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Development of bifunctional Pd/Nb2O5.nH2O catalysts for the production of tricarballylate plasticizers from citric acid.

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PURPOSE OF THE ABSTRACT

Increasing awareness of the bio-accumulating and endocrine disrupting properties of traditional ortho-phthalate plasticizers[1] has led to serious restrictions on these compounds and a growing interest in safe alternatives.[2] With the ongoing tendency to explore renewable resources for the production of drop-in chemicals or novel compounds, the potential of biobased plasticizers as safe alternatives is increasingly researched.[3] Here, the focus is on the production of tricarballylate plasticizers directly from the widely abundant and renewable citric acid. These tricarballylate plasticizers possess excellent plasticizing properties, comparable to or even better than those of traditional ortho-phthalates.[4]

Recently, a one-pot dehydration-hydrogenation of citric acid to tricarballylic acid was developed by applying a combination of a low Si/Al H-Beta zeolite as solid acid together with small amounts of Pd/C in water as a solvent (Figure 1, Route 1). Although high yields of tricarballylic acid were obtained in this green synthesis process, the corrosive citric acid also elicited Al leaching from the zeolite framework, which could be partially counteracted via a post-reaction realumination procedure.[5] In this work, niobium oxides and niobium phosphates were investigated as potential dehydration catalysts for citric acid in water as a solvent. From this screening, Nb2O5.nH2O was found to be an equally performant catalyst as the H-Beta zeolite, as a result of the high amount of Bronsted and Lewis acid sites. Interestingly, a strong involvement of the hydroxyl group of citric acid with the Nb2O5.nH2O surface was observed by 13C MAS NMR. This strong interaction likely activates the C-O bond of the hydroxyl group and therefore makes the adsorbed citric acid molecule more prone to dehydration when it encounters a strong Bronsted acid site in its close vicinity (Figure 1, centre). In addition, Nb2O5.nH2O was also proven to be a stable catalyst to the corrosive citric acid, since no Nb cations were detected in the reaction mixtures.

Considering this stability, efforts were made on the synthesis of bifunctional Pd/Nb2O5.nH2O catalysts via a low-temperature reduction method in propylene carbonate.[6,7] By this approach, the acid site density of the Nb2O5.nH2O support was preserved, which was not the case when a typical wet impregnation approach was applied for the synthesis of Pd/Nb2O5.nH2O (Figure 2). A higher reduction temperature was required in the latter case, which led to a loss of amorphicity and acid site density of the Nb2O5.nH2O support. The low-temperature reduction method also resulted in well-dispersed Pd-nanoparticles, which was evidenced by XAS, CO chemisorption and HAADF STEM. In presence of a 0.6 wt% Pd/Nb2O5.nH2O, high tricarballylic acid yields were achieved over multiple runs, while the selectivity towards tricarballylic acid remained high as well, which was not the case for the two-catalyst one pot system. This illustrates that by bringing both catalytic site in close intimacy to one another, high selectivity towards the hydrogenated product could be obtained, while the undesired decarboxylation to methylsuccinic acid was largely suppressed. Finally, a substrate scope investigation ensured the potential of these Pd/Nb2O5.nH2O catalysts for the sequential dehydration-hydrogenation of other monohydroxy (biobased) carboxylic acids.

After esterifying the obtained tricarballylic acid, tricarballylate plasticizers are obtained. However, the esterification and dehydration-hydrogenation processes can also be reversed, which shifts the challenge in the production of tricarballylate plasticizers to the dehydration-hydrogenation of citrate esters to tricarballylate esters (Figure 1, Route 2). To our delight, the developed Pd/Nb2O5.nH2O are also efficient to convert a variety of citrate esters to tricarballylate esters in high yields (up to 93%) in methyl cyclohexane as a solvent.

FIGURES

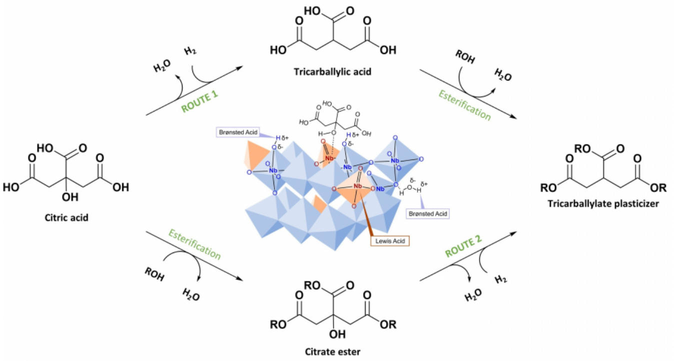
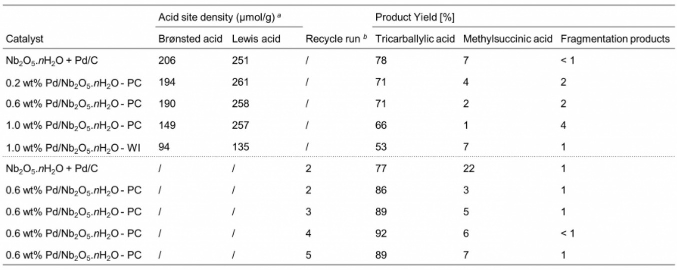


FIGURE 1

Possible routes for the production of tricarballylate plasticizers from citric acid, with a central role for the interaction of citric acid or citrate with the Nb2O5.nH2O surface.

No legend.



	Acid site density (μmol/g) [a]			Product Yield [%]		
Catalyst	Brønsted acid	Lewis acid	Recycle run [b]	Tricarballylic acid	Methylsuccinic acid	Fragmentation products
$Nb_2O_5.nH_2O$ + Pd/C	206	251	/	78	7	< 1
0.2 wt% Pd/$Nb_2O_5.nH_2O$ - PC	194	261	/	71	4	2
0.6 wt% Pd/$Nb_2O_5.nH_2O$ - PC	190	258	/	71	2	2
1.0 wt% Pd/$Nb_2O_5.nH_2O$ - PC	149	257	/	66	1	4
1.0 wt% Pd/$Nb_2O_5.nH_2O$ - WI	94	135	/	53	7	1
$Nb_2O_5.nH_2O$ + Pd/C	/	/	2	77	22	1
0.6 wt% Pd/$Nb_2O_5.nH_2O$ - PC	/	/	2	86	3	1
0.6 wt% Pd/$Nb_2O_5.nH_2O$ - PC	/	/	3	89	5	1
0.6 wt% Pd/$Nb_2O_5.nH_2O$ - PC	/	/	4	92	6	< 1
0.6 wt% Pd/$Nb_2O_5.nH_2O$ - PC	/	/	5	89	7	1

FIGURE 2

Sequential dehydration-hydrogenation of citric acid in presence of bifunctional Pd/Nb2O5.nH2O catalysts and their recycability.

Reaction conditions: Citric acid (0.2 mmol) in water (2 mL), 0.1 g catalyst, 1 mol% Pd in case of Pd/C, 10 bar H2, 160 °C, 20 h. a) Determined by pyridine FTIR. b) Direct recycling after isolation and drying, without addition of fresh catalyst.

KEYWORDS

Citric acid | Bifunctional catalysts | Phthalate plasticizers | Niobium oxides

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