



# Heterogeneous acid-catalysts for the production of furan-derived compounds (furfural and hydroxymethylfurfural) from renewable carbohydrates: A review



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## ABSTRACT

The production of value-added chemicals from renewable sources, such as biomass-derived carbohydrates, is an emerging field. The amount of publications in the field of pentose and hexose conversion to furfural and hydroxymethylfurfural has considerably increased in the recent years. Most of these studies focus on using heterogeneous acid-catalysts to selectively convert these carbohydrates into the desired products at optimized yields. This review aims to summarize the most significant studies reporting the conversion of C<sub>5</sub> and C<sub>6</sub> carbohydrates using different structured materials. The final goal is to provide with a general overview of the broad spectrum of heterogeneous catalysts studies and the correlation between their physicochemical properties, with a special attention on the pore structure, and the catalytic activity under different reaction conditions, such as solvents or temperature. In the case of furfural, as it is already a commercial product, a short overview of the manufacturing process and the current improvements will also be given. The future studies reporting the carbohydrate dehydration reactions to furfural and HMF could take advantage of this study to select the physicochemical properties of the catalysts required to achieve their specific goals.

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## 1. Introduction

The substitution of fossil-fuel derived precursors with biomass conversion intermediates and chemicals is becoming an essential requirement to gradually increase the production of chemicals and fuels from renewable sources. Among these, furfural (FUR) and hydroxymethylfurfural (HMF), derived from C<sub>5</sub> and C<sub>6</sub> carbohydrates respectively, present interesting properties as building-blocks for high value-added products. The production of FUR and HMF at high yields is relevant to achieve a significant production of interesting chemicals and biofuels. In this sense, one of the biggest challenges facing carbohydrate dehydration reactions to furanic aldehydes is the control of the secondary reactions leading to yield-loss reactions.

In this sense, current research activities focus on using two main strategies: the use of heterogeneous selective acid-catalysts and the improvement of reaction systems. The use of solid catalysts gathers most of the attention, especially since it shows the biggest potential of advancement beyond the current state-of-the-art, and especially due to their easy post-separation through a simple filtration step or its possible operation as fixed-beds. The catalysts

must feature surface acidity, product selectivity through textural property adjustment and enhanced hydrothermal stability.

The most studied solid acids are zeolites [1], which are highly structured crystalline microporous inorganic aluminosilicates containing channels with very well-defined pores of 5–13 Å, in which the catalytic groups are located [2,3]. Zeolites based on silica alumina-oxides can be strong acidic catalysts and show excellent thermal and chemical stability. The zeolite mechanism for catalysis is based on shape selectivity, where reagents and intermediate products can be selected according to the pore size. Since most of the catalytic groups are located inside the porous structure, the molecules must be able to diffuse into the zeolitic structure before reaction. However, the use of zeolites in catalytic processes cannot be applied to all types of molecules, mainly due to pore size restrictions. These types of materials are limited to products and reagents in the range of 5–13 Å sizes.

The concept of supramolecular chemistry was first proposed by Lehn, Cram and Pedersen (1987) suggesting that molecules can self-organize into defined structures without using covalent bonds but weaker interactions such as hydrogen bonding [1]. This concept was applied for mesoporous materials and the first materials in this field were discovered by Mobil Oil Company researchers (1992) with the so-called M41S structures [4]. Compared to zeolites, these materials offer product-selectivity in the mesopore range, show

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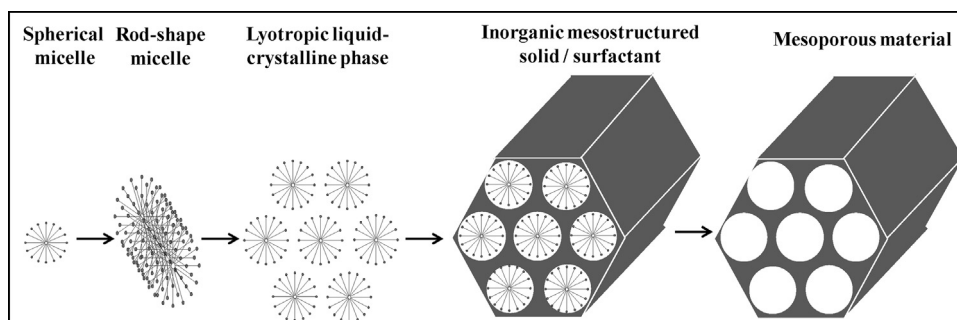


Fig. 1. True liquid-crystal template mechanism by structure-directing agents.

pore diameters around 20–100 Å and an amorphous silica wall [1]. The cylindrical shape of the pores allows fast molecule diffusion into them. Moreover, synthesis control allows pore tuning for product selectivity and for avoiding non-desired product formation, obtaining higher reaction rates. In theory, mesoporous materials enable to use more bulkier substrates than zeolitic materials [5] (Fig. 1).

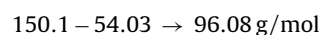
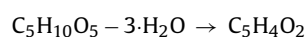
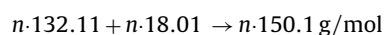
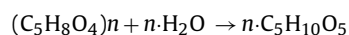
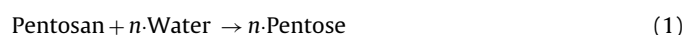
This review intends to draw a general picture of recent research developments achieved in the field of furfural and HMF production from carbohydrates, especially focused on the textural properties of different microporous and mesoporous heterogeneous acid-catalysts. This review aims to show the performance of zeolitic structures in the range below 2 nm and mesoporous materials with pores bigger than 2 nm. In order to provide sufficient information about the reaction parameters and to evaluate the influence of reagent and product diffusion in and out of the pores, the reaction yield values will be discussed as a function of the reaction temperature, source of carbohydrates, surface properties of the catalysts and reaction solvent. Moreover, the zeolitic and mesoporous catalysts that have been used to catalyze these reactions will be discussed classifying them into families according to their support' textural properties. As a general goal, this work intends to provide enough information to give an overall overview of heterogeneous acid-catalysts that can help future works develop more sustainable and greener renewable base-chemicals from biomass-derived carbohydrates through dehydration reactions.

## 2. State-of-the-art of the furfural production research

### 2.1. Production mechanism and current status

#### 2.1.1. Mechanism of furfural production from biomass

The following equations state the stoichiometry of the formation of furfural from pentosan-rich biomass by pentosan hydrolysis (1) and pentose dehydration (2) [6]:



So the theoretical furfural weight-basis yield from pentosan is: 72.7 wt.% from pentosan and 64 wt.% from pentose.

The dehydration reactions of pentose and hexose carbohydrates to furfural and HMF, respectively, follow similar reactions pathways. Different mechanisms have been proposed for both reactions, involving acyclic and cyclic dehydration pathways. The dehydration of these types of carbohydrates involves the protonation of 3 carbon atoms on the sugar ring to eliminate three water molecules and achieve the corresponding furanic molecules. The site requirements to achieve these products are similar in both reactions. Most studied catalysts feature Brønsted sites able to directly dehydrate the initial carbohydrate. Moreover, the use of Lewis acid-sites favors the isomerization of the carbohydrate and the subsequent dehydration via Brønsted sites. In addition to the reaction temperature, the source of carbohydrate and the reaction solvent, pentose and hexose dehydration reactions require similar textural properties. In these cases, the catalysts require specific pores adjusted to reagent and product diffusion to selectively produce the desired product.

**2.1.1.1. Pentosan hydrolysis to pentose sugars.** The hemicellulose polymers are mainly represented by xylan type sugars. Hemicellulose is hydrolyzed faster than cellulose, so this feature facilitates the extraction of pentoses from the biomass by dilute acid pretreatments [7]. The simplest model representing the hydrolysis suggests a series of irreversible reactions to hydrolyze xylans to xylose.

Pentosan polymers are C<sub>5</sub> rings linked by ether linkages, and their hydrolysis is usually carried out in several subsequent steps under dilute acid pretreatments or with steam in the presence of concentrated sulfuric acid (Fig. 2):

1. Protonation of the ether oxygen link leading to the formation of a trivalent oxygen
2. Cleavage of the oxygen bond to give a carbonium ion on one side and a hydroxyl group on the other side
3. Reaction of the carbocation with water
4. Liberation of the H<sup>+</sup> and thus the formation of the OH group

The use of strong mineral acid such as sulfuric acid or phosphoric acid accelerates the pentosan hydrolysis. However, their industrial use show several disadvantages, especially related to toxic effluents and corrosion issues. In some cases, the use of steam and the formation of organic acid fragments facilitates the protonation even in the absence of any catalyst.

**2.1.1.2. Pentose cyclodehydration to furfural.** The mechanism of pentose cyclodehydration consists of two subsequent 1,2-eliminations and one 1,4-elimination, as represented in Fig. 3 [7]. In the first instance, when a H<sup>+</sup> attacks a non-bonding electron pair of a hydroxyl oxygen bound to a carbon atom, it creates a trivalent positively charged oxygen atom. Oxygen is more electronegative than carbon, so the positive charge immediately shifts to the neighboring carbon to produce a fission of the C–O bond, a positively charged

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