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Synthesis of Bio-Based Methacrylic Acid by Decarboxylation of Itaconic Acid and Citric Acid Catalyzed by Solid Transition-Metal Catalysts

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Methacrylic acid, an important monomer for the plastics industry, was obtained in high selectivity (up to 84%) by the decarboxylation of itaconic acid using heterogeneous catalysts based on Pd, Pt and Ru. The reaction takes place in water at 200–250 °C without any external added pressure, conditions significantly milder than those described previously for the same conversion with better yield and selectivity. A comprehensive study of the reaction parameters has been performed, and the isolation of methacrylic acid was achieved in 50% yield. The decarboxylation procedure is also applicable to citric acid, a more widely available bio-based feedstock, and leads to the production of methacrylic acid in one pot in 41% selectivity. Aconitic acid, the intermediate compound in the pathway from citric acid to itaconic acid was also used successfully as a substrate.

Introduction

In recent years, environmental and economic concerns of our petroleum-based society have initiated the return to a bio-based origin for energy, fuel and chemical production. Green and sustainable sources of energy are under development using wind, solar radiation or hydropower, and biomass has become the focus of numerous research projects to produce fuels such as bioethanol and biodiesel. Similarly, the transition of the chemical industry towards the use of bio-based feedstocks has started, and many examples of the large-scale or near-market production of bio-based chemicals are emerging such as syngas, bioethanol, lactic acid and succinic acid.[1] An important branch of the chemical industry is engaged in the production of polymers that find numerous applications in our daily life. As far as plastics and materials are concerned, their substitution by bio-based equivalents can be envisaged following two strategies: either new polymers are produced directly from biomass (new bio-polymer strategy) or already known monomers are synthesised from biomass feedstocks instead of fossil resources (drop-in strategy). Examples of the first strategy are poly(lactic acid) and poly(hydroxyalkanoates), used mainly for packaging applications.[2] They present good degradability properties but their production and processing are new to the chemical industry, which implies a longer development time and higher capital costs. However, the drop-in strategy leads to the use of monomers identical to those obtained previously from fossil resources, which means that the production of polymers and their processing remain the same. Successful examples are already available on the market such as bioethylene and biopropylene,[3] and others, such as bio-based acrylic acid and adipic acid, are currently under development.[1e,f] Poly(ethylene furandicarboxylate) (PEF) is a new material that combines the two strategies mentioned above and uses a drop-in monomer, ethylene glycol (obtained from bioethylene), and a new bio-based monomer, 2,5-furandicarboxylic acid (FDCA), obtained from hydroxymethylfurfural (HMF).[4] PEF presents better properties than fossil-based polyethylene terephthalate (PET) (barrier properties, higher glass transition temperature), and commercial applications for food packaging are imminent.[5]

Methacrylic acid (MAA) and methyl methacrylate (MMA) are important monomers for the plastics industry.[6] They are mostly used for the production of poly(methyl methacrylate) (PMMA) but also enter the composition of methyl methacrylate-butadiene-styrene (MBS) co-polymers or modified poly(vinyl chloride) (PVC). Materials obtained from MAA and MMA are resistant, durable and transparent and can find numerous applications, for instance, as glass substitutes and optical fibres. MAA and MMA are also employed for the preparation of adhesives, paints and coatings.[6,7] Currently, MAA and MMA are produced from fossil resources through different industrial processes, such as the acetone cyanohydrin process or by the oxidation of isobutene or tert-butyl alcohol.[8] Currently, no commercial routes to bio-based MAA or MMA are available, but several companies and academic research groups have re-

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ported the synthesis of MAA or MMA from bio-based feed-stocks. Fermentative routes to MAA from renewable carbohy-drates have been envisaged by using non-natural micro-organ-isms, either in one process[9] or by combining the synthesis of 2-hydroxy-2-methylcarboxylic acid and a chemical catalytic de-hydration step.[10] Recently, Pyo et al. reported the production of MAA by two consecutive steps that involve an oxidative bio-conversion and a catalytic dehydration of 2-methyl-1,3-pro-panediol, which can be obtained from the fermentation of glycerol.[11] Isobutyric acid is a known precursor of MAA by cat-alytic oxidative dehydrogenation and it can be prepared by fermentative pathways.[12] It is also possible to consider the production of MMA through known processes such as the ace-tone cyanohydrin process or the oxidation of isobutene by using bio-based starting materials.[13] Other routes to bio-based MMA can start from ethylene, methanol and carbon monoxide, all obtainable from biomass, such as through the Alpha pro-cess developed by researchers at Lucite[14] and others.[15] Bio-based propylene glycol can also be used as a feedstock for MMA production by dehydration to propanal followed by the addition of methanol and the reaction with formaldehyde.[16]

2-Methylenesuccinic acid, or itaconic acid, is considered as an important platform chemical that can be obtained from biomass.[17] Its current global annual production is estimated at 80 000 tons and its main application is in polymer and co-poly-mer syntheses.[18] Carlsson et al. reported that itaconic acid can be converted to MAA by decarboxylation.[19] However, the pro-cedure uses near-critical and supercritical water conditions, that is, temperatures of 250–400 °C and pressures of 200–345 bar.[19,20] The best result was obtained at 360 °C with 72 % of MAA formed (molar yield). Citric acid is available more widely than itaconic acid and is present naturally in the juices of citrus fruits, as well as in agro-industrial rest streams, such as sugarcane molasses or vinasse. Citric acid is produced mainly by fermentation processes in high yields (up to 70 % of the theoretical yield with *Aspergillus niger*) with a total yearly production that reached 1.6 million tons in 2007[21] at a current price of ≈ 800 euro per ton. The full conversion of citric acid to MAA was also reported at temperatures above 320 °C but with poor selectivity and 6 % MAA yield.[19]

Here we report the synthesis of MAA from itaconic acid under reaction conditions that are significantly milder than the procedures reported previously. Solid transition-metal catalysts are employed to decrease the reaction temperature and pres-sure and to improve the MAA yield and selectivity. Moreover, the production of MAA from citric acid, a more widely avail-able bio-based feedstock, is also described.

Results and Discussion

Decarboxylation of itaconic acid using palladium on carbon

The high level of O atoms constitutes one of the main charac-teristics of biomass compared to naphtha, and is one of the main challenges to incorporate biomass into the chemical in-dustry, especially for fuel applications. Hence, many efforts have been dedicated to the development of biomass deoxyge-nation processes such as decarboxylation reactions performed either enzymatically[22] or chemically.[23] One typical example of the latter is the conversion of fatty acids to alkanes or alkenes used as biofuels.[24] Most of the time, anhydrous conditions are applied and reactions proceed at a high temperature (above 300 °C) and under elevated pressure using an inert gas or hy-drogen. Decarboxylation reactions in aqueous media are rarer but possible at a relatively low temperature (78 °C) by using acetonitrile as a co-solvent with, however, the use of a stoichio-metric amount of Ag salts as a catalyst.[25] Fatty acids can be converted into alkanes in near- and supercritical water by using activated carbon supports ($T > 370$ °C).[26] Similar condi-tions have been used to decarboxylate itaconic acid to MAA without a catalyst ($T = 250–400$ °C, $P = 200–345$ bar).[19,20] None-theless, supercritical water conditions are a potential problem for industrial applications because of their highly corrosive properties[27] and the capital costs linked to the required speci-fications of pressure reactors. Thus, it would be better if the decarboxylation of itaconic acid to MAA could be achieved at a lower temperature and pressure. One approach is the use of transition-metal catalysts as shown in some reports, in which Pt/C was used to decarboxylate fatty acids in water at 330 °C[28] or Pd/C was used to decarboxylate alkyl carboxylic acids in water at 250 °C and 40–50 bar.[29] Therefore, we decided to per-form an initial reaction using itaconic acid as the substrate in the presence of Pd/C (2.5 mol % Pd) in a basic aqueous solu-tion (0.1 M NaOH) at 250 °C for 1 h (Scheme 1).
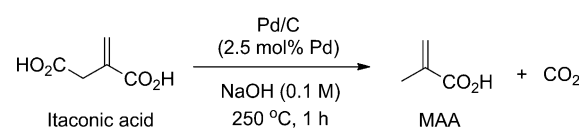
Scheme 1. Pd-catalysed decarboxylation of itaconic acid.

The reactor was filled at room temperature with 1 bar of Ar, and the internal pressure increased to 38 bar during heating. After cooling to room temperature, the catalyst was separated from the reaction mixture by micro-filtration. The resultant so-lution was then analysed by HPLC, and the composition of the different crude mixtures is depicted in Table 1.

First we noticed that the use of either 2-methylfumaric acid (mesaconic acid) or 2-methylmaleic acid (citraconic acid) as substrates gave comparable results to those obtained with ita-conic acid (similar conversion and selectivities). Hence, we be-lieve that the three compounds: itaconic acid, mesaconic acid and citraconic acid, are in equilibrium by fast isomerisation in the reaction mixture (Figure 1) and we consider all three of them as substrates. After reaction and work-up, the reaction mixture was analysed by HPLC, and the distribution and yields of the products were calculated from the calibration against the internal standard. We define the conversion (C) of the reac-tion as shown in Equation (1):

$$C = (1 - (Y_{IA} + Y_{MA} + Y_{CA})) \times 100 \qquad (1)$$

| Entry | Itaconic acid [M] | Conversion [%][b] | Product selectivity [%][c] | | | |
			MAA	Crotonic acid	Pyruvic acid	Others[d]
1	0.38	94	23	<1	n.d.	77
2	0.15	89	47	1	3	49
3	0.10	80	43	1	3	53
4[e]	0.15	78	17	<1	2	80

Table 1. Decarboxylation of itaconic acid using a Pd/C catalyst.[a]

[a] Reaction conditions: pressure reactors, 20 mL of 0.1 M NaOH, Pd/C (2.5 mol% of Pd), 250 °C, 1 h. Yields were determined by HPLC; [b] Conversion = $(1-(Y_{IA}+Y_{MA}+Y_{CA})\times 100)$; [c] Selectivity to a = (yield of a/conversion)×100; [d] Volatile degradation products such as propene, acetone and acetaldehyde; [e] 20 mL of H_2O as solvent.

in which Y_{IA} is the percentage of residual itaconic acid left after reaction, Y_{MA} is the percentage of mesaconic acid formed and Y_{CA} is the percentage of citraconic acid formed.

Product selectivity (S) for compound a is defined as shown in Equation (2):

$$S_a = (Y_a/C) \times 100 \qquad (2)$$

in which Y_a is the yield of compound a in the reaction mixture.

Our initial experiment that used a 0.38 M itaconic acid solution resulted in 94% conversion after 1 h at 250 °C (Table 1, entry 1). The MAA selectivity reached 23%, and the rest of the products consisted of degradation products. If we decreased the substrate concentration, the level of conversion decreased slightly but the selectivity of MAA increased to 47% and yield of degradation products decreased to 49% (Table 1, entry 2). If we decreased the substrate concentration further to 0.10 M, a lower conversion and MAA selectivity were obtained (Table 1, entry 3).

The absence of base had a critical influence on the selectivity towards MAA (Table 1, entry 4). The pH of the crude mixtures remained basic after reaction if NaOH was used, whereas it decreased to 2.5 for the reaction that started from neutral water. As the reaction medium is more acidic, one can assume

that more degradation occurs through the addition of water molecules to double bonds (Figure 1). Notably, in a blank reaction that used MAA under the same conditions as those used for entry 3 in Table 1 (20 mL of 0.1 M NaOH, Pd/C (2.5 mol% of Pd), 250 °C, 1 h), some degradation took place and a loss of 21% of MAA was observed. The presence of a stabiliser such as 4-methoxyphenol (100–500 ppm) had no influence on the level of MAA degradation. Therefore, if degradation occurs during the reaction, it is probably not caused by radical formation and polymerisation of MAA but is more likely because of the hydration of the double bonds, proven by the presence of traces of 2-hydroxyisobutyric acid in some reaction mixtures and of pyruvic acid in all of them (Figure 1, Table 1). It may also be because of a subsequent decarboxylation step to form propene, which is coherent with the observation of a slight increase of the internal pressure of 2–3 bar during the reaction and the report by Carlsson et al. who noted that up to 8% propene was formed during the reaction.[19] Numerous byproducts were analysed in the crude reaction mixture, and their formation can be explained by the competition between three main transformations: the isomerisation of double bonds, decarboxylation and the addition of water to double bonds. An overview of the different main byproducts can be seen in Figure 1.

According to the study by Li et al. on the kinetics of the non-catalysed reaction under near-critical water conditions,[20a] the rates of the three main reactions appear to be isomerisation > decarboxylation > hydration. In the mechanistic pathway, itaconic acid is isomerised quickly to mesaconic acid and citraconic acid and all three can be decarboxylated to produce either MAA or (E)-but-2-enoic acid, also called crotonic acid.

However, according to their calculations, it appears that MAA is more likely to be obtained from itaconic acid than from mesaconic or citraconic acid. They also postulate that the monoanion of itaconic acid decarboxylates faster than the neutral and dianion forms. This is because of the formation of a cyclic intermediate between the remaining acidic hydrogen
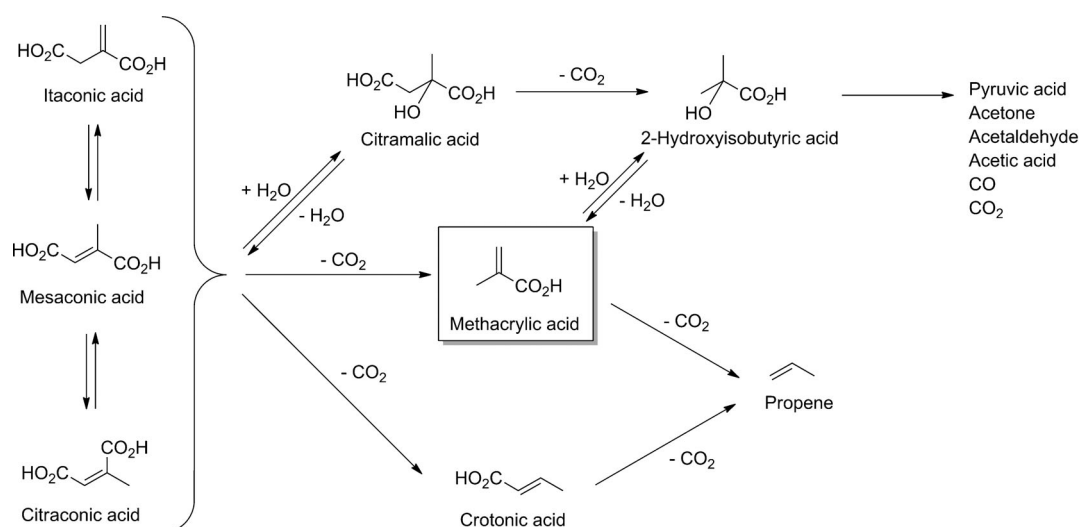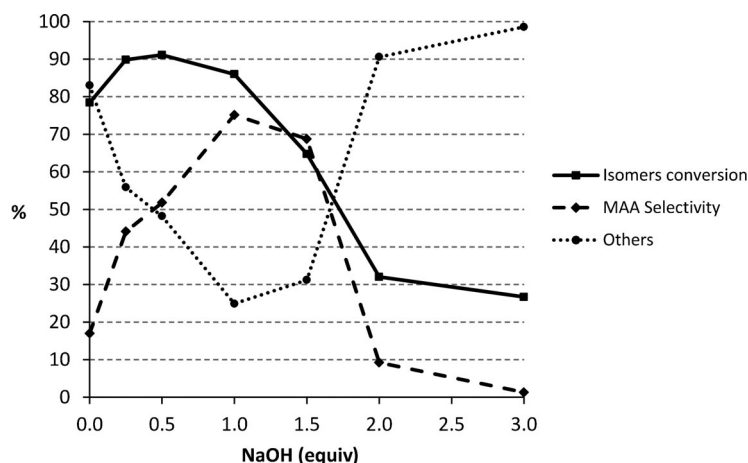

Figure 1. Possible reaction pathways that occur during the decarboxylation of itaconic acid.

atom and the unsaturation, which has a lower energy. Therefore, they proposed that the non-conjugated carboxylic group at the β position of the double bond in the itaconic acid structure is more likely to decarboxylate. In our case, as Pd has an affinity for double bonds,[30] the delocalised structure of the α-carboxylate and the unsaturation potentially coordinates to the metal surface, which stabilises the intermediates during the decarboxylation reaction. The other carboxylic function at the β position is likely to be adsorbed to the metal surface as well, upon which the decarboxylation takes place. Side reactions are also possible, such as a second decarboxylation to form propene (Figure 1). Under hydrothermal conditions, it is likely that water reacts with an unsaturated bond to form alcohols. 2-Hydroxy-2-methylsuccinic acid, or citramalic acid, can indeed be obtained from any of the three itaconic acid isomers. 2-Hydroxyisobutyric acid can also be produced from the hydration of MAA but it is also the decarboxylation product of citramalic acid. The further degradation of 2-hydroxyisobutyric acid leads to the formation of pyruvic acid, acetaldehyde, acetone and other volatile compounds. From our HPLC analyses, we observed the presence of MAA and the three isomers of the starting material as major products, and crotonic acid, pyruvic acid and 2-hydroxyisobutyric acid were observed in small quantities ($<3\%$). However, citramalic acid was not detected. Gas-phase analysis reported previously proved the production of propene and acetaldehyde.[19] For clarity, we are reporting the quantitative analysis of the starting material together with the two isomers (mesaconic and citraconic acids), MAA, and 'others' refers to any of the potential byproducts that result from side reactions (hydration) and further degradation of the intermediate products.

Figure 2. Pd-catalysed itaconic acid decarboxylation with different amounts of base (Reaction conditions: itaconic acid 0.15 M, 20 mL of aqueous NaOH, Pd/C (2.5 mol% Pd, 250 °C, 1 h; connecting lines were added for clarity).

Effect of base

Our initial series of experiments showed that without a base the selectivity of MAA was low (Table 1, entry 4) and a significant amount of side products was formed. Li and Brill also reported that the rate of the decarboxylation of itaconic acid is dependent on the pH of the reaction. The itaconate monoanion decarboxylates faster than the protonated itaconic acid, which in turn decarboxylates faster than the neutral and dianionic form of itaconic acid.[20a] Therefore, we checked this hypothesis by performing a series of reactions in which the amount of NaOH varied from zero to three equivalents (Figure 2). The conversion of itaconic acid and its isomers remained high ($>80\%$) if the amount of base varied from zero to one equivalent and then decreased significantly to $\approx30\%$ or less if more than 1.5 equivalents of base was used. Analyses show that the isomerisation of itaconic acid to its isomers is the major reaction that takes place. Without base, the MAA selectivity was poor (17%), which increased with the amount of NaOH to reach a maximum of 75% at one equivalent. Under more basic conditions, the MAA selectivity decreased significantly and remained lower than 10% with more than two equivalents of base. As mentioned earlier, it is likely that the nature of the byproducts of the reaction differs at high and low pH. At a low base concentration, the degradation of the starting materials and MAA can occur by the acid-catalysed addition of water molecules to double bonds. At a low pH, the MAA selectivity decreased probably because of degradation to volatile molecules. It appears that the optimum conditions for the decarboxylation of itaconic acid are reached with one equivalent of base. Similar results were achieved if other types of base such as calcium hydroxide were used.

Screening of transition-metal catalysts

Various transition metals have already been used as catalysts for the deoxygenation of biomass, and we selected a list of metals and typical supports to test their activity for the decarboxylation of itaconic acid (Figure 3).

First, blank reactions that used no catalyst and typical naked supports for heterogeneous catalysis were performed. High conversions were reached for all blank reactions, which shows that itaconic acid and its isomers are not stable under our reaction conditions (250 °C, 40 bar). MAA was formed in yields of 31–39%, which is slightly higher than reported previously under a higher pressure.[20b] Yields of 45–52% of byproducts were produced, which shows a poor selectivity toward the decarboxylative pathway to MAA. A series of Pd catalysts on different supports such as carbon, Al_2O_3 and $BaSO_4$ were then tested. Comparable results were observed with high MAA yields that ranged from 57% for $Pd(OH)_2$/C to 65% for Pd/$BaSO_4$. Pt/C led to a lower yield of MAA, and Pt/Al_2O_3 gave the best MAA yield of 68% with a low amount of byproducts (13%). A higher selectivity towards MAA was obtained compared to the non-catalysed reaction with all Pd and Pt catalysts. As mentioned earlier, it appears that these catalysts have a positive stabilisation effect on the itaconate monoanion and allow the decarboxylation to MAA to take place with a better selectivity. Ru/C presented a totally different reactivity with a high conversion, a low MAA yield and 94% yield of byprod-
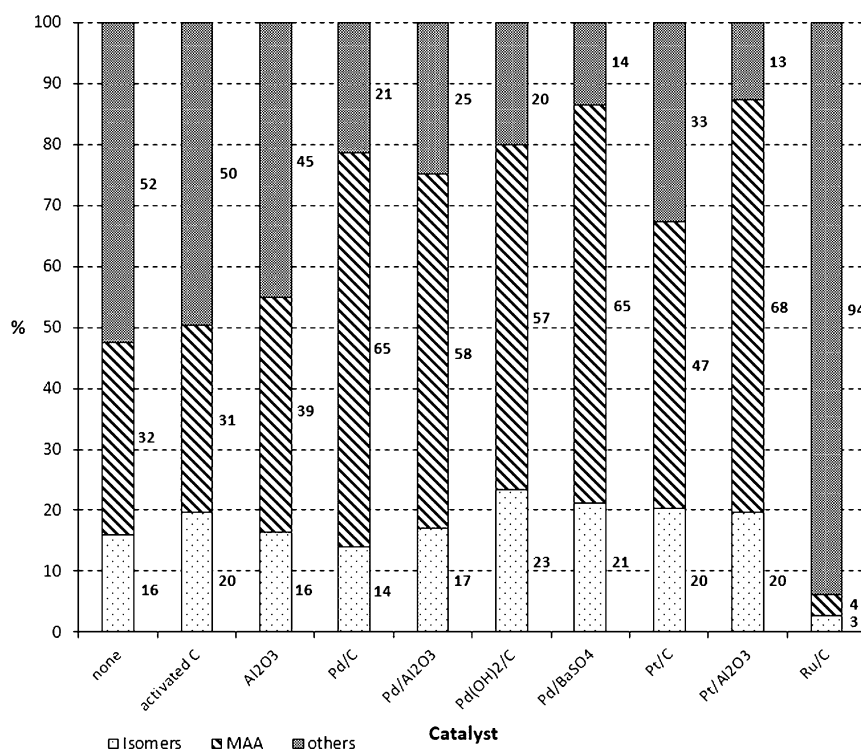
Figure 3. Catalyst screening for the decarboxylation of itaconic acid (Reaction conditions: itaconic acid 0.15 M, 20 mL of 0.15 M NaOH, 2.5 mol% of metal, 250°C, 1 h; Isomers = itaconic acid+mesaconic acid+citraconic acid).

Optimisation of the reaction conditions using Pt on alumina

The Pt/Al$_2$O$_3$ catalyst was used, and the temperature of the reaction was varied from 175–275 °C (Figure 5).

Similar to the reaction of Ru/C, the reaction performed at 175 °C resulted in a low isomers conversion and a poor MAA selectivity of 9%. If the temperature was increased to 200 °C, the isomers conversion was improved and the selectivity to MAA increased to 23%. At 225 °C, the MAA selectivity reached 44% with a better conversion. The best results obtained at 250 °C with 80% conversion and 84% MAA selectivity showed a lower quantity of the three isomers and byproducts. It is clear that the nature of the byproducts differs between the reactions performed at lower temperatures and those at temperatures higher than 250 °C. It appears that at 250 °C, the optimum conditions to promote the higher MAA selectivity by decarboxylation are reached with less hydration side reactions

ucts, probably because more deoxygenation reactions take place.

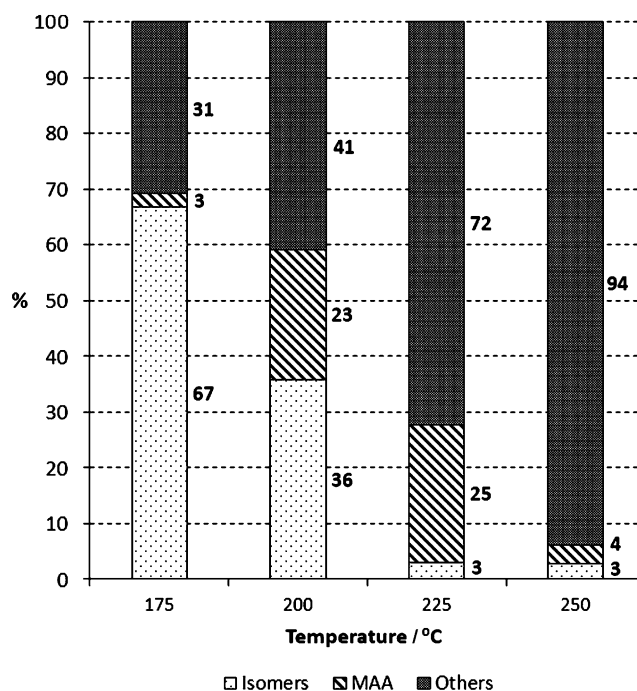## Optimisation of the reaction conditions using ruthenium on carbon

Amongst the catalysts screened, Ru/C presented a high level of byproduct formation. It is probable that those byproducts are also formed from MAA and that a better selectivity towards MAA production can be obtained at lower temperatures (Figure 4).

Under similar reaction conditions to those at 250 °C, the decarboxylation reaction was run at 175, 200 and 225 °C. At low temperature (175 °C), the conversion was incomplete and isomers were present as major compounds (67%). A low yield of MAA (3%) was observed, and it appears that degradation had already occurred from the observation of a 31% yield of byproducts. This amount increases drastically with temperature, and at intermediate temperatures (200 and 225 °C) the MAA yield was comparable at ≈23%. A reaction performed at 175 °C for 3 h led to a higher conversion with 16% of isomers left and a better yield of MAA (17%) but a high level of degradation with byproducts observed in 67% yield. All reactions performed with Ru/C led to an increase of the internal pressure (up to 5 bar), which suggests that the degradation products are volatile compounds. Although MAA yields can be improved at lower temperatures by using Ru/C as the catalyst, the level of side reactions remains high and the process appears to be less selective towards MAA than if Pd- or Pt-based catalysts are used at higher temperatures.
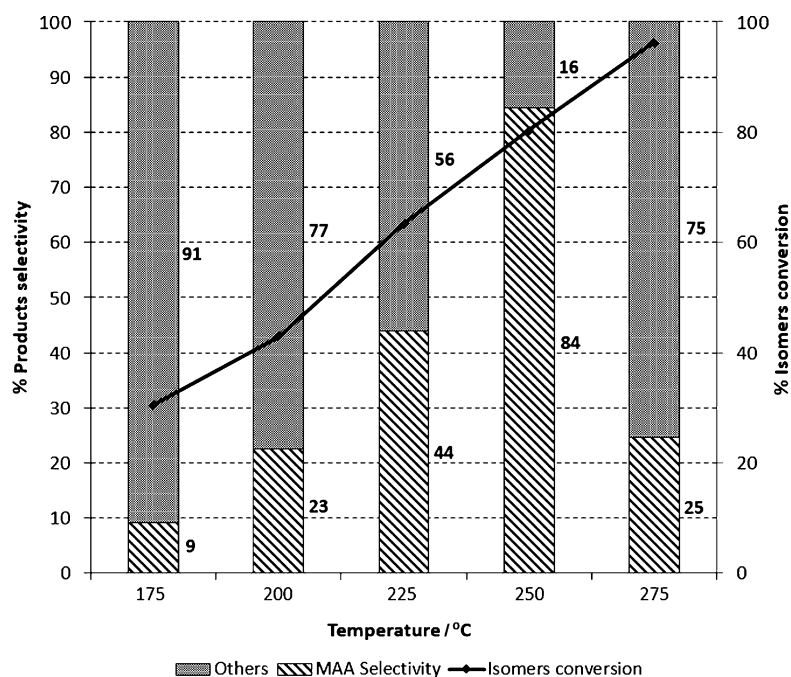

Figure 4. Decarboxylation of itaconic acid using 5 wt% Ru/C catalyst at different temperatures (Reaction conditions: itaconic acid 0.15 M, 20 mL of 0.15 M NaOH, 2.5 mol% of Ru, 1 h; Isomers = itaconic acid+mesaconic acid+citraconic acid).

Figure 5. Decarboxylation of itaconic acid using 5 wt% Pt/Al$_2$O$_3$ catalyst at different temperatures (Reaction conditions: itaconic acid 0.15 M, 20 mL of 0.15 M NaOH, 2.5 mol% of Pt, 1 h; Isomers = itaconic acid+mesaconic acid+citraconic acid).
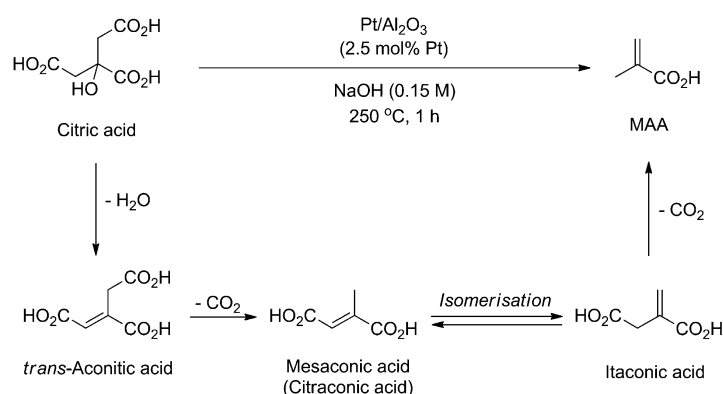
Conversion of citric acid to methacrylic acid

Direct conversion

Itaconic acid can be produced by micro-organisms by following the modified metabolic pathway of citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid),[17b] and it has been shown that itaconic acid can be obtained during the chemical catalytic dehydration of citric acid to (E)-prop-1-ene-1,2,3-tricarboxylic acid or aconitic acid.[32] Therefore, it is conceivable to think that MAA can be produced directly from citric acid. Carlsson et al. tested citric acid as substrate under near-critical and supercritical water conditions and observed that successive dehydration and double decarboxylation occurred, however, MAA was formed in a relatively low yield of 6%.[19]

The major products of the reaction were itaconic acid and its two isomers, which reached 76% yield overall. Thus, we investigated the use of citric acid under the metal-catalysed decarboxylation conditions (Scheme 2, Table 2). Citric acid was consumed almost fully in all of the reactions. No aconitic acid was detected in the crude mixtures, which shows that aconitic acid decarboxylation is faster than citric acid dehydration.

If we used Pt/Al$_2$O$_3$, after reaction for 1 h at 250 °C, the crude mixture was analysed and a full conversion of citric acid was observed (Table 2, entry 1). MAA was obtained with 35% selectivity, and the three isomers of itaconic acid were obtained in 19% yield. Shorter or longer reaction times did not improve the MAA selectivity (Table 2, entries 2 and 3). An im-

(equilibrium reaction) and less degradation by further decarboxylation to propene. Complementary reactions were performed at 225 and 250 °C for different reaction times without any improvement of the MAA selectivity. For longer reaction times at 250 °C the MAA selectivity was inferior by more than 20% with more degradation products present in the reaction mixtures. Shorter reaction times led to lower MAA selectivities and a higher amount of starting materials (itaconic acid and isomers). At 225 °C for longer reaction times, the amount of byproducts remained almost the same with a slight increase of the MAA selectivity (up to 43% for 3 h reaction), and the amount of starting materials decreased proportionally.

Down-stream processing and isolation of methacrylic acid

Several contributions from the patent literature describe the recovery and isolation of MAA from aqueous solutions either by simple extraction or a combination of azeotropic distillation and extraction.[31] We tested the combination of the two purification techniques one after the other and the other way around and we obtained similar isolated yields of MAA (≈50%, see Experimental Section). In both cases, the efficiency of the purification reached 80–85% of MAA recovery compared to the maximum theoretical isolated yields. As mentioned above, numerous examples of MAA purification from an aqueous solution have been reported by different chemical companies in the patent literature.[31] Therefore, the isolation of MAA, even on a large scale, is a known technology

and it will not constitute a major issue to scale up the process.

Scheme 2. One-pot conversion of citric acid to MAA.

Table 2. Parameter screening for the dehydration and double decarboxylation of citric acid.[a]

Entry	Catalyst (2.5 mol%)	NaOH [equiv.]	T [°C]	Reaction time [h]	Conversion of citric acid [%]	Product selectivity [%]		
						MAA	Isomers[b]	Others[c]
1	Pt/Al$_2$O$_3$	1	250	1	100	35	19	46
2	Pt/Al$_2$O$_3$	1	250	0.5	100	27	19	54
3	Pt/Al$_2$O$_3$	1	250	2	100	32	12	56
4	Pt/Al$_2$O$_3$	2	250	1	100	0	8	92
5	Pt/Al$_2$O$_3$	1	225	2	99	18	13	69
6	Pd/C	1	250	1	100	36	18	46
7	Pd/Al$_2$O$_3$	1	250	1	100	41	15	44
8	Ru/C	1	250	1	100	4	2	94
9	Ru/C	1	225	1	100	30	2	68
10	Ru/C	1	200	1	100	28	27	45

[a] Reaction conditions: pressure reactors, citric acid (0.59 g, 3.07 mmol), 20 mL of basic aqueous solution. Conversion and yields were determined by HPLC; [b] Isomers = itaconic acid+mesaconic acid+citraconic acid; [c] Volatile degradation products such as propene, acetone and acetaldehyde.

relatively good selectivity, which shows that citric acid could be a good feedstock for the production of bio-based MAA.

Two-step conversion with aconitic acid as intermediate

Aconitic acid is the dehydration product of citric acid and, therefore, a likely intermediate in the reaction pathway to itaconic acid and MAA (Scheme 2). Aconitic acid can be obtained by the catalytic dehydration of citric acid using a mineral acid with yields of 45–75% (Scheme 3).[32, 33] Aconitic acid also occurs naturally in plants and, for instance, is present in raw sugarcane juice at 1–2 g L^{-1}[34] and is up to 5% of the dry weight of sugarcane molasses.[35] Moreover, fermentation processes can produce aconitic acid selectively.[36] Therefore, we

Scheme 3. Two-step conversion of citric acid to MAA.

portant effect on the reaction with up to 92% of byproduct formation was observed with the increase of the number of equivalents of base (Table 2, entry 4). It is possible that under these conditions, citric acid was converted through an oxidative pathway to acetone dicarboxylic acid and subsequently to acetone instead of aconitic acid.[32] A reaction performed at 225 °C for 2 h led to a lower MAA selectivity (Table 2, entry 5). Pd/C and Pd/Al$_2$O$_3$ were also tested under the standard reaction conditions and showed a slightly better selectivity toward MAA with 36 and 41% yield, respectively (Table 2, entries 6 and 7). Reactions at lower temperature (225 °C) and longer times (2 h) did not improve the MAA selectivity. As observed with itaconic acid at 250 °C, the use of Ru/C resulted in a low selectivity and the production of byproducts (Table 2, entry 8). Notably, under these conditions a 6 bar increase of the internal pressure was observed during the reaction, probably caused by the formation of gaseous byproducts such as propene. If the reaction temperature was decreased to 225 °C, the amount of byproducts was decreased and only a pressure increase of 2 bar and a MAA selectivity of 30% were observed (Table 2, entry 9). A reaction performed at 200 °C for 1 h showed a slightly lower yield (28%) with, however, 27% of itaconic acid and isomers left (Table 2, entry 10). If the reaction time was increased to 2 h, the MAA yield was not improved. Compared to the work by Carlsson et al.,[19] in which citric acid was converted to MAA with 6% yield under supercritical water conditions, our metal-catalysed decarboxylation procedure is performed at 225–250 °C with no added pressure (the natural pressure increase reaches 40 bar) and results in the formation of MAA with 41% selectivity. Thus, the combination of one dehydration and two decarboxylation steps is possible in one pot with

tested aconitic acid as the substrate in the metal-catalysed decarboxylation reaction (Scheme 3). A similar optimisation study as for citric acid was performed with aconitic acid as the substrate (see Table 2 for reaction conditions and Table S1 for detailed results). The same reaction conditions were varied and the best result was obtained by using one equivalent of base with Pt/Al$_2$O$_3$ as the catalyst for 1 h at 250 °C with 47% MAA selectivity and 22% of itaconic acid isomers. Compared to the one-pot reaction with citric acid, a slightly lower amount of byproducts was observed (30%). Longer reaction times, lower temperatures and of the use of other catalysts did not improve this result.

The one-pot procedure that used citric acid as the substrate gave 41% selectivity to MAA. The decarboxylation step of the other route through the isolation of aconitic acid resulted in 47% MAA selectivity under similar reaction conditions as those of the one-pot procedure. Even if the H$_2$SO$_4$-catalysed dehydration reaction of citric acid to aconitic acid was quantitative, we can conclude that, at the current state of technology, the one-pot conversion of citric acid to MAA is the more efficient procedure. This is also validated by the fact that, in the case of the large-scale production of bio-based MAA, citric acid is a more widely available and cheaper feedstock than aconitic acid.

Conclusions

Solid Pd, Pt and Ru catalysts are able to perform the decarboxylation of itaconic acid to methacrylic acid (MAA) in water. The best MAA selectivity (84%) was obtained by using Pt/Al$_2$O$_3$ for 1 h at 250 °C. The Pd catalysts showed a similar activity with

slightly lower selectivities. Ru was a more active metal for the conversion of itaconic acid but led to lower MAA selectivity (< 25%). Compared to benchmark reaction procedures that are performed in near-critical and supercritical water conditions, MAA can be obtained at temperatures of 200–250 °C without any external added pressure. Moreover, an intensive optimisation of the reaction parameters was completed to attain better conversion and selectivity. Two different purification techniques were tested, and MAA was isolated in ≈ 50% yield.

Citric acid, a widely available bio-based feedstock, was successfully used as a substrate, and the one-pot dehydration–double decarboxylation pathway resulted in the formation of MAA with 41% selectivity by using a Pd/Al$_2$O$_3$ catalyst. A two-step procedure via the isolation of aconitic acid did not lead to better results.

Hence, the production of bio-based MAA, a precursor of bio-based poly(methyl methacrylate), can be achieved in one step in modest to good selectivity under relatively mild conditions from substrates available from biomass fermentation or raw fruit juices. Even if the overall molecular mass balance appears detrimental, for instance, there is a 55% molecular mass loss from citric acid to MAA, it is possible that this process could be economically viable. Firstly, it takes place in an aqueous medium and, therefore, is potentially compatible with the nature of fermentation broths obtained directly from the production of itaconic acid and citric acid. If these broths are used as the starting material, the purification of the aforementioned substrates before decarboxylation will be obsolete. Secondly, the solid catalysts that we employed are known to be recyclable and can be used in continuous processes, which will constitute an added benefit to the process. Both implementations of our decarboxylative synthesis of MAA, together with an economic feasibility study of large-scale production, are currently under investigation in our laboratory and will be reported in due course.

Experimental Section

MilliQ-grade water was used for all reactions. Sodium hydroxide (98%), calcium hydroxide (96%), itaconic acid (2-methylenesuccinic acid, 99%), citric acid (2-hydroxypropane-1,2,3-tricarboxylic acid, 99%), *trans*-aconitic acid ((*E*)-prop-1-ene-1,2,3-tricarboxylic acid, 98%) and CDCl$_3$ (99.8 atom% D) were purchased from Sigma–Aldrich. The catalysts had the following specifications and origins: Pd/C (5 wt%, Sigma–Aldrich), Pd/Al$_2$O$_3$ (10 wt%, Sigma–Aldrich), Pd/BaSO$_4$ (10 wt%, Fluka), Pearlman's catalyst (20 wt% Pd(OH)$_2$/C, Sigma–Aldrich), Ru/C (5 wt%, Sigma–Aldrich), Pt/C (10 wt%, Sigma–Aldrich), Pt/Al$_2$O$_3$ (5 wt%, Sigma–Aldrich). Ar gas was supplied by Linde Gas Benelux (Instrument argon 5.0). Unless stated otherwise, all chemicals were used as received and used without any further purification.

High-pressure reactions were performed in a parallel Parr system reactor (Series 5000, 6×75 mL, Hastelloy C-276) equipped with glass liners and glass-coated magnetic stirring bars at 1000 rpm. NMR spectra were recorded by using a Bruker Avance III spectrometer operated at 400.17 MHz (^{1}H) and 100.62 MHz (^{13}C). ^{1}H NMR chemical shifts are quoted in parts per million (ppm) referenced to the appropriate solvent peak. ^{13}C NMR spectra were fully decou-

pled by broad band decoupling. HPLC was performed by using a Thermo Fisher Scientific autosampler and pump (eluent: 12 mM H$_2$SO$_4$, pump flow: 0.6 mL min^{-1}), with an ROA Organic acid 150× 7.8 mm column (column temperature: 40 °C) and an injection volume of 50 µL. UV detection was performed at 210 nm, and the quantification of compounds was achieved by calibration with phthalic acid as an internal standard and checked by calibration from pure products. Retention times [min] were: citric acid (4.3), pyruvic acid (5.5), citraconic acid (6.4), itaconic acid (7.3), mesaconic acid (10.3), MAA (13.1), crotonic acid (14.5), phthalic acid (16.3, internal standard).

Typical experimental procedure for the decarboxylation of itaconic acid

In a typical experiment, itaconic acid (0.4 g, 3.07 mmol) and the solid transition-metal catalyst (2.5 mol% of metal) were weighed in air and placed in a glass liner with a stirrer bar. The liner was introduced into the reactor, and the atmosphere was purged twice with Ar. The basic aqueous solution was prepared in advance at the appropriate concentration (NaOH, 0.15 M) and degassed with Ar by bubbling gas through the solution for 1 h. The basic solution (20 mL) was added to the reactor with a syringe. The reactor was closed, purged three times with Ar, stirred (1000 rpm) and heating began (typically heating up to 250 °C was achieved in 30 min). The internal pressure reached 38 bar. The recorded reaction time started when the desired temperature was reached. After the allocated reaction time, the reactor was allowed to cool to RT (1–1.5 h) and the gas pressure was released. The crude solution was purified by micro-filtration (Millipore micro-filters, 0.20 µm), the pH was measured and an aliquot of the crude reaction mixture was diluted with MilliQ-grade water prior to analysis by HPLC.

Purification of crude reaction mixtures and isolation of MAA

With the aim to obtain an isolated yield from our metal-catalysed decarboxylation procedure, we performed two series of six identical reactions in our parallel reactors setup with itaconic acid (0.6 g) as the substrate, one equivalent of base in water (30 mL) and Pt/Al$_2$O$_3$ as the catalyst in each reactor. The purification of the two series of reaction was performed by distillation and solvent extraction.

Distillation followed by extraction: After the six identical itaconic acid decarboxylation reactions were performed (6×0.6 g of itaconic acid in 30 mL of 0.15 M NaOH solution, Pt/Al$_2$O$_3$ catalyst (2.5 mol% Pt)), the crude mixtures were filtered (micro-filtration 0.2 µm) and combined together to form the solution Crude1 (175 mL). HPLC analysis revealed the following composition: 60% of MAA, 3% of itaconic acid isomers and 37% of byproducts. The solution Crude1 (175 mL), was subjected to azeotropic vacuum distillation (20 mbar) to give a main fraction of 107 mL (20 mbar, vapour temperature of 54 °C). This fraction was analysed by HPLC and showed the following composition: 99.0% MAA, 0.7% crotonic acid, 0.2% pyruvic acid and 0.1% other compounds. Extraction with Et$_2$O (3×50 mL) followed by drying the combined organic layers over MgSO$_4$ and evaporation to dryness led to the recovery of a colourless oil. NMR spectroscopy showed the presence of pure MAA (1.22 g, 51% isolated yield, > 99.0% purity (HPLC)).

Extraction followed by distillation: Another set of six identical itaconic acid decarboxylation reactions was performed (6×0.6 g of itaconic acid in 30 mL of 0.15 M NaOH solution, Pt/Al$_2$O$_3$ catalyst (2.5 mol% Pt)). The crude mixtures were filtered (micro-filtration

0.2 μm) and combined together to form the solution Crude2 (174 mL). HPLC analysis revealed the following composition: 60% of MAA, 8% of itaconic acid isomers and 32% of byproducts. The solution Crude2 (174 mL) was extracted into Et_2O (3×75 mL), and the combined organic layers were dried over $MgSO_4$ and evaporated to dryness. NMR spectroscopy showed that MAA was present as the major product with traces of other organic acids such as acetic acid, pyruvic acid and crotonic acid. Purification by vacuum distillation was then performed (20 mbar, vapour temperature of 37–39 °C) to lead to the isolation of MAA as a pure product in 47% yield (1.12 g).

MAA: ^1H NMR ($CDCl_3$): $\delta = 1.96$ (dd, $^4J = 1.61$ and 1.04 Hz, 3H), 5.68 (m, 1H), 6.25 (m, 1H), 11.42 ppm (br s, 1H); ^{13}C NMR ($CDCl_3$): $\delta = 17.9, 127.9, 135.9, 173.2$ ppm.

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