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Stabilising Ni catalysts for the dehydration-decarboxylation-hydrogenation of citric acid to methylsuccinic acid

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A new reaction sequence of dehydration-decarboxylation-hydrogenation to transform citric acid into methylsuccinic acid, was recently developed using Pd as noble metal catalyst in water. In this work Ni catalysts were investigated as cheap, non-noble metal alternative. Several home-made and commercial catalysts were screened for this reaction. Citric acid was very reactive and full conversions were readily obtained in all cases. However, the selectivity to methylsuccinic acid was initially low, since typical Ni catalysts were not stable and therefore not able to hydrogenate the formed C=C double bonds. Due to the lower hydrogenation activity of Ni compared to Pd, new side products appeared. Especially hydration of the C=C double bonds made the reaction network more complex in this case. Fortunately, the formation of all hydration products – even the rather stable lactone, β-carboxy-γ-butyrolactone – was eventually shown to be completely reversible. Three routes were then studied to stabilise Ni catalysts and to enable the Ni catalyzed conversion of citric acid to methylsuccinic acid; partial neutralisation of the acid reactant, adding Fe to Ni/ZrO₂ or to the reaction mixture and coating Ni particles with carbon, all proved to stabilise Ni and all resulted in high to very high methylsuccinic acid yields. Furthermore, the role of Fe was unravelled by performing reference reactions with different Fe compounds and by in depth characterisation of the NiFe/ZrO₂ catalyst. Finally, the reaction conditions were optimised using the carbon-coated Ni nanoparticles and kinetic profiles were recorded to confirm the extended reaction network.

Introduction

Methylsuccinic acid is a versatile dicarboxylic acid, which can be used as a building block for the manufacture of solvents for cosmetics,[1] binders,[2] and biodegradable polyesters.[3–6] Incorporating methylsuccinic acid in *e.g.* polybutylene succinate enhances the biodegradability and the toughness of the polyester and simultaneously reduces the viscosity of this polyester's solutions.[4] Nowadays, methylsuccinic acid can only be produced via hydrogenation of itaconic acid.[7–10] Recently, Palkovits and co-workers reported an electrocatalytic system that enables the direct reduction of itaconic acid in a fermentation broth at room temperature, yielding up to 98% methylsuccinic acid.[11] However, in 2011 only 41.4 thousand tons of itaconic acid were produced via fermentation.[12]

The annual production volume of citric acid, on the other hand, was 2 million tons in 2016.[13] The solid-state fermentation of agricultural waste streams from *e.g.* corn or sugarcane, is increasingly being applied for the sustainable production of this biobased compound.[14] Citric acid has already been used as platform chemical for the synthesis of methacrylic acid, 2- and 3-methylbutyrolactone, 3-methyl-tetrahydrofuran and 3-(2'-hydroxyethyl)tetrahydrofuran.[15–18] In addition, we recently developed the one-step conversion of citric acid to methylsuccinic acid.[19] Citric acid was first dehydrated towards aconitic acid, subsequently decarboxylated to itaconic acid and finally hydrogenated to methylsuccinic acid. By using mild hydrogenation conditions and water as the solvent, carboxylic acid hydrogenation could be avoided. Moreover, the rates of decarboxylation and hydrogenation were carefully balanced to prevent further decarboxylation to *e.g.* methacrylic acid, and premature hydrogenation to propane-1,2,3-tricarboxylic acid. Besides, radical fragmentation of citric acid was proven to be minimal under more acidic conditions. Altogether these insights lead to high methylsuccinic acid yields; a yield of 84% was *e.g.* achieved by reacting citric acid in water for 40 min, using 0.5 mol% Pd/C as hydrogenation catalyst with 8 bar H₂ at 225°C.

The first step in the new reaction sequence of dehydration-decarboxylation-hydrogenation is acid-catalyzed, while the decarboxylation occurs spontaneously at temperatures higher than 150°C – although this step might also be aided by Pd. So intrinsically, the only metal-catalyzed step in this sequence is the hydrogenation of itaconic acid (or its isomers), an α,β-

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unsaturated carboxylic acid. Two metals are generally known to be suitable to catalyze the C=C hydrogenation of these α,β-unsaturated carboxylic acids, namely Pd and Ni.[20] This prompted us to investigate Ni catalysts for the conversion of citric acid to methylsuccinic acid.

Ni is a cheap, readily available non-noble metal, which makes it an interesting compound for the production of industrial catalysts. However, the acidic hydrothermal conditions and the presence of citric acid as a chelating compound render the use of Ni as hydrogenation catalyst for this reaction untrivial. Nevertheless, research by Lercher and co-workers encouraged us to start this investigation.[21] They showed that Ni^0 nanoparticles are stable during the hydrothermal hydrodeoxygenation of phenol; Ni/HZSM-5 is stable in dilute H_3PO_4 and even in 15 wt% acetic acid if the catalyst is pre-reduced.[21] In the latter conditions only around 4% Ni was leached into solution. Moreover, a passivated Ni/SiO_2 catalyst was almost completely reduced within 10 min under the aqueous reaction conditions (200°C, 35 bar H_2), indicating that reduction is faster than dissolution of Ni^{II} species.[21] Ni/HZSM-5 was also used for the hydrogenolysis of tetrahydrofurfuryl alcohol to 1,5-pentanediol and tetrahydro-pyran under hydrothermal conditions (250°C, 34 bar H_2).[22] In this case, the Ni catalyst was quite stable as well: only 5% Ni was leached into solution.

Furthermore, extensive research has been conducted to stabilise Ni catalysts for demanding reactions, such as methanation of CO and CO_2 or dry/steam reforming of hydro-carbons and ethanol.[23–32] For instance, adding Fe to Ni catalysts can improve the Ni dispersion, avoid sintering and facilitate the reduction of Ni.[23–28] Coating Ni particles with a metal oxide layer, such as SiO_2, Al_2O_3 or ZrO_2, can also prevent sintering and coke formation.[29–32] This method has been applied several times for the dry and steam reforming of CH_4. Besides, Ni particles encapsulated by carbon species have been reported for electrocatalytic applications in sensors, batteries and oxygen evolution reactions (e.g. in fuel cells).[33–35] To the best of our knowledge, carbon-coated Ni nanoparticles have so far not been reported as suitable chemocatalysts.

In this research we aim at identifying Ni-based catalysts and reaction conditions that enable the conversion of citric acid to methylsuccinic acid, while minimising the leaching of Ni.

Results and discussion

Screening of Ni-based catalysts and extending the reaction network

Initially, nine Ni-based catalysts were screened for their hydrogenation activity to transform citric acid into methylsuccinic acid (**Table 1**, entries 1-9). Among these catalysts were four home-made materials – synthesised via incipient wetness impregnation with $Ni(NO_3)_2$, see ESI for experimental details – and five commercial catalysts (entries 1-4 and 5-9, respectively). All these catalysts were pre-reduced and passivated to ensure safe handling in air. Keeping in mind the balancing of the hydrogenation and decarboxylation rate, the reaction conditions were changed to compensate for the lower hydrogenation activity of Ni compared to Pd in reference [19]. Citric acid was still reacted in water (2 mL, 0.1 M) for 6 h; the temperature was however decreased to 175°C to decrease the decarboxylation rate and the H_2 pressure was increased to 20 bar to increase the hydrogenation rate. Also the catalyst-to-substrate ratio was increased to 10 mol% for the same purpose.

Table 1. Dehydration-decarboxylation-hydrogenation of citric acid using Ni-based catalysts.[a]

	Catalyst	Conversion [%]	MSA [b]	2nd deca [c]	Fragmentation [d]	Itaconic isomers [e]	Isomer hydration [f]	Leaching Ni (Fe) [%]
					Selectivity [%]			
1	$Ni/MgAl_2O_4$	>99	3	13	6	22	19	23
2	Ni/TiO_2	>99	3	13	7	36	40	>99
3	Ni/ZrO_2	>99	2	6	4	50	38	>99
4	Ni/Al_2O_3	>99	2	13	3	27	23	>99
5	$Ni/SiO_2-Al_2O_3$	>99	9	16	7	30	34	>99
6	Ni/SiO_2	>99	4	11	5	39	37	>99
7	Katalco JM 11-4R [g]	>99	12	14	8	28	35	368 mg/L [h]
8	Katalco JM 23-8 [i]	>99	48	12	11	6	21	116 mg/L [h]
9	HTC Ni 500 RP [j]	97	44	12	7	6	21	238 mg/L [h]
10	Ni_5Fe_1/ZrO_2	>99	5	10	6	48	30	58 (43)
11	Ni_5Fe_3/ZrO_2	>99	36	10	15	9	26	28 (80)
12	$\mathbf{Ni_5Fe_5/ZrO_2}$	**>99**	**69**	**6**	**15**	**1**	**9**	**5 (93)**
13	$\mathbf{Ni_5Fe_5/ZrO_2}$ **(Ac)**	**>99**	**66**	**6**	**14**	**1**	**12**	**16 (97)**
14	**Ni-C NPs**	**>99**	**81**	**4**	**5**	**<1**	**10**	**20**
15	-	85	<1	2	4	62	32	-
16	$NiSO_4$	90	<1	3	5	59	33	-

[a] Reaction conditions: citric acid (0.2 mmol), catalyst (10 mol% Ni), water (2 mL), 175°C, 2 bar N_2 and 20 bar H_2, 6 h. [b] Methylsuccinic acid. [c] '2nd deca' represents methacrylic acid, 2-hydroxyisobutyric acid, isobutyric acid and butyric acid. [d] 'Fragmentation' represents acetone, acetic acid, pyruvic acid and lactic acid. [e] 'Itaconic isomers' represents itaconic acid, mesaconic acid and citraconic acid. [f] 'Isomer hydration' represents 2-(hydroxymethyl)succinic acid, β-carboxy-γ-butyrolactone and 2-hydroxy-2-methylsuccinic acid. [g] 3 mg. [h] The concentration of Ni in the reaction solution is given, since the precise catalyst composition is unknown. [i] 23 mg. [j] 8 mg.

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In all cases the conversion of citric acid was very high; on the other hand, the selectivity towards methylsuccinic acid was initially rather low (entries 1-9). The different products detected by ^{1}H-NMR can be explained by the reaction network in **Scheme 1**. There are some clear differences compared to the reaction using Pd as catalyst.[19] Due to the lower hydrogenation activity of Ni, even under the adapted reaction conditions, early hydrogenation of aconitic acid to propane-1,2,3-tricarboxylic acid was never observed. On the other hand, this also lead to the appearance of a new type of side reaction, namely hydration of the C=C double bonds. This hydration resulted in the formation of 2-hydroxy-2-methylsuccinic acid, 2-hydroxyisobutyric acid and 2-(hydroxymethyl)succinic acid; the latter can cyclise to β-carboxy-γ-butyrolactone. Besides, some further decarboxylation of itaconic acid and its isomers (mesaconic and citraconic acid) to methacrylic and crotonic acid, still occurred. These unsaturated monocarboxylic acids might be hydrogenated to form isobutyric and butyric acid. Finally, also acetone, acetic and pyruvic acid were produced via a radical pathway.[19] However, Ni has a stronger tendency to hydrogenate pyruvic acid to lactic acid,[20] which was observed more often than in the case of Pd – although still in minor quantities (≤6%). The ESI gives a detailed overview of the identification of the observed compounds.

In the initial screening the yield of methylsuccinic acid was always lower than 10% for the regular Ni/MeO$_x$ catalysts (**Table 1**, entries 1-6). It appears that Ni was rapidly and completely leached into solution under the demanding reaction conditions. Only for Ni/MgAl$_2$O$_4$ the leaching

appeared to be limited to 23%; this was probably due to the incorporation of oxidised Ni^{II} species in the layers of the layered double hydroxide. To make sure that Ni^{II} is not active for the hydrogenation, a reference reaction was performed using NiSO$_4$ as catalyst (entry 16). The result coincided with the blank reaction (entry 15); this clearly indicates that Ni^0 is needed for the C=C hydrogenation. In these reactions citric acid was converted for 85-90% and the majority of the products were itaconic acid and its isomers, which were partly hydrated to mainly β-carboxy-γ-butyrolactone. A minor amount of the itaconic isomers was further decarboxylated to methacrylic acid and around 5% was fragmented to form mainly acetone and acetic acid. The product distributions of the Ni catalyzed reactions generally correspond to the one in the blank reaction (entries 1-6 and 15). Nevertheless, besides the minor hydrogenation to methylsuccinic acid, the conversions of citric acid are now complete, which is most probably due to the faster dehydration facilitated by the supports. Moreover, more 'further decarboxylation' products were observed. This observation was most pronounced for Ni/MgAl$_2$O$_4$ and Ni/Al$_2$O$_3$, where also more than 30% of the products was lost from solution, next to the formation of 13% of secondary decarboxylation products. Mass loss from solution primarily occurred through extensive decarboxylation and formation of propene (**Scheme 1**).[19] The acceleration of the decarboxylation might be mediated by Mg^{2+} and Al^{3+} leached into solution.[36–38] Finally, three catalysts generously supplied by Johnson Matthey, especially Katalco JM 23-8 and HTC Ni 500 RP, showed to maintain some hydrogenation activity, resulting in the formation of 12-48% methylsuccinic
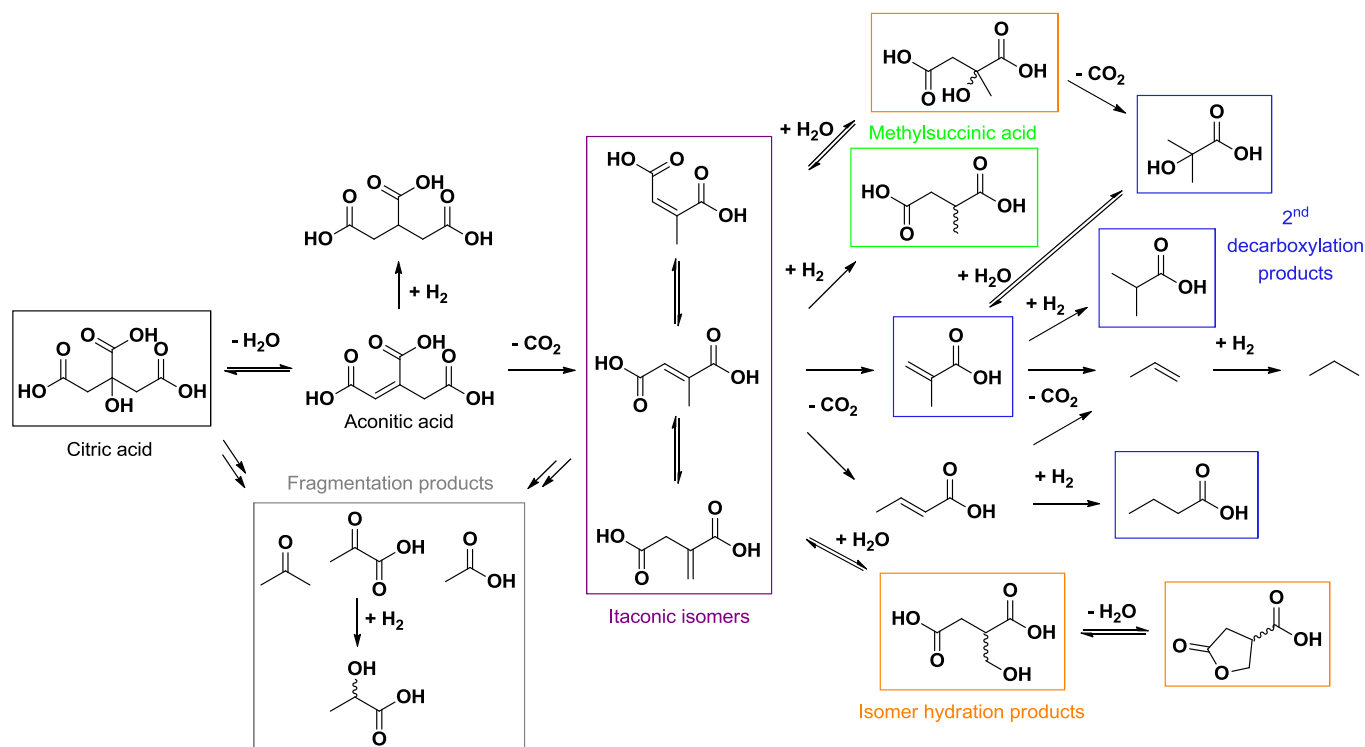
Scheme 1. Extended reaction network for the dehydration-decarboxylation-hydrogenation of citric acid, built on the reaction network in reference [19]. The ESI gives a detailed overview of the identification of the observed (framed) compounds. The colour codes of the different product groups will be further used in the following figures.

acid (entries 7-9). However, a significant amount of Ni was still leached into solution.

Subsequently, to gather more information about the fragmentation and hydration side reactions under these conditions, several blank reactions were performed starting from intermediates in the reaction network (**Table 2**). Fragmentation products were observed starting from aconitic acid, itaconic isomers and methacrylic acid. This means that in the absence of adequate hydrogenation, radical fragmentation not only proceeds directly from citric acid,[19] but also from unsaturated compounds further along the reaction network. Furthermore, itaconic and mesaconic acid were shown to be converted mainly via isomerisation and hydration; 2-hydroxy-2-methylsuccinic acid, 2-(hydroxymethyl)succinic acid and β-carboxy-γ-butyrolactone indeed originated from these itaconic isomers (entries 2 and 3). Moreover, itaconic acid is more reactive than mesaconic acid, which is probably due to the stronger delocalisation of the C=C double bond in mesaconic acid. Finally, it is clear that 2-hydroxyisobutyric acid can also be produced via hydration of methacrylic acid (entry 4), next to via hydration of the itaconic isomers followed by decarboxylation (**Scheme 1**).[19]

Stabilising Ni/ZrO$_2$ with Fe

Encouraged by the somewhat better stability of Katalco JM 23-8 and HTC Ni 500 RP and inspired by previous research on stabilising Ni catalysts,[23–28] Fe was added to the Ni/ZrO$_2$ catalyst. ZrO$_2$ was selected as stable support and Fe(NO$_3$)$_3$ was co-impregnated with Ni(NO$_3$)$_2$ in three different ratios: 1, 3 and 5 wt% Fe *vs.* 5 wt% Ni. The reduction and passivation conditions were the same as for the regular Ni/ZrO$_2$ catalyst (see ESI for further details). The three new catalysts were screened using the conditions in **Table 1** (entries 10-12). There was a remarkable positive correlation between the amount of Fe added and the yield of methylsuccinic acid. For Ni$_5$Fe$_5$/ZrO$_2$ a yield of 69% was already achieved. This positive trend corresponded to a clear increase in the stability of Ni; the Ni leaching steadily decreased from >99%, when no Fe was added, to only 5%, when Fe was stoichiometrically added (**Table 1**, entries 3 and 10-12). However, now a large part of the Fe leached into solution. In addition, this resulted in a clear increase of the fragmentation side products to around 15% due to the presence of oxidised Fe species as electron

acceptors. A similar result could be obtained with a NiFe catalyst based on acetate precursors (**Table 1**, entry 13).

To elucidate the peculiar role of Fe, several reference reactions were performed, including blank reactions with the support and different Fe compounds, as well as addition of these compounds to the regular Ni/ZrO$_2$ catalyst (**Table 3**). The reaction with ZrO$_2$ alone confirms that this support accelerates (de)hydration reactions, since the citric acid conversion was complete and the product selectivity shifted towards the 'isomer hydration' products (entry 2). The different Fe compounds seem to have some hydrogenation ability, however, also further decarboxylation and especially fragmentation were accelerated (entries 3-6). The latter is most pronounced for fine Fe^0 powder, which quickly dissolved in the citric acid solution, and for Fe(NO$_3$)$_3$, where NO$_3^-$ might act as an additional electron acceptor. When Fe(NO$_3$)$_3$ and Fe(CH$_3$COO)$_2$ were added to a reaction mixture with Ni/ZrO$_2$, we noticed a stabilising effect: only 3% and 11% Ni were leached into solution, respectively (entries 7 and 8). This means that ionic Fe species might catalyze the reduction of Ni with H$_2$ under the reaction conditions, stabilising the Ni particles. For Fe(CH$_3$COO)$_2$ this resulted in a decent methylsuccinic acid yield of 45%, whereas in the case of Fe(NO$_3$)$_3$ only 13% yield was obtained. This can be explained by the increased fragmentation rate in this case. On the other hand, Fe^0 might act as a sacrificial reductant, in this way stabilising the Ni against oxidation (only 7% leaching) and enabling a methylsuccinic acid yield of 55% (entry 9). Sun *et al.* showed that the dissolution of Fe^0 indeed induces a more reducing environment.[39] In the case of Fe(CH$_3$COO)$_2$ and Fe^0, the effect on the stability of the Ni catalyst through a (subtle) increase in *pH* cannot be excluded (*cfr. infra*),[39] although this amount of Fe^0 did not result in a measurable *pH* increase. When Fe^0 was dissolved in the citric acid solution, the *pH* remained at 2.2.

To clarify the role of Fe in the NiFe/ZrO$_2$ catalysts, the Ni/ZrO$_2$ and Ni$_5$Fe$_5$/ZrO$_2$ catalysts were characterised by scanning transmission electron microscopy (STEM) in combination with energy dispersive X-ray spectroscopy (EDX) and by X-ray photoelectron spectroscopy (XPS). Additionally, these catalysts were also analysed by N$_2$ physisorption and powder X-ray diffractometry (XRD). The N$_2$ adsorption-desorption isotherms showed a behaviour that is typical for a mesoporous structure (**Table S1**, **Figure S1** and **S2**), and the

Table 2. Reactivity of intermediates in the dehydration-decarboxylation-hydrogenation of citric acid under blank reaction conditions.[a]

		Conversion	Selectivity [%]				
	Substrate	[%]	MSA[b]	2nd deca[c]	Fragmentation[d]	Itaconic isomers[e]	Isomer hydration[f]
1	Aconitic acid	>99	<1	4	1	52	44
2	Itaconic acid	76	<1	4	1	19[g]	44
3	Mesaconic acid	36	<1	7	3	52[h]	38
4	Methacrylic acid	45	-	59[i]	3	-	-

[a] Reaction conditions: substrate (0.2 mmol), water (2 mL), 175°C, 2 bar N$_2$ and 20 bar H$_2$, 6 h. [b] Methylsuccinic acid. [c] '2nd deca' represents methacrylic acid and 2-hydroxyisobutyric acid. [d] 'Fragmentation' represents acetone, acetic acid and pyruvic acid. [e] 'Itaconic isomers' represents itaconic acid, mesaconic acid and citraconic acid. [f] 'Isomer hydration' represents 2-(hydroxymethyl)succinic acid, β-carboxy-γ-butyrolactone and 2-hydroxy-2-methylsuccinic acid. [g] Mesaconic acid and citraconic acid. [h] Itaconic acid and citraconic acid. [i] 2-Hydroxyisobutyric acid.

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Table 3. Reference reactions to elucidate the role of Fe.[a]

	Catalyst	Additive	Conversion [%]	Selectivity [%]					Leaching Ni (Fe) [%]
				MSA[b]	2nd deca[c]	Fragmentation[d]	Itaconic isomers[e]	Isomer hydration[f]	
1	-	-	85	<1	2	4	62	32	-
2	ZrO_2[g]	-	>99	<1	4	3	53	41	-
3	Fe/ZrO_2	-	>99	2	7	12	39	33	- (93)
4	-	Fe^0	>99	9	12	38	26	15	- (>99)
5	-	$Fe(NO_3)_3$	>99	4	8	32	25	19	-
6	-	$Fe(CH_3COO)_2$	>99	5	9	21	34	31	-
7	Ni/ZrO_2	$Fe(NO_3)_3$	>99	13	5	42	6	5	3
8	**Ni/ZrO_2**	**$Fe(CH_3COO)_2$**	**>99**	**45**	**7**	**17**	**3**	**22**	**11**
9	**Ni/ZrO_2**	**Fe^0**	**>99**	**55**	**7**	**27**	**<1**	**12**	**7 (>99)**

[a] Reaction conditions: citric acid (0.2 mmol), catalyst (10 mol% Me), additive (10 mol% Fe), water (2 mL), 175°C, 2 bar N_2 and 20 bar H_2, 6 h. [b] Methylsuccinic acid. [c] '2nd deca' represents methacrylic acid, 2-hydroxyisobutyric acid, isobutyric acid and butyric acid. [d] 'Fragmentation' represents acetone, acetic acid, pyruvic acid and lactic acid. [e] 'Itaconic isomers' represents itaconic acid, mesaconic acid and citraconic acid. [f] 'Isomer hydration' represents 2-(hydroxymethyl)succinic acid, β-carboxy-γ-butyrolactone and 2-hydroxy-2-methylsuccinic acid. [g] 24 mg ZrO_2.

metal loadings (5 wt%) were too low to distinguish characteristic metal peaks in the X-ray diffractogram (**Figure S3**). In literature, the beneficial effect of Fe addition to Ni has been ascribed to an improved dispersion and/or a facilitated reduction.[23–28] In this work, the effect of Fe on the dispersion of Ni could not be confirmed by STEM, since few metal particles were observed due to the low contrast between Ni and zirconia (**Figure 1-(a)** and **-(e)**). Simultaneous EDX analysis did confirm that Ni and Fe are intimately mixed in the Ni_5Fe_5/ZrO_2 catalyst (**Figure 1-(h)** and **-(i)**). However, an effect of Fe on the dispersion seems unlikely to be decisive for the stabilisation of Ni, since Fe almost completely leaches into solution. Finally, XPS analysis showed that the surface of the Ni particles is indeed oxidised by the passivation procedure; before reaction Ni is mainly present as NiO and $Ni(OH)_2$ (**Table 4**, entries 1 and 2; **Table S2** and **S3**; **Figure S4** and **S5**). The low amount of metallic Ni observed, might be due to the limited information depth of the XPS analysis.[40,41] These results indicate that the outer oxidised Ni layer should indeed be reduced during the initial stages of the reaction,[21] which can be faster in the presence of Fe. The latter occurs in an oxidised state, mainly as Fe_2O_3, but the presence of other oxides cannot be excluded due to interference of Ni Auger peaks with the Fe 2p signal (**Table S3**, **Figure S6**).[42] This means that Fe might stabilise Ni in the $NiFe/ZrO_2$ catalysts by promoting the reduction of Ni as catalyst in an ionic form using H_2 as reductant.

Stabilising Ni/ZrO₂ by partial neutralisation of the reactant

In our previous research using Pd as catalyst for the direct production of methylsuccinic acid from citric acid, we demonstrated that the addition of base was detrimental for the methylsuccinic acid yield due to a strong increase of fragmentation reactions.[19] Nevertheless, the influence of small amounts of NaOH and KOH on the hydrogenation activity of Ni/ZrO₂ was investigated. First, 10 and 20 mol% of the mineral bases were added to the reaction mixture using the screening conditions in **Table 1** (**Figure 2**). Separate *pH* measurements showed for both bases that the *pH* of the citric acid solution slightly increased from 2.2 to 2.5 and 2.7 for 10 and 20 mol%,
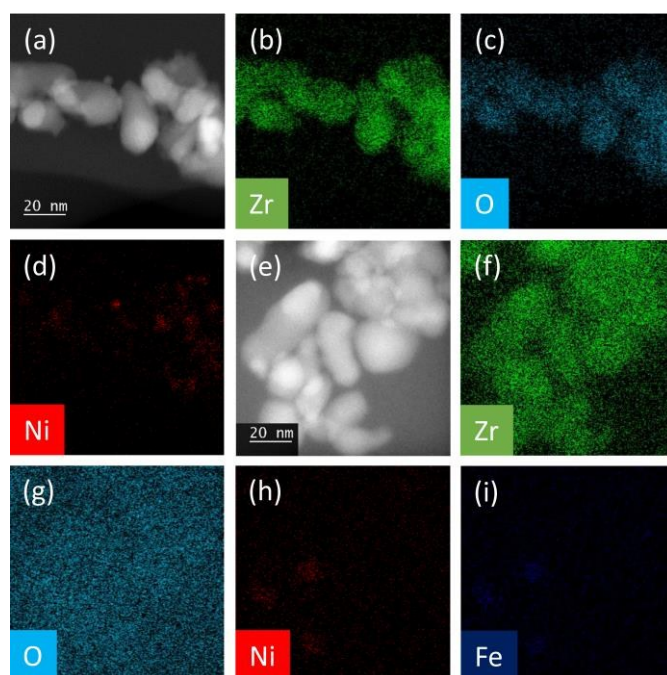

Figure 1. (a) & (e) STEM images and (b-d) & (f-i) EDX elemental maps of Ni/ZrO₂ (a-d) and Ni₅Fe₅/ZrO₂ (e-i).

Table 4. Summary of XPS results.

	Catalyst	Fraction of Ni species [%]		
		Ni^0	NiO	$Ni(OH)_2$
1	Ni/ZrO_2	0.4	46.4	53.2
2	Ni_5Fe_5/ZrO_2	3.7	48.8	47.6
3	Ni-C NPs	>99	<1	<1

respectively. These low amounts of base did not have a significant effect on the fragmentation side reactions. However, the effect on the stability of Ni/ZrO₂ and the concomitant increase of the methylsuccinic acid yield were remarkable. For NaOH the yield increased from 2% to 48% and further to 58%, while the Ni leaching decreased from >99% to 14% and further to only 4% at 20 mol% NaOH. The same trend

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was observed for KOH, where the yield increased to 57% and further to 72%, while the Ni leaching decreased to 7% and further to only 2% at 20 mol% KOH. Furthermore, when the H_2 pressure was increased from 20 bar to 30 bar under these conditions, the hydrogenation rate increased (**Figure 3**). This resulted in an even more enhanced yield of methylsuccinic acid of up to 81%. The increased pressure did not further stabilise Ni/ZrO$_2$, since the mean Ni leaching at 30 bar H_2 remained the same as at 20 bar (7%).
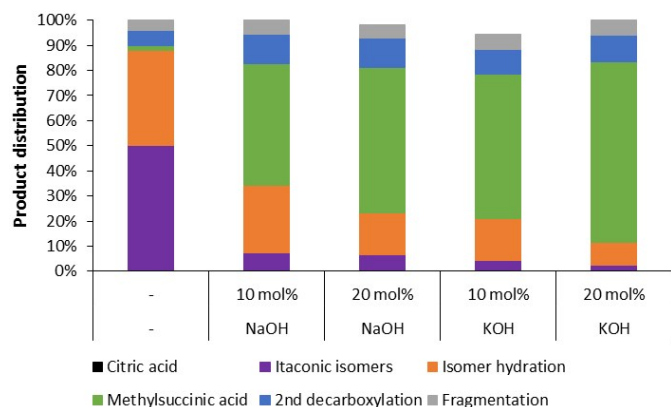
Figure 2. Effect of small amounts of mineral bases on the hydrogenation activity of Ni/ZrO$_2$. Reaction conditions: citric acid (0.2 mmol), Ni/ZrO$_2$ (10 mol% Ni), water (2 mL), 175°C, 2 bar N_2 and 20 bar H_2, 6 h.
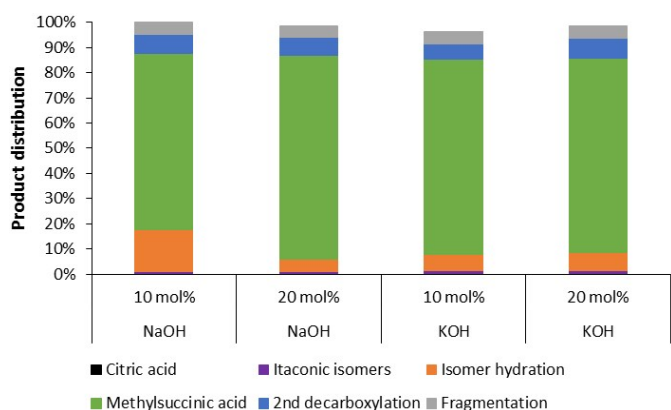
Figure 3. Effect of small amounts of mineral bases on the hydrogenation activity of Ni/ZrO$_2$ at higher H_2 pressure. Reaction conditions: citric acid (0.2 mmol), Ni/ZrO$_2$ (10 mol% Ni), water (2 mL), 175°C, 2 bar N_2 and 30 bar H_2, 6 h.

Stabilising Ni nanoparticles with a carbon coating

The previous stabilisation methods both resulted in high methylsuccinic acid yields, however, additives – mineral bases or Fe – were always necessary. Therefore we explored the use of a coating to stabilise the Ni nanoparticles and avoid the use of additives. Unsupported carbon-coated Ni nanoparticles (Ni-C NPs) were purchased; they were prepared via laser evaporation and have an aerodynamic particle size of 20 nm.[43] The protective carbon layer prevented the Ni from oxidation when in contact with air. XPS confirmed that Ni is only present in its metallic state (**Table 4**, entry 3; **Table S4**; **Figure S7**). Moreover, from XRD it is also clear that Ni has its metallic, face-centred cubic (fcc) structure (**Figure 4**).[44] The N_2

adsorption-desorption isotherms reveal that the particles had a BET surface area of only 26 m^2/g, which matches the nominal value that was anticipated for nanoparticles of the specified size range (*i.e.* 33.7 m^2/g geometrical surface area for perfect spheres of 20 nm size). Hence, this indicates that the carbon coating does not contain significant nanoporosity (**Figure S9**). Nevertheless, this material was tested as well using the screening conditions in **Table 1** (entry 14). Surprisingly, a high methylsuccinic acid yield of 81% was obtained and the Ni leaching was limited to 20%. Since the carbon layer was impermeable, this means that the layer should contain imperfections, such as cracks. The catalyst was therefore subjected to a thorough analysis using transmission electron
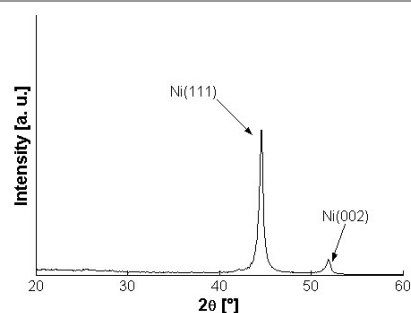
Figure 4. X-ray diffractogram of the carbon-coated Ni nanoparticles.
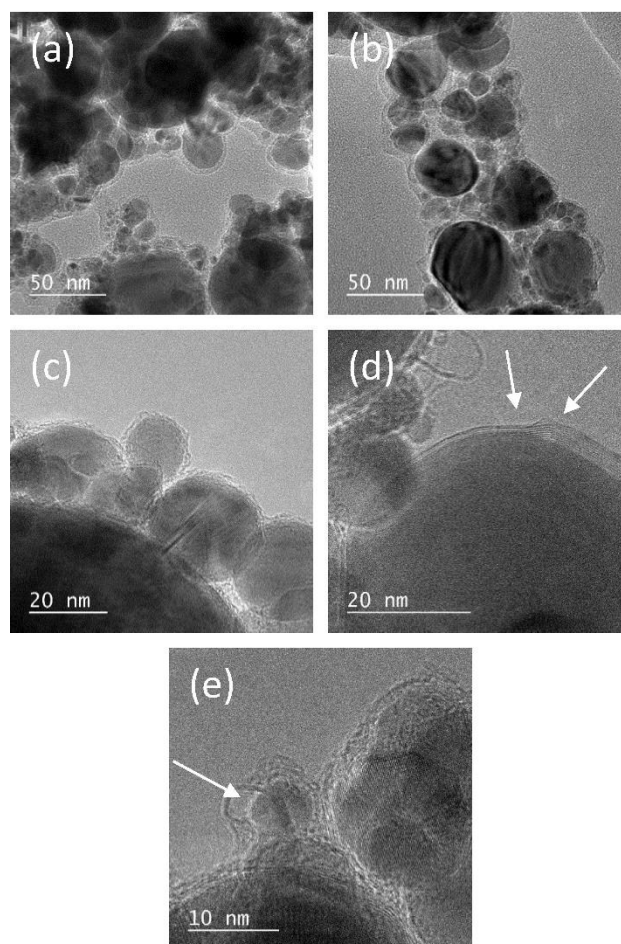

Figure 5. TEM images of the carbon-coated Ni nanoparticles. Zones with a very thin or even absent carbon coverage are indicated by white arrows.

microscopy (TEM) to try to visualise some of these imperfections (**Figure 5**). First of all, the TEM images show that the catalyst consisted of particles with a very broad size distribution, surrounded by a carbon matrix (**Figure 5-(a-c)**). Close inspection of the 2D images shows some peculiarities. The carbon layer varied in thickness (**Figure 5-(d)**), and some parts of the Ni were hardly covered by carbon (**Figure 5-(e)**).

The Ni-C NPs were able to catalyze the hydrogenation in the conversion of citric acid to methylsuccinic acid without the use of any additives; they eventually gave the highest methylsuccinic acid yield (81%) under the screening conditions in **Table 1**. Therefore, the reaction conditions were optimised for this catalyst. First, the effect of the H_2 pressure was investigated (**Figure 6**). A minimum H_2 pressure of 20 bar appears to be necessary for an adequate hydrogenation of the intermediate itaconic isomers. At 30 bar the methylsuccinic acid yield slightly increased to 83%. Under these conditions a time profile was subsequently gathered (**Figure 7**). This kinetic profile is consistent with the reaction network in **Scheme 1**. It demonstrates that the fragmentation products are formed from the start of the reaction in a parallel path and that 'further decarboxylation' products are indeed only formed after a few hours. It is also clear that the itaconic isomers are intermediates in this reaction sequence. Moreover, the 'isomer hydration' products are intermediates as well, since their formation is shown to be completely reversible. So eventually, also β-carboxy-γ-butyrolactone can be reconverted to the itaconic isomers and hydrogenated to the desired methylsuccinic acid. This is why the yield increased to 89% after a longer reaction time of 24 h. In addition, for this reaction the Ni leaching was only 5%. This shows that also if the Ni particles are appropriately protected by carbon, the catalyst's activity remains high enough to result in a very high yield of methylsuccinic acid. Furthermore, reusability studies showed that the methylsuccinic acid yield after 6 h gradually decreased from 80% to 76% and further to 55% at the third run (**Figure S10**), which is consistent with limited Ni leaching and minor catalyst loss during the recycling process.

Next, the influence of the temperature was studied (**Figure 8**). At 150°C the dehydration-decarboxylation of citric acid was much slower, resulting in a conversion of only 24% after 6 h. Conversely, when the reaction temperature was increased to 200°C, the reaction sequence was faster: now all the intermediate 'isomer hydration' products were already converted to methylsuccinic acid after 6 h. On the other hand, further decarboxylation and fragmentation side reactions clearly increased with raising the temperature from 150°C to 200°C. Therefore, the methylsuccinic acid yield at 200°C after 6 h was slightly lower than the yield at 175°C after 24 h (86% vs. 89%).

Finally, lowering the amount of Ni to 5 mol% was considered (**Figure 9**). This decrease in catalyst-to-substrate ratio slowed down the hydrogenation and thus the reaction sequence to methylsuccinic acid. After 6 h with only 5 mol% Ni there were still some itaconic isomers left (8%), next to 16% of 'isomer hydration' products. However, a reaction time of 24 h sufficed to reach complete conversion of citric acid and all

intermediate compounds, resulting in a methylsuccinic acid yield of 91%.
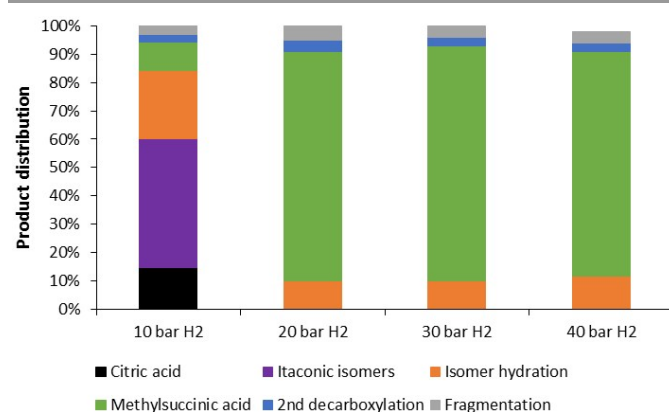
Figure 6. Effect of H_2 pressure on the conversion of citric acid to methylsuccinic acid using the carbon-coated Ni nanoparticles. Reaction conditions: citric acid (0.2 mmol), Ni-C NPs (10 mol% Ni), water (2 mL), 175°C, 2 bar N_2, 6 h.
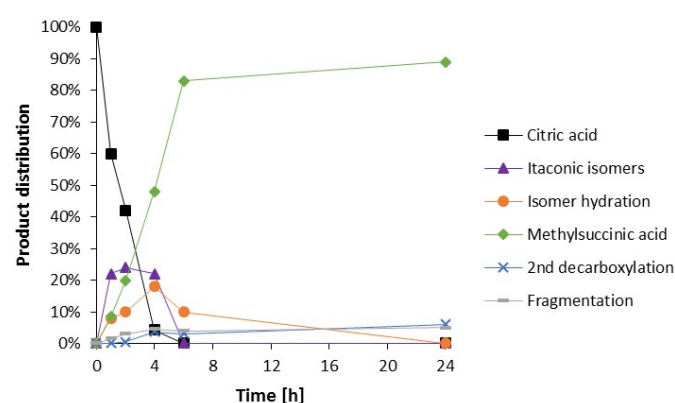

Figure 7. Time course of the dehydration-decarboxylation-hydrogenation of citric acid using the carbon-coated Ni nanoparticles. Reaction conditions: citric acid (0.2 mmol), Ni-C NPs (10 mol% Ni), water (2 mL), 175°C, 2 bar N_2 and 30 bar H_2.
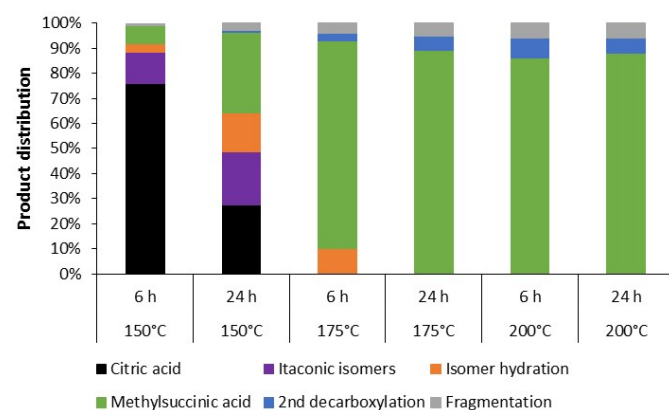

Figure 8. Effect of temperature on the conversion of citric acid to methylsuccinic acid using the carbon-coated Ni nanoparticles. Reaction conditions: citric acid (0.2 mmol), Ni-C NPs (10 mol% Ni), water (2 mL), 2 bar N_2 and 30 bar H_2.
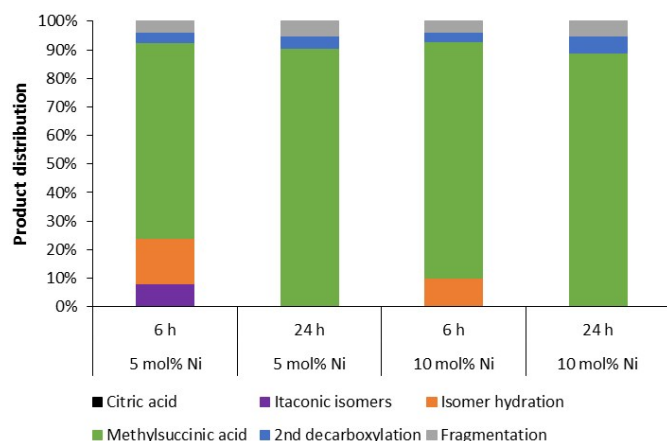
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Figure 9. Effect of a lower catalyst-to-substrate ratio on the conversion of citric acid to methylsuccinic acid using the carbon-coated Ni nanoparticles. Reaction conditions: citric acid (0.2 mmol), Ni-C NPs, water (2 mL), 175°C, 2 bar N_2 and 30 bar H_2.

Conclusions

Citric acid can be transformed to methylsuccinic acid via the new reaction sequence of dehydration-decarboxylation-hydrogenation. Regular Ni catalysts are not stable under the demanding conditions of an aqueous citric acid solution at natural *pH*, and are thus not able to hydrogenate the intermediate itaconic isomers. On the one hand, partial neutralisation of the reactant results in a much slower corrosion of the Ni particles and maintains the hydrogenation activity of Ni/ZrO$_2$, leading to methylsuccinic acid yields up to 81%. On the other hand, adding Fe to either the Ni/ZrO$_2$ catalyst or directly to the reaction mixture, results in a more reducing environment for the Ni particles, since the added Fe may act either as a sacrificial reductant (in the case of Fe^0 powder), or as reduction catalyst to keep Ni in its zerovalent state with H_2 as reducing agent. This ensures a better stability and hydrogenation activity of the Ni catalysts; however, Fe also strongly increases the fragmentation side reactions, limiting the maximum yield of methylsuccinic acid. Finally, also protecting the Ni particles with a carbon layer avoids fast corrosion of the metallic Ni. Optimising the reaction conditions for these carbon-coated Ni nanoparticles results in an optimal yield of 91% methylsuccinic acid without using additives, at 175°C with 30 bar H_2 and 5 mol% Ni after 24 h. In all three cases (Ni + base, Ni + Fe, Ni + C) the Ni leaching could be minimised to around 5%. These concepts in improving the stability of Ni catalysts may be expanded to the conversion of other biobased compounds and further research on the stabilisation of Ni catalysts is still necessary in order to make them completely recyclable. This would benefit the greenness of the Ni-based catalytic systems, also because the high temperature catalyst synthesis procedures have a considerable energy demand.

Author contributions

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgements

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