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SETTING THE SCENE FOR THE CONTINUOUS FLOW HMF OXIDATION: Au/Pd-DECORATED ELECTROSPUN MEMBRANES AS CATALYTIC SYSTEMS FOR FDCA PRODUCTION

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PURPOSE OF THE ABSTRACT

In the last decade, the need to decrease the dependence on fossil resources has led researchers to look for bio-derived chemicals to replace the already existing ones. For instance, 2,5-furandicarboxylic acid (FDCA) has been pointed out as the bioderived counterpart of terephthalic acid for the synthesis of polyesters. In fact, FDCA could be obtained by means of selective oxidation of 5-hydroxymethylfurfural (HMF), a bio-derived platform molecule produced by glucose hydrolysis. HMF oxidation to FDCA is generally performed under batch conditions, being supported metal nanoparticles (NPs), such as alloyed Au/Pd NPs, the most studied catalysts, since high yield of FDCA can be obtained [1]. On the other hand, apart from a few reports [2], the possibility to perform such reaction under continuous conditions has not yet been extensively studied.

Recently, polymer/inorganic composites have been demonstrated to be useful tools in several industrial fields, such as catalysis, considering their low cost, chemical stability, and tunable hydrophobic/hydrophilic properties. Among all the paths to produce such composites, electrospinning provides a convenient approach to prepare them and could represent an useful strategy to prepare catalytic membranes which can be used in continuous processes for biomass valorization.

In this work, the production of Au/Pd NPs (Au/Pd molar ratio 6) decorated polymeric/inorganic membranes have been studied. Preformed NPs were directly electrospun using stable suspension containing the metal, TiO2 and the polymer. Two strategies have been designed (Fig. 1): 1) Electrospinning of Polyacrylonitrile (PAN) and TiO2 supported Au/Pd NPs in DMF [3]; 2) Electrospinning of Nylon 6,6 [4], Au/Pd NPs and TiO2 suspension in formic acid and CH2Cl2.

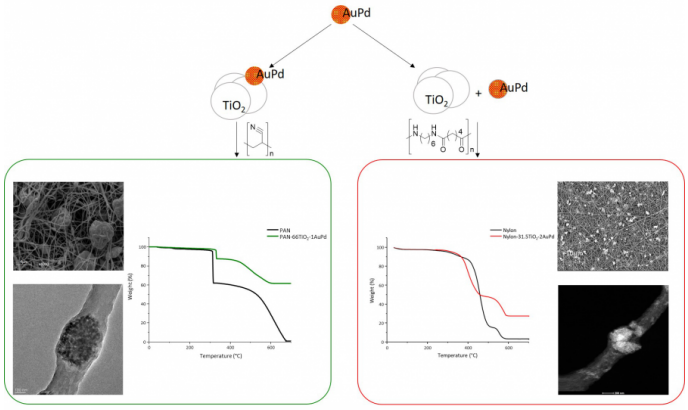
Both suspensions were successfully electrospun and the obtained membranes have been characterized by means of SEM, HRTEM, BET, TGA and tested as catalyst in the batch HMF oxidation under aqueous conditions, in order to discern how synthetic protocol and supporting polymer properties affect membrane activity.

Smooth filaments containing agglomerates were detected in both samples by SEM (Figure 1). The HRTEM and EDX analysis of the electrospun membrane revealed that such agglomerates are made of TiO_2. In addition to this, in the Nylon sample, Au/Pd NPs are more concentrated over the TiO_2 aggregates, probably due to the electrostatic interactions that take place during electrospinning, which preferentially lead NPs onto TiO_2 surface. Moreover, TEM images (Fig. 1) seem to suggest that the inorganic components are coated by a polymer layer. TGA analysis revealed that the synthetic protocol leads to the quantitative introduction of the inorganic components in the polymeric fibers, since the inorganic residues after thermal treatment well compare to the nominal value of the inorganic loading.

Catalyst screening showed that both membranes are active in HMF oxidation, and among them, the Nylon-based one leads to higher FDCA yield and lower carbon loss. This feature is more pronounced when the tests are performed at high temperature, indicating that PAN membrane suffers from severe diffusional limitations respect to the Nylon one (Fig. 2). This difference in activity has been ascribed to the different glass transition temperature (Tg) of the two polymers: indeed, Nylon Tg (around 62°C) is lower than both reaction temperatures tested, thus tentatively leading to an improved accessibility of the catalytic active sites with respect to PAN, whose Tg (around 100°C) is higher or at least close to the testing conditions.

In conclusion, this work showed that electrospinning is a suitable technique to obtain catalytically active membranes, whose activity, being dependent on the active site exposure, is strictly correlated to the possibility of operating at temperature above the Tg of the polymeric component. Thus, among the two membranes tested, Nylon showed the most promising properties.

FIGURES



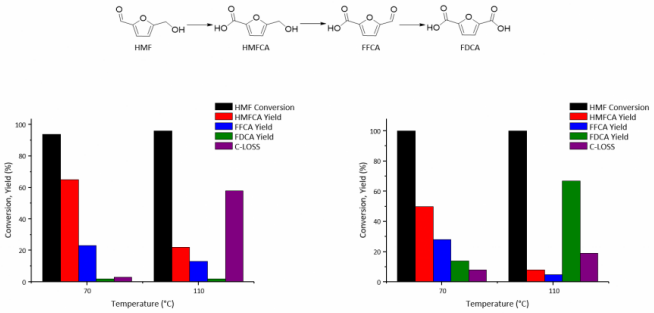


FIGURE 1

Fig. 1

Strategies for polymeric/inorganic PAN (left) and Nylon 6,6 (right) based membrane preparation

FIGURE 2

Fig. 2

HMF conversion and product yield for PAN and Nylon 6,6 based membranes (right and left, respectively). Reaction conditions: 4h, at 10bar of O2, 70°C and NaOH/HMF molar ratio equal to 2. A suitable quantity of composite membranes (as small squares with ave

KEYWORDS

HMF conversion | Catalytic membranes | Electrospinning | Nanoparticles

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