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A new renewable route for succinic acid: the aqueous phase catalytic transfer hydrogenation of bio-based maleic acid with bio-based formic acid.

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PURPOSE OF THE ABSTRACT

Succinic acid (SAC) has multiple applications in the pharmaceutical, food, detergent, cosmetic, textil, photography, agrochemical industries and in the production of polyamides and polyesters. Besides, SAC is also an intermediate in the production of gamma-butyrolactone, 1,4-butanediol and tetrahydrofuran from maleic anhydride or maleic acid (MAC).

Until recently, SAC was only produced from petrochemical maleic anhydride. More recently, fermentation of sugars is becoming competitive. However, fermentation presents drawbacks associated with the handling of microorganism, the precise control of pH and other operation variables, its low space-time yield (long fermentation times are required) and serious issues in the separation-purification of succinic acid from the fermentation broth. In this work we demonstrate a different renewable route based in the aqueous phase hydrogenation of MAC and using liquid formic acid (FAC) as hydrogenating agent.

Although both FAC and MAC are currently derived from fossil feedstocks, their potential production from lignocellulosic feedstocks has already been technically demonstrated. Bio-based FAC is possible by the so-called OxFA process or as a by-product in the production of levulinic acid from lignocellulose. Bio-based MAC can be produced by oxidation of different lignocellulose derived platforms, i.e. butanol, levulinic acid, hydroxymethylfurfural and furfural. Within this context, a very advantageous process to produce MAC is the oxidation of furfural to MAC using liquid H₂O₂. In such case one molecule of FAC is released per molecule of MAC formed [1] and consequently this reaction mixture could thus be used to produce biogenic SAC without the incorporation of external FAC, provided that the reaction could be conducted in aqueous media and with the stoichiometric amount of FAC. This is our novelty: to conduct the hydrogenation in water and with the stoichiometric amount of FAC, and not using organic solvents and higher amounts of FAC as it has previously been used.

Recently Zheng et al. [2] have reported the production of succinic acid, but from fumaric acid, the trans isomer of MAC, and using twice the stoichiometric amount of aqueous FAC and a difficult to reuse homogeneous Pd(AcO)₂ catalyst. The incorporation of Xantphos ligand was also required to render high SAC yields. A much simpler catalyst formulation was identified in our work. This article demonstrates that, among the different supports and supported noble metal tested and under the optimised reaction conditions, 5 wt. % Pd/C catalyst was the most active, selective and stable catalysts for conducting the reaction at similar T and P used in the petrochemical

process.

No deactivation could be noted in Figure 1 when catalyst was used in continuous flow (contact time of 12 h⁻¹) for 450 h on stream at two different reaction temperatures (130 and 110 ° C). At 130 °C (full conversion) the space time yield was above 0.30 g SAc·g⁻¹cat·h⁻¹. Other formulations with other supports or noble metals resulted in worse performance. Finally, it was also verified that the catalyst is able of processing MAc and FAc recovered from the oxidation of furfural with H₂O₂, confirming that fully renewable SAc is possible.

Isotopic kinetics and ¹H and ²D NMR experiments with deuterated maleic and formic acids and with D₂O allowed us to conclude that the indirect hydrogenation with H₂, arising from FAc decomposition, is a minor route. The reaction mainly proceeds with the direct transfer of the formyl hydrogen from formic acid to C=C of maleic acid. The second hydrogen required to complete the hydrogenation (when using stoichiometric FAc) is the acid proton of FAc or is supplied by water.

Finally, characterisation by XPS analysis and CO chemisorption-DRIFT allow us to detect in the used catalyst both Pd(0) and Pd(2+) at the surface of the Pd particles, posing the question of the relevance of Pd(2+) as active sites to conduct the reaction.

FIGURES

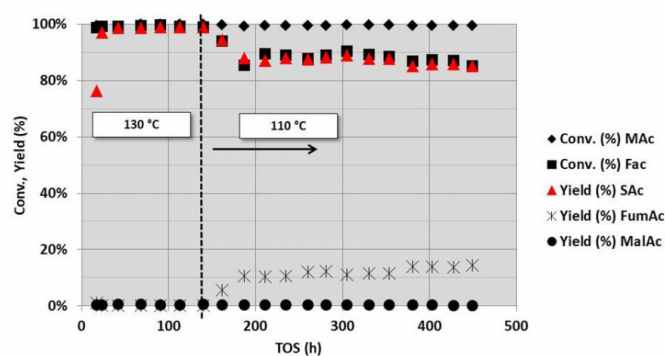


FIGURE 1

Figure 1

Long term catalytic properties of Pd/C catalyst under continuous operation incorporating NaOH to partially neutralize MAc and Fac. 2.5 wt.% of MAc, WHSV = 12 h⁻¹, FumAc = fumaric acid, MalAc = malic acid

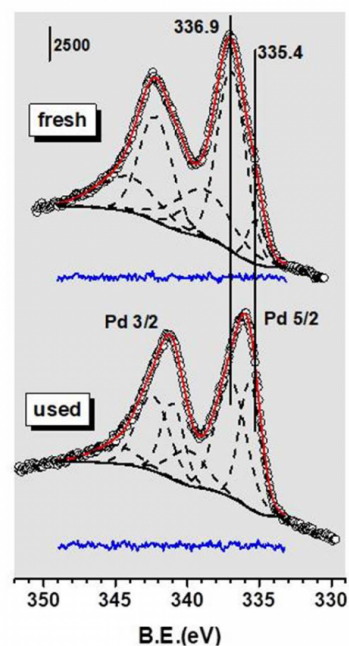


FIGURE 2

Figure 2

Pd 2p core level of fresh and used Pd/C catalyst. Symbols: empty circles = raw data; dashed lines = deconvoluted peaks; red line = sum of all the deconvoluted peaks; black line = baseline; blue line = difference between raw data and deconvolution.

KEYWORDS

Renewable chemicals | Succinic acid | Maleic acid | Catalytic transfer hydrogenation

BIBLIOGRAPHY