



# Insights into the influence of feed impurities on catalytic performance in the solvent-free dimerization of renewable levulinic acid

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## ABSTRACT

Bio-jet fuel precursors can be produced from the solvent-free aldol dimerization of levulinic acid. The influence of the most common impurities accompanying the levulinic acid produced in lignocellulosic biorefineries (sulfuric acid, water, formic acid, and furfural) has been studied on the catalytic performance of different kinds of heterogeneous acid catalysts: (i) sulfonic acid-based materials, such as propyl-sulfonic acid-modified SBA-15, and the sulfonic acid resin Amberlyst-70, and (ii) commercial acid zeolites, such as H-Beta-19 and H-Beta-75. Furfural is the impurity that produces the greatest detrimental effect on the performances of all the catalysts tested. Catalyst deactivation is observed due to the formation of organic deposits on the catalyst surface (identified by TGA and acid-base titration), phenomenon that is accentuated when furfural is present in the reaction medium. Amberlyst-70 can recover almost totally the initial catalytic activity with a regeneration step based on washing with an acid solution under reflux. For Beta zeolites, the original activity of the catalyst can be easily and totally recovered through a regeneration process by calcination. H-Beta-19 zeolite is shown as the most suitable catalyst for the aldol dimerization of renewable LA, as its activity is not significantly affected by the presence of most of the impurities in the levels herein analyzed. In addition, a simultaneous mixture of all the impurities produces a synergistic effect, even improving the initial activity of the H-Beta-19 zeolite as a consequence of the sulfuric acid contribution to the catalytic effect.

## 1. Introduction

The air transport sector accounts for approximately 2–3 % of global CO<sub>2</sub> emissions worldwide, and air travel is predicted to double in the next 15 years. The International Air Transport Association (IATA) resolved to achieve net-zero carbon emissions from the global air transport industry operations by 2050 [1]. One of the proposed measures to reduce the carbon footprint of the air transport sector is the large-scale and cost-competitive production of Sustainable Aviation Fuels (SAFs) to replace the equivalent fossil kerosene [2,3].

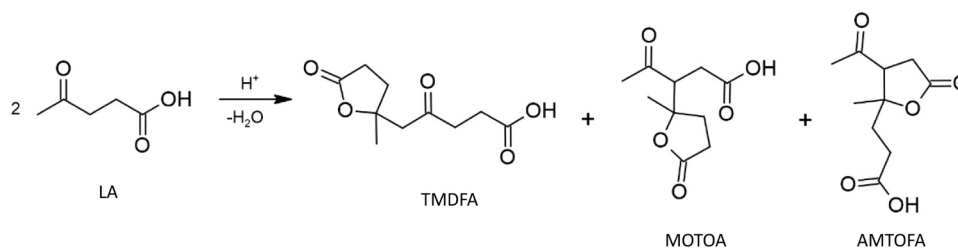
Among the different raw materials for aviation biofuel production, lignocellulosic biomass displays the greatest potential due to its low cost and high availability [4]. In particular, and owing to its high versatility, lignocellulosic biomass can be converted into a wide range of bio-based chemicals or bio-fuels [5,6]. Among them, levulinic acid (LA, C<sub>5</sub>H<sub>8</sub>O<sub>3</sub>) is considered as one of the top building-block chemicals coming from biomass, which can be easily and economically produced from cellulosic materials by commercial-scale acid-catalyzed hydrolysis process [7–9]. LA is a versatile chemical containing both a ketone carbonyl group and

an acidic carbonyl group, and it has been proposed as platform chemical for the preparation of fuels, organic chemicals, polymers, flavor substances, etc. [10].

LA upgrading can be accomplished via self-aldol condensation reaction, taking advantage of the presence of the carbonyl moiety. This reaction increases the length of the carbon chain, to C10 oxy-compounds (Scheme 1), that in a subsequent hydrodeoxygenation process can be converted into branched alkanes within the range of jet-fuel. Although this transformation can be carried out using either base or acid catalysis, the use of solid bases is neither environmentally benign nor economical from an atomic point of view since the presence of the carboxylic group in LA can neutralize/deactivate base catalytic sites, leading to low efficiencies [11]. Therefore, a potential alternative to perform this process in a more sustainable way is the use of solid acid catalysts, such as commercially available acid zeolites [12] or sulfonic mesostructured SBA-15 silicas [13], as we have recently reported [14,15]. Particularly, H-Beta zeolites performed outstandingly owing to a unique combination of microporous structure, excellent textural properties, and an adequate balance of aluminum acid sites in terms of coordination and acid

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**Scheme 1.** Reaction scheme for the aldol dimerization of LA to C10 dimers [16].

strength. On the other hand, the activity and selectivity shown by the sulfonic acid-functionalized mesostructured materials is superior to those of conventional sulfonic acid resins due to an enhanced accessibility and dispersion of the  $\text{SO}_3\text{H}$  sites.

In the global context of a lignocellulosic biorefinery [17], chemicals derived from one process (reagents, catalysts or by-products) can be fed to subsequent processes being able to poison catalysts used downstream, even at small concentrations. The influence of such impurities will greatly depend on the nature of the catalyst (i.e., structure, pore size, and particle size), reactor configuration, and reaction conditions (i.e., concentration, solvent, temperature, etc.) under which the catalysts will be employed [18]. Hence, catalyst deactivation by feeding impurities is another challenge to overcome for the efficient valorization of biomass.

The production of LA from biomass sources will typically involve treatment of cellulose in dilute solutions of mineral acids, mainly sulfuric acid [19,20]. When not completely removed, such mineral acid impurities are expected to negatively affect the downstream catalytic processes for LA transformations. In addition to sulfuric acid, byproducts from LA synthesis, such as furanic derivatives like furfural, as well as coproduced formic acid or water, can remain in small quantities accompanying the produced LA, which can have a significant impact on catalyst stability [21]. Furthermore, the furanic compounds can undergo side reactions (e.g., polymerization of furfural) resulting in the formation of high molecular weight compounds, typically denoted as *humins*, which might cause fouling of the catalyst surface.

The influence of LA impurities on the stability and performance of the catalysts has been described in the literature mainly for the hydrogenation of bio-derived LA to  $\gamma$ -valerolactone [18,21–25]. However, although several catalytic systems have been reported for the self-condensation of LA into bio-jet fuel precursors [11,14–16,26–29], all the studies used pure LA as feedstock employing reaction conditions that may not be suitable for using in a process operating with contaminated LA streams derived from a real lignocellulosic biorefinery. Therefore, the purpose of the present work is to give one step further in the study of the solvent-free acid-catalyzed dimerization of renewable LA, via aldol condensation, evaluating the influence of the most common impurities from the production of LA on the catalytic performance, such as sulfuric acid, water, formic acid, and furfural.

## 2. Experimental

### 2.1. Catalysts and reagents

The commercial acid catalysts were acquired from different suppliers: ion-exchange sulfonic resin Amberlyst-70 (Rohm & Haas), zeolite H-Beta-19 (Zeolyst International - CP814C), and H-Beta-75 (Zeolyst International - CBZ 150). Propylsulfonic acid-functionalized mesostructured silica (Pr-SBA-15) was synthesized following a previously reported procedure [30], using Pluronic 123 ( $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ , Sigma Aldrich) as a template block-copolymer along with tetraethylorthosilicate as the silica precursor (TEOS, Sigma-Aldrich, 98 % purity), and (3-mercaptopropyl)trimethoxysilane (MPTMS, Sigma-Aldrich, 95 % purity) as the sulfonic acid precursor.

For the aldol condensation reactions, levulinic acid (Acros Organics,

**Table 1**

Main physicochemical, textural and acidity properties of sulfonic-acid catalyst and zeolites.

Sulfonic-acid materials					
Catalyst	Type of catalyst	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )	$D_{\text{p}}^{\text{b}}$ ( $\text{\AA}$ )	Acid capacity <sup>d</sup> ( $\text{meq H}^+/\text{g}$ )	$\text{SO}_3\text{H}$ groups density <sup>f</sup> ( $\mu\text{eq H}^+/\text{m}^2$ )
Amberlyst-70	Sulfonic resin	36	220	2.68	70.8
Pr-SBA-15	Mesostructured silica	673	83	1.16	2.5
Acid zeolites					
Catalyst	Structure	$S_{\text{BET}}^{\text{a}}$ ( $\text{m}^2/\text{g}$ )	$D_{\text{p}}^{\text{b}}$ ( $\text{\AA}$ )	Acid capacity <sup>c</sup> ( $\text{meq H}^+/\text{g}$ )	Si/Al <sup>g</sup>
H-Beta-19	BEA	726	5.6 – 7.7	0.57	23
H-Beta-75	BEA	573	5.6 – 7.7	0.21	103

<sup>a</sup> Surface area calculated by the BET method. <sup>b</sup> Mean pore size from the adsorption branch of the  $\text{N}_2$  isotherm. <sup>c</sup> Pore size range corresponding to each crystalline structure. <sup>d</sup> Acid capacity determined by acid-base titration. <sup>e</sup> Total acid capacity as determined by  $\text{NH}_3$ -TPD. <sup>f</sup> Acid sites density defined as the ratio between acid capacity from acid-base titration and the BET surface area. <sup>g</sup> Si/Al molar ratio as measured by ICP-OES.

+98 % purity) was used as the substrate, sulfolane (Merk, synthesis grade) as the internal standard, and furfural (Sigma-Aldrich, 99 % purity), formic acid (Scharlau, 98–100 % purity), sulfuric acid (PanReac AppliChem, 95–98 % purity, pharma grade), and Milli-Q water as the impurities. Hydrochloric acid (Sigma-Aldrich, ACS reagent, 37 % purity), ethanol absolute (Scharlau, synthesis grade), tetraethylammonium chloride hydrate (TEACl, Thermo Scientific, 99 % purity), NaOH 0.01 M solution prepared from sodium hydroxide 0.1 N (standardized solution, Thermo Scientific), acetone (PanReac AppliChem, analysis grade), and chloroform deuterate (Eurisotop, 99.80 % D) were used for the characterization of the catalysts and the product analysis.

### 2.2. Catalysts characterization

X-Ray powder diffraction (XRD) was used to determine the structural ordering of the catalysts by means of a Phillips X'Pert diffractometer, recording from  $0.6^\circ$  to  $5^\circ$  ( $2\theta$ ), using the  $\text{Cu K}\alpha$  line, with a step size of  $0.02^\circ$  for the mesostructured Pr-SBA-15, and from  $5^\circ$  to  $60^\circ$  ( $2\theta$ ) with a resolution of  $0.04^\circ$  for the zeolites. A Micromeritics TriStar 3000 unit was used to determine the textural properties of the acid-functionalized mesostructured silica Pr-SBA-15 at  $-196^\circ\text{C}$  (77 K) by nitrogen adsorption-desorption. In the case of the beta zeolites, textural properties were calculated from argon adsorption-desorption isotherms at  $-186^\circ\text{C}$  (87 K) recorded using an Auto-Sorb equipment (Quantachrome Instruments). The Brunauer-Emmett-Teller (BET) method was used in both cases to determine the total surface area of the catalysts, while the pore size distributions was assessed by the Barret-Joyner-Halenda (BJH) method with the Kruk-Jaroniec-Sayari correction. The concentration of sulfonic acid sites, herein denoted as acid capacity, of the sulfonic acid catalysts was characterized by titration using an Eco

Titration Metrohm 9100 unit. The acid sites of the catalysts were exchanged for 30 min using a suspension of 0.05 g of the catalyst in TEACI 2 M solution and then titrated with a NaOH 0.01 M solution with continuous stirring. A Micromeritics Autochem 2910 (TPD/TPR) unit coupled to a TCD detector was used to determine the total acid capacity of the zeolites via temperature-programmed desorption of ammonia ( $\text{NH}_3$ -TPD). Organic content was evaluated through thermogravimetric analyses (TGA) accomplished in a Mettler-Toledo SDT 2960 Simultaneous DSC-TGA Star System device with an air flow of 100 mL/min and heating ramp of 5 °C/min. In the case of zeolites, aluminum content was determined by Inductively-Coupled Plasma Optical Emission Spectroscopy (ICP-OES) with a Varian Vista AX apparatus. In the sulfonic acid-based catalysts, sulfur content was assessed by means of elemental analysis (HCNS) in a Thermo Scientific Flash Smart Elemental Analyzer apparatus. Table 1 shows a summary of the most relevant physico-chemical, textural and acidity properties of the different catalysts tested in this work.

### 2.3. Reaction procedure

The solvent-free dimerization of LA (Scheme 1) leads to three main products: tetrahydro-2-methyl-5,  $\gamma$ -dioxo-2-furanpentanoic acid (TMDFFA), 3-(2-methyl-5-oxotetrahydrofuran-2-yl)-4-oxopentanoic acid (MOTOA), and 3-acetyl-2-methyltetrahydro-5-oxo-2-furanpentanoic acid (AMTOFA) [16]. All of them are interesting precursors for bio-jet fuel production, so they have been pooled together as C10 dimers.

The catalytic reactions were carried out in ACE pressure glass reactors with continuous stirring and with temperature control (oil bath). Upon completion of the respective catalytic run, the reactor was removed from the oil bath and samples are withdrawn for analysis. Based on our previous works [14,15], the reaction conditions were fixed as follows: 1.16 g of LA (10 mmol), 0.1 g of sulfolane as internal standard, 0.15 g of catalyst, 150 °C, and 3 h. The reaction time was limited to 3 h to avoid working under saturating conditions (that is, keeping low conversion), to allow for a better discrimination of the real effect of impurities on the catalytic performance of each catalyst under study. The catalysts tested in this work were four different acid heterogeneous catalysts: two zeolites (H-Beta-19 and H-Beta-75), a cationic-exchange sulfonic resin (Amberlyst-70) and a SBA-15-supported sulfonic catalyst (Pr-SBA-15). Before use, the zeolites were activated via calcination at 550 °C for 6 h with a heating ramp of 1.8 °C/min, while the acid resin Amberlyst-70 was washed with methanol to remove absorbed water and dried overnight at 110 °C. Pr-SBA-15 was used without any activating

pretreatment. The impurities analyzed and their concentration levels were: sulfuric acid (0.5–1 mol%), water (15–30 mol%), formic acid (3–5 mol%), and furfural (3–5 mol%). Such concentrations correspond to the typical ranges expected in unpurified LA, or partially-purified LA, in real biorefinery crude streams [31].

### 2.4. Product analysis

Gas chromatography (GC) and nuclear magnetic resonance (NMR) spectroscopy were combined to analyze the samples after reaction. While samples were still hot and under continuous stirring, 0.3 mL was taken and dissolved in 2.8 mL of acetone, filtered with 0.2  $\mu\text{m}$  Nylon filters to remove the heterogeneous catalyst, and analyzed in a Varian CP-3900 GC. This chromatograph was equipped with an Agilent CP-WAX 52 CB column (30 m  $\times$  0.25 mm  $\times$  0.25  $\mu\text{m}$ ), a Varian CP-8400 automatic injector and a flame ionization detector (FID), and it allowed for the quantification of the remaining nonreacted LA to calculate its conversion. Calibration of the GC analysis unit was done with pure LA and using sulfolane as the internal standard. In parallel, another sample of 0.1 mL was taken from the reactor and dissolved in 0.7 mL of deuterated chloroform, filtered, and analyzed by means of  $^1\text{H}$  NMR using a Varian Mercury Plus spectrometer at 400 MHz. The NMR analysis allowed for the quantification of C10 dimers. The processing of the  $^1\text{H}$  NMR data was that previously reported by Zhang et al. [26] and Amarasekara et al. [16]. Representative  $^1\text{H}$  NMR spectrum and GC chromatogram of the reaction mixture can be found in our previous work [14]. For each catalyst, the influence of the impurities has been evaluated in terms of activity (LA conversion,  $X_{\text{LA}}$ ), and in terms of yield ( $Y_{\text{C10}}$ ) and selectivity ( $S_{\text{C10}}$ ) towards the products, C10 dimers (Eqs. 1–3).

$$X_{\text{LA}}(\%) = \frac{\text{Reacted mol of LA}}{\text{Initial mol of LA}} \cdot 100 \quad (1)$$

$$Y_{\text{C10}}(\%) = \frac{2 \cdot \text{Formed mol of dimerization product}}{\text{Initial mol of LA}} \cdot 100 \quad (2)$$

$$S_{\text{C10}}(\%) = \frac{2 \cdot \text{Formed mol of dimerization product}}{\text{Reacted mol of LA}} \cdot 100 \quad (3)$$

### 2.5. Catalysts regeneration

Within this work, we have also assessed the stability of the catalysts in a second consecutive use. After the corresponding reaction, the catalyst was recovered by filtration, washed with acetone under

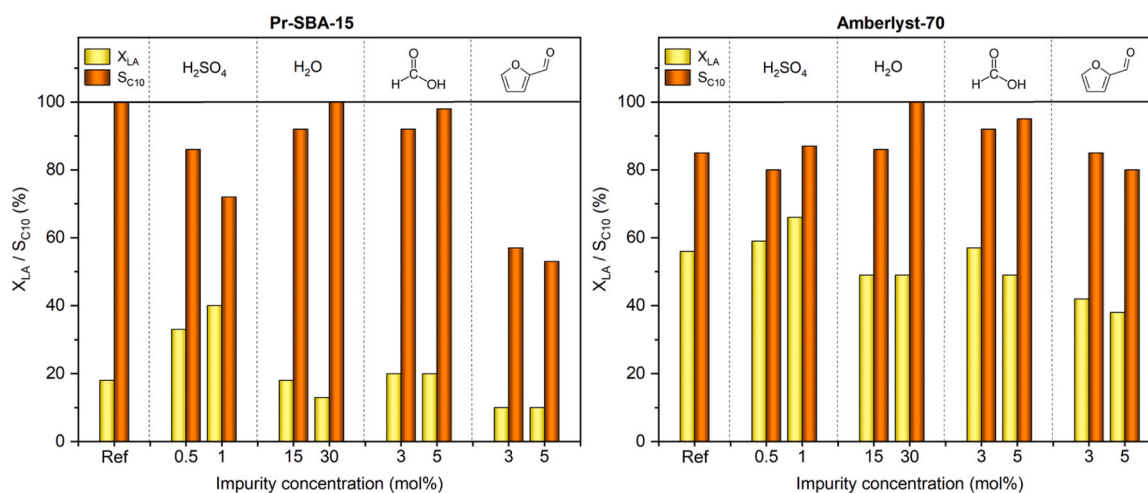
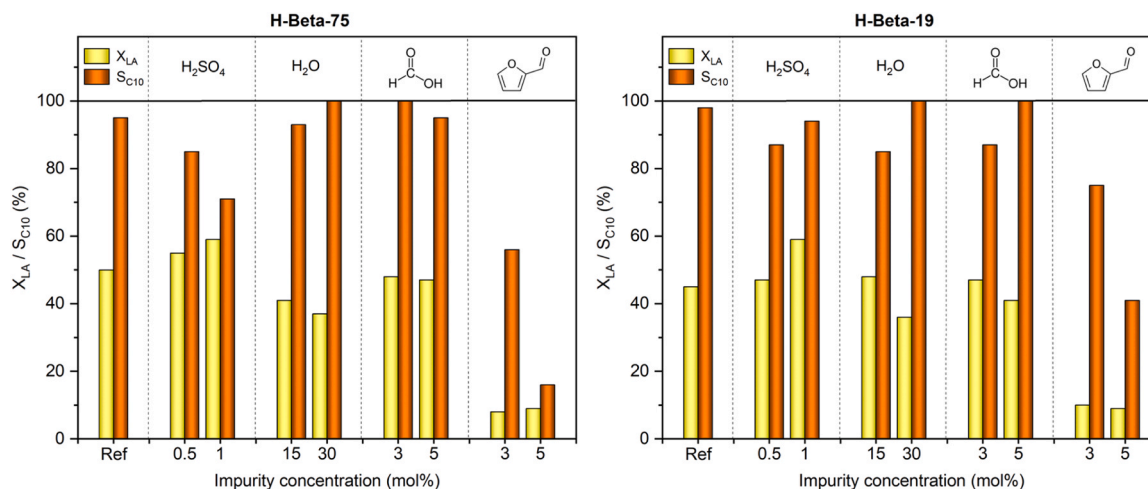


Fig. 1. Aldol dimerization of LA over sulfonic acid-functionalized materials (left = Pr-SBA-15, right = Amberlyst-70) using different impurities and concentrations. Ref = reaction without impurities. Reaction conditions: LA: 10 mmol; T: 150 °C; reaction time: 3 h; catalyst loading: 0.15 g.



**Fig. 2.** Aldol dimerization of LA over beta zeolites (left = H-Beta-75, right = H-Beta-19) using different impurities and concentrations. Ref = reaction without impurities. Reaction conditions: LA: 10 mmol; T: 150 °C; reaction time: 3 h; catalyst loading: 0.15 g.

continuous stirring for 30 min and finally dried at 110 °C overnight. In the case of Amberlyst-70 two different regeneration treatments were carried out. In a moderate one, the catalyst was suspended and stirred in a solution of 0.1 M HCl in water for 30 min at room temperature, filtered, and washed with MilliQ water until the pH increased to 7. Finally, the catalyst was dried overnight. In a second more intense regeneration treatment, Amberlyst-70 was washed in a solution of 0.05 M HCl in ethanol, keeping under reflux during 4 h. For beta zeolites, a calcination treatment was applied to regenerate the catalyst, following the same procedure described for the activation of the fresh zeolites.

### 3. Results and discussion

#### 3.1. Homogeneous catalysis

In this work, the influence of different impurities on the self-condensation of LA into jet-fuel precursors has been studied. Two of the impurities chosen are acid compounds, formic acid and sulfuric acid, that could possess the capacity to promote the reaction under study, thus behaving as homogeneous co-catalysts. Hence, some blank reactions, without solid catalyst, were carried out: (1) without any impurity; (2) adding 5 mol% of formic acid as impurity; (3) adding 1 mol% of sulfuric acid as impurity. The amount of each impurity was set at the corresponding high addition level, and the reaction conditions were: LA 10 mmol, 150 °C and 3 h of reaction time.

In the first blank test (results not shown) no activity is observed, obtaining an insignificant conversion of LA. This confirms that, under the reaction conditions of the study, the LA used as reaction reagent is not capable of autocatalyzing the aldol condensation reaction, most likely because its acid strength is not enough. Similar result was obtained with the addition of 5 mol% of formic acid, as it is also a weak carboxylic acid. On the other hand, the results obtained in the third test confirm that sulfuric acid promote the transformation of LA even at only 1 mol% concentration, giving place to a LA conversion of 38 % which can be attributed to the high acid strength of sulfuric acid.

#### 3.2. Influence of impurities

The influence of impurities was tested over different kinds of acid heterogeneous catalysts, including sulfonic acid-based materials and commercial acid zeolites. Reaction conditions were fixed as follows: temperature 150 °C, catalyst loading 0.15 g, and reaction time 3 h. Fig. 1 shows the catalytic results for the aldol dimerization of LA over the

synthesized propyl-sulfonic acid-modified SBA-15 mesoporous silica, Pr-SBA-15, and the commercial sulfonic acid resin Amberlyst-70, using different impurities and concentrations. These catalysts were chosen based on our previous work in which Pr-SBA-15 was the most active and selective catalyst in the LA dimerization among different SO<sub>3</sub>H-functionalized materials due to an optimal combination of textural properties, moderate strength, and surface density of sulfonic acid groups [14]. As a reference catalyst, the commercial sulfonic acid macroporous resin Amberlyst-70 is also evaluated, as its maximum operating temperature is high enough for this application (190 °C according to the supplier).

The presence of formic acid does not significantly affect the activity of both catalysts, at the concentration levels tested. Although formic acid is an acid compound, due to its low acid strength its presence in the reaction medium does not improve the results, but neither does it negatively affect the LA conversion and the selectivity to the desired condensation products.

On the other hand, an increasing trend in the LA conversion is observed for both catalysts as the amount of sulfuric acid in the reaction medium increases, since, as we discussed above, this acid is able to transform the substrate LA acting as a co-catalyst in the system. Despite this beneficial effect, it must be noted that the presence of sulfuric acid is detrimental from the point of view of security, materials corrosion, and handling. In the case of the synthesized Pr-SBA-15 material, the presence of well-ordered mesopores with narrow pore size distributions favors the progress of the aldol dimerization process minimizing side reactions, as the results at the reference level without impurities show, reaching a 100 % of selectivity C10 dimers. However, a decrease in this value is observed in the presence of sulfuric acid since this strong acid compound promotes other side reactions. The sulfonic resin Amberlyst-70 displays a lower specific surface area but a higher acid capacity, leading to a high surface SO<sub>3</sub>H density (70.8 μeq H<sup>+</sup>/m<sup>2</sup>, Table 1). This can explain its increased activity for undesired side reactions and therefore the lower selectivity obtained, 85 %, as compared to Pr-SBA-15 at the reference level. Hence, the effect of the presence of sulfuric acid in the reaction medium with Amberlyst-70 is not observed to the same extent as with Pr-SBA-15.

With the addition of water, a slight decrease in the LA conversion is observed and also an improvement in the selectivity to the desired dimers. In sulfonic acid-based materials this reduction is attributed to the strong interaction between SO<sub>3</sub>H groups and water molecules, since this compound is adsorbed on their surface and interacts with the sulfonic groups of the catalysts (very hydrophilic), forming a coordination sphere around them. This phenomenon can cause a decrease in the accessibility of the sulfonic acid sites of the catalysts, leading to a decrease in their



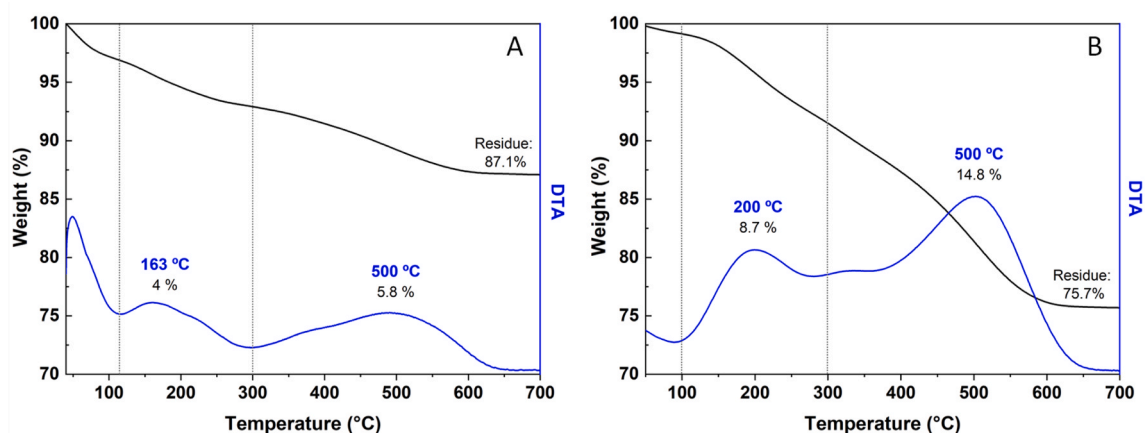


Fig. 3. Thermogravimetric profile of H-Beta-19 zeolite: (A) after the reaction without impurities (reference level); and (B) after the reaction with furfural as impurity (5 mol%).

catalytic activity.

Finally, furfural is the impurity that causes the most negative effects on the catalytic activity of this type of catalysts, decreasing both the LA conversion and the selectivity. However, the resin Amberlyst-70 tolerates in a better way the presence of this compound, most likely due to the high acid sites concentration and the more open structure that would help minimizing the detrimental effects of formed organic deposits coming from furfural polymerization.

In Fig. 2 the effect of the impurities on the catalytic performance of beta zeolites is shown. In our previous work, H-Beta zeolites were shown to be promising catalysts for the aldol dimerization of LA due to a unique combination of microporous structure, excellent textural properties and a suitable balance of acid sites nature and strength [15]. Therefore, H-Beta-19 and H-Beta-75 were selected for this study in order to evaluate different Al content and acid strength. As in the case of the sulfonic catalysts, formic acid is the species with the lower impact on the catalytic performance of both zeolites, remaining almost constant both LA conversion and selectivity to C10 dimers. In contrast, the co-feeding of sulfuric acid improves LA conversion, with a slight loss of selectivity. Again, it is possible to observe a cooperative catalytic effect from this strong mineral acid. However, it also promotes unwanted side reactions reducing the selectivity to the products of interest (C10 dimers). The presence of water leads to a decrease in the LA conversion, similar to the reduction observed for sulfonic catalysts, maintaining in terms of C10

selectivity. Such a decrease is also attributed to the solvation of acid protons within the zeolitic BEA structure.

Last, furfural is again the impurity that produces the greatest negative effect on the performance of the zeolites, sharply reducing their catalytic activities. The high instability of the furfural and its ease for polymerizing at high temperatures in the presence of acid catalysts, lead to the formation of *humins*. Non-soluble *humins* tend to deposit on the catalysts surface, especially around the acid sites, drastically reducing the access of LA molecules to the catalyst's acid centers. The detrimental effect of furfural is more pronounced in these materials than in the SO<sub>3</sub>H-based catalysts, probably due a lower availability of acid sites, together with a more restricted pore size that would enhance pore blocking (Table 1). It is important to note that in literature is described the cross-condensation reaction of furfural with levulinic acid under acid zeolites catalysts. However, under the reaction conditions tested in this study, no peaks corresponding to these products have been detected, probably due to the higher reaction temperature leading to a rapid furfural degradation instead. To confirm the cause of catalyst deactivation, a thermogravimetric analysis was performed on the H-Beta-19 zeolite after the reaction, comparing with the TG analysis of the catalyst after the reaction at the reference level, without impurities (Fig. 3).

As shown in Fig. 3, the first weight loss up to 100 °C corresponds to water molecules adsorbed on the catalyst surface. A second weight loss is then observed around 150–200 °C, that can be attributed to the LA

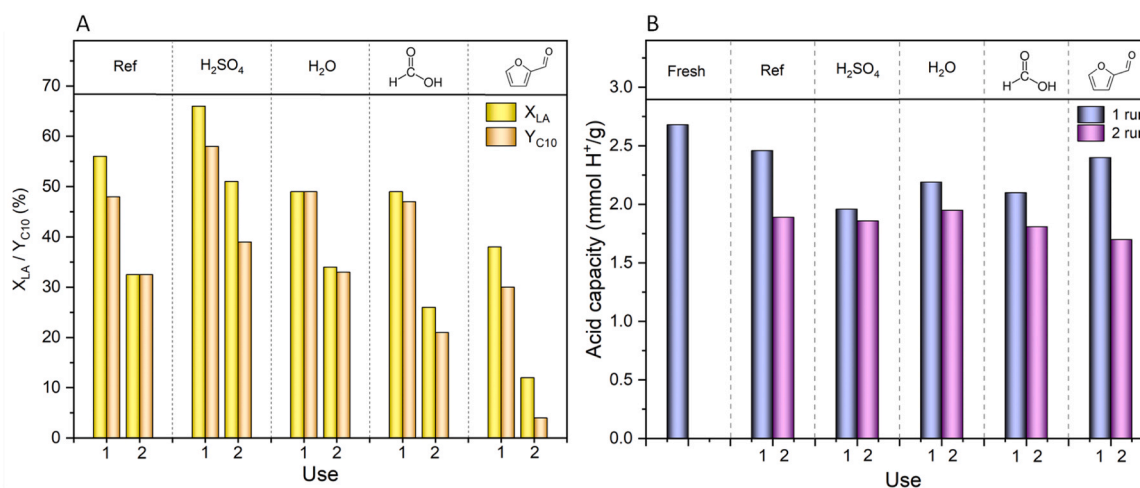
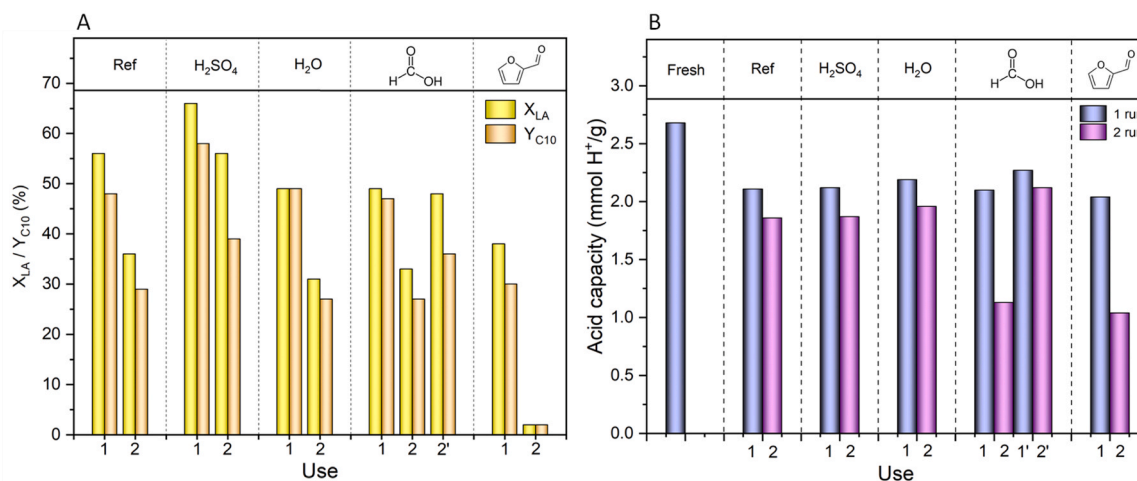


Fig. 4. Stability of Amberlyst-70 for the aldol dimerization of LA using different impurities. A: catalytic results; B: acid capacity of the catalyst after 1 and 2 reaction cycles. Ref = reaction without impurities. Reaction conditions: LA: 10 mmol; T: 150 °C; reaction time: 3 h; catalyst loading: 0.15 g. Catalyst washed with acetone at room temperature after each use.



**Fig. 5.** Stability of Amberlyst-70 for the aldol dimerization of LA using different impurities. A: catalytic results; B: acid capacity of the catalyst after 1 and 2 reaction cycles. Ref = reaction without impurities. Reaction conditions: LA: 10 mmol; T: 150 °C; reaction time: 3 h; catalyst loading: 0.15 g. After each use: catalyst regenerated at room temperature (1 and 2); catalyst regenerated under reflux (1' and 2').

condensation products obtained during the reaction. Finally, thermogravimetric analysis of the post-reaction H-Beta-19 zeolite confirms the presence of significant, strongly adsorbed organic species, whose decomposition around 500 °C is consistent with polymeric compounds such as residues from furfural. Comparing both thermogravimetric profiles, an increase of these polymeric compounds on the catalyst surface is observed for the zeolite after a reaction cycle with furfural as impurity. We conclude that the main reason of catalyst deactivation is by organic fouling of the active sites.

In order to minimize the side reactions of furfural and therefore the generation of deactivating organic deposits, the temperature of the reaction was reduced to 120 °C using the zeolite H-Beta-19 as catalyst. Under these reaction conditions and without the presence of any impurity in the reaction medium, a LA conversion of 10 % (100 % of selectivity) was obtained, and by adding 3 mol% of furfural the conversion dropped to 4 %, maintaining the selectivity to the desired products. Hence, it is confirmed that by using lower reaction temperatures the negative effect of furfural can be ameliorated, in consonance with a reduction of the extent of side reactions. However, the catalytic activity is still affected in a strong way by the presence of furfural.

### 3.3. Stability of the catalysts

In addition, the stability of the catalysts in a second consecutive use was assessed at the highest level of the impurities: 5 mol% of formic acid, 30 mol% of water, 1 mol% of sulfuric acid, 5 mol% of furfural. For this study Amberlyst-70 and H-Beta-19 zeolite were chosen as representatives of both types of materials. The effect of furfural as an impurity has been addressed only for Amberlyst-70 since the activity of H-Beta-19 drops drastically even in the first use, as it has been described above. The evaluation of the stability was performed reusing the catalysts under the same reaction conditions: temperature 150 °C, catalyst loading 0.15 g, and reaction time 3 h.

In the case of Amberlyst-70, different procedures of recovery and regeneration after reaction were studied (described in the Experimental section). First, the catalyst was recovered, washed with acetone at room temperature and used in the next reaction, without applying any regeneration treatment. As shown in Fig. 4A, the sulfonic resin Amberlyst-70 suffers a significant deactivation in the second consecutive use, with all the impurities tested but also even in the reference level. This detriment of activity is attributed to the progressive loss of acid capacity of the catalyst after the reaction, as determined by acid-base titration (Fig. 4B). It is important to note that the acid capacity was measured using a large exchange cation such as TEA<sup>+</sup>, compared to

the most commonly used Na<sup>+</sup> cations, in order to quantify only the acid sites accessible by molecules the size of LA. Also, the organic and polymeric nature of the resin, consisting of polyvinylbenzene chains, would be prone to retain and incorporate the possible humins formed during the reaction. This might also lead to an additional deterioration of its catalytic properties.

The organic deposits formed during the reaction of aldol condensation of LA without impurity in the presence of Amberlyst-70 could be the same as those formed with formic acid after the first use, since formic acid does not affect the catalytic performance as described before. During the second reaction cycle, organic deposits formation would increase, blocking a greater number of sulfonic acid sites, and leading to a significant decreasing of the activity (both LA conversion and yield to C10 dimers). With the presence of sulfuric acid in the reaction medium, a loss of selectivity and acidity is observed after the first use, which may be due to the presence of organic deposits on the catalyst surface coming from the side reactions promoted by the sulfuric acid. The presence of water during the condensation reaction leads to a loss of activity, but not of selectivity after the second reaction cycle. The catalyst is being modified, but to a lesser extent than when there are no impurities in the medium, so the presence of water may be minimizing the deposition of organic compounds on the catalyst surface. Finally, although the presence of furfural did not greatly affect the activity of the resin Amberlyst-70 as described in the previous section, it caused a large catalyst deactivation that becomes evident in the second reaction cycle in which both the catalytic results and the acid capacity decrease.

Next, a moderate regeneration treatment of the catalyst recovered after the reactions was tested to check the possibility of recovering the original activity of the catalyst. In that case, the Amberlyst-70 was washed with an acidic aqueous solution at room temperature. As seen in Fig. 5A, with this procedure little recovery of activity is obtained and similar results (only slightly higher in some cases) are obtained. There are no significant differences in the acidity values either (Fig. 5B). For formic acid and furfural, a noticeable decreasing in the acid capacity is observed even after the second catalytic cycle, which confirms that the regeneration method followed is not effective enough to remove the entrapped organic deposits and to recover the catalyst activity.

Finally, a more intense regeneration treatment was applied to the catalyst recovered from the reaction with formic acid as impurity: the recovered resin was washed with an acidic (HCl) solution in ethanol under reflux (shown in the Fig. 5 as 1' and 2'). It can be seen how the activity is recovered, reaching conversion values like those of the first use, although with a lower yield for the products of interest. The acid capacity is lower than the fresh catalyst but keeping a constant value

**Table 2**

Acidity properties of the fresh Amberlyst-70 and reused under different regeneration treatments.

	Acid capacity (meq H <sup>+</sup> /g)		Elemental analysis (%)	
	Sulfur content <sup>a</sup>	Titration <sup>b</sup>	S	C
Fresh Amberlyst-70	2.54	2.68	8.1	44.2
Without regeneration				
1st use	-	2.19	-	-
2nd use	1.39	1.95	4.4	55.9
Regeneration at RT				
1st use	1.74	2.10	5.6	51.0
2nd use	1.41	1.13	4.5	53.0
Regeneration under reflux				
1st use	2.28	2.27	7.3	49.5
2nd use	2.11	2.12	6.7	49.1

<sup>a</sup> Acid capacity determined indirectly from sulfur content obtained via elemental analysis. <sup>b</sup> Acid capacity determined directly by acid-base titration using TEA<sup>+</sup> as exchange cation.

around 2 mmol H<sup>+</sup>/g, avoiding the decrease that was observed with the more moderate regeneration treatment.

To further investigate the causes of the catalyst deactivation, the quantification of the sulfur content by means of elemental analysis (HCNS) of the fresh Amberlyst-70 and the catalysts after one or two consecutive catalytic runs was carried out (Table 2). The acid capacity values measured indirectly via sulfur content and directly by acid-base titration for the fresh Amberlyst-70 are similar, which indicates that all the acid sites of the catalyst are accessible to the LA. For catalysts recovered after reaction and washed with acetone without any regeneration step, both acidity values decrease. Two possible reasons can explain this trend: leaching of sulphonic groups, not very likely due to the moderate reaction and regeneration conditions tested, or the presence of organic compounds entrapped in the polymeric network that reduce the acid sites concentration due to the dilution effect. The latter is the most likely option due to the already mentioned formation of *humins* coming from side reactions. Similar results were obtained for catalysts recovered after reaction and subjected to a moderate regeneration

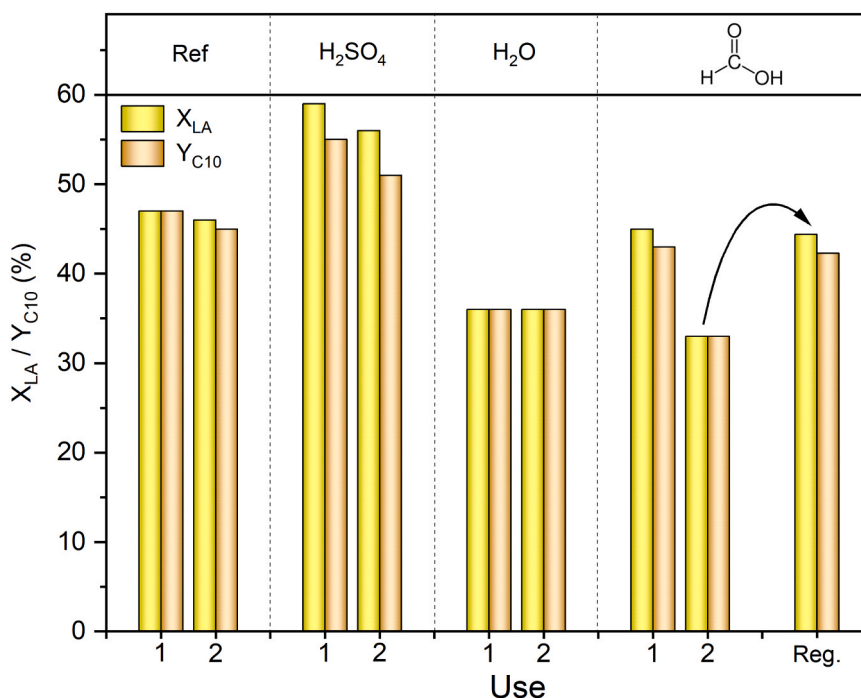
process at room temperature. However, when a reflux regeneration process is carried out, both values are similar, indicating that all the active centers are again accessible. Still, slightly lower values than those of the fresh catalyst were obtained, which implies that there are some remaining adsorbed organic compounds on the catalyst surface, apparently not interfering with the SO<sub>3</sub>H active sites. Similarly, a higher carbon content is observed for those catalysts used and regenerated with moderate conditions, which confirms the presence of organic compounds deposited on the catalyst surface.

Therefore, we conclude that the main reason of catalyst deactivation for Amberlyst-70 is the fouling of the catalyst surface by undesired organic deposits, that must be removed with an acid solution during the regeneration step in order to recover almost the original activity of the catalyst.

On the other hand, using H-Beta-19 zeolite, when sulfuric acid or water is present in the reaction media, no significant loss of activity is observed (Fig. 6). However, with formic acid, deactivation is observed since both the conversion of LA and the yield to condensation products decrease to 33 %.

In order to determine the main cause of deactivation and propose a suitable regeneration step for this catalyst, a thermogravimetric analysis of H-Beta-19 recovered after reaction was carried out (Fig. 7). Comparing the weight loss of this catalyst (Fig. 7B) with the ones of the catalyst after a reaction cycle without impurities (Fig. 7A), similar amount of LA condensation products adsorbed over the catalyst surface (150–200 °C) is observed for both catalysts. However, an increase of polymeric organic deposits, reaching a weight loss of ca. 10%, is detected for the zeolite after a reaction cycle with formic acid as impurity, the same as previously observed with the presence of furfural (Fig. 3). In view of these results, the regeneration treatment of the used catalyst with formic acid is proposed to be a calcination step to remove all the strongly adsorbed organic compounds that hinder the accessibility of the reagents to the active acid sites.

As can be seen in Fig. 6, after the calcination step in air (6 h at 550 °C), the initial catalytic activity is fully recovered, obtaining the same LA conversion and yield to C10 dimers as in the first use. Therefore, the fouling of the catalyst surface is reversible by such a thermal



**Fig. 6.** Stability of H-Beta-19 zeolite for the aldol dimerization of LA using different impurities. Ref = reaction without impurities. Reaction conditions: LA: 10 mmol; T: 150 °C; reaction time: 3 h; catalyst loading: 0.15 g. Catalyst washed with acetone at room temperature after each use.

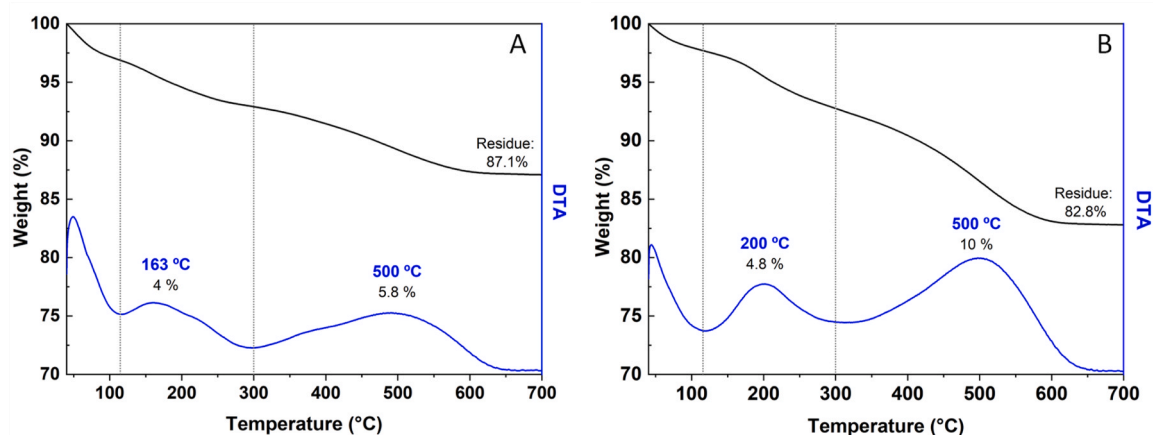


Fig. 7. Thermogravimetric profile of H-Beta-19 zeolite: (A) after a reaction cycle without impurities (reference level); and (B) after a reaction cycle with formic acid as impurity.

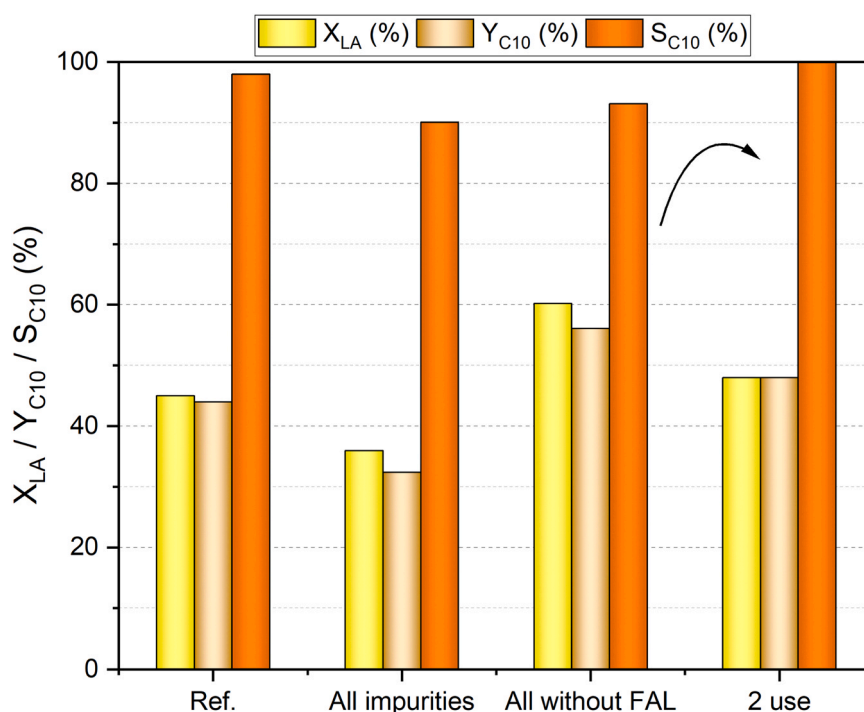


Fig. 8. Aldol dimerization of LA over H-Beta-19 zeolite using different mixtures of impurities. Ref = reaction without impurities. Reaction conditions: LA: 10 mmol; T: 150 °C; reaction time: 3 h; catalyst loading: 0.15 g.

treatment. As a conclusion, the zeolite deactivation was due to the formation of carbonaceous deposits on the surface and the recovery of the activity can be achieved easily and completely after a calcination treatment in between consecutive uses.

Being H-Beta-19 zeolite the most stable catalyst in this reaction, the study of the simultaneous effect of all the impurities on catalytic performance was proposed at the lowest level of the impurities. Fig. 8 depicts the catalytic results in terms of LA conversion, and yield and selectivity to the desired dimerization products without adding impurities, adding simultaneously all the impurities, and adding all the impurities except furfural. As can be seen, the combined presence of all the impurities seems to have a synergistic effect, as only a slight decrease in the catalytic activity is observed, maintaining also a high selectivity towards the products of interest. If we exclude the addition of furfural in the mixture of impurities, an increase in the catalytic activity is achieved, reaching yield values for the products of interest close to 60%

together with a selectivity close to 100%. Moreover, the zeolite shows a surprisingly good stability when all the impurities, but furfural are present, since only a slight decrease in the catalyst activity is observed in the second use of the catalyst and without having carried out any regeneration treatment. This positive effect might be ascribed to the synergistic effect of H<sub>2</sub>SO<sub>4</sub> on the catalytic performance. This result suggests that the LA used as substrate for this reaction would not need an exhaustive purification of certain types of compounds such as sulfuric acid, water, or formic acid, thus lowering the cost of the process.

#### 4. Conclusions

Commercially available acid zeolites are the most suitable catalyst for the aldol dimerization of renewable LA since their activity is not significantly affected by the presence of the most common impurities of the LA produced from lignocellulosic biomass reaching also high



selectivity to the desired C10 dimers. Within this study we have proved that furfural is the impurity that produces the greatest negative effect on the performance of SO<sub>3</sub>H-based catalysts and beta zeolites in the solvent-free dimerization of LA. Formic acid, sulfuric acid and water affect to a lesser extent. Regarding the reusability of the catalysts, deactivation is observed due to the formation of organic deposits on the surface (identified by TGA and acid-base titration), accentuated when there is furfural in the reaction medium. In the case of the sulfonic resin Amberlyst-70, catalytic activity can be recovered with a regeneration step based on washing with an acid solution under reflux. For beta zeolites, the original activity can be easily and totally recovered through a regeneration process by calcination. In addition, the mixture of impurities produces a synergistic effect, due to the presence of sulfuric acid, even improving the initial activity of the catalyst. Therefore, the presence of some of these impurities at the suitable level would positively enhance the activity and/or selectivity in the dimerization reaction. This can be advantageously taken into account in the design of the purification process of raw levulinic acid when destined to this particular application.

### CRedit authorship contribution statement

**Marta Paniagua:** Conceptualization, Methodology, Supervision, Writing- Original draft preparation. **Gabriel Morales:** Conceptualization, Writing- Reviewing and Editing, Funding acquisition. **Juan A. Melero:** Supervision, Writing- Reviewing and Editing, Funding acquisition. **Daniel García-Salgado:** Investigation, Data curation, Writing-Original draft preparation.

### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

### Data availability

Data will be made available on request.

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