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## Direct transformation of fructose into FDCA mediated by metal-functionalized acid resins as bifunctional catalysts

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### PURPOSE OF THE ABSTRACT

Polyethylene furanoate (PEF) is a real 100% bio-based alternative to petroleum-based PET [1]. Its synthesis involves the preparation of furandicarboxylic acid (FDCA), the key monomer of PEF, which is synthesized from C6 sugars through dehydration to hydroxymethyl furfural (HMF) and subsequent selective air oxidation to FDCA. Carrying out both transformations in a single step would allow increasing product yields and decrease production cost, making PEF a cost competitive bioplastic. Nonetheless, this option, scarcely reported, requires driving, at the same time, two types of reactions which usually find opposite optimal reaction conditions -acid media for dehydration and usually basic conditions for air oxidation- [2]. In addition, different types of catalytic functionalities need to be present to accomplish proper product yields, so that, this alternative requires combining acid sites and air oxidation active phases together in the same catalytic system.

Within this contribution we present the synthesis, characterization and testing of bifunctional catalysts bearing sulfonic acid groups and different metal particles. These materials have been prepared from Amberlyst A70®, a sulfonated PS-DVB acid resin, as catalyst support. Different metal particles were incorporated to the polymer beads (4wt% metal loading), including Pt(Bi-promoted), Au-Pd and Au-Pt bimetallics. Samples were prepared by incipient wetness impregnation with aqueous solutions of the metal precursors (H<sub>2</sub>PtCl<sub>6</sub>·2H<sub>2</sub>O, HAuCl<sub>4</sub>·H<sub>2</sub>O, and Pd(NO<sub>3</sub>)<sub>2</sub>), followed by reduction with aqueous solutions of formaldehyde or hydrazine.

Comparison between formaldehyde and hydrazine revealed a much better performance of the latter in the reduction of all the metal precursors, yielding almost quantitative metal contents, homogeneously distributed metal particles (figure 1), with a smaller size (dp = 35-60 nm) as compared to those obtained with formaldehyde. Interestingly, no negative influence was observed on the acidity of the organic resin in terms of acid capacity, regardless the metal content or the used reducing agent.

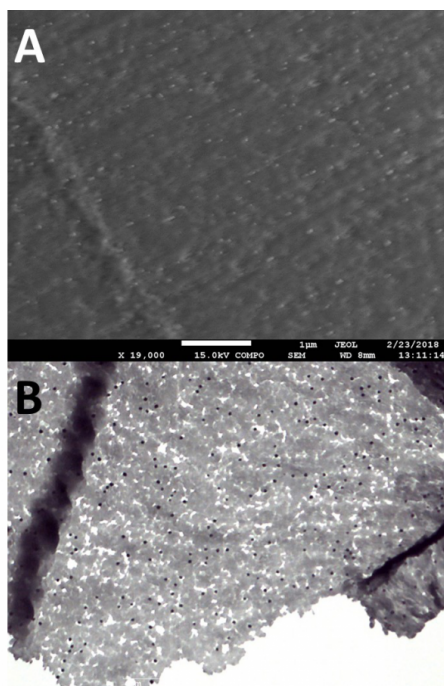
Catalytic tests were performed by treating fructose (50mM) with air at 40 bar, 100°C during 6 h in the presence of the bifunctional catalysts (fructose:metal = 100 mol:mol), in different reaction media. Quantification of the reaction products was performed by HPLC using a Hilex H+ column operating with 0.025N H<sub>2</sub>SO<sub>4</sub> as mobile phase.

Fructose dehydration was tested in different solvents, in the presence of commercial A70 resin. Best results, in terms of HMF yield, were obtained when using mixtures of 1,4-dioxane and DMSO (90:10 vol). Under these conditions A70 resin provided 88% yield of the starting fructose as HMF, in 6 hours, confirming the good performance of these catalysts to drive the first stage of the reaction cascade from fructose to FDCA.

As for the catalytic tests performed in the presence of bifunctional catalysts, results evidenced the possibility of coupling the acid driven dehydration of fructose with the oxidation of the evolving HMF. Nevertheless, the use of 1,4-dioxane:DMSO mixtures as reaction media evidenced a depressed intrinsic catalytic activity in all the tested metallic catalysts, as compared to that showed in water media, accordingly to literature data. However, all the catalysts displayed high catalytic activity in the production of HMF (40-50% yield) as well as a moderate conversion of HMF into oxidation derivatives (9% hydroxymethylfurfural; 9% diformylfuran), although only the

Pt(Bi) catalyst was able to produce quantifiable amounts of highly oxidized products such as 5-formyl furan carboxylic acid (FFCA, 3%), accompanied with tiny amounts of 2,5-furandicarboxylic acid (FDCA). Further studies aiming the enhancement of the catalytic activity of these materials in oxidation reactions are being accomplished through the increasing of the reaction temperature and pressure as well as through the dosage of water to the reaction media.

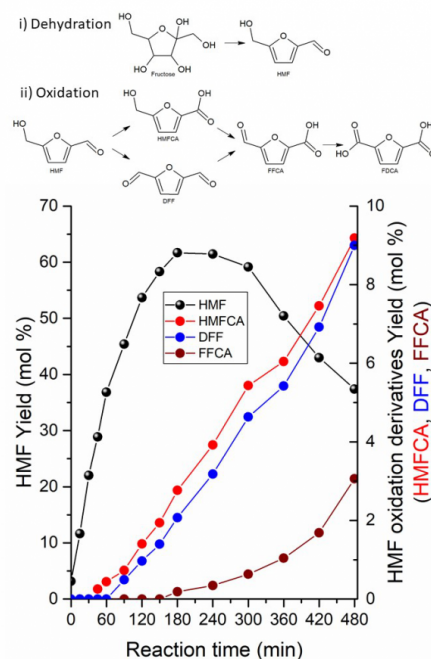
## FIGURES



**FIGURE 1**

Electron microscope images recorded for Pt(Bi)-A70 bifunctional catalyst.

A: SEM and B: TEM



**FIGURE 2**

Reaction scheme for the two coupled transformations and product yield profiles obtained in the conversion of fructose into HMF oxidation products in presence of Pt(Bi)-A70 catalyst.

Reaction conditions: 170°C, 40 bar, fructose starting concentration = 50 mM; fructose:Pt = 100:1 mol:mol

## KEYWORDS

FDCA | Cascade reaction | Selective oxidation | Bifunctional catalyst

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