



# Conversion of furfuryl alcohol to ethyl levulinate using porous aluminosilicate acid catalysts



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## ABSTRACT

The following porous aluminosilicates were tested as acid catalysts in the reaction of furfuryl alcohol (FA) with ethanol, at 140 °C: micro/mesoporous composite Beta/TUD-1 and the correspondent nanocrystalline (large pore) zeolite H-Beta; ITQ-2 and its zeolite counterpart (medium pore) H-MCM-22; mesoporous Al-TUD-1. The target product ethyl levulinate (EL) was formed with a yield up to 80%, at 24 h reaction (100% FA conversion). Relationships between the catalytic results and the acid and texture properties of the catalysts were established. Comparative studies for the aluminosilicates and the well-known sulfonic acid resin Amberlyst<sup>TM</sup>-15 were reported on the basis of EL yields, the undesirable formation of diethyl ether, and catalyst stability (regeneration and reuse). A study of the reaction products was carried out by comprehensive two-dimensional gas chromatography combined with time-of-flight mass spectrometry.

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## 1. Introduction

In the context of biorefineries the sugar platform derived from non-edible, relatively low-value lignocellulosic biomass, is promising for the sustainable production of liquid biofuels or fuel additives among other chemicals [1–10]. The sugar platform can complement that of vegetable oils in the production of bioesters. The acid-catalysed conversion of carbohydrates (polysaccharides) in aqueous phase may give levulinic acid (LA) (Scheme 1), one of the target chemicals (from the sugar platform) with most potential [7] and a wide-range of applications [8,11–16]. Using an alcohol medium instead of water, the carbohydrates may be converted to levulinate esters (LEs), which are interesting for different sectors of the chemical industry (e.g., polymers, flavour, fragrances, fuels) [6,11,16–20]. In essence, the synthesis of LEs may occur via two different catalytic routes depending on whether the feedstock is based on hexoses (e.g., D-glucose and D-fructose) or pentoses (e.g., D-xylose) (Scheme 1). These routes involve the acid-catalysed hydrolysis of polysaccharides into the constituent monosaccharides, and the subsequent dehydration of the latter into furanic compounds. In water, the relevant furanic products are furfural

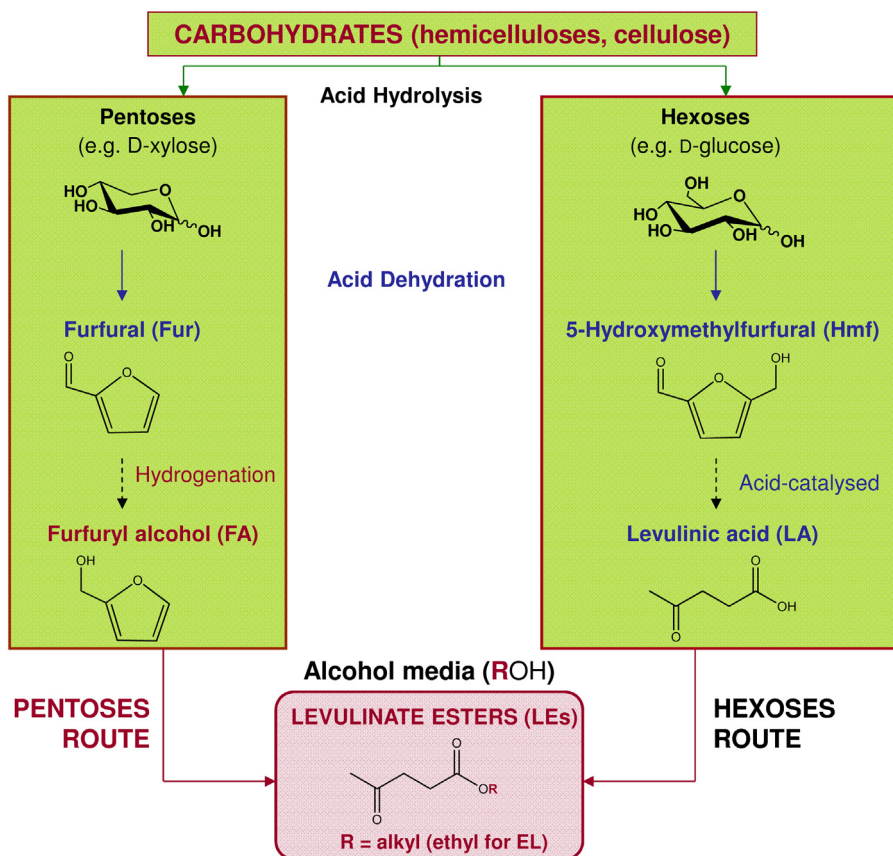
(Fur) from pentoses, and 5-hydroxymethylfurfural (Hmf) from hexoses [6,10,14,15,21–24], whereas in an alcohol medium LEs may be obtained as target end products (Scheme 1). While the hexose route may lead to LEs in an integrated process involving a series of acid-catalysed reactions, the pentose route involves an intermediate hydrogenation step of Fur into furfuryl alcohol (FA), which is converted into LEs via reaction with an alcohol over an acid catalyst. The pentose route for the production of Fur and FA has been implemented on an industrial scale for decades [22,25,26], and has been less explored for the synthesis of LEs. Recently, Li et al. [27] reported the formation of LA and methyl levulinate in the conversion of xylose using a methanol/water solvent mixture and Amberlyst<sup>TM</sup>-70 as catalyst, but the yields of these products were small (<3% at 170 °C, 3 h reaction).

The patent literature related to the production of LA and LEs is quite focused on the use of sulfuric acid or organic catalysts possessing sulfonic acid groups [28–34]. Sulfuric acid is a toxic and corrosive liquid (requiring the use of costly corrosion-resistant materials for operating equipment), neutralisation steps are necessary (leading to the co-production of inorganic salt wastes), and it may decompose and lead to the formation of sulfur-containing by-products. Sulfonic acid ion-exchange resins are organic-solid acids, less corrosive, easier/safer to handle than liquid acids and may perform as heterogeneous catalysts, which is advantageous for continuous-flow operation mode. Nevertheless, the regeneration and reuse of organic-solid acid catalysts in these reaction systems

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**Scheme 1.** Simplified representation of the pentose and hexose catalytic routes to levulinate esters (LEs).

may be seriously compromised by their limited thermal and chemical stabilities [35]. In this sense, fully inorganic porous solid acids present advantages over catalysts possessing organic components.

Aluminosilicates, such as zeolites, are relatively cheap, stable catalysts and versatile materials. Although zeolites are widely employed in the petrochemical industry their use as catalysts in the liquid-phase reaction conversion of biomass or related platform chemicals has drawbacks associated with their microporosity. These drawbacks include limited accessibility of active sites to the reagent molecules, and the existence of strong internal diffusion limitations. Concerning the conversion of FA to ethyl levulinate (EL), Lange et al. [35] noted the limited accessibility of the acid sites accessibility of zeolites. Moreover, Fernandes et al. [36] studied the esterification of LA into EL and concluded that the formation of the transition states likely takes place in zeolite catalysts with large cavities.

Breakthroughs in obtaining aluminosilicate catalysts with improved texture properties were accomplished through different synthetic strategies, such as: (i) use of an organic template for introducing mesoporosity and obtaining relatively narrow pore-size distributions (e.g., Al-TUD-1, [37–40]); (ii) reducing the crystallite sizes of zeolites to the nano-scale, and embedment of nanocrystalline zeolites in mesoporous silica matrices (e.g., nanocrystals of zeolite H-Beta in TUD-1 mesoporous silica to obtain the composite Beta/TUD-1 [41,42]); (iii) delamination of lamellar precursors of zeolites (e.g., of Pre-MCM-22(P) to give ITQ-2 [43–47]). Here, the reaction of FA with ethanol to give ethyl levulinate (EL) is investigated using porous aluminosilicate acid catalysts of the type (i)–(iii). Their catalytic performance is compared with the performance of the commercial sulfonic-acid resin Amberlyst™-15, one of the best catalysts (in terms of EL

yields) for this reaction, amongst various types of sulfonic-acid resins [35]. The reaction products are identified by comprehensive two-dimensional gas chromatography (GC × GC) combined with time-of-flight mass spectrometry (ToFMS).

## 2. Experimental

### 2.1. Catalysts

The catalysts tested herein were previously reported: mesoporous Al-TUD-1 [48], nanocrystalline (large pore) zeolite H-Beta (ca. 20 nm crystallite sizes) [49], composite Beta/TUD-1 [49] (medium pore) zeolite H-MCM-22 consisting of very thin (150–300 nm thick) platelet particles, prepared from Pre-MCM-22(P) [50], and mesoporous ITQ-2 obtained from delamination of Pre-MCM-22(P) [50]. In previous studies these solid acids were successfully used as catalysts in the aqueous phase acid-catalysed dehydration of D-xylose to Fur at 170 °C, exhibiting high catalytic activities and stabilities [48–50]. Table 1 summarises the acid and texture properties of these materials [48–50]. The cation-exchange resin Amberlyst™-15 (a macroporous styrene-divinylbenzene copolymer bearing benzenesulfonic acid groups) was acquired from Fluka Chemika. All catalysts were manually ground using an agate pestle and mortar and subsequently sieved to give a powder with particle sizes of less than 106 μm width.

### 2.2. Catalytic tests

Batch catalytic experiments were performed in tubular glass micro-reactors with pear-shaped bottoms and equipped with an appropriate PTFE-coated magnetic stirring bar and a valve for

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