Novel Palladium Magnetic Catalysts for 5-Hydroxymethylfurfural Oxidation

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Abstract
During latest years, significant research efforts have been focused on the conversion of biomass into platform chemicals and biofuels. In particular furan derivatives, such as 5-hydroxymethylfurfural (HMF) have high potential for the synthesis of chemicals and fuels [1]. For instance, 5-hydroxymethyl-2-furancarboxylic acid (HFCA) derived from the selective oxidation of the aldehyde moiety of HMF, serves as a monomer for the synthesis of various polyesters, but also shows antitumor activity. Much more research interest has been devoted to the synthesis of 2,5-furandicarboxylic acid (FDCA) considered as an alternative monomer for the replacement of terephthalic acid [2,3]. The aim of this study is the environmentally friendly synthesis of HFCA and FDCA through heterogeneously catalyzed reactions working in water under mild conditions. Pd-doped Fe_3O_4 was synthesized following a novel MW-assisted solvothermal approach. This magnetic system resulted as easily recoverable and versatile catalyst being able to reach up to 86% yields of HFCA when subjected to 10 atmospheres of O_2 and 60°C in the as-synthesized form. On the contrary, this catalyst can reach up to 70% FDCA yields when working at 40°C and atmospheric O_2 pressure in a mildly reduced form, as shown by XPS analysis.
In order to design a truly sustainable process, biomass derived HMF raw liquors must be employed. The direct use of the raw hydrolysis solution avoids complex, expensive and inefficient HMF purification processes, adjourning them to the refinement of the final product. Therefore, the novel catalysts here proposed were also tested in a cascade process of biomass valorization using raw hydrolysates derived from cellulose. These aqueous liquors obtained by hydrolysis and dehydration with a solid acid contained mostly HMF and furfural as well as small amounts of unreacted sugars. Quite good results were obtained from the cascade process using Pd-doped Fe_3O_4 leading to 81% yield of HFCA, 4% FDCA and 80% yield of furoic acid (main furfural oxidation product). These results evidence the robustness of this catalyst and the high feasibility of this cascade approach.

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