Article

Selective Synthesis of Levulinic Ester from Furfural Catalyzed by Hierarchical Zeolites

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Abstract: Furfural is a platform molecule that can be catalytically converted using a cascade series of reactions into levulinic esters, essential compounds used as fuel additives. Bifunctional catalysts containing Lewis and Brønsted acid sites such as zeolites are commonly used for these conversions. However, microporous zeolites often present diffusional restriction due to the size similarity of furfural and other molecules to the zeolites’ micropores. Thus, incorporating mesopores in these materials through post-synthetic protocols is a promising pathway to circumvent these limitations. This study presents the creation of hierarchical beta and mordenite using Si or Al removal and their employment in the furfural conversion to isopropyl levulinate (PL). Mordenite zeolite did not produce satisfactory mesopores, while the beta was more efficient in generating them by both acid and alkaline treatments. Beta zeolite treated in an alkaline solution presented larger mesopores (14.9 and 34.0 nm), maintaining a total acidity value close to its parent zeolite and a higher Lewis/Brønsted ratio. The combination of these features led to an improved diffusion of bulkier products and the highest furfural conversion (94%) and PL selectivity (90%), suggesting that a post-modification of beta zeolites produced efficient catalysts for upgrading abundantly available furfural.

Keywords: hierarchical zeolite; furfural; levulinic ester; dealumination; desilication

1. Introduction

Today, fossil fuels are in great demand as an energy source and as carbon-based products (cosmetics, paints, plastics, pharmaceuticals, etc.) and are thus indispensable feedstock for our society [1]. As a non-renewable source, many discussions center around the depletion of reserves and its implications for the environment [2–6]. Thus, the use of lignocellulosic biomass appears as a promising alternative for the production of biofuels, green solvents, and other value-added chemical products. This is a renewable feedstock and carbon-neutral source that is abundantly available in nature through photosynthesis from water, sunlight, and carbon dioxide present in the atmosphere [2–6].
From the viewpoint of using lignocellulosic biomass as feedstock, its derivative platform molecules such as furfural (FUR), in a unique manner, have the potential to be converted into other compounds of vital industrial interest [7–10]. FUR is primarily formed by the dehydration of xylose, a five-carbon sugar in the hemicellulose fraction. It can be converted into assorted functional molecules via catalytic processes such as hydrogenation, oxidation, hydrogenolysis, and carboxylation [7–10]. Among these products, alkyl levulinites have been revealed as promising molecules for applications as fuel additives and green solvents [11].

The direct conversion of FUR to a levulinic ester, usually called the domino reaction, comprises a sequence of catalytic reactions: hydrogenation, hydrolysis, ring-opening, and lactonization reactions promoted by Lewis acids and Brønsted acids [8,9,12–15]. Among the most common acid catalysts used for domino reactions, zeolites are particularly interesting, as they possess both acid sites, are cheaper, and are widely commercially available in several topologies (from the 1D to 3D pores array), Si/Al ratios and tunable acidities [16]. Here, it is worth mentioning that, despite some studies reporting a more efficient obtention of isopropyl levulinate in higher yields than zeolites, they typically employ a sequential addition of catalysts to promote the catalytic hydrogen transfer (CHT) for converting FUR to furfuryl alcohol and a second catalyst to promote further reactions [17,18]. In contrast, other studies reported using a one-pot strategy employing bifunctional catalysts, such as ZrO/SBA-15 [19], or metal oxide combinations [18]. However, preparing these materials often presents some drawbacks, as they deploy more expensive reactants, are time-consuming, and result in the generation of residues.

In addition, the conventional microporosity of zeolites reduces the diffusion of bulky molecules into their channels and to the active sites, leading to the micropores’ occlusion. This effect would consequently lead to the catalyst’s deactivation or might provide a lower number of acid sites required for the domino reaction [14–16,20,21].

In this setting, hierarchical zeolites (containing micro-and mesopores) emerge as an alternative to this diffusional limitation [22–27]. They are obtained by incorporating mesopores into their structure via pre-synthetic or post-synthetic methods. In this fashion, desilication and dealumination are post-synthesis methods that remove Si and Al through alkali and acid treatment, respectively. These are simple and cheaper methods that allow for starting from commercial zeolites. The hierarchical structure of pores facilitates the diffusion into the zeolite crystal, increases the access to the active sites, and also might create stronger acid sites due to the chemical treatments. Beta (BEA) and mordenite (MOR) zeolites are promising for the catalytic upgrading of FUR since they possess a wide range of Si/Al and a good concentration of Brønsted and Lewis acid sites and are classified as large-pore zeolites [21].

From this perspective, this paper reports the use of hierarchical mordenites and beta zeolites prepared from commercial zeolites using a post-synthetic approach (desilication or dealumination). All the zeolites were characterized in terms of their crystalline, morphological, textural, and acidic properties and were applied as catalysts for the domino reaction of FUR conversion PL under different reaction conditions. The superiority of the chemically treated beta zeolites in the acidic or alkaline medium resulted from larger mesopores and new acid sites, such as Lewis acid sites. Additionally, the reaction parameters, namely, catalyst loading, temperature, FUR amount, and solvent/FUR ratio, were also examined.

2. Results
2.1. Crystalline, Textural, and Morphological Properties

The X-ray diffractograms of the commercial and treated beta and mordenite zeolites are presented in Figure 1. The reaction conditions used in zeolite modification processes, such as dealumination and desilication, can affect their crystalline structure through the
formation of amorphous phases and the partial destruction of the zeolites’ framework [22,24,28].

![XRD diffractograms](image)

**Figure 1.** XRD diffractograms of the (a) beta and (b) mordenite zeolite samples.

The typical structure of beta zeolite (JCPDS 48-0074) and mordenite (JCPDS 06-0239) were preserved in both acid and alkali treatments. The characteristic peaks of the BEA topology (≈7.74 and 22.11°) and MOR (6.51; 9.77; 22.20; 25.63, and 27.67°) were maintained, indicating the structural integrity of the zeolites and the absence of impurities as secondary crystalline phases [29,30]. Zeolites with a lower Si/Al ratio possess more stability against alkali attack, thus avoiding these materials’ high dissolution and amorphization [30]. This occurs due to the high aluminum content, which prevents such dissolution and thus allows for the formation of mesopores in these materials [30].

However, the diffraction peak intensities decreased after these treatments, substantiating that a portion of the crystallinity was lost after changes provoked in the Si/Al ratios, mainly for the dealuminated mordenite MOR-A and desilicated beta zeolite BEA-B (Table 1). This is consistent with the literature, where the decrease in aluminum content is related to the partial loss of zeolite crystallinity. Furthermore, the partial removal of silicon reduces the microporosity [26,31,32]. XRF experiments (Table 1) confirmed the efficiency of the acid and alkali treatments employed to remove aluminum and silicon in the commercial beta and mordenite zeolites. A higher efficiency of the dealumination of beta zeolite was observed compared to mordenite, as suggested by the total difference of Si/Al ratios in Table 1. It is worth mentioning that parent beta zeolite (commercial material) was dealuminated by oxalic acid. In the mordenite sample, nitric acid was employed, as commonly reported in the literature for these two types of zeolites [29,33]. The dealumination with oxalic acid furnished a more efficient Al removal due to its mutual role as an acid and chelating agent [34]. In addition, it has been proposed that the lower Si/Al ratio of the parent mordenite sample and the one-dimensional pore channels in this structure led to a lower demetallation degree than that in the case of the beta zeolite. This fact can be observed by the lower Si/Al value deviation compared to that for commercial zeolites (BEA and MOR) [35,36].
The nitrogen physisorption isotherms and pore distribution curves are presented in Figure 2, and the textural properties are displayed in Table 1. The commercial beta zeolite BEA showed an isotherm type I with the presence of a small hysteresis loop at high relative pressures (P/P0 > 0.8) assigned as the interparticle condensation of nitrogen molecules in the void spaces in beta zeolite grains [39–41]. On the other hand, the beta zeolites with chemical treatments (BEA-A and BEA-B) displayed isotherms classified as a mixture of type I and IV, characteristic of hierarchical zeolites [42]. In addition, their hysteresis loops (at p/p0 > 0.8) are classified as H3 type, which is typical of non-rigid aggregates of particles and also the creation of intra-crystalline mesopores [34,43]. It is essential to highlight that the micropore volume slightly decreased, while the mesoporosity was developed in all the samples. The sample BEA-B presented a larger hysteresis loop at a p/p0 higher than 0.8, assigned to the condensation of N2 in the large mesoporosity developed between interparticle sizes. This sample showed a broader pore distribution than its parent material or the acid-treated one [39]. Additionally, there was a mixture of the type I and IV isotherms for the treated mordenite zeolites (MOR-A and MOR-B) with hysteresis loops classified as H4, a characteristic of mesoporous zeolites in which aggregation occurs between crystals [43]. However, N2 physisorption on the mordenite without treatment displayed only a type I isotherm characteristic of microporous materials [33].

The pore distribution curves of the beta and mordenite samples are shown in Figure 2. There was a bimodal pore distribution, with two maximums for the commercial beta zeolite sample discernible; the first one is located in the micropores region (<2 nm), and the other one is at 7.5 nm. The second peak occurs due to mesopore generation from zeolites crystals aggregation [28,41,43], as affirmed by the SSw and mesopore volume values observed for this sample. This second peak was shifted to 10.4 nm for the dealuminated beta zeolite BEA-A due to mesopore creation in the dealumination procedure. In addition, the desilicated sample BEA-B presented a broader peak centered at 14.9 nm due to a larger mesopores creation in the alkali treatment, as corroborated by the values of the external surface area and mesopore volume stated in Table 1. This sample also presented the third peak of pore distribution centered at 34.0 nm due to the rearrangement of the beta zeolite crystals after the NaOH treatment [30,40,44]. The mordenite samples, MOR and MOR-A, presented similar profiles of pore size distribution with a maximum <2 nm, thus being predominantly microporous materials, as suggested by the values declare in Table 1. In contrast, the MOR-B sample presented a bimodal pore size distribution curve with a second maximum at 11.0 nm and was assigned to the mesopore formation. Moreover, it is proposed that the lower Si/Al ratio and one-dimensional pore channels array of mordenite zeolite led to a lower efficiency in terms of silicon or aluminum removal from its structure compared to beta zeolite [35,36].

Table 1. Physical-chemical properties of the beta and mordenite zeolites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Si/Al a</th>
<th>Stotal (m²g⁻¹)</th>
<th>Smicro (m²g⁻¹) b</th>
<th>Smeso (m²g⁻¹)</th>
<th>Vp (cm³g⁻¹)</th>
<th>Vmicro (cm³g⁻¹) b</th>
<th>Vmeso (cm³g⁻¹) b</th>
<th>Dp c (nm)</th>
<th>Cryst (%) d</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEA</td>
<td>11.3</td>
<td>597</td>
<td>368</td>
<td>206</td>
<td>0.26</td>
<td>0.17</td>
<td>0.09</td>
<td>10.9</td>
<td>100</td>
</tr>
<tr>
<td>BEA-A</td>
<td>27.8</td>
<td>630</td>
<td>371</td>
<td>263</td>
<td>0.29</td>
<td>0.16</td>
<td>0.13</td>
<td>11.9</td>
<td>80.6</td>
</tr>
<tr>
<td>BEA-B</td>
<td>7.5</td>
<td>625</td>
<td>347</td>
<td>351</td>
<td>0.29</td>
<td>0.11</td>
<td>0.19</td>
<td>10.8</td>
<td>75.5</td>
</tr>
<tr>
<td>MOR</td>
<td>5.2</td>
<td>575</td>
<td>556</td>
<td>19</td>
<td>0.04</td>
<td>0.02</td>
<td>0.02</td>
<td>3.6</td>
<td>100</td>
</tr>
<tr>
<td>MOR-A</td>
<td>8.8</td>
<td>565</td>
<td>532</td>
<td>33</td>
<td>0.06</td>
<td>0.02</td>
<td>0.04</td>
<td>3.5</td>
<td>46.2</td>
</tr>
<tr>
<td>MOR-B</td>
<td>6.3</td>
<td>548</td>
<td>507</td>
<td>41</td>
<td>0.08</td>
<td>0.02</td>
<td>0.06</td>
<td>5.3</td>
<td>73.4</td>
</tr>
</tbody>
</table>

* a Obtained by XRF analyses. b Calculated by t-plot analyses [37,38]. c Average pore diameter. d Crystallinity was calculated using each commercial zeolite as a reference [28].
Figure 2. N2 adsorption–desorption isotherms and pore size distribution curves for the (a,c) beta and (b,d) mordenite samples.

The Scanning Electron Microscopy (SEM) images for the commercial and chemically treated beta and mordenite zeolite samples are presented in Figures 3 and S1. The commercial beta zeolite grains showed a quasi-spherical morphology with a microscopic size and were formed by smaller grains deposited on their surface, which furnished this material with a rugous feature (Figure S1) [39]. The treatment with acid or alkali yielded additional wrinkled grains of beta zeolite and presented a more significant number of smaller particles and a more significant amount of debris deposited over its grains, as seen in Figures 3 and S1.

From the images depicted in Figure 3, it can be perceived that the commercial and treated mordenite zeolites showed elongated clusters. Clusters of needle-shaped crystals typically characterize these materials’ morphology since the crystal growth occurs preferentially in a single direction due to the one-dimensional pore system [36,45]. Furthermore, the treated mordenite zeolite in acid or alkali media presented small particles as debris over the microscopic grains. However, comparing the treated beta and mordenite samples revealed a more severe attack of the leaching agents over the beta structure, corroborating the higher mesopore volume and external specific surface area (Table 1).
2.2. Acidic Properties

The acidity of the beta and mordenite zeolite samples was characterized using the temperature-programmed desorption of ammonia (TPD-NH₃) and Fourier-transform infrared with pyridine adsorption (FTIR-pyridine), as displayed in Figure 4. In addition, Table 2 presents the total number of acid sites obtained by integrating TPD-NH₃ curves and the concentration of Brønsted and Lewis acid sites acquired by integrating the FTIR-pyridine spectra, as described by Tamura and co-workers [46].

Table 2. Acidic properties of the beta and mordenite zeolites.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Number of Acid Sites (mmol g⁻¹)</th>
<th>C_B (μmol g⁻¹)</th>
<th>C_L (μmol g⁻¹)</th>
<th>C_L/C_B</th>
</tr>
</thead>
<tbody>
<tr>
<td>BEA</td>
<td>1.67</td>
<td>94</td>
<td>37</td>
<td>0.39</td>
</tr>
<tr>
<td>BEA-A</td>
<td>0.80</td>
<td>21</td>
<td>59</td>
<td>2.82</td>
</tr>
<tr>
<td>BEA-B</td>
<td>1.55</td>
<td>28</td>
<td>31</td>
<td>1.11</td>
</tr>
<tr>
<td></td>
<td>MOR</td>
<td>1.96</td>
<td>80</td>
<td>16</td>
</tr>
<tr>
<td>--------</td>
<td>------</td>
<td>------</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>MOR-A</td>
<td>1.75</td>
<td>77</td>
<td>34</td>
<td>0.43</td>
</tr>
<tr>
<td>MOR-B</td>
<td>1.80</td>
<td>48</td>
<td>18</td>
<td>0.37</td>
</tr>
</tbody>
</table>

* Obtained by NH₃-TPD analyses. * Calculated by the integration of FTIR-pyridine spectra [46].

Figure 4. Acid characterization of the beta and mordenite samples using (a,b) TPD-NH₃ and (c,d) FTIR-pyridine.

For the acid-treated zeolite samples (BEA-A and MOR-A), there was a marked decrease in the total number of acid sites (Table 2). This effect was more drastic for the beta zeolite than for the mordenite structure. The higher reduction of the total acidity of the beta zeolite is ascribed to the more efficient Al removal procedure, which employed oxalic acid [34]. It is suggested that this strategy removed extra-framework aluminum (EFA) and thus decreased the total number of acid sites in the sample BEA-A [34]. This dealumination procedure also created new strong acid sites (>350 °C), which might be attributed to the deposition of soluble aluminum oxyhydroxide and aluminum oxalate species inside the micropores, as already suggested by Possato and co-workers [34].

From the FTIR-pyridine spectra and the values presented in Table 2, it can be seen that either alkali or acid chemical treatment in beta zeolite provoked a decrease in the total acid amount (TPD-NH₃). It changed the concentration of Lewis and Brønsted acid sites compared to its parent zeolite BEA. The acid-treated material BEA-A presented a marked decrease in the concentration of Brønsted acid sites and an increase in Lewis acid sites. This outcome was already expected, since acid leaching often leads to a significant reduction in the Si/Al ratio (Table 1), thus removing tetracoordinate aluminum in the zeolite’s framework responsible for creating Brønsted acidity [42]. Under this proposition,
the increase in the Lewis acid sites concentration occurs due to the deposition of AlOx species in the zeolite’s channels, as it creates new Lewis acid sites during the oxalic acid leaching [28,34,47,48]. In this context, the sample BEA-A presented the highest Lewis/Bronsted concentration (2.82) due to the high dealumination degree caused by a marked reduction in its Bronsted acidity and the formation of new Lewis acid sites. The alkali-treated beta zeolite BEA-B also presented a considerable decrease in the concentration of both acid site types compared to its parent zeolite BEA. However, despite this decrease observed in the FTIR-pyridine spectrum, its total acidity was notably close to the value displayed by the non-treated material, as shown in Table 2 and Figure 4; the desilication process is known in the literature to be more efficient in not affecting the total acidity of zeolites compared to dealumination procedures [30,40,47–49]. The silicon removal from the zeolite’s surface will not directly affect the distribution of Brønsted and Lewis acid sites [35]. The desilication procedure using alkaline solutions can also remove some aluminum ions from the zeolite framework, thus creating EFA species that might act as Lewis acid sites [48]. Thus, it is worth mentioning that the BEA-B sample presented a good balance of Lewis/Bronsted acid sites (1.11) and preserved a good value of total acid sites compared to its parent zeolite.

The parent mordenite zeolite presented the highest total number of acid sites (Table 2) due to its lower Si/Al ratio. A high aluminum content is directly related to the Brønsted acidity, as has been reported by Pastvova and co-workers for parent mordenite microporous zeolites. A majority are Bronsted acid sites, since most of the Al species are present in the zeolite’s cages [33]. Thus, a low concentration of Lewis acid sites is often observed. The commercial MOR sample presented the lowest Lewis/Brønsted ratio (0.19) among all the zeolites analyzed in this study. It is noticeable that the acid-treated mordenite MOR-A showed a higher concentration of Lewis acid sites compared to its parent material. Some studies in the literature report a decreasing Lewis/Brønsted ratio upon the acid treatment of mordenite and ascribe it to the aluminum removal and the formation of EFA species that might act as Lewis acid sites [33,49], On the other hand, the desilication procedure (MOR-B sample) on mordenite zeolite led to a marked decrease in the Brønsted acid site concentration. This occurred due to the removal of both the aluminum and silicon species, causing an increase in the Lewis/Brønsted ratio (0.37) compared to that of the MOR sample (0.19) [33].

2.3. Catalytic Evaluation

Before discussing each zeolite’s catalytic performance and product distribution, it is essential to mention some details of the domino reaction in converting FUR to PL. Scheme 1 presents the reaction pathway for a cascade conversion of lignocellulosic biomass-derived FUR into other value-added compounds. In this reaction, a secondary alcohol (isopropyl alcohol, IPA) is often used as a hydrogen donor and a bifunctional catalyst comprising Brønsted and Lewis acid sites, such as zeolites. Firstly, FUR is hydrogenated to FA catalyzed by a Lewis acid site and consumes an IPA molecule as a hydrogen donor. The reaction proceeds via an MPV (Meerwein-Ponndorf-Verley)-type mechanism [8,9,12,50]. In addition, FUR can be converted to a less-value-added product over a Brønsted acid site following a dehydration reaction, which produces an acetal compound called DPMF (2-(diisopropoxymethyl)furan). Once an FA molecule is formed, it can go through a reaction with an IPA molecule through an etherification mechanism catalyzed by a Brønsted acid site and generate the PMF (2-(isopropoxymethyl)furan) compound. Next, PMF can readily undergo a ring-opening reaction followed by esterification with IPA catalyzed by a Brønsted acid site and thus form the desired product PL [11]. The ensuing PL molecule might undergo further cyclization and the elimination of an IPA molecule catalyzed by a Brønsted acid site. This reaction yields an α-AL (α-angelica lactone) molecule, which can be further isomerized to β-AL (β-angelica lactone) [51].

The initial catalytic screening of furfural conversion deploying the commercial and treated beta and mordenite zeolites is presented in Figure 5. The commercial beta zeolite
BEA showed a quantitative FUR conversion and 48.6% of selectivity to the desired product, PL. However, this material also presented a high selectivity to the acetal DPMF (27.4%) and to the intermediate product PMF (21.8%), which might further be converted to PL [12]. On the other hand, commercial mordenite zeolite presented 62.3% of FUR conversion and only 19% of PL selectivity.

Scheme 1. Catalytic conversion of furfural to isopropyl levulinate through a domino reaction. DPMF = 2-(diisopropoxymethyl)furan, FUR = furfural, FA = furfuryl alcohol, PMF = 2-(isopropoxymethyl)furan, PL = isopropyl levulinate, α-AL = α-angelica lactone, β-AL = β-angelica lactone.

Figure 5. Catalytic evaluation of the commercial and treated zeolite (a) beta and (b) mordenite samples in the domino reaction of furfural upgrading. FUR = furfural conversion, PL = isopropyl levulinate, DPMF = 2-(diisopropoxymethyl)furan, AL = α-angelica lactone, PMF = 2-(isopropoxymethyl)furan. Reaction conditions: 0.34 mmol of FUR, 50 mg of catalyst, 1500 μL of isopropanol, 110 °C, and for 24 h.

The commercial and untreated MOR sample exhibits a lower conversion of FUR and PL selectivity compared to the commercial BEA, which can be attributed to the smaller channel pores (8 member-ring, MR) of the mordenite zeolite and their one-dimensional array [33]. These features of MOR zeolite can lead to a diffusional restriction and thus hinder the further conversion of FUR to bulkier molecules, such as PL [21]. Consequently, it is essential to highlight that Lewis acid sites are mainly located inside the mordenite cages [33], and these acid sites are required in the first step of the domino reaction (FUR→
FA). From this point of view, it is proposed that the MOR sample converted FUR molecules mainly on the external surface sites. In contrast, BEA zeolite had a more facilitated diffusion pathway and, importantly, additionally facilitated access to Lewis acid sites in the interior of this material. In this way, the major product observed for the MOR sample was the acetal DMFF formed upon exposure to the Brønsted acid sites. This acid site is present in higher concentrations in the mordenite structure (in the 8 and 12 MRs), as previously reported by Pastvova and co-workers [33].

Interestingly, after the chemical treatments performed in the beta zeolite (BEA-A and BEA-B), these samples displayed a higher selectivity for PL than its parent material BEA. A decrease in FUR conversion was observed for the acid-treated sample BEA-A due to its lower acidity (Table 2). The alkali-treated beta zeolite BEA-B presented the highest PL selectivity (~81%) among all the studied samples and only a slightly decreased FUR conversion. It is worth mentioning here that this material’s acidity was not significantly affected by the alkaline procedure used for creating mesopores (Table 2). In addition, both BEA-A and BEA-B offered mesopores creation due to the chemical treatments employed (Table 1), thus demonstrating the beneficial role of material with larger pores for the FUR and the diffusion of the intermediate product.

Moreover, these two samples also presented higher Lewis/Bronsted, which suggests that the domino reaction is well performed to form PL when an adequate number of Lewis acid sites are created. In addition, the high concentration of Brønsted acid sites in this material gets reduced. This fact can be closely related to the reaction mechanism, in which the hydrogenation reaction to convert FUR to FA is the crucial step in the domino reaction requiring strong Lewis acid sites [52].

Although the MOR-A and MOR-B samples presented a higher FUR conversion, they were not efficient in selectively obtaining the desired ester PL. This observation is ascribed to the lower effectiveness for the mesopore creation in mordenite zeolite compared to that for the beta samples (Table 1). In this situation, the mordenite-treated samples could not afford a good enough FUR diffusion inside the material’s micropores to access the required Lewis acid sites for the first reaction step. Furthermore, these samples also presented comparatively lower Lewis/Bronsted ratios (Table 2), thus suggesting a lower concentration of Lewis acid sites for this first reaction step [52].

Since the beta zeolite treated in alkaline conditions BEA-B presented the best catalytic performance among the produced samples, this material was chosen to evaluate essential parameters in the domino reaction, such as temperature, catalyst loading, FUR concentration, and solvent volume (Figure 6). The detailed procedure for these catalytic runs is presented in the Supplementary Material. Firstly, the reaction temperature was evaluated, and at the lowest studied reaction temperature (90 °C), a low FUR conversion (~10%) and PL selectivity (21%) were noticed, where PMF was the primary product formed (79%). A further increase in the temperature to 110 °C led to a rise in the FUR conversion (36%). PL was now the main product formed, with 62% of selectivity, suggesting that PMF was an intermediate product and that the ring-opening of this compound to create PL is favored at higher temperatures [8,9,12,52], which is consistent with the domino reaction presented in Scheme 1. The optimal temperature for the conversion of FUR and PL selectivity was achieved at 130 °C, which is in good agreement with previous reports in the literature [8,9].

A nearly quantitative FUR conversion was achieved when 0.17 mmol of this compound was used in the domino reaction using the sample BEA-B as a catalyst; good PL selectivity was observed (~70%). A further increase in this starting material to 0.34 mmol for the same amount of the catalyst led to the highest PL selectivity (90%). However, using a more concentrated reaction medium, i.e., 0.68 mmol, the number of active sites furnished by the zeolite BEA-B was not enough to afford a good FUR conversion to PL, which was suggested by a high selectivity of the intermediate PMF (40%). Again, these results are consistent with the domino reaction presented in Scheme 1.
A low amount of the catalyst in the reaction medium (25 mg) could not convert a high amount of FUR since a small number of active sites were available. This catalyst loading represents 12 mol % considering the total acidity of the BEA-B zeolite (Table 2), and despite the low FUR conversion (35%), a satisfactory selectivity of PL (97%) was attained. When the catalyst amount was doubled, i.e., 50 mg (or 24 mol%, considering the total acidity of BEA-B), the highest FUR conversion (94%) and PL selectivity (90%) were achieved. However, a further increase in the catalyst loading to 75 mg did not lead to any improvement in either FUR conversion (45%) or PL selectivity (84%) when a higher amount of α-angelica lactone (~6% of selectivity) was observed. This suggests that AL might be obtained at a higher concentration of active sites in the reaction medium. This increase in the catalyst loading might also promote the FUR polymerization reaction due to a higher concentration of acid sites [50,53,54].

The IPA/FUR ratio was crucial in the FUR conversion and PL selectivity. A more concentrated reaction medium (IPA: FUR =14) led to a low FUR conversion (40%) and low PL selectivity (22%). In this case, the highest selectivity was discerned for the intermediate PMF (80%), which might be explained by a low diffusion of FUR into the zeolite’s pores and the further promotion of the conversion of this compound to PL. The best FUR conversion and PL selectivity were noticed when the reaction was performed using an IPA/FUR equal to 28, which agrees with previous studies using beta zeolite as a catalyst [9]. However, when the reaction medium was further diluted (IPA: FUR =56), a good FUR conversion (95%) was preserved, and a lower PL selectivity (72%) was achieved due to its conversion to AL (20%), as expected by the domino reaction.
Figure 7 presents the evaluation of commercial (BEA) and alkaline-treated beta zeolite (BEA-B), and Figure S3 shows their results for the experiments performed in triplicate. In addition, Figures S4 and S5 present the chromatogram and mass spectra for the catalytic reaction under optimized conditions for BEA-B material. A Nuclear Magnetic Resonance (NMR) of the isolated and purified PL obtained from the same optimized conditions is presented in Figure S6. The commercial beta zeolite gave a nearly quantitative conversion, even in the second reuse reaction (Figure 7a). However, the PL selectivity was significantly affected by the catalyst reuse, thus presenting a decrease from 48.6% in the reaction using fresh material to 11.7% in the second reuse. Moreover, the DPMF selectivity was markedly increased from 27.4% to 85.7%, suggesting a noticeable deactivation of this commercial beta zeolite without the chemical treatment for mesopores creation. On the other hand, the hierarchical beta zeolite BEA-B (Figure 7b) kept a high PL selectivity even in the second reuse reaction, decreasing from 89.9% to 64.5%. This effect suggests that the mesopore creation in the beta zeolite was advantageous in retaining the catalytic activity and in avoiding deactivation.

The deactivation of solid acid catalysts mainly occurs through the deposition of polymerization products from furfural called humins, as has been often reported in the literature [9,10,12,20,55]. Thermogravimetric analysis (TGA) was employed to investigate the formation of humins for both of the reused catalysts recovered after the second reaction, as displayed in Figure S2. It is noticeable that the commercial beta zeolite presented a higher weight loss (~30%) compared to the alkaline-treated beta zeolite (~15%) in the region typically used to observe the decomposition of organic matter, i.e., temperatures higher than 250 °C [56]. Thus, these results suggest the stability of the hierarchical beta zeolite obtained from alkaline leaching to avoid the formation of humins due to its mesoporosity, which circumvents the restricted diffusion of furfural and the products of the domino reaction. In addition, it was demonstrated that, through a re-calcination of the reused solid from the second reaction, the initial FUR conversion and PL selectivity were virtually restored, as displayed by the fresh BEA-B sample.

3. Materials and Methods

3.1. Materials

The commercial mordenite zeolite (Si/Al = 6.5) and beta (Si/Al = 14) were supplied by Zeolyst International® and Eurecat®, respectively. These samples were labeled
as BEA and MOR and referred to in the text as parent zeolites. Isopropanol (HPLC grade), Furfural (98%), Oxalic acid dihydrate (P.A. ACS), Nitric acid (65%), Sodium hydroxide (ACS, >97%), Ammonium chloride (ACS, >99.5%) and Ethanol (HPLC grade) were procured from Sigma-Aldrich® and used without further purification.

3.2. Hierarchical Beta Zeolite Synthesis

Desilication: In a round-bottom flask, 30 mL of 0.2 mol L⁻¹ NaOH was added, stirred, and heated using an oil bath up to 65 °C. Then, 1.0 g of commercial beta zeolite was added to the solution under magnetic stirring (500 rpm) and heated for 30 min. Subsequently, the sample was vacuum filtered, washed with distilled water until pH~7, and dried at room temperature [30]. This sample was labeled as BEA-B.

Dealumination: In a round-bottom flask, 1.0 g of zeolite beta was added to 20 mL of 0.5 mol L⁻¹ oxalic acid solution under magnetic stirring at room temperature. After 1 h of stirring, the sample was vacuum filtered, washed with distilled water until pH~7, and dried at room temperature [29]. This sample was labeled as BEA-A.

Ion Exchange: After drying all the samples, the ion exchange was performed with ammonium chloride to obtain the zeolites' ammoniacal form. In a beaker, the 0.5 mol L⁻¹ NH₄Cl solution was stirred and heated in an oil bath to 60 °C. Then, the zeolite was added (1.0 g of zeolite/100 mL of solution). After 3 h, the sample was vacuum filtered, washed with distilled water, and dried at room temperature. This procedure was performed three times for each sample. Finally, the zeolites in their acidic forms were obtained by calcination at 550 °C for 5 h (10 °C min⁻¹) in a static air atmosphere.

3.3. Hierarchical Mordenite Zeolite Synthesis

Desilication: Thirty milliliters of a 0.2 mol L⁻¹ NaOH solution were initially stirred and heated in an oil bath at 85 °C. Then, 1.0 g of the zeolite was added to this solution, remaining under magnetic stirring and heating for 2 h. Afterward, the sample was vacuum filtered, washed with distilled water, and dried at room temperature [33]. This sample was labeled as MOR-B.

Dealumination: In a three-necked round-bottom flask, 1.0 g of zeolite was added to 30 mL of stirred 3 mol L⁻¹ nitric acid solution and heated to 80 °C. After 40 min, the sample was vacuum filtered, washed with distilled water, and dried at room temperature [33]. This sample was labeled as MOR-A.

After drying all the samples, ion exchange with ammonium chloride was performed following the same procedure described for beta zeolites. Then, mordenite samples in their acid form were obtained, employing calcination at 550 °C for 3 h (10 °C min⁻¹) under a static air atmosphere [33].

3.4. Materials Characterization

A Rigaku Miniflex II diffractometer recorded the diffraction patterns for zeolites with CuKα radiation (λ = 1.540 Å). Measurements were performed with 2θ between 5° and 80°, using a step of 0.05° and a counting time of 1.0 s per step. XRF analysis was performed using an X-ray spectrometer, model ED-720, Shimadzu, using an X-ray generator tube with a target of rhodium (Rh).

The textural characterizations were performed at the boiling temperature of liquid nitrogen (~196 °C) in Micromeritics equipment (ASAP 2420). The samples were treated under vacuum at 300 °C for 240 min to eliminate water and physically adsorbed gases. The surface area was determined by the B.E.T method. The pore size distribution was determined by the B.J.H. method [43,57]. S_{micro}, V_{micro}, and S_{tot} were obtained using the t-plot method described by Desmurus and co-workers and Galarneau and co-workers [37,38].

The Scanning Electron Microscopy (SEM) characterizations were performed in Field-Emission Gun Scanning Electron Microscopy equipment (JEOL JEM 2100F) with a
secondary and backscattered electrons detector. A small amount of the powder samples was initially deposited in the SEM sample holder on carbon tape, and then the sample was blown with compressed air to remove the excess from the sample holder.

Ammonia desorption analysis at a programmed temperature (TPD-\text{NH}_3) was performed in Micromeritics AutoChem II 2920 equipment. The samples were treated at a temperature of 350 °C for 1 h and then exposed to a flow of \text{NH}_3 (10% vol. in He) at 120 °C for 30 min. Next, the excess and physically adsorbed \text{NH}_3 was purged at 120 °C using a He flow for 1 h. The programmed desorption of ammonia was carried out between 120 and 550 °C (holding for 45 min at this final temperature and using a heating rate of 15 °C min\(^{-1}\)).

The Nuclear Magnetic Resonance spectrum was recorded on a Varian Mercury 500 MHz (Palo Alto, Santa Clara, CA, USA) spectrometer at a [1H] frequency of 500 MHz. Chemical shifts (\(\delta\)) are given in ppm relative to the respective NMR solvent. Apparent peak multiplicities are described as s (singlet), d (doublet), t (triplet), or hept (heptet), where appropriate. Coupling constants (J) are reported in hertz after integration.

The number of Brønsted (\(B\)) and Lewis (\(L\)) acid sites of the catalysts was determined by in situ adsorbed pyridine with a Fourier Transformed Infrared (FTIR) analysis using a transmission cell with a CaF\(_2\) window and a Bruker spectrometer (Vertex 70) equipped with an MCT detector. For the analyses, a 10 mg pellet of the sample (pressed with 5 tons) was pre-treated at 350 °C under an argon atmosphere (100 mL min\(^{-1}\)) for 1 h. Then, the system was cooled to 150 °C, and the sample was saturated with gaseous pyridine. The excess and physically adsorbed pyridine was purged with argon (100 mL min\(^{-1}\)), and FTIR spectra were collected at 150 °C, with a resolution of 4 cm\(^{-1}\) in the range of 4000 to 1000 cm\(^{-1}\). The spectra from the samples with and without adsorbed pyridine were subtracted. The integrated extinction coefficients (\(\varepsilon_L = 1.73 \text{ cm}/\mu\text{mol}\) and \(\varepsilon_B = 1.23 \text{ cm}/\mu\text{mol}\)) determined by Tamura and co-workers [46] were used, and the concentration of Lewis and Brønsted acid sites in mmol/g was calculated based on the equations below (1–3), where \(A_B(\text{cm}^2), A_L(\text{cm}^2), m_p \text{ (mg)}, \) and \(S_p \text{ (cm}^2\) are the areas of the bands at \(\sim1545\) and \(\sim1450 \text{ cm}^{-1}\)—the mass and area of the pellet, respectively.

\[
C_B = \frac{A_B}{\varepsilon_B \alpha} 
\]
\[
C_L = \frac{A_L}{\varepsilon_L \alpha} 
\]
\[
\alpha = \frac{m_{\text{cat}}}{\pi r^2} 
\]

3.5. Catalytic Evaluation

For a typical catalytic evaluation, it followed an adapted procedure previously reported in the literature [8,9] in sealed AceTube\textsuperscript{®} pressure under constant stirring and was heated in an oil bath. After 24 h, the reaction mixture was filtered with a syringe filter (0.45 \(\mu\text{m}, PFTE\) and injected in a Shimadzu GCMS-QP2010 gas chromatograph with a SupelcoWax column (30 m × 0.25 mm × 0.25 \(\mu\text{m}\)) that was coupled with a mass spectrometer under the following operating parameters: inlet temperature of 250 °C and oven temperature ramp from 80 to 250 °C at a rate of 10 °C min\(^{-1}\).

The FUR conversion was calculated using Equation (4):

\[
X_{\text{FUR}} = 100\% - A_{\text{FUR}}(\%) 
\]

whereas \(A_{\text{FUR}}\) is the area of the FUR peak detected in each chromatogram. The selectivity of the \(X\) product was calculated using Equation (5), where \(A_s\) is the area of the peak detected in the chromatogram and the denominator is the total sum of the area of all the peaks of the products observed:
4. Conclusions

In this study, hierarchical beta and mordenite zeolites were prepared by a post-synthesis modification using silicon or aluminum leaching to create mesopores in commercial zeolite materials. The alkaline treatment was generally more efficient for creating larger mesopores than the acid treatments (using oxalic or nitric acid). The aluminum leaching using acid treatment led to a substantial modification of the total acidity of these materials, whereas the silicon leaching using sodium hydroxide was efficient in maintaining the total acidity of these materials closer to their parent zeolites. The mordenite samples did not display a sufficient creation of mesopores and thus restricted access to the reactant molecules inside the zeolite’s channels. Although these mordenite samples showed high FUR conversion, the acetal DPMF was the main product detected by GC-MS.

On the other hand, the beta zeolite samples presented a proper generation of mesopores due to their post-synthetic treatments and higher FUR and PL selectivity. Furthermore, the larger mesopores, high acidity, and adequate Lewis/Brønsted ratio were observed for the beta zeolite treated in an alkaline medium, thus illustrating the highest FUR conversion (94%) and PL selectivity (90%). The good catalytic efficiency of this sample is attributed to the higher accessibility of the reactant molecules inside the material’s pores, a proper concentration of Lewis acid sites (created by the alkaline treatment), and diminution in the Brensted acid sites. The re-use reactions demonstrated that this hierarchical material could maintain a good PL selectivity compared to the commercial material due to the lower formation/deposition of humins, a consequence of the lower diffusional restriction of furfural and the products of the domino reaction. This study has demonstrated that the post-synthetic treatment of beta zeolites might be a promising pathway to achieving a good conversion of lignocellulosic-derived molecules and a comparatively more selective production of alkyl levulinate—desired compounds for several industrial applications, including their usage as fuel additives.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/article/10.3390/catal12070783/s1. Figure S1. SEM images for the (a,b,c) beta and (d,e,f) mordenite samples. Figure S2. TGA analyses of the (a) commercial beta zeolite and (b) alkali-treated beta zeolite after the 2nd reuse in the furfural upgrading reaction. Figure S3. Experiments performed in triplicate for the commercial beta zeolite and alkali-treated beta zeolite in the furfural upgrading reaction. Figure S4. Typical chromatogram for the catalytic upgrading of furfural via domino reaction using BEA-B as a catalyst. Figure S5. Mass spectra of the products detected in the catalytic upgrading of furfural via domino reaction zeolites as catalysts. Figure S6. 1H-NMR spectrum of isopropyl levulinate obtained from the reaction performed at optimized conditions using BEA-B as a catalyst. (500 MHz, CDCl3). References [8,9,46,57] are cited in supplementary materials.

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\[ S_x = \frac{A_x}{A_x + A_y + A_z + \cdots} \times 100\% \]
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