



Microwave-assisted dehydration of fructose and inulin to HMF catalyzed by niobium and zirconium phosphate catalysts



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ARTICLE INFO

Article history:

Received 7 November 2016

Received in revised form 11 January 2017

Accepted 22 January 2017

Available online 24 January 2017

Keywords:

Fructose

5-Hydroxymethyl-2-furaldehyde

Phosphate acid catalysts

Microwaves

Response surface methodology

ABSTRACT

5-Hydroxymethyl-2-furaldehyde (HMF) is a key bio-based platform for the production of renewable monomers and bio-fuels. However, most of its syntheses are carried out under not sustainable conditions. In this work, the production of HMF from fructose and inulin was investigated following the Green Chemistry principles, adopting aqueous medium, appreciable substrate concentration (10 wt%), low loading of heterogeneous acid catalyst (niobium or zirconium phosphate) and microwave heating. Both the catalysts resulted very active and promising, in particular zirconium phosphate and the performances were related to their different acid characteristics. The optimization of HMF synthesis with zirconium phosphate was also supported by a statistical modelling, which shows that the highest yield to HMF (about 40 mol%) is ascertained at high temperature (190 °C) and short reaction time (8 min). The catalysts resulted recyclable maintaining their starting activity almost unchanged.

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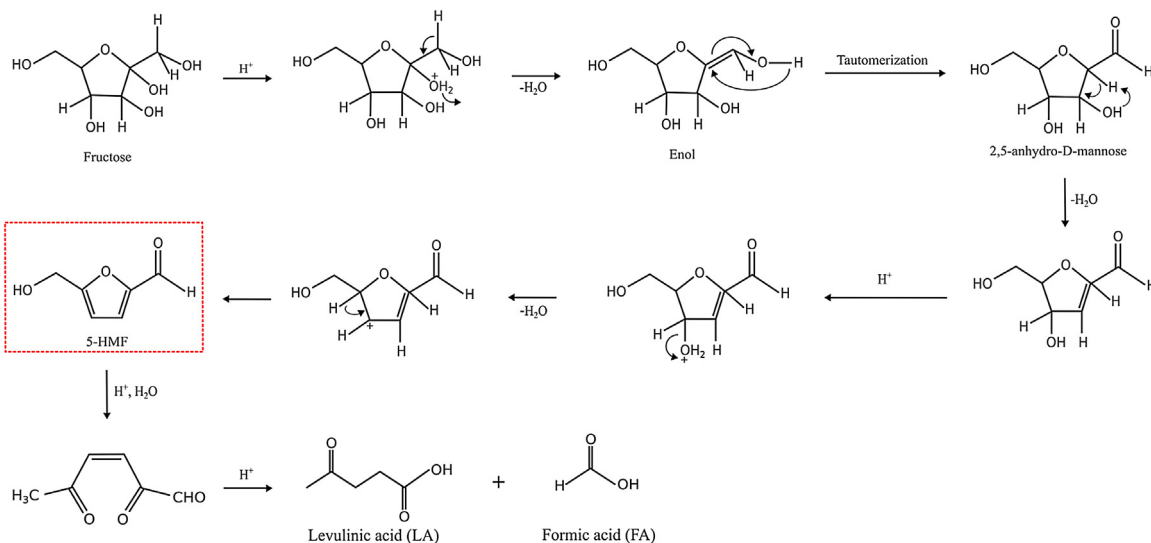
1. Introduction

In the last years environmental problems, such as pollution, greenhouse effect and the dwindling supply of fossil materials, have driven the interest of the scientific community towards the valorisation of lignocellulosic biomass. This last represents a renewable, plentiful and cheap material for the industrial production, not only in the energy field but also as feedstock for the manufacture of chemicals, solvents and materials. This idea is included in the concept of "bio-refinery", which aims to a complete valorization of the lignocellulosic biomass to obtain an array of added-value products [1–11]. In this scenario 5-hydroxymethyl-2-furaldehyde (HMF) represents a key molecule, evaluated by the US Department of Energy as one of the most important bio-based compounds [12]. HMF is referred in the literature as a "sleeping giant" due to its high potentialities [13–16]. In fact, this platform chemical can be employed as an intermediate for the synthesis of a number of fine-

chemicals, bio-fuels and monomers [10]. Some polysaccharides and monosaccharides, in particular fructose, represent the ideal starting materials for HMF synthesis [13–18]. Under acidic conditions, fructose undergoes a complex set of chemical reactions, leading to intermediates, HMF and reaction by-products. HMF is formed by fructose dehydration, and then is converted (at least in part) into by-products. HMF rehydration results in the formation of levulinic (LA) and formic (FA) acids, whereas humins are obtained from HMF polymerization [19,20]. These reactions are favoured by the presence of water, compelling many researchers to carry out the fructose dehydration in organic solvents [21–25], ionic liquids [26,27] and biphasic systems [28–31]. Considering safety, economic and environmental reasons, these solvents are less sustainable than water from the green chemistry perspective. Several mechanisms for the formation of HMF by acid-catalyzed dehydration of hexoses have been reported in the literature [15]. The mechanistic pathways can be divided in two groups. The first one assumes the reaction to proceed via acyclic intermediates, whereas the second type, largely reported in the literature, hypothesizes cyclic intermediates [32]. Scheme 1 shows the possible mechanism involving cyclic intermediates for the conversion of fructose to HMF and then to LA and FA. The dehydration of fructose is initiated by the proto-

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Scheme 1. Mechanism of fructose dehydration.

nation of the most basic hydroxyl group of the molecule, directly attached to the ring in the alpha position to the oxygen. The protonated form undergoes spontaneous dehydration and generates the cyclic intermediate enol, 2,5-anhydro-D-mannose, formed in the tautomerization step. The loss of water leads to the formation of HMF.

Both homogeneous and heterogeneous acid catalysts have been employed for the HMF synthesis but nowadays increasing research is focused on the use of heterogeneous ones. In fact, they are more suitable from an industrial perspective because avoid corrosion problems and facilitate catalyst separation and recycling. The most studied heterogeneous catalysts are ion-exchange resins [33,34], zeolites [35–37] and phosphates of transition metals (such as Nb, Zr, V, Cu, Ti) [38–45]. In particular, this last type of heterogeneous catalysts is very interesting because these systems keep their strong acidic properties in polar liquids [45], including water, also at high temperature [42,47,48]. Moreover, they can be easily reactivated by thermal treatments, as reported in the literature [45,49]. Carlini et al. [41] have carried out several studies regarding the fructose dehydration employing metal phosphates. They performed experiments on aqueous solutions containing 6 wt% of fructose at 100 °C in the presence of commercial niobium phosphate, employing substrate/catalyst ratio (RAC) from 1.4 to 1.7 wt/wt. Although the amount of catalyst was high, the reaction turned out to be slow but very selective, leading to 48 mol% conversion of fructose into HMF at 67 mol% selectivity. When they employed a more concentrated fructose solution (10 wt%), a decrease of HMF selectivity was ascertained. The same authors [40] investigated the fructose dehydration with zirconium and titanium phosphates under similar experimental conditions (100 °C, 6 wt% fructose in aqueous solution, RAC of 1.8 wt/wt) achieving higher HMF yields than those obtained with niobium phosphate, accounting for around 44 mol% for zirconium phosphate and 41 mol% for titanium phosphate. The same group considered the catalytic conversion of inulin into HMF under similar reaction conditions, reaching results similar to those reached from fructose. Recently, Zhang et al. [45] have studied the fructose dehydration, employing a synthesized niobium phosphate catalyst, working at 130 °C for 30 min with 8 wt% fructose in water. The authors reported high yields, up to 45 mol%, but adopting a too low substrate/catalyst ratio (1 wt/wt), which cannot be applied. Finally, Asghari et al. [38] claimed very high HMF yields, up to 50 mol%, when fructose was dehydrated for very short times, ranging from 60 s to 240 s, in aqueous medium using zirconium phosphate as a

catalyst. However, also in this case, the adopted conditions are not acceptable from an applicative perspective because of the very low fructose concentration (1 wt%), and too low substrate/catalyst ratio (2 wt/wt).

On the other hand, microwave heating has recently become a fast growing research area because it can improve the efficiency of many processes. In fact, thanks to the interaction between the microwaves and the polar molecules, the heating starts from the core, resulting in faster temperature increase, thus reducing the reaction time and the energy consumption. Moreover, microwave irradiation enables a more efficient reaction control, generally affording higher yields of the target products [50–53].

In this context, now we have studied the catalytic dehydration of fructose and inulin to HMF in water adopting MW heating and heterogeneous acid catalysis. The effect of the main reaction parameters has been studied using two different heterogeneous catalysts (niobium and zirconium phosphate). To the best of our knowledge, this is the first work that reports the HMF synthesis in water under microwave heating with these catalytic systems.

2. Materials and methods

2.1. Materials

5-hydroxymethyl-2-furaldehyde (98%), formic acid (99.8%) and levulinic acid (98%) were purchased from Sigma-Aldrich and used as received. Fructose was food grade and used without any further purification. Inulin from *Dahlia Tubers* ($[\alpha]_D^{20} = -37.0$ and $M_n \approx 5000$) was purchased from Fluka and used as received. Niobium phosphate, kindly provided from CBMM (Companhia Brasileira de Metalurgia e Mineração), was treated at 255 °C for 6 h under high vacuum (5 Pa) before reaction.

2.2. Synthesis of zirconium phosphate

Zirconium Phosphate (ZrPO) was prepared as reported by Kamiya et al. [54] through the precipitation of $ZrOCl_2 \cdot 8H_2O$ (32 mL of 1 M aqueous solution) and $NH_4H_2PO_4$ (64 mL of a 1 M solution), at a molar ratio of P/Zr = 2. The precipitate was filtered, washed with water, dried at 100 °C, and calcined at 400 °C for 3 h before reaction.

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