



16th INTERNATIONAL CONFERENCE ON CARBON DIOXIDE UTILIZATION

Aspects of the direct carboxylation of C5 acid to C6 diacids with inorganic carbonates: is CO₂ necessary?

Francesco Nocito,^a Angela Dibenedetto^{a,b} and Michele Aresta^{b,c}

^aDepartment of chemistry, University of Bari, Campus Universitario, Bari 70126, IT

^bCIRCC, via Celso Ulpiani 27, 70126 Bari, IT

^cIC2R srl, Lab H124, Tecnopolis, via Casamassima km 3, 70018 Valenzano, IT

Keywords: valorization of polyols C5 fraction, carboxylation, synthesis of FDCA, role of metals, role of CO₂

The utilization of non-edible renewable feedstock for the production of chemicals and materials is a must for a sustainable Chemical Industry.[1] Ligno cellulose is an abundant material that can find several uses. After separation into its main fractions (cellulose, emicellulose and lignine) cellulose and emicellulose can be depolymerized to C6 and C5 polyols “platform molecules”. Glucose is converted into 5-hydroxymethylfurfural (5-HMF), origin of a variety of hydrogenated and oxidized products.

Recently, our Group has investigated the conversion of C6 into 5-HMF and the selective aerobic oxidation of the latter into several products, either molecular compounds [2-4] or monomers for polymers, such as FDCA.[5] (Fig. 1) The great interest is in the utilization of FDCA, bio-sourced,

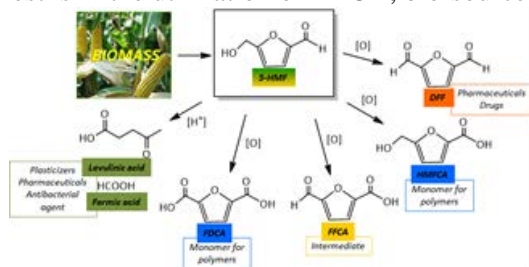


Figure 1. From C6 to 5-HMF and added value products.

as monomer for polymers, supplanting terephthalic acid, derived from fossil-carbon.

Very recently, furoic acid, formed from furfural, has been used as substrate for the synthesis of FDCA, via a carboxylation carried out using Cs₂CO₃ and CO₂[6]. (Fig. 2) Our interest in the carboxylation of organic substrates [7] and biosourced molecules has pushed us to discover cheaper promoters than Cs for the conversion of furoic acid into FDCA.

We have investigated the role of several metals (s-p Groups and Transition Metals) in different reaction

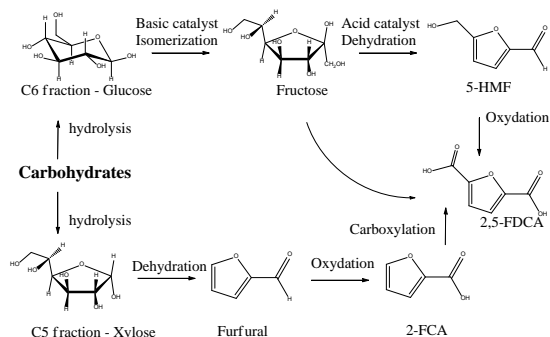


Figure 2. From C6 and C5 to FDCA.

conditions (temperature, presence and absence of CO₂) in order to gather information about a possible reaction mechanism, not disclosed so far, and identify the carboxylating agent.[8]

In this paper we shall discuss the chemistry of such interesting system and the role of metals and CO₂.

References

- [1] M. Aresta, A. Dibenedetto, F. Dumeignil, Biorefineries, De Gruyter, 2015
- [2] M. Ventura, F. Lobefaro, E. de Giglio, M. Distaso, F. Nocito, A. Dibenedetto, *ChemSusChem*, 2018, 11 (8), 1305-1315
- [3] M. Ventura, D. Williamson, F. Lobefaro, M. D. Jones, D. Mattia, F. Nocito, M. Aresta, A. Dibenedetto, *ChemSusChem*, 2018, 11 (6), 1073-1081
- [4] M. Ventura, M. Aresta, A. Dibenedetto, *ChemSusChem*, 2016, 9 (10), 1096-1100
- [5] M. Ventura, A. Dibenedetto et al, Submitted
- [6] G. R. Dick, A. D. Frankhouser, A. Banerjee, M. W. Kanan, *Green Chemistry*, 2017, 19 (13), 2966-2972
- [7] A. Dibenedetto, J. Zhang, M. Trochowsky, A. Angelini, W. Macyk, M. Aresta, *Journal of CO₂ utilization*, 2017, 20, 97-104
- [8] M. Aresta, A. Dibenedetto and F. Nocito, Patent pending

Acknowledgments

We acknowledge the financial support from Apulia Region, Tecnonidi. Programm