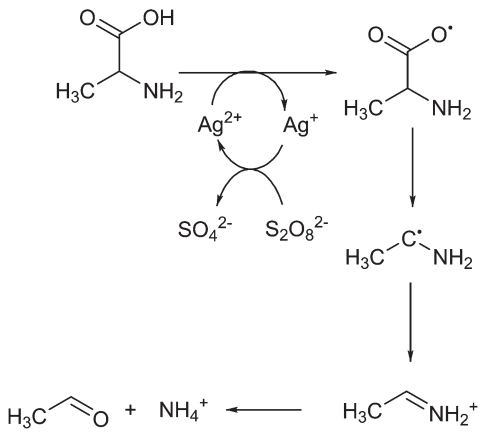

Fig. 2 Amino acid decarboxylation by silver(II).

Table 2 Decarboxylation of anisic acid to anisole[a]

Catalyst	Amount catalyst (mol%)	Ligand[b]	Additive[c]	Solvent	Temp (°C)	Yield (mol%)
Ag_2O	5	Phen[d]	—	NMP/quin[e]	170	22
Ag_2O	5	Phen[d]	—	NMP	170	85
Ag_2O	5	Phen[d]	—	NMP	120	60
AgOTf	10	Phen[d]	—	NMP	120	0
AgOAc	10	Phen[d]	—	NMP	120	70
AgOAc	10	PPh_3	—	NMP	120	0
AgOAc	10	—	—	NMP	120	24
AgOAc	10	—	K_2CO_3	NMP	120	98
AgOAc	10	—	K_2CO_3	NMP	80	60

[a] Reaction conditions: 16 h. [b] 10 mol%. [c] 15 mol%. [d] 1,10 phenanthroline. [e] Quinolone.

market scale of about 0.3 million tons per year.[75] Levulinic acid is a compound formed by the hydration of hydroxymethylfurfural (HMF), which itself is formed by the dehydration of glucose (or fructose) in the presence of (Lewis or Brønsted) acid catalysts.[76] These steps are shown in Fig. 3. HMF is a platform chemical in its own right,[39] being capable of being transformed into several other industrially relevant compounds including furandicarboxylic acid (FDCA) or caprolactam.[77] HMF has also been shown to undergo selective decarbonylation to furfural alcohol using Ir based catalysts.[78] Fructose is either found in nature as a monosaccharide and is significantly more active than glucose for the formation of HMF and levulinic acid.[79] The reaction from glucose is considered to proceed *via* the transformation into fructose, but is shown in the diagram as glucose is sourced from both starch and cane sugar sources and thus has a wider application. Levulinic acid has the potential to be a platform molecule for the production of chemicals such as 2-methyl tetrahydrofuran (a novel solvent or fuel oxygenate),[80] diphenolic acid (a novel monomer),[81] or used in the form of levulinic esters as fuel.[82] However, originally the impact of this molecule may be somewhat diminished as the estimated cost of production has risen in recent years from a low \$0.10/kg^{-1} up to a substantially higher \$10 per kg.[76] In the decarboxylation of levulinic acid with silver(I) phosphate and sodium peroxydisulphate in an aqueous buffer solution of citric acid and sodium hydrogen phosphate, the rate of reaction relies upon the availability of carboxylate groups for the silver(I) ions to coordinate to.[83] Thus, a sharp peak of activity occurs at pH 4 and above, resulting in an increase from almost 0 to 30% yield of butanone, with the conversion of levulinic acid changing from <5% to nearly 80%. At a pH lower than 4, they report no butanone production and that the main product is acetone. This is reported to be a side product of their buffer, citric acid, degrading in the reaction conditions instead of levulinic acid. The best yield of butanone was 43% after 30 minutes at 140 °C in an autoclave, at a selectivity of just over 60%. They also report production of methyl vinyl ketone when copper(I) was used in place of silver(I), but no clear yield analysis was undertaken.

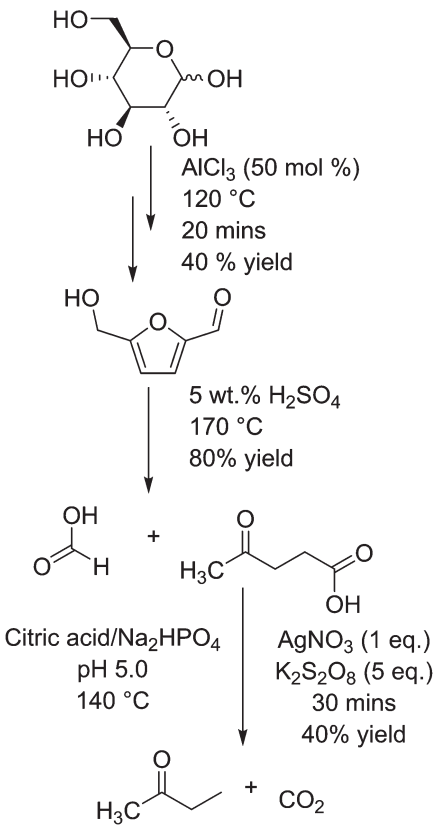

Fig. 3 Formation of butanone from glucose *via* hydroxymethylfurfural and levulinic acid.

2.2. Palladium decarbonylation

Carbonylation reactions are readily used in industrial scales, such as in the petrochemical synthesis of acetic acid amongst others.[84] This process relies upon the presence of an $Ir(CO)_2I_2$ catalyst in solution. Before this was the Monsanto process based on $Rh(CO)_2I_2$ catalysis.[85] Palladium(II) also shows carbonylation activity. However, its activity is less attractive than rhodium or iridium.[86] However, when it comes to decarbonylation, at least of furfural, palladium-based catalysts show markedly higher activity compared to other transition metals.[87]

Furfural is a major product from the dehydration of C_5 sugars, mainly xylose and arabinose, originating from the hemicellulose component of lignocellulose.[88] The amount of hemicellulose is between 5% for softwoods and up to 25% of the dry weight for hardwoods.[89] Bagasse from sugarcane also contains between 26 and 30% pentosan sugars by weight,[90] and some foodstuff by-products such as corn husks contain up to 28 wt% xylose.[91] Given that these materials would otherwise be used for their caloric value, these feedstocks are preferable to wood in an industrial capacity. Due to the low overall yield involved with the production of furfural at large scale, the estimated market price of furfural is around 1700 \$ per ton.[88] The decarbonylation of furfural can be used to produce furan, an intermediate in the production of tetrahydrofuran (THF), a widely used solvent (Fig. 4). Furfural is also a promising intermediate for the synthesis of chemicals or fuel applications. Examples include methyl tetrahydrofuran and ethylfurfuryl ether as fuel oxygenates, as well as complex aldol condensation routes to C_{10} and C_{15} molecules which can be hydrogenated to form branched alkanes.[82]

Shown in Fig. 5 is the mechanism elucidated for the decarbonylation of fatty acids by palladium(II)-based homo-

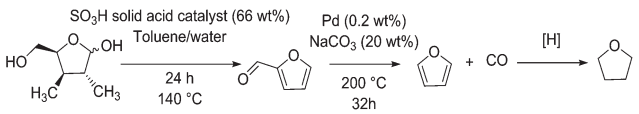

Fig. 4 Formation of tetrahydrofuran (THF) *via* furfural from xylose.

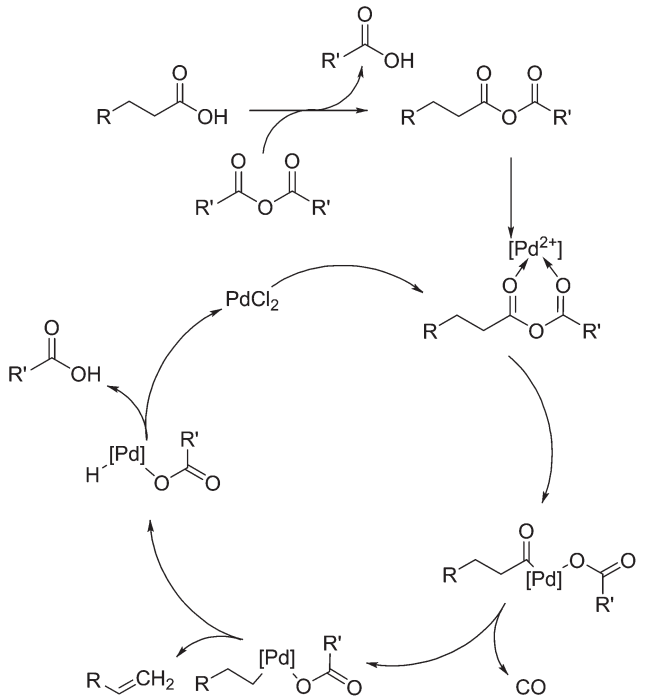

Fig. 5 Palladium-catalysed decarbonylation of fatty acids *via* anhydride formation.

geneous catalysts, as proposed by Gooßen *et al.*[92] and extended by others. This mechanism is reinforced by the detail that Gooßen *et al.* showed that the reaction takes place in an analogous fashion when an enol ester is substituted for the anhydride.[93,94] It is thought that decarbonylation proceeds *via* the formation of an anhydride, which then allows the coordination of the palladium(II) salt. The anhydride is cleaved to produce an acyl anion, which then coordinated to the palladium atom. As the product of this reaction is an alkene, isomerisation of the double bond is an issue, but it can be eliminated by the use of correct conditions and ligands.

Originally, the use of bis(2-diphenylphosphinophenyl)ether (DPEPhos) ligands and 125 °C was selected as a means of limiting the products to only 1-alkenes. It was shown that the use of pivalic anhydride can produce the required anhydride to promote decarbonylation, but further research shows the use of acetic anhydride produced comparable results.[95] The use of stearic acid anhydride as a substrate also proceeded to 94% yield with a production of 93% stearic acid, indicating the addition of an auxiliary anhydride may not be necessary. Maetani *et al.* also showed that palladium(II) is not necessary either, showing a successful decarbonylation occurring with iron(II) chloride as a catalyst.[96]

One other conclusion from Gooßens work is that DPEPhos is needed as a ligand for $PdCl_2$ to improve activity and selectivity in the transformation of phenylbutanoic acid, as the use of other phosphorus-based ligands allows for too-rapid isomerisation and loss of selectivity. By this same transformation method it was shown that palmitic acid could be transformed into 1-pentadecene with 64% yield after 16 h reaction time with 3 mol% catalyst in 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU), see Table 3. DPEPhos is not always required when isomerisation is not an issue, such as the decarbonylation of hydrocinnamic acid (described in 3.5) to hydroxystyrene, or of succinic acid monoester to acrylic acid ester.[97] The conclusion drawn is that the much cheaper PPh_3 ligand is almost as effective as DPEPhos in these reactions, indicating the role of this ligand as a moderator for by-product formation. In a similar reaction with $IrCl(CO)(PPh_3)_2$, the reaction conditions required to achieve good yields are much more stringent (250 °C rather than 110 °C).[98] Under most circumstances, this catalyst shows a high selectivity for isomerisation at such high temperatures and in some cases produces less than 1% terminal alkenes. The follow-up work of this paper shows that the complex $Fe(CO)(Cl)_2$ can be substituted for palladium in these reactions, although they show that the problem of isomerisation of the double bond can account for up to 9% of the final product, such as in the use of phenylbutanoic acid.

Significant work has been performed by the group of Gooßen *et al.* into the use of palladium(II) based catalysts as centres for aryl carboxylate decarboxylation, particularly for coupling reactions (Fig. 6).[99,100] For Heck-type coupling reactions, the mechanism proceeds *via* a reductive elimination in order to remove carbon dioxide, so an oxidant is required to drive the reaction. The original work on this field uses silver nitrate as an oxidant,[101] but this can be replaced with oxygen as the electron acceptor,[102] without significant impact on yields or selectivity. For decarboxylative cross coupling, the

Table 3 Decarbonylation of fatty acids by Pd or Fe salts and anhydrides

Fatty acid R =	Anhydride R′ =	Catalyst	Ligand	Solvent	Yield 1-alkene (mol%)	Yield other alkene (mol%)
$PhCH_2CH_2$	^{t}Bu[a]	$PdCl_2$	DPE-Phos	NMP	70	<2
n-$C_{13}H_{27}$	^{t}Bu[a]	$PdCl_2$	DPE-Phos	DMPU	64	—
$PhCH_2CH_2$	Me[b]	$FeCl_2$	DPPPent[c]	—	56	2
n-$C_{13}H_{27}$	Me[b]	$FeCl_2$	DPPPent[c]	—	65	6
n-$C_{15}H_{31}$	n-$C_{17}H_{35}$[b]	$FeCl_2$	DPPPent[c]	—	94	—

[a] 2 eq. Anhydride, 3 mol% cat. 9 mol% ligand, 110 °C, 16 h. [b] 10 mol% cat. 20 mol% ligand, 1 eq. KI, 1 eq. anhydride, 240 °C, 3 h, CO (20 atm). [c] 1,5-Bis(diphenylphosphino)pentane.

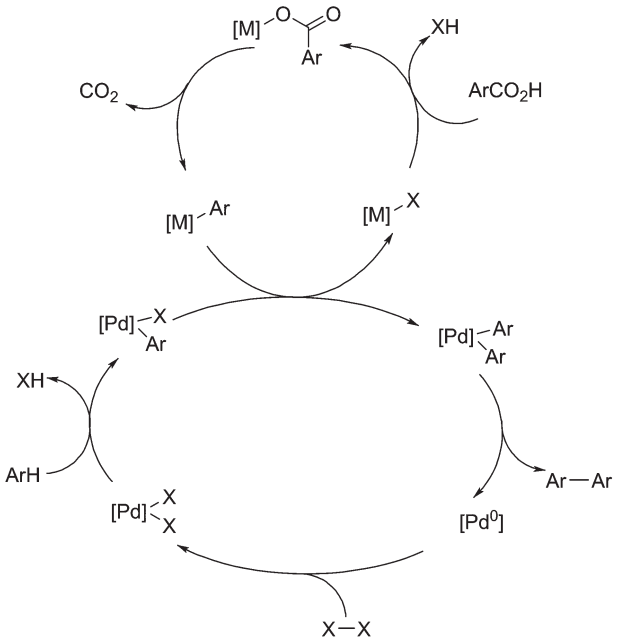

Fig. 6 Decarboxylative coupling with Pd(II) and a second metal (M = Cu(I), Ag(I)).

primary mechanism is by transmetalation of aryl ligands and subsequent reductive elimination, shown below in Fig. 6. Because palladium(II) is not a very active decarboxylation catalyst, copper(I) or silver(I) is used to promote decarboxylation, and subsequently transfer the resulting aryl groups over to palladium.[103] There they can be coupled with groups from aryl halides,[104] other aryl carboxylates,[105] or aryl groups produced by C–H activation.[106] This reaction is useful for the utilisation of benzoic acid derivatives and producing compounds for azo dyes or other coloured compounds. In addition, the ability for this to activate C–H aryl bonds gives it added purpose in the utilisation of lignin-derived compounds.

2.3. Henkel reaction

Henkel decarboxylation can be used to disproportionate the presence of carboxyl groups on aromatic molecules. Research on this reaction was originally performed for the production of terephthalate from benzoate, discovered in 1952 by Henkel et Cie.[107] to work over cadmium salts at 500 °C. Terephthalic acid is used in the production of poly(ethylene terephthalate) (PET), a plastic used for its controllable crystallinity, transparency and low permeability of gases, and has a global production of above 40 million tons per year.[108] Unlike the mechanism for silver-catalysed decarboxylation, this reaction proceeds *via* two-electron abstraction of CO_2, and the use of cadmium(II) allows for proton abstraction, as shown diagrammatically in Fig. 7. It would appear that the catalyst is required for the selectivity for thermodynamic products, as Henkel-like activity has been observed in the pyrolysis of coal products at 425 °C, but the main product observed is phthalic acid rather than terephthalic acid.[109] The mix of products in the reaction

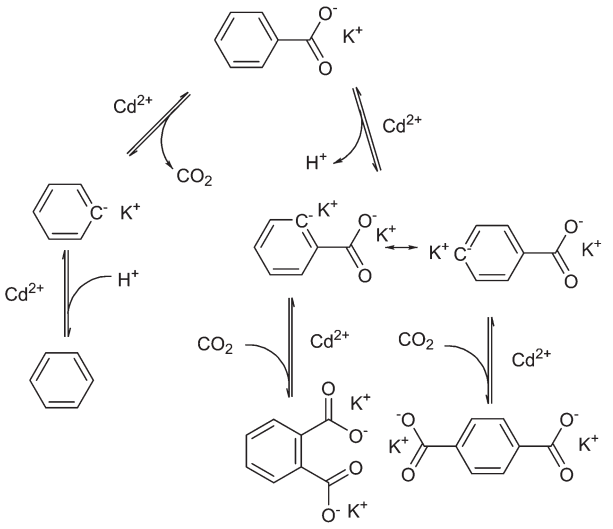

Fig. 7 Radical rearrangement of Henkel reaction products.

system eventually disproportionates and rearranges to form the products, benzene, and the thermodynamic product 1,4-terephthalate.[110]

It is worth mentioning here that terephthalic acid can also be derived from other biomass sources such as *via* the oxidation of biomass-derived xylene.[111] Xylene can also be formed by dimerization of isobutene, produced by glucose fermentation to isobutene[112] or dehydrated bio-isobutano.[113] Other methods include the oxidation of *para*-cymene,[114] and the Diels–Alder reaction of muconic acid and ethylene followed by aromatisation.[115] These are attractive processes for the production of 'drop-in' compounds from bio-based origins, however they are beyond the scope of this review.

Analogous to the Henkel route to terephthalic acid from benzoic acid, this reaction can be applied to furoic acid, derivable from furfural to form 2,5-furandicarboxylic acid (FDCA).[116,117] Pan *et al*. showed an 86% selectivity for FDCA when this reaction was performed at 250 °C under 38 bar CO_2 for 3 hours with zinc chloride as a catalyst, see Fig. 8.[118] FDCA, when used in place of terephthalic acid to produce poly(ethylene furandicarboxylic acid) (PEF) can have similar physical properties to PET.[119] FDCA can also be produced by the oxidation of 5-hydroxymethylfurfural, shown in section 2.1 to be able to be obtained from glucose by dehydration. This oxidation is reported to occur by the use of stoichiometric potassium permanganate,[120] but recently has

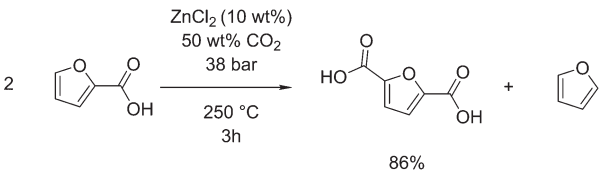

Fig. 8 Henkel reaction performed on furoic acid.

been found to occur readily with the use of gold nanoparticles on cerium oxide supports, giving as much as 99 mol% selectivity at 130 °C in water with air as an oxidant.[121] One benefit of the Henkel reaction is that it produces furan as a side product, which itself can be hydrogenated to tetrahydrofuran or 1.4-butanediol. This was proposed by Pan *et al.* as a carbon-efficient means of producing polymers from furfural, using 1,4-butanediol and FDCA as precursors to produce poly(butyl furandicarboxylic acid), thus utilising 100% of the input carbon.[118] The highest selectivity disproportionation was performed in a sealed reactor at 250 °C, using 0.1 g zinc chloride as a catalyst per gram of substrate, and in supercritical carbon dioxide. They report no activity when other metals such as cadmium, copper or nickel, were used, although a small amount of conversion was observed for lanthanum. They also show that chloride ions are a required counter ion, observing no activity when zinc oxide or zinc acetate were used instead.

2.4. Kolbe reaction

The Kolbe reaction is a means of coupling two carbon chains together with subsequent oxidative decarboxylation. This electrochemical reaction is interesting from a technological point of view as the oxidation is carried out at the electrode, requiring no auxiliary compounds and thus, in theory, improving atom efficiency. This property has highlighted electro-synthetic reactions as particularly applicable to the aspects of Green Chemistry[122] and several applications of this reaction can be seen in Fig. 9. However, the technical challenges of electro-synthetic reactions, especially the separation of the products from the solution and the necessary separation of anodic reactions from cathodic reactions, are significant.[122] It was originally discovered as an electro-oxidation reaction,[123] occurring on the anodic side of a reaction vessel, where oxidations take place. Mechanistically, this reaction is disagreed upon in its basic elements.[124–126] The reaction however is generally agreed to proceed *via* the formation of a carboxyl radical and subsequent decarboxylation into an alkyl radical. Sufficiently stable radicals at this step can go on to form n-1 length alkanes, alkenes or alcohols, but with the correct substrate a radical coupling reaction can occur, creating 2n–2 length carbon backbones. This reaction can be directed by the use of pressure,[127] in the case of pentanoic acid, 1.1 MPa was sufficient to boost selectivity for *n*-octane from 42% to 63% (scheme ii and iii, Fig. 9). As this reaction was originally observed for the formation of ethane from acetic acid, applications of this reaction are centred around the decarboxylative coupling of fatty acids, upgrading them to longer chains.[128,129] Recent work has been shown to be able to use this technique for cross coupling nitrile terminated fragments in the production of adiponitrile, derived from glutamic acid.[130] They show a yield of 78 mol%, indicating the selectivity of this reaction to carboxylate components. Adiponitrile has a global scale of around 1.5 million tonnes, and is selectively hydrogenated producing high-purity 1,6 hexanediamine for the production of nylon-6,6 (scheme i), Fig. 9).[131]

2.5. Bio- and organocatalysis

There are a number of potential sources of proteins and amino acids[132,133] including feathers[134] and vinasse (by products of sugar cane production)[135] that can be used to produce a variety of interesting chemicals *via* deoxygenation. Enzymes are an attractive catalyst choice as they are capable of high selectivity for substrates in low concentrations in an aqueous environment. One of the main challenges in the use of amino

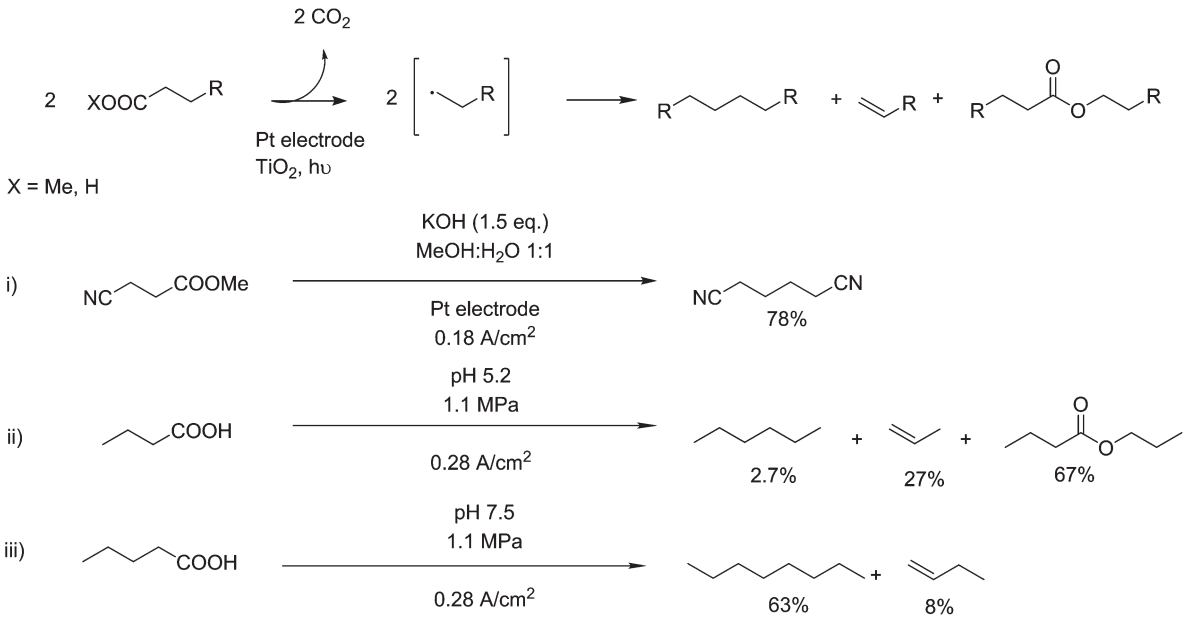

Fig. 9 Kolbe reactions of different substrates.

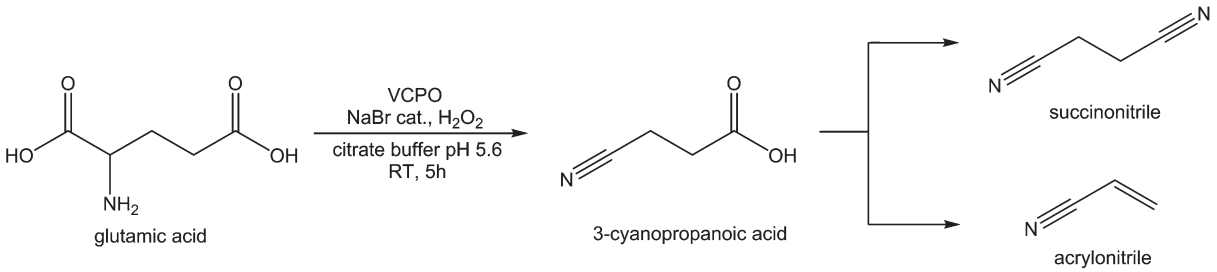

Fig. 10 Production of succinonitrile from glutamic acid.

acids is the ability to obtain pure amino acids for a synthetic route. However, as enzymes are substrate specific, this allows for potentially selective transformation in mixed streams, and potential separation as a result of the changed charge characteristics, for example by decarboxylation.[136]

An alternative strategy in obtaining amino acids may be obtained using microorganisms. For example by the production of the storage protein, cyanophycin (multiarginyl-poly-[L-aspartic acid]) produced by cyanobacteria.[137] It has been shown that this well-defined molecule can be produced from complex amino acid containing aqueous mixtures.[138] It is accumulated in the cell bodies and can be filtered out of the broth, allowing for simpler production of a concentrated stream of just two amino acids. When hydrolysed, only aspartic acid and arginine are produced.[139] Arginine can be used to produce 1,4-diaminobutane *via* hydrolysis to ornithine and subsequent decarboxylation.[46] 1,4-Diaminobutane is a monomer for the production the polymer nylon-4,6 (Stanyl®) produced, by DSM. Aspartic acid can be alpha-decarboxylated to form beta-alanine by the use of aspartate alpha-decarboxylase, an intermediate that could be used for the synthesis of acrylamide.[45] Other examples include the production of gamma-amino butyric acid from glutamic acid by enzymatic decarboxylation,[44] which can be used for the production of for example *N*-methylpyrrolidone[140] or *N*-vinyl pyrrolidone. Phenylalanine can be deaminated by the use of phenylalanine ammonia lyase (PAL) to obtain cinnamic acid that is subsequently converted by deoxygenation to styrene by either direct decarboxylation[72] or to styrene and acrylic acid by ethenolysis.[141] Other simple amines can be produced by the decarboxylation of amino acids, such as ethanolamine from serine, or ethylamine from alanine.[74]

Amino acids also be oxidatively decarboxylated to form nitriles, using NaOCl and NaBr to form 3-cyanopropanoic acid, and subsequently succinonitrile, from glutamic acid.[142,143] Nitriles such as succinonitrile are used mostly for their ability to be selectively hydrogenated to diamines for the production of nylons. 3-Cyanopropanoic acid can be readily converted into acrylonitrile, a monomeric starting compound for the production of acrylonitrile-butadiene-styrene (ABS) and nitrile butadiene rubber (NBR). Acrylonitrile can also dimerised to from adiponitrile,[144] or hydrated to form acrylamide.[145] As such, the market scale for acrylonitrile reaches around 6 million tonnes.[143] The reaction of methylglutamate to 3-cyanopropanoic methyl ester requires 3 equivalents of NaOCl and catalytic amounts of NaBr at 4 °C to give 70% isolated yield, and proceeds *via* the production of "Br^+" equivalences, the activity of these is sufficient to decarboxylate glutamic acid. This reaction is not within the bounds of Green Chemistry as large amounts of waste salt are produced and the requirement for cooling makes for an expensive process,[146] however this reaction remains interesting as enzymatic routes using vanadium bromoperoxidases and chloroperoxidases have been shown to oxidatively decarboxylate valine,[147] and appear to produce the same "Br^+" activity using hydrogen peroxide. Recently, vanadium chloroperoxidase has been used to perform the oxidative decarboxylation of glutamic acid using hydrogen peroxide as an oxidant and a catalytic amount of bromide salts, with a near 100% selectivity for 3-cyanopropanoic acid (Fig. 10).[148]

Amino acids are not the only substrate that can be enzymatically deoxygenated, as the use of P450-based enzymes such as OleTJE have resulted in the enzymatic decarbonylation of stearic acid.[149] They report a selectivity for 1-tridecene of >90% from myristic acid and hydrogen peroxide at 28 °C for 2 hours, with much of the byproduct being the beta-hydroxy alkane.

The decarboxylation of amino acids can be performed using non-metal based organocatalysts in an effective route to the formation of amines. The first paper on this topic shows amino acid transamination by the Strecker degradation,[150] where alloxan is used as an electron and ammonia acceptor, turning into the purple murexide. Strong electrophiles such as ninhydrin[151] also promotes decarboxylation, but are so active that amine hydrolysis is not possible and instead aldehydes are produced. Pyridoxal is a cofactor in many decarboxylase enzymes, but can also be used as a decarboxylation catalyst capable of converting about 50 mol% of phenylglycine in 30 minutes at 100 °C in water. It has the issue that it produces less than 50% yield of amines, preferring to transaminate amino acids to aldehydes.[152] Both the activity and selectivity can be enhanced greatly by the use of an enzyme mimic to prevent amino acid hydrolysis.[153] This can be as much as 16 times faster for the decarboxylation of phenylalanine in water. The same group goes on to show that they can perform selective transaminative decarboxylation using the same catalyst.[154]

Table 4 Decarboxylation of amino acids by ketones[a]

Amino acid	Hydrolysis method[b]	Yield amine product (mol%)	Yield transamination product (mol%)
Phenylglycine	A	80	<1
Phenylalanine	A	90	<1
Tyrosine	B	80	0
Histidine[c]	B	61–81	0
Tryptophan	A	50	0
Leucine	A	90	0
Lysine	B	25	0

[a] Reaction conditions: use of *o*-methoxyacetophenone (100 mol%), 100–240 °C. [b] A = 3 M NaOH, 100 °C, 3 h, B = conc. HCl, 100 °C, 3 h. [c] 200 mol% ketone used.

Other catalysts that promote the decarboxylation of amino acids include benzaldehyde,[155] or aromatic ketones, such as acetophenone and its derivatives,[156] but significant quantities of Schiff bases are reported, sufficient for the authors to require boiling concentrated hydrochloric acid to hydrolyse to produce as much as 90% phenethylamine from phenylalanine, when *o*-methoxyacetophenone was used at equimolar concentrations, as shown in Table 4. A good selectivity was achieved for many of the amino acids used, however the selectivity for lysine conversion is reduced, possibly due to the second amine group on the molecule.

3. Heterogeneous catalysis

3.1. Titanium dioxide photodecarboxylation

Titanium dioxide (TiO_2) surfaces are known for their photoactive behaviour, and have been studied extensively for their ability to degrade organic compound, however it is a difficult process to make selective. Control of this process can be found by affecting the crystal structure *i.e.* by selecting between anatase, brookite and rutile phases. Further, adjusting the particle size, concentration of surface defects and applied gas pressure affects the photoactivity of titanium dioxide particles.[157] anatase/rutile-TiO_2 is active as a decarboxylation agent for levulinic acid, primarily producing methyl ethyl ketone before further degradation towards CO_2 at higher concentrations (Fig. 11).[158] The conversion of this feedstock is poor, but the selectivity for the desired product reaches 95%. It even shows a good activity of photodegradation of fatty acids such as valeric acid, resulting in a rapid (0.71 mmoles h^{-1}) degradation to isobutane,[159] implying it could be active on longer fatty acids also. Malic acid, a byproduct formed by the fermentation of sugars into lactic acid,[160] can be photo-degraded by TiO_2 coated fibers, and produces malonic acid and other small intermediates such as pyruvic acid, fumaric acid and maleic acid, *via* a photo-Kolbe oxidation mechanism.[161] Alternatively, TiO_2 can be used to photo-deformylate tryptophan into kynurenine under black light with up to 90 mol% selectivity.[162] Kynurenine can be used to produce alanine and, by further decarboxylation over zeolite catalysts, bio-based aniline.[163]

3.2. Platinum/palladium heterogeneous decarboxylation

In similar fashion to the use of palladium and rhodium[164] in a homogeneous phase, significant work has been performed in using heterogeneous palladium[165] or platinum on a solid support to decarboxylate fatty acids[166] into fuel-compatible alkanes. Three competing reactions are at play on these metal surfaces: decarboxylation, decarbonylation, and ketone formation where two alkyl chains cross-couple (Table 5).[167] The specificity of product formation appears to be controlled first by choice of metal: platinum produces more alkenes, palladium produces more alkanes.[168] The use of the correct support is important: γ-alumina has been observed to convert canola oil into 77% light gases at 500 °C,[169] but selectively produce stearone from stearic acid at 300 °C (Table 5, entries 1 and 2).[170] Palladium or platinum on mesoporous carbon seems to show a much greater selectivity: palladium on carbon shows 92% selectivity for undecane formation from lauric acid at 270 °C (Table 5, entry 3),[171] and platinum on carbon reaches 95% selectivity for decarboxylation of linoleic acid at 330 °C (Table 5, entry 4).[172] This has been independently investigated by Ford *et al.*, showing that palladium on carbon gives the greatest (96%) selectivity for decarboxylation, and palladium on silica (at 8.4% dispersion) gave the lowest (2.8%).[173] Other supports are also successful: decarboxylative coupling can be used to form 5-nonanone from pentanoic acid (derived from levulinic acid *via* gamma-valerolactone) by the use of a palladium on niobium oxide catalyst (Table 5, entry 5).[174] The addition of hydrogen gas into this reaction allows for a competing deoxygenation reaction to occur. In a similar mechanism, palladium on carbon gave 93% conversion of

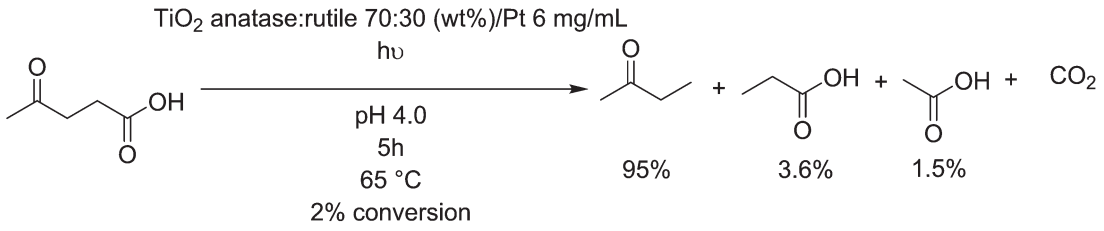

Fig. 11 Photocatalytic degradation of levulinic acid.

Table 5 Decarboxylation of fatty acids by heavy metals

Entry	Fatty acid R =	Catalyst	Time (h)	Temp (°C)	Solvent	Yield alkane (mol%)	Yield 1- alkene (mol%)	Yield cross-coupled ketone (mol%)
1	$C_{15}H_{31}$	Pd/γ-Al_2O_3	24	250	Dodecane	100	0	0
2	$C_{15}H_{31}$	γ-Al_2O_3	24	250	Dodecane	0	0	100
3	C_9H_{19}	Pd/C	0.5	270	Dodecane	92	<1	—
4	$C_{15}H_{31}$	Pt/C	2.5	330	H_2O	95	—	—
5	GVL[a]	Pd/Nb_2O_5	0.1[b]	350	H_2O	—	—	57[c]

[a] Gamma-valerolactone. [b] WHSV/h^{-1}. [c] Also gave 6 mol% pentanoic acid.

stearic acid at 300 °C,[175] but the addition of hydrogen under argon continues to allow decarboxylation despite conditions for deoxygenation.[176,177] In fact, more hydrogen appears to slow the reaction as carbon monoxide adsorbs onto palladium surfaces, selectively blocking them[178] and promoting decarbonylation instead.[179] palladium on carbon catalysts can also decarbonylate furfural,[180] with a tendency to produce difuran and other polyfuranic species.

3.3. Hydrotreating catalysts in decarboxylation and decarbonylation

Hydrodeoxygenation (HDO) is a competing reaction type used on large scales where oxygen is removed from a molecule *via* the addition of hydrogen, yielding water and an alkane. Typically, these catalysts are unselective for which heteroatom they remove from a molecule, simultaneously performing hydrodenitrogenation and hydrodesulphurisation in crude oil feeds. Catalysts for this reaction are often molybdenum-based, such as Mo_2C or NiMo alloys on alumina supports, but also Pd and Pt as described earlier.[48] The main active sites of these catalysts are reported to be on the MoS_2 crystal edges, formed after sulphidation of the catalyst.[181] As these are particularly active on aryl compounds, the main biomass use for these catalysts is the conversion of lignin-derived phenols.[182] Up to 35% of natural wood is lignin,[183] and the separation of the lignocellulosic components has a strong history in the pulp and paper industries. There has been several alternative techniques investigated for the isolation of lignin.[184,185] Depolymerisation of lignin would lead to a source of (oxygenated) aromatic ring structures. While some effort has been made, there are significant issues surrounding the isolation and depolymerisation of this feedstock.[186–188] The desired products of benzene, toluene and xylenes (BTX) have a market scale of between 250 and 300 million tons.[189] Lignin deoxygenation proceeds faster for more oxygenated molecules such as syringol rather than phenol, and is remarked to be rather unselective, producing a chain of intermediates before finally producing benzene and toluene, however cleavage of aryl groups was not observed.[190] HDO catalysts suffer significantly from deactivation which is correlated to the acidity of the feedstock. Lignin derivatives are commonly phenol-based, which have a high pH, and can coke easily on catalysts.[191]

HDO is also used for the deoxygenation of fatty acids, where both decarboxylation and hydrodeoxygenation reactions are taking place on the same catalyst. The two reactions however occur at different rates depending on the conditions. For example, considering the HDO of waste cooking oil rich in C_{18} fatty acids: after 40 hours at 350 °C, a CoMo/Al_2O_3 catalyst produced alkanes of which 20% were C_{17} decarboxylation product, but under the same conditions a NiW/Al_2O_3 catalyst produced up to 50% C_{17} alkanes. Because chain length shortening only occurs by decarboxylation or decarbonylation, this implies that the NiW/Al_2O_3 catalyst promotes these reactions better.[192] Sulphided tungsten derivatives can also be effective HDO catalysts. The proportion of hydrogenation and decarboxylation can be tuned based on whether tungsten oxide (38% conversion, 91% decarboxylation) or tungsten carbide (81% conversion, 15% decarboxylation) are used as a catalyst. Both of these are supported on carbon nanofibres, and the conclusions are based on results from the HDO of stearic acid at 350 °C for 5 hours with 50 bar H_2, 12.5 wt% catalyst, in dodecane.[193] Jatropha is a hardy plant that grows in poor soil conditions, and produces an oil rich in C_{18} and C_{16} triglycerides.[194] Hydrodeoxygenation of this oil over NiMo/SiO_2 using 800 mL H_2 at 4 MPa per mL solution and 250 °C for 10 h produced 82.9 wt% C_{11-20} alkanes and 4.3 wt% C_{1-4} alkanes, effectively hydrolysing and reducing the glycerol in one step (Fig. 12). Some decarboxylation and decarbonylation

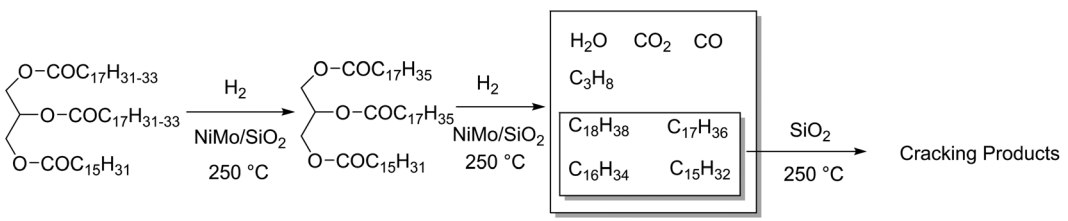

Fig. 12 NiMo catalysed hydrotreatment of Jatropha oil to C_{18-15} alkanes and subsequent cracking products.

reactions were observed, accounting for the presence of C_{17}/C_{15} molecules in the product distribution. Further investigation into the selectivity for hydrodeoxygenation *versus* hydrodecarboxylation has been reported, investigating the use of CoMo catalysts on several grades of Al_2O_3 support, using triglyceride-rich rapeseed oil as a substrate. Decarboxylation and decarbonylation are also avoided at higher temperatures, producing a 16 : 1 ratio of C_{18} : C_{17} alkanes for CoMo on an organised mesoporous alumina support at 280 °C, compared to a 12 : 1 ratio at 250 °C, implying a negative relationship between decarboxylation and reaction temperature. Pressure plays a significant role, increasing the reaction pressure from 0.7 to 7 MPa changes the resulting alkanes from a 3 : 1 ratio of C_{18} to C_{17} to 16 : 1 at 280 °C.[195,196] Conversely, when sunflower oil was used on a $CoMo/Al_2O_3$ catalyst with 40 bar H_2,[197] a reaction temperature of 380 °C produces 11.7% C_{17} alkanes and 70.3% C_{18} alkanes. At 300 °C the same conditions produced 2% C_{17} alkanes and 27% C_{18} alkanes, displaying a positive relationship between temperature and rate of decarboxylation.

4. Thermal decarboxylation

4.1. High temperature water treatment

Citric acid is produced fermentatively by *Aspergillus niger* at high productivities, over 70% theoretical yield,[198] and has a market in the nutraceutical field of about 0.4 million tons per year.[199,200] When citric acid is exposed to high temperature water (HTW) close to supercritical conditions (320 °C and 34.5 MPa), it is converted into 6% methacrylic acid and 35% itaconic acid, with a wide spectrum of intermediates such as citraconic acid, mesaconic acid and acetic acid, as shown in Fig. 13.[201] When pure itaconic acid was subjected to the same reactor at 360 °C with 20 mol% NaOH, it produces 71% methacrylic acid, with the main byproducts being acetic acid, crotonic acid and hydroxyisobutyric acid. More recently it has been shown that methacrylic acid can be obtained from itaconic acid with yields up to 58% using 1 equiv. of NaOH at temperatures between 250 and 350 °C, 200 bar pressure, and a residence time of 520 seconds in continuous reactors.[202] Itaconic acid is a novel molecule produced from biomass that has uses as a comonomer in plastic production,[203] and as a surfactant, and is able to be transformed into molecules such as 3-methyl tetrahydrofuran, 3-methyl *N*-methylpyrrolidone, and 3-methylpyrrolidine. It has a current market scale of around 150 000 tons per year globally,[204] growing fast from 15 000 tons in 2001. It is primarily produced fermentatively by fungi, however there are recent efforts in producing itaconic acid in other species such as plants.[205] Methacrylic acid is a monomer produced at a scale of around 2.2 million tons per year for the manufacture of poly(methyl methacrylate), a polymer used for its high transparency.[206]

HTW conditions also allow for controlled oxidation conditions with the addition of hydrogen peroxide, which can selectively remove carbon-rich molecules from a waste stream, without producing the oxides of sulphur and nitrogen that are associated with pyrolysis. This has been used on vanillic acid as a model compound for lignin to some success, showing catechol, cresol and phenol produced.[207] Fatty acids have also been tested, and at 400 °C a wide range of diacids and ketones were formed.[208] Glucose, when treated to similar conditions at 374 °C for 120 min with 4.5 mol% hydrogen peroxide in 100 mL gave a wide range of organic products (from propanoic acid to benzaldehyde), with 42% CO_2 being produced at the same time.[209]

Amino acids and proteins have also been studied under HTW conditions as a means of reclaiming material from protein-rich side streams. An example is the reclamation of seafood waste, where HTW was used to hydrolyse the protein down, but only around 7% selectivity was observed at 250 °C.[210] Investigation into this showed that significant non-selective decarboxylation and deamination reactions were occurring in the reaction conditions. A myriad of different products were formed, but deamination of aspartic acid was noted to be a predominant mechanism, forming fumaric acid, and serine underwent a retro-aldol condensation to form glycine.[211] In the case of dipeptides, a significant amount of cyclisation also was found to occur.[212] Phenylalanine is able to react with 1 eq. 2,4-decadienal at 180 °C in water at 9.8 atm for 60 min with a sodium phosphate buffer at pH 6, being converted to styrene by as much as 6 mol%.[213] At 280 °C and 6.4 MPa in HTW for 60 minutes, phenylalanine conversion is at 97 mol%, producing 68 mol% phenethylamine and 4 mol% styrene, however 19 mol% of the mass is not accounted for.[214] This process is shown diagrammatically in Fig. 14.

4.2. Pyrolysis

By applying heat to biomass in an anaerobic environment, a significant amount of oxygen can be removed from the material, and liquefaction is achieved leading to what is called bio-oil.[215] The liquefaction of soybean straw and vegetable oil has been attempted at 400 °C, where a significant amount of decarboxylation (88 wt%) takes place.[216] In the gas phase, 3 wt%

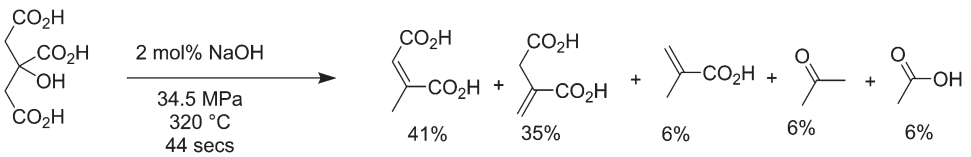

Fig. 13 High temperature water decarboxylation of citric acid.

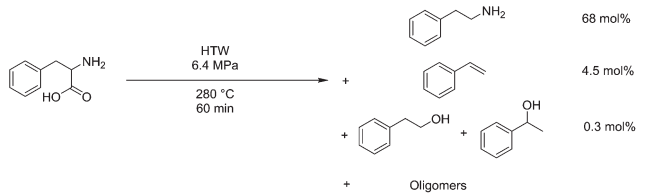

Fig. 14 Degradation of phenylalanine in HTW conditions.

short alkanes (3 carbons or less) were formed, and at much as 50% yield of alkanes was shown, but only in the case where pure sunflower oil was used was no char formed, otherwise between 20–30 wt%. A wide range of compounds were formed in addition to char.

The production of bio-oil from the high temperature liquefaction of lignocellulosic biomass is mainly performed over zeolite catalysts at a temperature of 600 °C. For example, a pine wood and methanol mix can be converted to 14 mol% aromatic molecules and 9.4 mol% olefins, with 26 mol% coke formation and 32 mol% carbon monoxide.[217] Bio-oil is not a good replacement for petroleum, as it has a very high oxygen content (up to 60 wt%), is acidic, and often has a high water content.[218] Pyrolysis has been used to stabilise a water soluble bio-oil by deoxygenation, but up to 32 mol% of char can be formed. A combined pyrolysis and hydrogenation technique using 4.8 g H_2/100 g carbon at 52 bar over ruthenium on carbon at 125 °C succeeded in reducing char to 17.4 mol%, with a shift towards aromatic molecule production.

Instead of attempting to eliminate the production of char, it can be promoted by the use of hydrothermal carbonisation. Yields of 66% char from 72 hours under pressure at 200 °C have been reported for wood,[219] and a marked reduction in O/C ratio from 0.58 to 0.17 has been achieved, alongside a reduction in H/C ratio, indicating aromatisation. Unfortunately, due to the wet nature of biomass and the requirement for water in this reaction, extracted organic compounds are always present and thus carbonisation does not proceed to completion.

5. Summary and outlook

In this review we have looked at various methods of catalytic deoxygenation, using multiple Biobased substrates. In order to be able to draw conclusions on the suitability of certain catalysts with substrates for deoxygenation (in the form of decarboxylation and decarbonylation) a uniform entity should be defined. Due to the variability of the reaction conditions this is not trivial. For efficient industrial application the volumetric productivity would be a useful comparison. However volumetric productivity is linked to the maximum density of active sites per unit volume and the maximum turnover frequency of each active site. On laboratory scale, the maximum site density per unit volume is of less significance therefore making comparison of published data unrealistic. Instead, the turnover frequency (TOF) (moles substrate converted per mole catalyst per minute) has been selected as a suitable indication as to reactor productivity independent of type (plug flow, batch, *etc.*).

From Table 6, it can be seen that the many reactions can be broken down to their fundamental reaction characteristics such as reaction rate, temperature and concentration based on literature data. The rates given have been calculated at a point where the reaction is close to linearity as possible. From this data we can see one very clear result, that all heterogeneous catalysts are tested at 250 °C and above, all homogeneous catalysts are between 280 and 70 °C, and all biocatalysts are 20–50 °C.

In order to calculate the TOF, it is required to calculate the amount of active sites in contact with the substrate. For homogeneous and biocatalysts the concentration of catalyst in solution is used for this value. For heterogeneous catalysts, the active surface area of the catalyst surface area has been calculated from the BET data (for pure oxidic material) or particle size information (for metal). This method was not applied to mixed metal catalysts such as CoMo and NiMo HDO catalysts, due to the uncertainty in active site location – whether only the particle adjuncts are active for decarboxylation, or the Ni particles dramatically changes the calculated number of sites and thus the TOF. Finally, with the TOF data compiled, it is possible to show a trend of TOF with temperature in Chart 1.

From Table 6 and Chart 1 it can be concluded that, the substrate does not seem to have a significant effect on the TOF, *e.g.* the use of silver peroxydisulphate reaction on lauric acid and pivalic acid does not significantly affect the resultant TOF. As well as this it can be seen that there is a strong correlation between increasing specific activity (TOF) and increasing temperature for metal based catalysts either homogeneous or heterogeneous thus one is not more active than the other at the same temperature. Given that heterogeneous catalysts are more robust and easier to re-use, it could be considered that, at an industrial scale, heterogeneous catalysts are the most suitable choice for application.

However this trend is not followed by biocatalysts. Biocatalysts have significantly higher TOFs even at low temperatures. However the low volumetric productivities of biocatalytic processes lead to limitations. Reactor design will play an important role in overcoming this. One could consider increasing concentrations of substrate and enzyme. However in the case of exothermic reactions care needs to be taken as biocatalysts can often not be used at elevated temperatures without significantly affecting their stability. Biocatalysts are generally not as stable as traditional metal-based catalysts and often deactivate over time so developments to improve enzyme stability will be required. Most frequently they require an aqueous environment, which might be prohibitive for some desired reactions, although this has been shown to not always be true, and examples exist to ionic liquids,[220] supercritical fluids[221] and organic solvents[222] have been reported.

In conclusion, in the deoxygenation by decarboxylation and decarbonylation of biomass-derived molecules the primary

Table 6 Deoxygenation (decarboxylation and decarbonylation) of multiple substrates

Entry	Reactor design	Catalyst type	Catalyst	Substrate	Reaction temp (°C)	Reaction time (min)	Reaction pressure (atm)	Reaction solvent	Yield of desired product (mol%)	Rate (g min^{-1})	Active sites (mol)	Turnover frequency (mol conv./min/mol sites)
1[147]	Batch	Bio	Bromoperoxidase and NaBr	Valine	21	90	1	Water	0.9	0.30×10^{-4}		
2[45]	Batch	Bio	Aspartate Decarboxylase	Aspartic acid	30	300	1	Water		0.0002×10^{-4}	2×10^{-9}	8.8
3[44]	CSTR	Bio	Glutamic acid Decarboxylase	Glutamic acid	30	3000	1	—	1	5	4×10^{-4}	7.9×10^{1}
4[148]	Batch	Bio	Vanadium Chloroperoxidase and NaBr	Glutamic acid and H_2O_2	21	240	1	Water	1	0.006×10^{-4}	9×10^{-12}	4.62×10^{3}
5[136]	CSTR	Bio	Lysine Decarboxylase	Lysine	37	1440	1	Buffer	1	0.8×10^{-4}	2.5×10^{-8}	6.5×10^{3}
6[46]	Batch	Bio	Ornithine Decarboxylase	Ornithine HCL	30	8	1	Buffer	1	0.006×10^{-4}	2×10^{-10}	2.7×10^{6}
7[73]	Batch	Homo	Silver(I) picolinate	2-(2-Phenylcyclopropyl)-glycine	70	60		Water	0.34	50×10^{-4}	800×10^{-4}	3.54×10^{-4}
8[58]	Batch	Homo	Silver picolinate	Pivalic acid	85	720	1	Acetonitrile–water	0.7	22×10^{-4}	20×10^{-4}	1.1×10^{-2}
9[92]	Batch	Homo	$PdCl_2$	Phenylbutyric acid	110	960	1	NMP	0.7	1×10^{-4}	0.3×10^{-4}	2.4×10^{-2}
10[64]	Batch	Homo	Silver nitrate and copper nitrate	Palmitic acid	78	20	1	Water–acetonitrile 5 : 9	0.5	500×10^{-4}	78×10^{-4}	2.5×10^{-2}
11[96]	Batch	Homo	$FeCl_2$	Stearic anhydride	240	180	20	—	0.74	23×10^{-4}	0.2×10^{-4}	2.1×10^{-1}
12[164]	Batch	Homo	Rhodium triphosphine	Stearic acid	280	60	1	—	0.9	4260×10^{-4}	0.77×10^{-4}	1.9×10^{1}
13[83]	Batch	Hetero	Silver nitrate	Levulinic acid	100	30	1	100 ml buffer	0.3	116×10^{-4}	100×10^{-4}	1×10^{-2}
14[165]	Batch	Hetero	Pd on non-oxidised CNF	Stearic acid	250	20	5.92	Dodecane	0.05	25×10^{-4}	2.8×10^{-4}	3.2×10^{-2}
15[190]	Batch	Hetero	WO_3	Methyl stearate	350	300	49.3	Dodecane	0.20	14×10^{-4}	1×10^{-4}	3.4×10^{-2}
16[167]	Batch	Hetero	Pd/Al_2O_3	Stearic acid	250	1440	6.91	—	0.1	6×10^{-4}	0.6×10^{-4}	3.4×10^{-2}
17[118]	Batch	Hetero	$ZnCl_2$	Furoic acid	250	180	42.9	CO^2 (1 g)	0.53	58×10^{-4}	15×10^{-4}	3.5×10^{-2}
18[170]	Batch	Hetero	Pd/C	Stearic acid	300	240	2	Dodecane	0.96	64×10^{-4}	3×10^{-4}	6.7×10^{-2}
19[193]	PFR	Hetero	Ni on Al_2O_3	Rapeseed oil	270	120	34.5	—	0.78	2586×10^{-4}	75×10^{-4}	1.2×10^{-1}
20[168]	PFR	Hetero	Pd/C	Lauric acid	270	75	9.86	Mesitylene	0.26	303×10^{-4}	7.5×10^{-4}	2.0×10^{-1}
21[165]	Batch	Hetero	Pd on oxidised CNF	Stearic acid	250	20	5.92	Dodecane	0.4	200×10^{-4}	2.8×10^{-4}	2.5×10^{-1}
22[166]	Batch	Hetero	Pt/Al_2O_3	Octanoic acid	330	60	1	Tetradecane	0.89	685×10^{-4}	7.5×10^{-4}	6.3×10^{-1}
23[173]	PFR	Hetero	Pd/C	Stearic acid	300	330	—	Dodecane	0.11	158×10^{-4}	0.3×10^{-4}	1.6
24[165]	Batch	Hetero	Pd/C	Stearic acid	300	360	5.92	Dodecane	0.95	119×10^{-4}	12×10^{-4}	4.6
25[190]	Batch	Hetero	W_2C	Methyl stearate	350	300	49.3	Dodecane	0.93	62×10^{-4}		
26[169]	Batch	Hetero	Pt/C	Stearic acid	330	150	—	Water	0.85	3×10^{-4}		
27[87]	Batch	Hetero	Palladium	Furfural	200	1920	1	Dibutyl phthalate 400 ml	1	302×10^{-4}		
28[121]	Batch	Hetero	$Au–CeO_2$	HMF	65	480	9.89	Water (20 ml)	1	8×10^{-4}		
29[158]	PFR	Hetero	TiO_2 and 1% Pt	Levulinic acid	65	300	1	15 ml water	0.66	77×10^{-4}		
30[174]	PFR?	Hetero	1% Pt/Ce_2O_5	Gamma valerolactone	350	600	34.5	Water	0.46	269×10^{-4}		

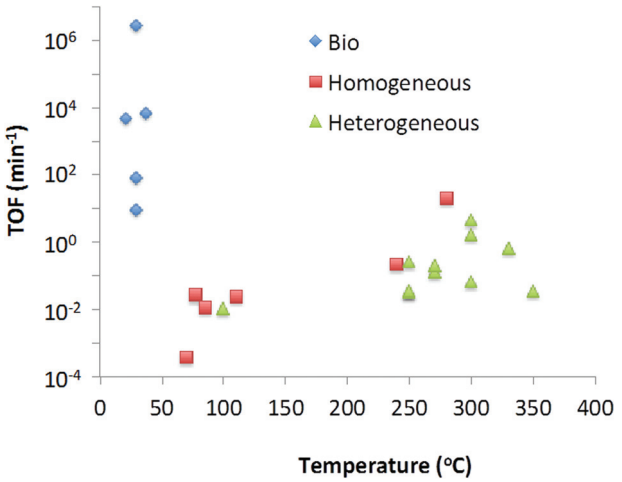

Chart 1 TOF as a function of temperature for different classes of catalyst.

means of controlling the activity of a catalyst is by altering the reaction temperature. Depending on the reaction, substrate catalyst type and cost, this tool allows choices to be made for developing the process of choice. For biocatalysts this does not apply and although TOFs are high at low temperatures, improvements in enzyme stability and improvements in volumetric productivity should be made.

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