



Synergy effect between solid acid catalysts and concentrated carboxylic acids solutions for efficient furfural production from xylose



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ABSTRACT

An efficient furfural formation from xylose was demonstrated combining a concentrated aqueous solution of acetic acid and solid acid catalysts. Higher furfural yields and selectivities were obtained by comparison to the catalytic performances obtained in pure water. The evident synergy effect observed at 150 °C between the aqueous carboxylic acid solution and the solid acid catalysts is tentatively explained by the occurrence of two phenomena: 1) the contribution of Lewis acid sites which would operate in cooperation with the homogeneous weak Brønsted acidity brought by the aqueous acetic acid solution. According to the literature, the two steps mechanism involving the xylose-xylulose isomerization over Lewis acid sites and the successive Brønsted acid catalyzed cyclodehydration to furfural would be the prevailing reaction pathway in the heterogeneous-homogenous catalytic system at 150 °C. 2) an enhancement of the surface solid acid coverage by the carbohydrate and furfural owing to the presence of carboxylic acid in the aqueous solution as shown by comparative liquid phase adsorption experiments done in pure water and in aqueous acetic acid solutions. Among a series of solid acid catalysts, ZrW, Cs₂HPW₁₂O₄₀, HY (Si/Al = 15), K10 and NbOH, the latter one, NbOH used non-calcinated was shown to be active, selective and stable in the aqueous acetic acid media. HY and K10 are as active and selective for furfural formation but suffer for a strong Al leaching which precludes their utilization as true solid acid catalyst in acetic acid media.

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1. Introduction

Upgrading the carbohydrates biomass into high value-added chemicals is a current research topic of high interest [1]. Among the principal sources of carbohydrates, cellulose, a hexose biopolymer, has already well established applications, mainly in the paper industry. By contrast, hemicelluloses have limited identified applications and are still considered as an agriculture waste for example in bagasse sugarcane. In this xylan rich biomass, hemicelluloses are composed mainly of pentoses and the principal commercial product derived from them is furfural, obtained from the dehydration of the C5 units forming the polysaccharide (Scheme 1). This is an industrial process known since the earlier 1900, and the world production is about 250,000 tons annually. The potential of the furfural yield depend on the composition of the biomass and may ranges from 150 to 220 kg of furfural produced per metric ton of dry biomass [2].

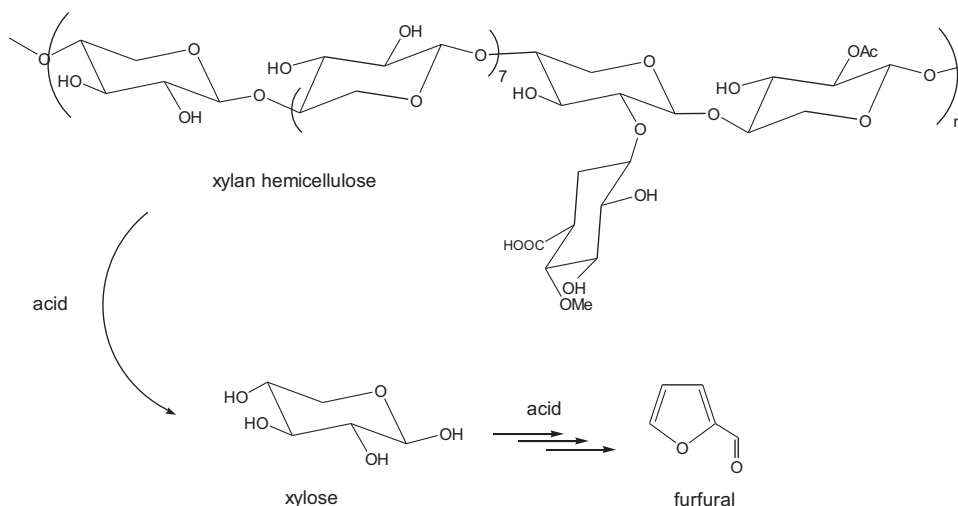
Today, the most widely used process in the industry is the Quaker Oats process, which uses sulphuric acid as catalyst and a

furfural steam distillation. This process is characterized by a limited yield in furfural, 35% due to side reactions and by an excessive water vapour consumption [3]. Other new processes have been developed but are not yet commercialized such as the SupraYield process which claims a furfural production (up to 50%) thanks to a discontinuous reactor working at high temperatures (200–225 °C) and high pressures (15–30 bars) but at a low contact time [4]. Nowadays, there is a need to develop a sustainable process which might avoid the use of strong mineral acids, such as sulphuric acid, and their drawbacks: low selectivity, equipment corrosion, health and environmental issues, impossibility of catalyst recycling. This justifies the growing interest in the search for heterogeneous acid catalysts for conducting in an efficient and sustainable way the furfural production from xylose dehydration.

One of the first reports on the use of a heterogeneous catalyst for the transformation of xylose in furfural is from Moreau et al. in 1998 [5]. They reported the use of H-mordenite and H-faujasite zeolites in a biphasic medium composed of water and toluene or MIBK (methyl isobutyl ketone) as furfural extractive solvent. This methodology allows the furfural extraction from the water phase, in order to avoid its degradation. The furfural selectivity achieved 82% for a xylose conversion of 51%. Since this pioneering work, others zeolites such as ZSM-5 [6], HUSY, H-Beta [7–9], H-mordenite

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Scheme 1. Furfural formation from xylan hemicelluloses.

[7,10], SAPO-11 [8,9] and solid acids like niobic acid [11] or even sulphonated graphenes [12] have been introduced for this reaction. It can be mainly concluded from all these studies that zeolites with small pore size and a low mesoporous volume, are more effective for the dehydration of xylose and more selective when used in the presence of an extractive solvent, leading to high furfural yields.

Indeed, as evocated above, in the more general field of catalytic sugars cyclodehydration, most of the studies have been carried out in the presence of an extractive solvent to increase the furanic derivatives yields. Cabezas et al. and Corker et al. studied the influence of the solvent employed during the extractive reaction. They reported that furfural is easily degradable due to side reactions forming humins when the reaction occurs in water, at high temperature [13,14]. Thus, various systems have been evaluated in order to determinate the benefit of using either MIBK, toluene, isobutyl acetate or alcohols such as methyl-2-butanol and 2-ethyl-1-hexanol. Alkyl-phenols are also applied with success to get high furfural yields [15]. Toluene appeared to be the most efficient solvent, leading to the highest furfural yields up to 80%. Despite its toxicity and unlikely industrial large scale application, this solvent has been further studied with different catalytic systems. Dias et al. used this solvent, in proportion of 70 wt%/water to explore the activity of several solid catalysts. Whatever their catalytic activity and selectivity in furfural in pure water, heteropolyacids (PW, SiW and PMo) [16,17], cesium-based heteropolyacids [18], titanium and niobium nanosheets [19], niobium-based silicates [20] and silica supported sulphated zirconia [21] have greater catalytic performances when used with toluene as extractive solvent. Note that DMSO, when used as co-solvent added to the aqueous phase, has also a positive influence to the furanic derivatives yields. Its role is less documented, but it was proposed in the similar reaction of glucose dehydration into 5-hydroxymethyl furfural (5-HMF), that adding DMSO to water might favor the furanose form of hexoses which exists in negligible proportion in pure water. It was also proposed that DMSO addition to water could reduce the condensation reactions and the successive rehydration of 5-HMF associated by the reduced proportion of water [22]. However, beside the efficiency of the extractive reaction methodology applied to sugar dehydration, it is scarcely underlined that due to the low partition coefficient of furfural to the organic solvent, its efficient extraction depends on salts addition in high amounts leading to complex reaction media [15]. If this methodology can suit well to the use of homogeneous mineral acids, it will not be compatible with the use of a heterogeneous solid acid, due to the possible solid acid catalyst

deactivation via cationic exchange as evocated recently by Dumesic et al. [23].

In order to go further in the development of an environment-friendly process, we decided to study sugars cyclodehydration in aqueous media without resort to an organic extractive solvent with potential toxicity. Previous works from our group have shown the benefit to perform hexoses dehydration in concentrated aqueous solutions of carboxylic acids. From fructose, 5-HMF yields of 60% were achieved in concentrated aqueous solutions of lactic acid. In pure water, from the screening of a large panel of solid acid catalyst, we have shown that the most efficient one was niobium hydroxide acid (NbOH) which led to a maximum 5-HMF yield of 30% [24]. Notably, this 5-HMF yield was obtained only when a high catalyst to sugar ratio was used. When NbOH was used in catalytic proportion, 5 wt%, the 5-HMF yield was limited to 10%.

To go further in the development of an efficient and green way to dehydrate monosaccharides, the present work aims to evaluate a large panel of different solid acid catalysts for xylose cyclodehydration in pure water and to perform a comparative evaluation of a concentrated aqueous solution of acetic acid as reactive medium, in the absence or in the presence of added solid acids. It was expected from this methodology to evidence or not, the occurrence of a synergy effect between the homogeneous weak Brønsted acid, acetic acid and the solid acid catalysts.

2. Experimental

2.1. Catalysts

Tungstated zirconia (ZrW) was prepared by anionic exchange according to an optimized method [25]. The acidic cesium salt of phosphotungstic acid $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ (Cs_2HP) was prepared by precipitation through a previously reported procedure [26]. Niobium hydroxide (NbOH) was obtained from CBMM (Brazil) and used as received without calcination. Zeolites HY (Si/Al = 15), ZSM-5 (Si/Al = 40) were provided by IFPEN. K10 was purchased from Aldrich.

2.2. Catalysts characterization

The specific surface areas were determined by nitrogen adsorption at -196°C using a Micrometrics ASAP 2020 equipment. Samples were previously degassed at 150°C under vacuum (10^{-3} Pa) for 5 h. Surface areas were calculated using the Brunauer–Emmet–Teller (BET) methods.

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