Catalytic synthesis of adipic acid using biomass-derived raw materials

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Significance and Relevance

Adipic acid market in 2022 reached 5.6 Bln $, with a CAGR of 4.8% it is expected to reach 8.2 Bln $ in 2030[1]. At industrial level, it is traditionally produced by Du Pont process[2] involving fossil-type resources and two main steps, the former leading to KA-oil and the latter forming adipic acid by oxidation in HNO_3. Here, more sustainable processes are described, using renewable raw materials to obtain adipic acid. Among the biomass-derived substrates, MW-assisted conversion of 2,5-furandicarboxylic acid over Rh/Al_2O_3 gave the best results (>99% conversion, 78% selectivity) under milder conditions than those reported[2], and opening the way to the possibility of a one-pot reaction.

Preferred and 2nd choice for the topic: Green chemistry and biomass transformation, renewable resources conversion and Circular economy
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

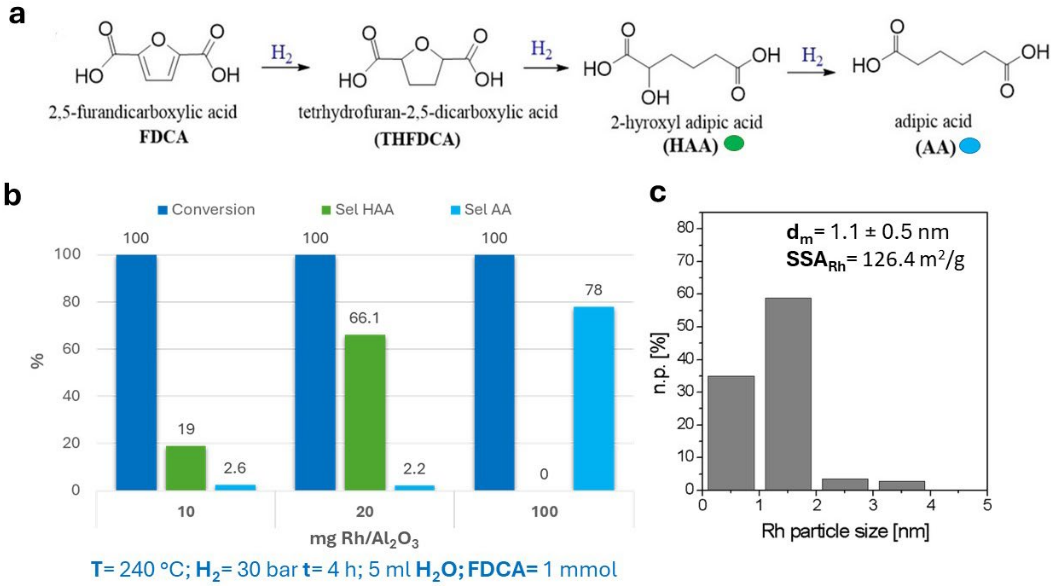
Adipic acid covers the main market share to produce synthetic fibers, but also finds applications in the production of pharmaceuticals, cosmetics, lubricants, fertilizers and much more[1]. Adipic acid production encompasses different industrial and biotechnological processes[2,3,4], which must face several issues: on one hand, the use of petrol-derived raw materials, NO_x emissions, the use of acids, high cost of H_2O_2 and, on the other hand, low yields and the need to find new bio-synthetic routes and suitable micro-organisms. Therefore, the possibility to design competitive catalytic processes to obtain adipic acid starting from molecules derived from lignocellulosic biomass is of great interest. In this frame, the use of microwaves (MW) guarantees lower heat dispersion due to the MW transparency of the containers allowing rapid heating and temperature homogeneity. This results in both energy savings and an increase in yield and selectivity compared to conventional heating[5], along with a reduction in reaction time. In this study, levulinic acid, mucic acid and 2,5-furandicarboxylic acid were used in the MW-assisted production of adipic acid over different commercial and lab-made catalysts. The optimization of reaction parameters and the effect of the nature of the metal and of the support are investigated.

Materials and Methods

Commercial and lab-made supported metal catalysts were tested in the MW-assisted production of adipic acid (AA) from levulinic acid (LA), mucic acid (MA) and 2,5-furandicarboxylic acid (FDCA). Synthwave multimode microwave (MW) reactor allowing to carry out the reaction under controlled atmosphere and temperature was used. Products were analyzed by GC-MS and GC-FID. TEM, XRD, TGA and FT-IR spectroscopy have been employed to establish structure-activity relationships.

Results and Discussion

The MW-assisted synthesis of adipic acid from levulinic acid afforded mainly γ-valerolactone (GVL), and neither the use of levulinic esters to avoid cyclization produced better results. The conversion of mucic acid (MA) to AA involves a deoxydehydration reaction; various tests led only to the first reaction intermediate, 2,3-dihydroxyhex-4-endioic acid. However, it was not possible to go on with the subsequent steps, obtaining mainly the formation of decarboxylated by-products and lactones. The MW-assisted synthesis of AA starting from FDCA (**Figure 1a**), involves several steps and initially the reaction was divided into two steps: [3,6] in the first one the aromatic system is reduced, while the second one involves the opening of the furan ring and the elimination of the hydroxyl group with subsequent hydrogenation of the unsaturation produced. As for the first step, complete conversion and selectivity were achieved under operating conditions (140 °C, Pd/C, 10 bar H_2, methanol, 1 hour) much milder than those reported in the literature [5] (140 °C, Pd/SiO_2, 52 bar H_2, acetic acid, 3 hours). Working with water instead of methanol allowed to produce adipic acid in a one-pot reaction (**Figure 1b**). Temperature, pressure, time, amount and type of catalyst (testing different metals and different supports) were varied to obtain the optimized reaction conditions summarized in **Figure 1b**.



T= 240 °C; H_2= 30 bar t= 4 h; 5 ml H_2O; FDCA= 1 mmol

Figure 1. a) Main steps of AA production from FDCA. **b)** Effect of the catalyst amount on conversion and selectivity. **c)** Particle size distribution of the commercial Rh/Al_2O_3 catalyst.

The best catalyst for the optimized reaction was commercial Rh/Al_2O_3: the initial screening of the catalysts revealed first that Rh is more active than Pd and Ru, and furthermore two other catalysts yielded interesting results, namely Rh/TiO_2 and Rh-Re/γ-Al_2O_3 (obtained by US-assisted impregnation with a Rh precursor of ReO_x/Al_2O_3). To correlate the morphological-structural properties to the catalytic activity, an extended characterization was performed on these catalysts. Rh/Al_2O_3 contains homogeneously dispersed nanoparticles with d_m= 1.1± 0.5 nm and a rather narrow size distribution (**Figure 1c**), with 95% of the nanoparticles having size <2 nm (specific surface metal area equal to 126.4 m^2/g of catalyst). Alumina has a rod-like morphology, and it is predominantly amorphous, as confirmed by XRD. Moreover, the results of FT-IR spectroscopy of adsorbed CO indicate that different Rh sites are exposed at the surface of the catalysts depending on the nature of the support. In conclusion, the use of a substrate deriving from renewable resources, combined with microwaves (determining a lower demand for energy consumption) in the presence of a heterogeneous catalyst (easily separable from the substrate) and an aqueous solvent that does not involve toxicity risks allowed to design a more sustainable adipic acid synthesis process.

References

1. https://www.reportsinsights.com/search.php?qry=adipc+acid.
2. Lang, M.; Li, H. *ChemSusChem* **2022**, 15, e202101531.
3. J. C. J. Bart, S. Cavallaro, *Ind. Eng. Chem. Res.* **2015**, 54, 1.
4. E. Skoog, J. H. Shin, V. Saez-Jimenez, V. Mapelli, L. Olsson, *Biotechnology Advances* **2018**, 36, 2248.
5. Roberts, B. A.; Strauss, C. R. Acc. *Chem. Res*. **2005**, 38 (8), 653–661.
6. S. V. de Vyver, Y. Román-Leshkov, Y. *Catalysis Science & Technology* **2013**, 3, 1465.

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