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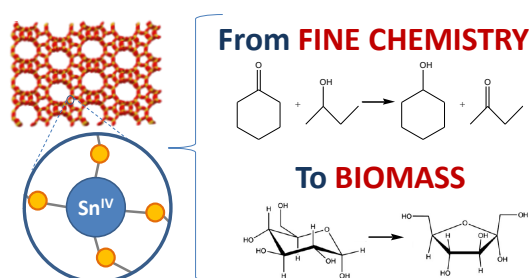
**State of the art of Lewis acid-containing zeolites: lessons from fine chemistry to new  
biomass transformation processes**

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New transition metal-containing zeolites presenting Lewis acid character show unique catalytic applications in fine chemistry processes and novel biomass-transformations

## Abstract

The former synthesis of TS-1 opened new catalytic opportunities for zeolites, especially for their application as selective redox catalysts in several fine chemistry processes. Interestingly, isolated Ti species in the framework positions of hydrophobic zeolites, such as high silica zeolites, offer unique Lewis acid sites even in presence of protic polar solvents (e.g. as water). Following this discovery, other transition metals (such as Sn, Zr, V, Nb, among others) have been introduced in the framework positions of different hydrophobic zeolitic structures, allowing their application in new fine chemistry processes as very active and selective redox catalysts. Recently, these hydrophobic metallozeolites have been successfully applied as efficient catalysts for several biomass-transformation processes in bulk water. The acquired knowledge from the former catalytic descriptions in fine chemistry processes using hydrophobic Lewis acid-containing zeolites, has been essential for their application in those novel biomass transformations. In the present review, I will describe the recent advances in the synthesis of new transition metal-containing zeolites presenting Lewis acid character, and their unique catalytic applications both in fine chemistry and novel biomass-transformations.

## Keywords

Zeolite, Lewis acid, catalysis, fine chemistry, biomass

## 1.- Introduction

The discovery of Titanium Silicalite-1 (TS-1) in 1983 by ENI researchers was a clear breakthrough in materials science because it broadened the application of zeolites as heterogeneous catalysts beyond Brønsted acid processes and opened new opportunities for selective redox catalysis, especially in fine chemistry processes.<sup>1</sup> The isomorphic substitution of isolated Ti<sup>IV</sup> species in tetrahedral coordination into the framework of Silicalite (pure silica bidirectional medium pore zeolite with MFI structure) confers unique Lewis acid character to these metal sites that promotes the selective oxidation of diverse hydrocarbons using hydrogen peroxide as oxidizing agent.<sup>2</sup> Indeed, several industrial oxidation processes have become more efficient and greener (reducing waste and hazards) by using TS-1 as heterogeneous catalyst and H<sub>2</sub>O<sub>2</sub> as oxidant,<sup>3</sup> instead of the former homogeneous catalysts and the expensive organic hydroperoxides or peracids.<sup>4</sup>

One of the most interesting features of TS-1 is the ability to maintain this remarkable Lewis acidity even in presence of protic polar solvents, such as water.<sup>3a</sup> It is important to note that protic polar solvent often suppress Lewis acidity by hindering coordination or decomposing catalytic sites.<sup>5</sup> However, the crystalline framework of TS-1 is mainly formed by silicon dioxide, and consequently, this high-silica structure presents hydrophobic void spaces, which allow preserving the Lewis acid nature of isolated Ti centers even in the presence of bulk water phase.<sup>3a</sup> Among others, TS-1 has been applied as industrial catalyst in diverse reactions using aqueous solutions of H<sub>2</sub>O<sub>2</sub> as oxidizing agent, such as phenol hydroxylation, cyclohexanone ammoxidation, and propene oxide synthesis.<sup>2-3,6</sup>

The excellent catalytic activities achieved on medium-pore TS-1 are attributed to the selective activation of H<sub>2</sub>O<sub>2</sub> by the isolated tetrahedral Ti atoms, forming Ti-OOH species, which lead to the selective oxidation of hydrocarbons.<sup>7</sup> However, the applicability of TS-1 was limited to reactions involving medium-sized molecules since the pores of TS-1 show an effective diameter of 5.5 Å. Bulky organic molecules either suffer from severe diffusion limitations or they are unable to reach the active sites in the pores. In the late 90s, a very intense research period started on the synthesis of open micro- and mesoporous materials featuring ordered materials with pores ranging from 6.5 to 40 Å.<sup>8</sup>

From the reported titanosilicates with open architectures, one of the most interesting materials was the highly hydrophobic titanosilicate Beta zeolite synthesized by Corma et al. following the fluoride synthetic route.<sup>9</sup> The presence of fluoride anions balances the positive charges introduced by the organic structure directing agent (OSDA) used to direct the crystallization of the Beta zeolite (tetraethylammonium cation, TEA<sup>+</sup>), clearly reducing the amount of structural defects (note that in regular zeolite syntheses in alkaline media, the positive charges of the OSDAs are balanced by SiO<sup>-</sup> groups, which yield to Si-OH after elimination of the OSDA). Compared to previously Ti-Beta materials synthesized with prior methods, the new defect-free Ti-Beta showed improved physico-chemical properties, including higher hydrothermal stability, crystallinity, and hydrophobicity. Consequently, increased catalytic activity and selectivity in different oxidation reactions, such as olefin epoxidation reactions, were achieved because the lack of silanols (structural defects) avoided the opening of the epoxides towards undesired diols.<sup>10</sup>

The successful results achieved using Ti-containing silicates inspired the incorporation of other transition metals in framework positions in order to introduce different isolated Lewis acid sites to be used in new catalytic opportunities. However, the introduction of transition metals in crystalline framework positions is not an easy task because framework insertion depends on the ionic radius of the metal, the rigidity of the zeolitic crystalline framework, as well as on the synthesis conditions (presence of cations, pH or metal sources).<sup>11</sup> In recent years, these metal-containing hydrophobic silicates with Lewis acid character, especially tin and zirconium-containing zeolites, have been synthesized and used as very efficient catalysts in different chemical processes. The range of applications has spanned from the synthesis of fine chemistry to biomass-transformation processes.

Since the syntheses and applications of titanosilicates are already reported in great detail in the literature,<sup>2-3,8</sup> in the present review I will only focus on the recent advances in the synthesis of new transition metal-containing zeolites presenting Lewis acid character, particularly those with isolated tin and zirconium atoms. A strong focus will be placed on their novel catalytic applications, especially those related to biomass-based transformations for the synthesis of key platform molecules. It will be shown that the acquired knowledge from the former catalytic descriptions of water-resistant Lewis acid-containing zeolites in fine chemistry processes, has been essential for the application of these solid Lewis acids in novel biomass transformations in bulk water.

## **2.- Tin-containing microporous materials**

### **2.1.- Synthesis of tin-containing zeolites**

Prior attempts to introduce tin atoms into the framework of different zeolites (FAU or Beta) were performed by post-synthetically substituting a fraction of framework aluminum atoms with tin. These materials were tested in diverse acid hydrocarbon conversion processes, including cracking and alkylation of aromatics.<sup>12</sup> The first report on isomorphic substitution of Si by Sn was described by Ramaswamy et al. for the direct synthesis of the Sn-MFI zeolite in alkaline media.<sup>13</sup> In this case, the authors confirmed the insertion of tin atoms into the framework both by tracking the increase of the unit cell volume as the Sn content was progressively increased, and by IR spectroscopy. These Sn-MFI materials were tested for the hydroxylation of phenol, achieving similar results that those observed for the TS-1;<sup>14</sup> and for the oxidation of ethylbenzene, where Sn-MFI was found more active than TS-1.<sup>15</sup> The same authors also reported the direct synthesis of large-pore Sn-Beta in alkaline media, but in this preparation was always required the presence of aluminum atoms in the synthesis, which were selectively removed by a post-synthetic acid treatment.<sup>16</sup> This Sn-Beta material was tested in the oxidation of bulky substrates, as *m*-cresol or 1,3,5-trimethylbenzene, showing improved activities compared to Sn-MFI.

The need to develop an efficient heterogeneous catalyst for the Baeyer-Villiger oxidation of ketones to form the corresponding lactones, in the presence of other functional groups that could also be oxidized, prompted Corma and co-workers to rationalize the preparation of the first truly Al-free hydrophobic Sn-Beta.<sup>17</sup> Up to that moment, all the used catalysts increased the nucleophilicity of H<sub>2</sub>O<sub>2</sub> to react with the corresponding ketone,<sup>18</sup> but could not avoid the reaction of the peroxide with other functional groups present in the molecule (e.g., double bonds), thereby reducing the chemoselectivity. Corma et al. introduced a new concept wherein the catalyst would

selectively activate the carbonyl group.<sup>17</sup> Given the propensity of Lewis acid catalysts to activate carbonyl groups,<sup>19</sup> and judiciously selecting from a potential list of metals with Lewis acid nature, the authors hypothesized that well dispersed isolated tin atoms into a hydrophobic zeolitic material could be the best candidate to activate carbonyl groups. In this sense, isolated tin atoms in the framework of Beta zeolite could be the adequate catalyst since Sn has higher electronegativity than other heteroatoms (e.g. Ti), and Beta zeolite structure would permit the diffusion of reactants and products through its large pores. Sn-Beta zeolite was prepared following the fluoride synthetic route, under similar synthesis conditions to hydrophobic Ti-Beta. The full crystallization of Al-free Sn-Beta material prepared in fluoride media was achieved after 20 days at 140°C, and the presence of isolated tin atoms within the zeolitic framework was confirmed by <sup>119</sup>Sn MAS NMR of a Beta zeolite prepared with a tin source enriched with the NMR-active <sup>119</sup>Sn isotope.<sup>17</sup>

## **2.2.- Unique catalytic behavior of tin-containing zeolites in fine chemistry oxidation processes: Baeyer-Villiger and Meerwin-Ponndorf-Verley (MPV) reactions**

As Corma et al. predicted, Sn-Beta zeolite performs as an exceptional catalyst for the Baeyer-Villiger oxidation of ketones for the selective formation of the corresponding lactones.<sup>17</sup> Interestingly, high activity and chemoselectivity were maintained when using unsaturated ketones (e.g., dihydrocarvone) performing much better than organic peracids or other metallosilicates (see Table 1).<sup>17,20</sup> The use of *m*-chloroperbenzoic acid (mCPBA) yielded to a complex mixture of products (lactone, epoxide and epoxy lactone), Ti-Beta zeolite produced the epoxide product, and Sn-Beta was able to produce selectively the desired lactone (see Table 1).

In addition to the Baeyer-Villiger, Corma et al. have also reported that Sn-Beta is a very efficient heterogeneous catalyst for the MPV reduction of aldehydes and ketones to the corresponding alcohols (see Figure 1).<sup>21</sup> The MPV reaction mechanism occurs through a hydride transfer from an alcohol to the carbonyl group of the aldehyde or ketone when both reactants are coordinated to a Lewis acid metal center (see Figure 1).<sup>22</sup> The authors proposed that the activity and selectivity of MPV reaction could be improved if the adequate catalyst able to activate the carbonyl group of the aldehyde or ketone was used, and in this sense, the higher electronegativity of Sn than other metals in the zeolitic framework, such as Ti, would offer to Sn-Beta the potentiality to be a reasonable candidate. As seen in Figure 2, Sn-Beta shows much more activity for the selective MPV reduction of cyclohexanone using 2-butanol as reductant compared to other metal-containing Beta zeolites.<sup>23</sup> In addition, the same authors reported that the surface organic modification of Sn-Beta in order to make the catalyst more hydrophobic, allowed their use in the MPV reaction even in the presence of up to 10%wt of water in the reaction medium.<sup>23</sup> It is important to note, that this water resistance is an important issue, because the commercial catalysts are aluminum *iso*-propoxides, which suffer irreversible deactivation with water.

## **2.3.- Determination of catalytic sites and reaction mechanisms by theoretical and characterization techniques**

### Catalytic active sites

Two catalytic active sites could be found in the Sn-Beta zeolite, partially hydrolyzed tin framework centers (-Si-O)<sub>3</sub>Sn-OH or fully-coordinated tin framework atoms (-Si-O)<sub>4</sub>Sn

(see Figure 3). DFT calculations, IR spectroscopy and catalytic tests confirm that the most active site is the partially hydrolyzed tin framework center for the selective Baeyer-Villiger oxidation of cyclic ketones to form the corresponding lactones.<sup>24</sup> The concentration of both tin centers in the catalyst can be easily tuned during the calcination process (dry or wet atmosphere), and interestingly, a linear correlation can be observed between the initial rate for the oxidation of cyclic ketones and the amount of partially-hydrolyzed tin centers in the catalyst.<sup>24</sup>

#### Multisite reaction mechanisms

Once the partially-open tin center has been elucidated as the catalytic site for the Sn-Beta material, the reaction mechanisms for the Baeyer-Villiger oxidation and MPV reduction have been studied by combining molecular mechanics and quantum-chemical calculations.<sup>25</sup>

In the case of the Baeyer-Villiger oxidation, it was found that the catalytic active site is formed by two centers. On one hand, the carbonyl group of the cyclic ketone is activated on the Lewis acidic Sn atom, and on the other hand, the oxygen atom of the Sn-OH defect interacts with H<sub>2</sub>O<sub>2</sub> through a hydrogen bond (see Figure 4a).<sup>25a</sup> The complete mechanism involves into the oxidation and subsequent rearrangement to form  $\epsilon$ -caprolactame and water (see Figure 4a).

Theoretical calculations for the MPV reduction of cyclohexanone with 2-butanol using Sn-Beta show that the bifunctional Lewis acid center is initially coordinated to the carbonyl group of ketone and to the alcohol (see Figure 4b).<sup>25b</sup> Then, the proposed reaction pathway presents three steps: 2-butanol deprotonation by the Sn-OH to give the corresponding alcoholate intermediate and a water molecule, hydride shift between the ketone and deprotonated alcohol both bonded to the Sn atom, and the final proton transfer from the zeolite to form cyclohexanol (see Figure 4b).

As it can be seen, the presence of the Sn-OH group plays a pivotal role in both reaction pathways, activating H<sub>2</sub>O<sub>2</sub> for the Baeyer-Villiger reaction and performing the alcohol deprotonation for the MPV reaction.

#### **2.4.- Application to other fine chemistry processes**

The excellent activities and selectivities achieved for the Baeyer-Villiger and MPV reactions using water-resistant Sn-Beta opened the possibility for the application of this catalyst to the green production of some fine chemicals, such as fragrances, cosmetics, aromatizers, among others.

The synthesis of the industrial fragrance  $\delta$ -decalactone, which has a creamy-coconut aroma and is an important flavor in many products, was performed using homogeneous percarboxylic acids as oxidants.<sup>26</sup>  $\delta$ -decalactone presents two different enantiomers, but only the *R*-isomer has industrial interest.<sup>27</sup> The use of Sn-Beta as catalyst and hydrogen peroxide as green oxidant allows the production of the *R*-enantiomerically enriched  $\delta$ -decalactone under solvent free conditions starting with delfone as reactant (see Figure 5a).<sup>28</sup> This reaction occurs through a Baeyer-Villiger reaction.

Substituted phenols, and particularly 4-alkoxy derivatives, are important intermediates for agrochemicals, drugs, or dyes.<sup>29</sup> These 4-alkoxyphenols can be prepared through a Baeyer-Villiger oxidation of aromatic aldehydes but using different organic peracids as oxidants and producing large amount of waste during the reaction.<sup>30</sup> In contrast, the use of Sn-Beta zeolite as catalyst combined with H<sub>2</sub>O<sub>2</sub> permits the selective oxidation

of aldehydes containing alkoxy substituents to the corresponding formate esters which are hydrolyzed to the desired phenols (see Figure 5b).<sup>31</sup>

Melonal is another attractive industrial fragrance with melon and cucumber aromas, which mainly was produced through reacting 6-methyl-5-hepten-2-one with ethylchloroacetate to form an epoxy ester that finally must be saponified and decarboxylated to produce the desired product.<sup>32</sup> A much greener novel halogen-free strategy for the synthesis of melonal has recently been proposed, performing first the aldol condensation of 6-methyl-5-hepten-2-one with acetaldehyde into citral, and second the chemoselective oxidation of citral into melonal (see Figure 5c).<sup>32</sup>

Finally, the synthesis of (-)-menthol, an aromatizer with large relevance in cosmetics and pharmaceuticals, has also been improved by using Sn-Beta as heterogeneous catalyst. The synthetic route for the preparation of (-)-menthol used a Lewis-acid catalysts for the cyclisation of citronellal to (-)-isopulegol, and later this intermediate was hydrogenated to (-)-menthol (see Figure 5d). The most efficient reported Lewis acid catalyst was zinc bromide which provided very high diastereoselectivity towards (-)-isopulegol (higher than 90),<sup>33</sup> but the large amount of ZnBr<sub>2</sub> required in the process produced high waste disposal problems. The use of Sn-Beta allows the synthesis of desired isopulegol with almost 90% diastereoselectivity, while avoiding the formation of waste during the reaction.<sup>34</sup>

### **3.- Synthesis of other Lewis acid metal-containing zeolites (metal = Zr, V, or Ta)**

The efficient fluoride synthetic route followed for the preparation of the hydrophobic Ti- and Sn-Beta zeolites<sup>10,17</sup> has allowed the design of new metallosilicate Beta polymorphs, including isolated zirconium, niobium and tantalum metals as novel Lewis acid sites.<sup>35</sup> Fluoride medium shows a clear advantage against alkaline medium, since the former permits the availability of the metal precursors while in an alkaline medium the metal precursor can be precipitated as the metal oxide, precluding the metal incorporation into the zeolitic framework.

Al-free Zr-Beta zeolite synthesized in fluoride medium using Beta nanocrystalline zeolite seeds has been reported.<sup>35a</sup> Following this synthetic procedure, up to 1.3% framework substitution of Zr in the Beta zeolite structure, corresponding to a Si/Zr molar ratio of 75, can be achieved. The acidic properties of Zr-Beta zeolite were evaluated by infra-red spectra after adsorbing pyridine, revealing the exclusive presence of Lewis acid sites on the catalyst. Interestingly, this Zr-Beta catalyst is also a very active catalyst for the MPV reduction of several alkyl- and aryl-substituted cyclohexanones.<sup>35a</sup>

On the other hand, other metals with large charge to radius ratio, as Nb and Ta, have been incorporated into the framework of the Beta zeolite.<sup>35b</sup> Their incorporation into the zeolitic structure and Lewis acid properties has been proven by X-ray absorption (EXAFS and XANES) and infra-red spectroscopy, respectively. Those Lewis-acid metallosilicates show high activity and diastereoselectivities for the intramolecular carbonyl-ene reaction of citronellal to isopulegol (see Figure 5d).<sup>35b</sup>

### **4.- Catalytic application of hydrophobic metal-containing zeolites to novel biomass transformations into platform molecules**

The chemical knowledge acquired from the use of hydrophobic Lewis-acid containing molecular sieves in the production of several fine chemicals has served to rationalize



the use of these metal-containing zeolites in novel chemical transformations involving biomass-derived feedstocks. Indeed, the increased interest in the use of biomass as a sustainable source of carbon to produce fuels and chemicals, the fact that most of the involved biomass molecules contain carbonyl functionalities, and that the preferred solvents for biomass transformations are protic polar solvents (especially water), have promoted water-resistant Lewis acid zeolites as essential heterogeneous catalysts for efficient biomass transformations.

#### **4.1.- Sugar isomerization**

The isomerization of glucose to fructose is the largest immobilized biocatalytic process worldwide to produce high-fructose corn syrup.<sup>36</sup> However, the use of an immobilized enzyme (xylose isomerase) presents important operation drawbacks, such as the need of purification to selectively remove impurities from the feed that can inhibit the enzyme activity, the requirement of a buffered solution to maintain neutral pH values, low reaction temperatures to maximize enzyme lifetime, and finally, high operating costs from the periodic replacement of deactivated catalyst bed. The design of an inorganic catalyst able to isomerize sugars would offer several advantages compared to enzymes, including higher resistance to impurities, wider range of operating temperatures and pHs, and longer lifetimes.

In order to find a potential inorganic catalyst candidate, the enzymatic glucose isomerization mechanism was previously evaluated.<sup>37</sup> A three-stage mechanism has been proposed in the enzymatic glucose to fructose isomerization: first, the glucose ring is opened to form its acyclic form, next the isomerization of the linear sugar at C-2 and C-1 position occurs through a metal assisted hydride shift, and finally, the ring closes to form the cyclic form of fructose (see Figure 6a).<sup>37</sup> Davis et al. proposed the use of Sn-Beta as a potential catalyst to perform the glucose to fructose isomerization reaction in aqueous media,<sup>36</sup> based on the hypothesis that Sn-Beta is a very active catalyst for the MPV reduction of carbonyl compounds, where a hydride shift from an alcohol to the carbonyl group of the ketone molecule occurs.<sup>21</sup> Sn-Beta is not only able to isomerize glucose to fructose in water with similar activities that those reported for the enzymatic process, but also is very active over a wide temperature range (343-413 K) and acidic solutions (pH < 2).<sup>36</sup> <sup>13</sup>C and <sup>1</sup>H NMR spectroscopy on isotopically-labeled glucose demonstrates that the sugar isomerization mechanism using Sn-Beta takes place through a Lewis acid intra-molecular hydride shift from the C-2 to C-1 position (as seen in Figure 6b).<sup>38</sup> Additional characterization data and theoretical calculations have confirmed that Sn-Beta isomerizes glucose to fructose following analogous reaction pathways to enzymes, including glucose ring opening in the Lewis acid center, intra-molecular proton shift to form fructose, and finally, ring closure to form the cyclic form of fructose.<sup>39</sup> A similar pathway has been described for the isomerization of xylose to xylulose also using Sn-Beta as Lewis acid catalyst in aqueous media.<sup>40</sup>

On the other hand, it has been observed a competitive isomerization reaction when the glucose isomerization reaction is carried out using Ti-Beta zeolite as catalyst in water or methanol.<sup>36,41</sup> In this case, the glucose-sorbose isomerization also occurs in parallel to glucose-fructose through a C1-C5 intramolecular hydride shift, achieving fructose as the main product in the aqueous medium and sorbose in methanol.<sup>41</sup> Interestingly, this direct Lewis acid mediated mechanism to obtain sorbose from glucose is the first example among heterogeneous or biological catalysts. <sup>13</sup>C and <sup>1</sup>H

NMR spectroscopy on isotopically-labeled glucose reveals that the glucose-sorbose isomerization occurs through an intramolecular C5-C1 hydride shift. Sorbose sugar is largely used in the synthesis of L-ascorbic acid, which is a form of vitamin C.<sup>42</sup>

#### **4.2.- Sugar epimerization to synthesize rare sugars**

Only seven of all possible pentoses or hexoses (D-glucose, D-galactose, D-mannose, D-fructose, D-xylose, D-ribose and L-arabinose) can be found in nature with large amount, while the other sugars are called "rare".<sup>43</sup> However, rare sugars are very demanded in the preparation of antiviral drugs, anti-inflammatory agents, and as chiral building blocks.<sup>44</sup> Most of the synthesis processes of rare sugars from abundant ones involve biochemical processes, where different enzymes are used (epimerases). These enzymes, as the ones used for the sugar isomerization, show several operation drawbacks, and in this sense, the design of stable inorganic catalysts able to perform the sugar epimerization is highly required.

Román-Leshkov et. al. found that the rational combination of Sn-Beta and borate salts cooperatively catalyzes the epimerization of sugars in aqueous media.<sup>45</sup> The intermediate complexes formed by the interaction of the borate salts with the initial sugars react on the Lewis acid sites of Sn-Beta by an epimerization pathway through an 1,2-intramolecular carbon shift (see Figure 7).<sup>45</sup> NMR spectroscopy studies reveal the key role of borate salts to promote the epimer products instead of the isomers.<sup>46</sup> This combined methodology has been successfully described for different monosaccharides (glucose, xylose, or arabinose), mainly producing the epimer products (mannose, lyxose, or ribose, respectively), instead of the isomer product (fructose, xylulose, or ribulose, respectively).

Davis et al. have recently reported a different reaction system to direct sugar epimerization using Sn-Beta without borate salts.<sup>47</sup> In this case, the reaction of glucose on Sn-Beta when using methanol as solvent mainly produces the epimer product (mannose),<sup>47</sup> while the isomer product (fructose) is the preferred product when the reaction is performed in pure aqueous media.<sup>36</sup> At this point, the effects of methanol molecules on the mechanism reaction remain unclear, but the authors suggest that methanol molecules could interact with framework Sn sites, affecting to the intermediate transition state.

#### **4.3.- Sugar to lactic acid derivatives**

Lactic acid is a very attractive chemical product with large application in the synthesis of biodegradable polymers and solvents. The preferred industrial production of lactic acid is mainly through microbial fermentation of glucose and sucrose.<sup>48</sup>

In a previous communication, Christensen et al. nicely reported the production of lactate esters through the isomerization-esterification of trioses in methanol using Lewis acid zeolites, especially hydrophobic Sn-Beta, which gives 99%wt yield of methyl lactate.<sup>49</sup> The authors propose that the reaction mechanism also involves the MPV reaction pathway through an intramolecular 1,2-hydride shift (see Figure 8a).

The excellent catalytic activities achieved using trioses as feedstock for the production of lactic acid derivatives served as motivation to use other less expensive substrates compared to trioses. Indeed, the use of hexose sugars is a very challenging issue because these monosaccharides show several alternative reaction pathways, including dehydration and polymerization reactions, and therefore, the overall yield towards the

desired product could be diminished. Taarning et al. described the direct formation of high yields of methyl lactate (up to 70%) in methanol using Sn-Beta as catalyst, and glucose, fructose or sucrose as initial common sugars.<sup>50</sup> The proposed reaction mechanism involves a retro aldol fragmentation of the hexose that is favored at high temperature, followed by the isomerization of the formed trioses through a 1,2-hydride shift (see Figure 8b).

#### **4.4.- Rearrangement of $\beta$ -pinene epoxide into myrtanal**

Myrtanal is a natural monoterpene that find application in cosmetics, pharmaceutical, and flavors.<sup>51</sup> This product can be extracted from plants, such as *Geur urbanum* roots,<sup>52</sup> or *Greek Paeonia taxa*.<sup>53</sup> Interestingly, myrtanal could be obtained by transposition of  $\beta$ -pinene epoxide, and this epoxide from the epoxidation of  $\beta$ -pinene.<sup>54</sup> Indeed, it has been described that  $\beta$ -pinene can be efficiently achieved from biomass by distillation of the white spirit of pine resin.<sup>55</sup>

A very efficient epoxide rearrangement of  $\beta$ -pinene into myrtanal by using isolated Lewis acid sites in zeolites has been demonstrated.<sup>56</sup> Myrtanal selectivities of up to 94% using Zr-Beta as catalyst and acetonitrile as solvent have been reported. Sn-Beta showed lower myrtanal yields. Probably, the higher interaction of the carbonyl group of the myrtanal molecule over the Lewis acid sites of Sn-Beta increases its adsorption time on the active sites, favoring other rearrangement reactions towards undesired by-products.

#### **4.5.- “One-pot” synthesis of furfural-derived products from monosaccharides**

Different furfural-based molecules can be considered as some of the most important target molecules to be achieved from biomass, in order to obtain chemicals and fuels.<sup>57</sup>

From those furfural-based molecules, probably 5-(hydroxymethyl)furfural (HMF) is the most interesting precursor of high valuable polymers and biofuels.<sup>58</sup> A very challenging process is the efficient production of HMF from glucose since this monosaccharide is the most abundant.<sup>59</sup> However, glucose ring is relatively stable compared to other monosaccharides, making glucose transformation to furan derivatives a difficult process with poor activities and selectivities. Nevertheless, the recent description reported by Moliner et al. for the glucose to fructose isomerization, which can be performed efficiently in water even at very low pHs,<sup>36</sup> has allowed rationalizing a “one-pot” biphasic process to improve the HMF yield from glucose.<sup>60</sup> In this sense, Nikolla et al. have combined Sn-Beta and HCl in a biphasic water/THF biphasic reactor system for the glucose to HMF transformation. Sn-Beta is able to perform the isomerization of glucose to fructose in the aqueous phase, and the formed fructose rapidly is dehydrated to HMF by the inorganic acid also in the aqueous phase (see Figure 9). Produced HMF is mainly extracted to the organic phase, thus precluding its degradation to undesired by-products by the presence of the inorganic acid in the aqueous phase. HMF yields over 70% have been reported using this biphasic system.<sup>60</sup> Similarly, Lobo et al. have reported a one-pot methodology using Sn-Beta combined with a Bronsted acid as catalysts to produce furfural from xylose.<sup>40a</sup> Unfortunately, the achieved yields of furfural are very low (~20%wt) due to the reaction is carried out in a single aqueous phase, and then, the formed furfural can undergo undesired degradation reactions in presence of Brønsted acids.

Tsapatsis et al. have combined Sn-Beta with a heterogeneous Brønsted acid catalyst, such as Amberlyst 131, to perform the one-pot reaction of glucose to 5-(ethoxymethyl)furfural [EMF] in ethanol.<sup>61</sup> This is a very interesting reaction because EMF has been proposed as a potential biofuel alternative, presenting an energy density similar to gasoline (30.3 MJ/L).<sup>62</sup> Taking as a reference the previous work of Nikolla et al.,<sup>60</sup> where high HMF yields can be achieved by combining Lewis and Brønsted acids, Tsapatsis et al. are able to introduce a new catalytic step to efficiently transform HMF into EMF using the Brønsted acid catalyst (Amberlyst 131, see Figure 10). The overall EMF yield following this one-pot methodology from glucose in ethanol is 31%, which is a significant amount but could be improved by optimizing the catalytic conditions.

#### **4.6.- Production of $\gamma$ -valerolactone (GVL) from furfural**

GVL is also considered as a versatile chemical for the production of liquid alkenes, solvent for biomass reactions, fuel additive, and polymer precursor.<sup>63</sup> GVL can be produced through a multistep reaction, where sugars are transformed to levulinic acid (LA), and a noble-metal based catalyst selectively reduces LA to GVL with H<sub>2</sub>.<sup>64</sup> The use of precious-metal catalysts (Ru or Pt) and high H<sub>2</sub> pressures limits the large-scale application of this process. Very recently, Roman-Leshkov et al. have reported an alternative domino reaction to obtain GVL from furfural in a single reactor.<sup>65</sup> A transfer-hydrogenation reaction, as MPV reaction, has been proposed as an alternative to high-pressure molecular H<sub>2</sub> for the selective reduction of carbonyl functional groups. Lewis acid zeolites, particularly Zr-Beta, have been previously introduced as efficient catalysts to perform the MPV reaction for fine chemistry processes.

The overall process proposed by Roman-Leshkov et al. requires the combination of zeolites with Lewis and Brønsted acid sites, approaching a GVL yield of 80% from furfural when Zr-Beta and Al-MFI with nanosheet morphology are used.<sup>65</sup> Figure 11 summarizes the complete reaction mechanism, involving the Lewis acid mediated MPV reduction of furfural into furfuryl alcohol (FA), the Brønsted acid conversion of FA into LA and butyl levulinate, their successive transformation to 4-hydroxypentanoates through a second Lewis acid mediated MPV reaction, and finally GVL formation by lactonization.

#### **4.7.- Synthesis of optically pure $\gamma$ -lactones from pyrolysis products**

A very recent example of a biomass transformation using Lewis acid zeolites shows the production of highly valuable optically pure products, as unsaturated chiral  $\gamma$ -lactones, which have been reported for the synthesis of many drugs, aromatizers, and antiviral agents.<sup>66</sup> Indeed, this type of chiral  $\gamma$ -lactones can be achieved from levoglucosenone (LGO), which is a very interesting dehydrated sugar presenting two chiral and six different functional carbon atoms (see Figure 12), and it can be obtained in high yields from acid-catalyzed pyrolysis processes.<sup>67</sup> The selective oxidation of LGO to the intermediate formate lactone (FBO, see Figure 12) occurs through a Baeyer-Villiger reaction, and the former reported catalysts to undergo the oxidation processes were homogeneous organic peracids, such as peracetic acid or m-chloroperbenzoic acid.<sup>68</sup> At this point, Paris et al. introduced water resistant Lewis acid zeolites as catalysts (Sn-Beta and Zr-Beta) and hydrogen peroxide as oxidant agent for the green production of HBO in a one-pot process.<sup>69</sup> Indeed, previous descriptions of water resistant Lewis acid

zeolites as efficient catalysts to undergo the Baeyer-Villiger reaction in fine-chemistry processes have been essential for their application in this attractive biomass transformation to achieve optically pure lactones. Depending on the reaction conditions, the overall yield towards the desired HBO product range between 75 to 90%.<sup>69</sup> The optical purity of the achieved HBO product has been demonstrated by using different characterization techniques.

## 5.- Perspectives

In the last few years, a large amount of new catalytic applications involving water-resistant Lewis acid containing zeolites have been reported, most of them being related to biomass transformation processes. This fact can be explained by noting that most chemical routes for biomass conversion involve molecules containing carbonyl functional groups, and require the presence of polar protic solvents such as water. In this sense, the presence of large hydrophobic void environments in this type of zeolites allows selective adsorption of organic reactants excluding liquid water from these hydrophobic void spaces, clearly improving the overall stability of the catalysts, and also the activity and selectivity of the chemical processes.<sup>70</sup>

Biomass has become an important fundamental research area for the development of technologies to reduce our dependence on fossil fuels. Therefore, the large interest in this research area permits us to envision that new biomass-conversion processes to produce efficiently chemicals and fuels will be discovered in the near future using Lewis acid containing zeolites. Recent examples have allowed performing multistep reactions in a single reactor, achieving high yields of some of the considered platform chemicals, including optically pure chiral molecules. Lewis acid zeolites are playing a key role in the efficient preparation of fuels and chemicals in the presence of water.

Nevertheless, more efforts have to be done in the development of processes involving C-C bond formation. This type of reactions would be interesting to upgrade short-chain molecules. It has been intensively described that Lewis acids can undergo some C-C bond forming reactions, as for instance Michael additions and aldol condensations.<sup>5a</sup> However, very few examples related to C-C bond formation using a Lewis acid zeolite can be found in the literature.<sup>32,34</sup>

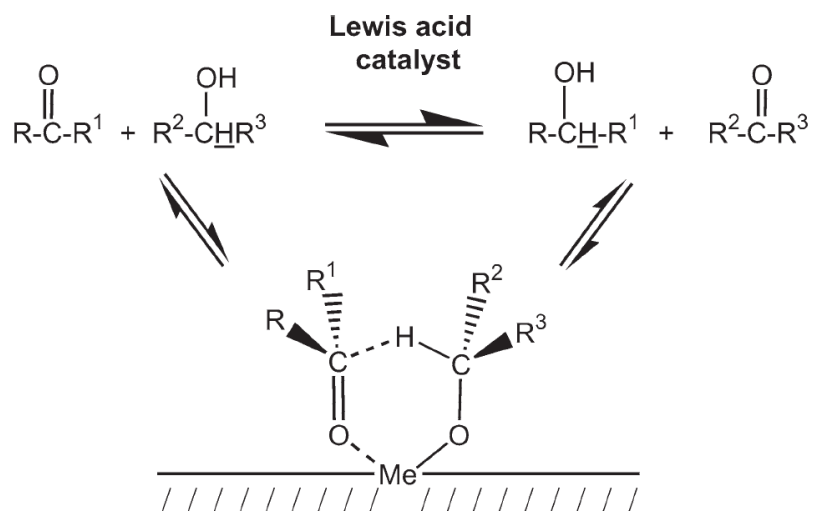
Finally, new Lewis acid containing zeolites must be designed, either introducing new metals or synthesizing new structures with novel framework topologies that allow directing different activities and selectivities by shape-selective issues. Some recent improvements have been described in the last two years related to the zeolite synthesis of tin-silicates. On one hand, new synthetic descriptions have allowed the preparation of the nanosized Sn-Beta zeolite by simple post-synthetic methods,<sup>71</sup> and tin-silicates zeolites with nanosheet morphology,<sup>72</sup> both presenting lower diffusion limitations than Sn-Beta synthesized in fluoride media. On the other hand, the required time to crystallize Sn-Beta following the fluoride route (~20 days) has been notoriously decreased using steam-assisted conversion, seeding methodology or post-synthetic treatments to 5 hours to 2 days.<sup>73</sup> The reduction of the required time to achieve highly crystalline Sn-Beta offers new motivations for industrial applications.

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Figure 1: MPV reaction mechanism (R= alkyl or aryl, R<sup>1</sup> and R<sup>3</sup>=alkyl or hydrogen, M=metal). Reproduced from <sup>23</sup>



**Figure 2: Results achieved for the MPV reduction of cyclohexanone using 2-butanol as reductant and different metal-containing Beta zeolites. Reproduced from <sup>23</sup>**

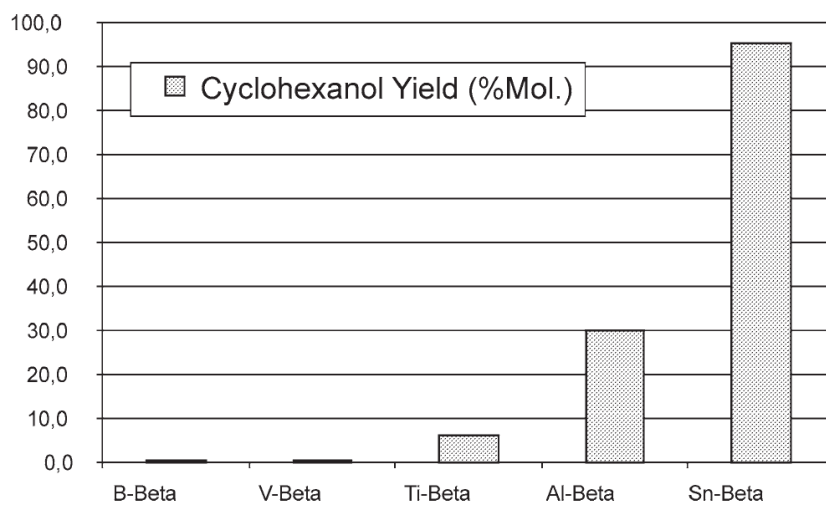




Figure 3: Two possible catalytic active sites in Sn-Beta catalyst. Reproduced from <sup>24</sup>

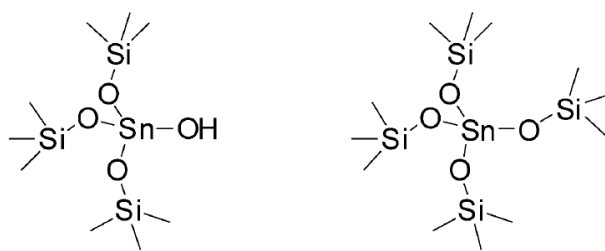


Figure 4: Proposed reaction mechanism for the Baeyer-Villiger (a) and MPV (b) reactions using Sn-Beta as catalyst. Reproduced from <sup>25a</sup> and <sup>25b</sup>, respectively

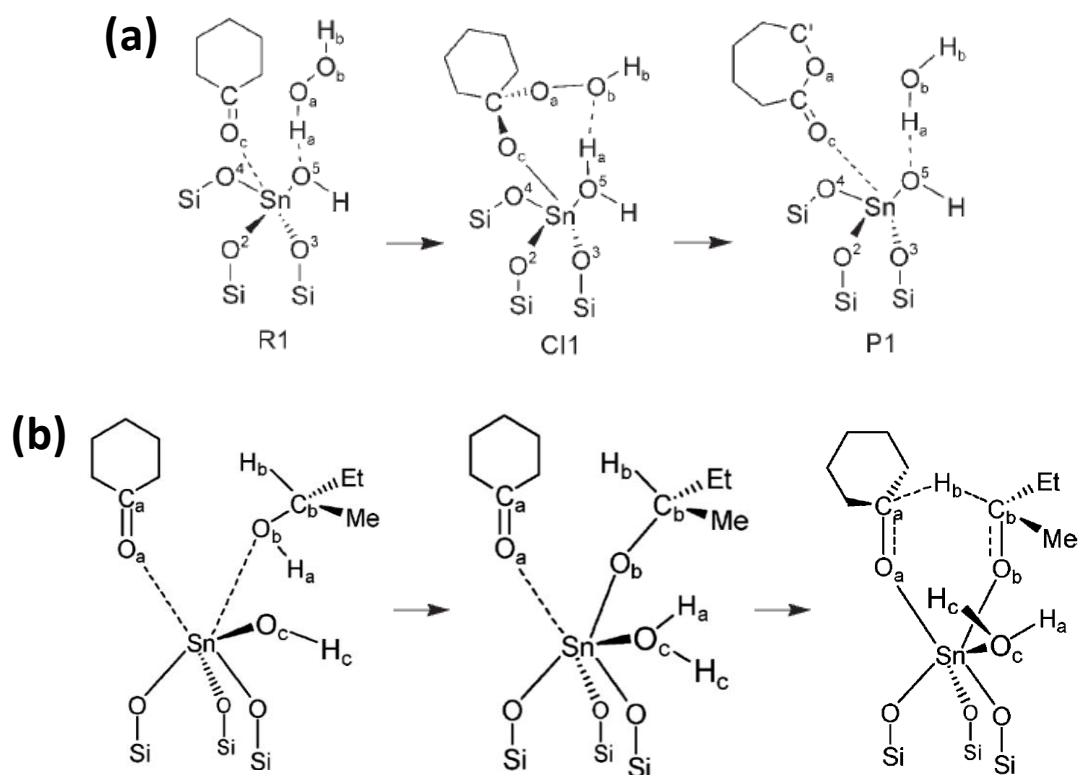


Figure 5: Synthesis of melonal (a),  $\delta$ -decalactone (b), phenols (c), and menthol (d) using Lewis acid-containing zeolites

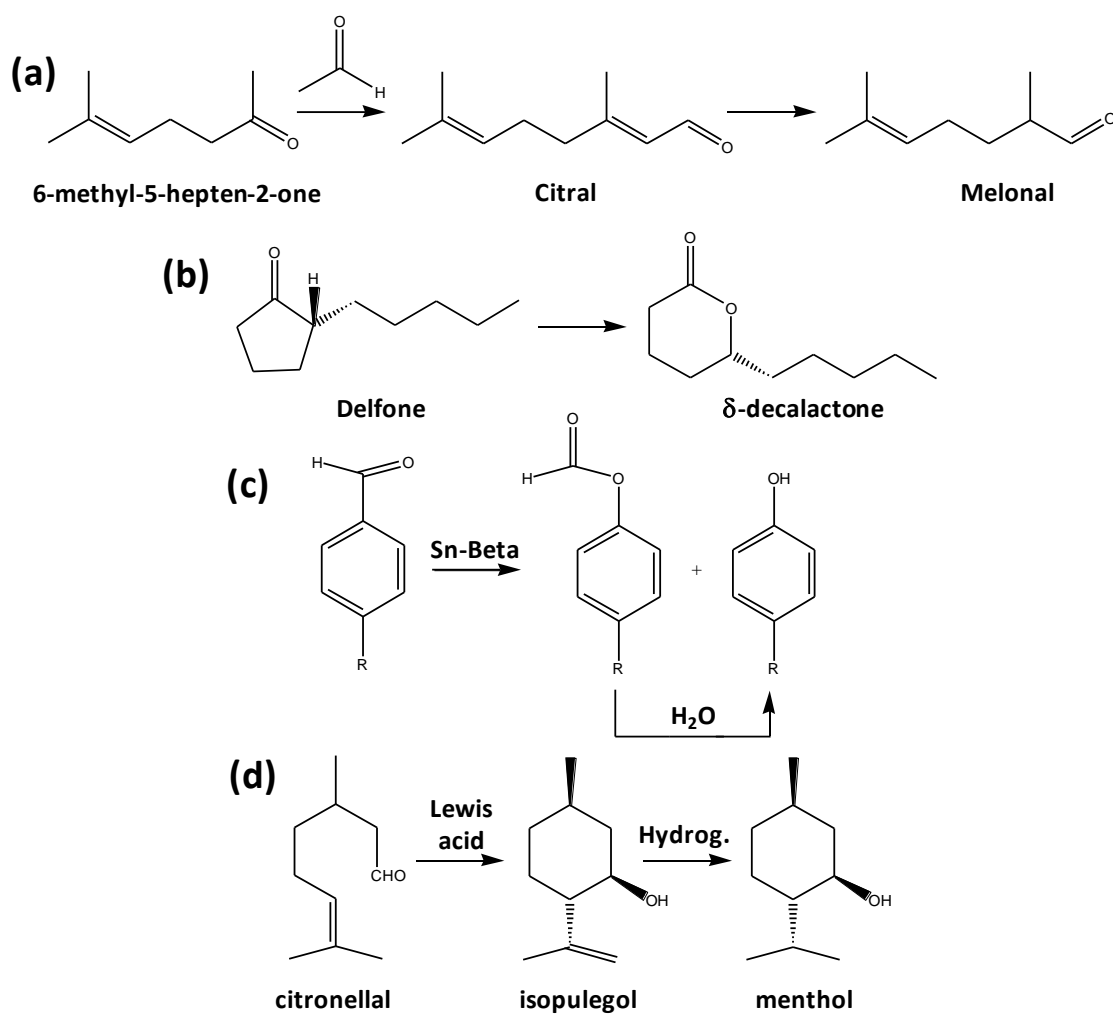


Figure 6: (a) Scheme for the isomerization of glucose to fructose, and (b) scheme for the metal-catalyzed proton shift. Reproduced from <sup>39</sup> and <sup>36</sup>

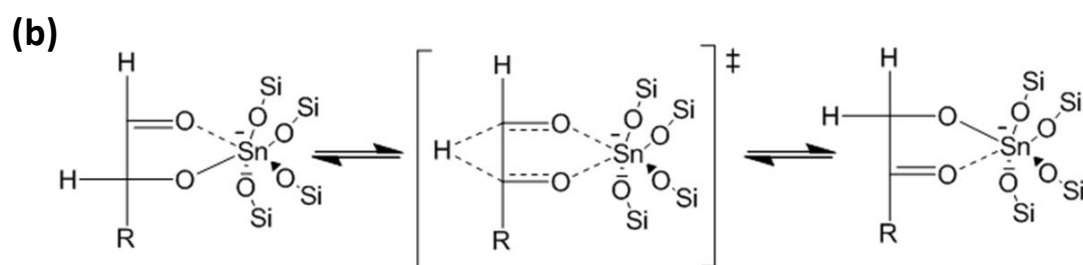
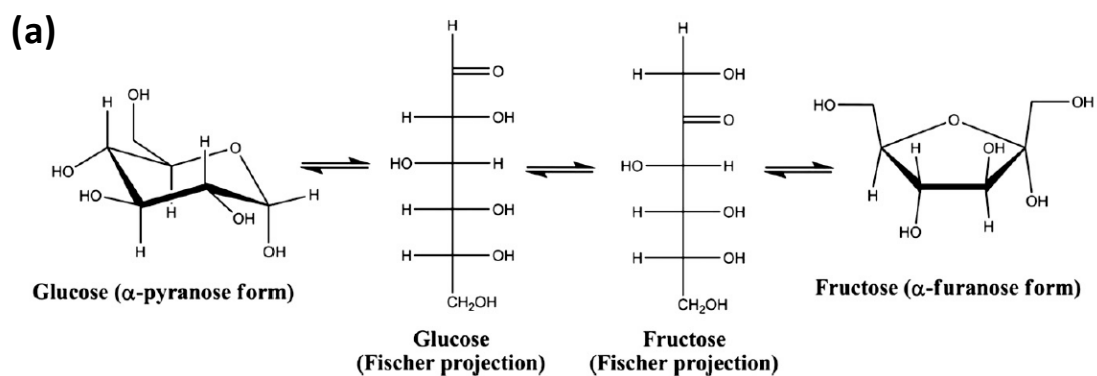


Figure 7: Epimerization reaction of glucose to mannose through 1,2-intramolecular carbon shift

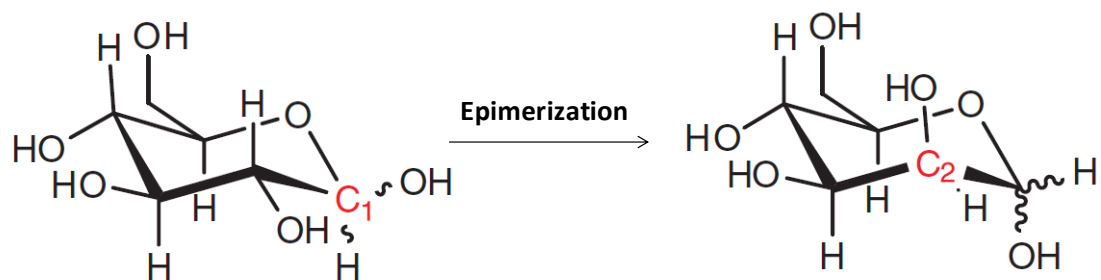


Figure 8: (a) MPV reaction mechanism followed to synthesize methyl lactate, and (b) reaction pathway for the fructose conversion to methyl lactate. Reproduced from <sup>49</sup> and <sup>50</sup>

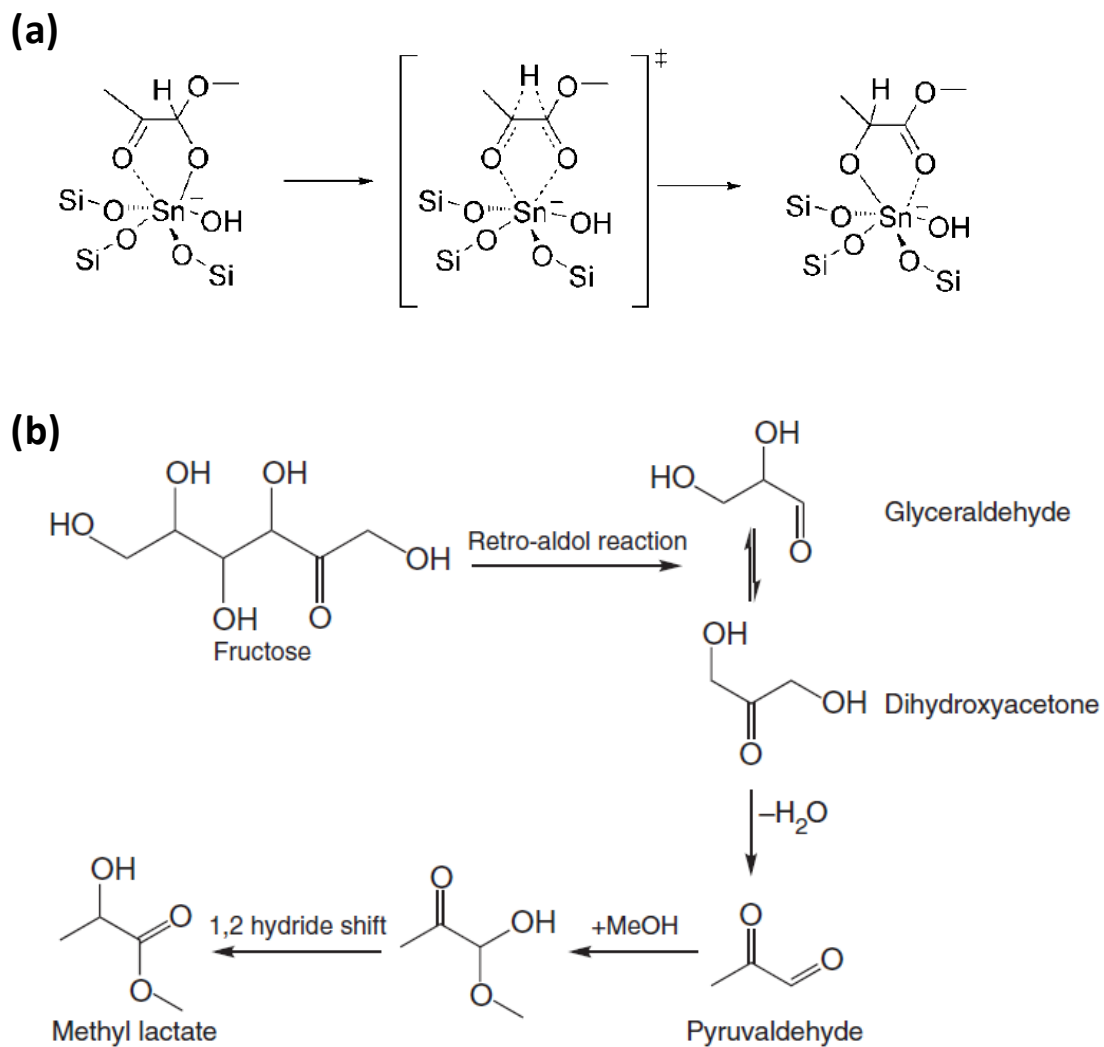


Figure 9: Scheme for the reaction pathway of glucose to HMF using Sn-Beta and HCl as cooperative catalysts in a biphasic system. Reproduced from <sup>60</sup>

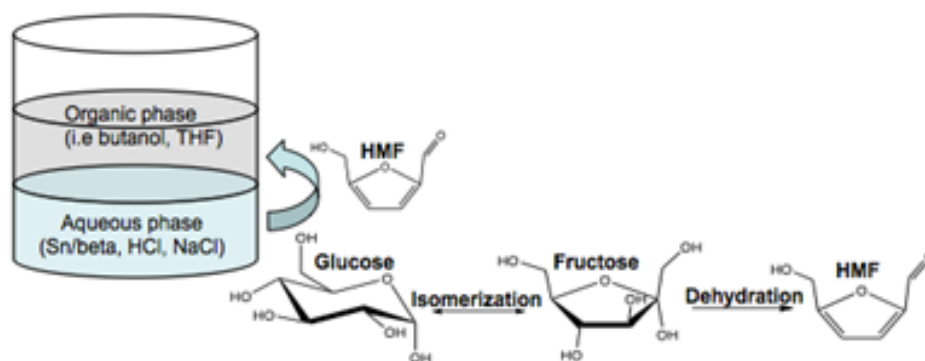


Figure 10: Scheme for the one-pot reaction of glucose to 5-ethoxymethyl)furfural

[EMF]. Reproduced from <sup>61</sup>

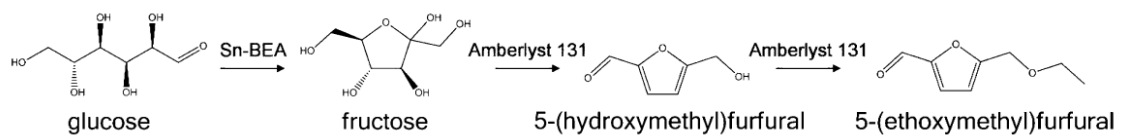
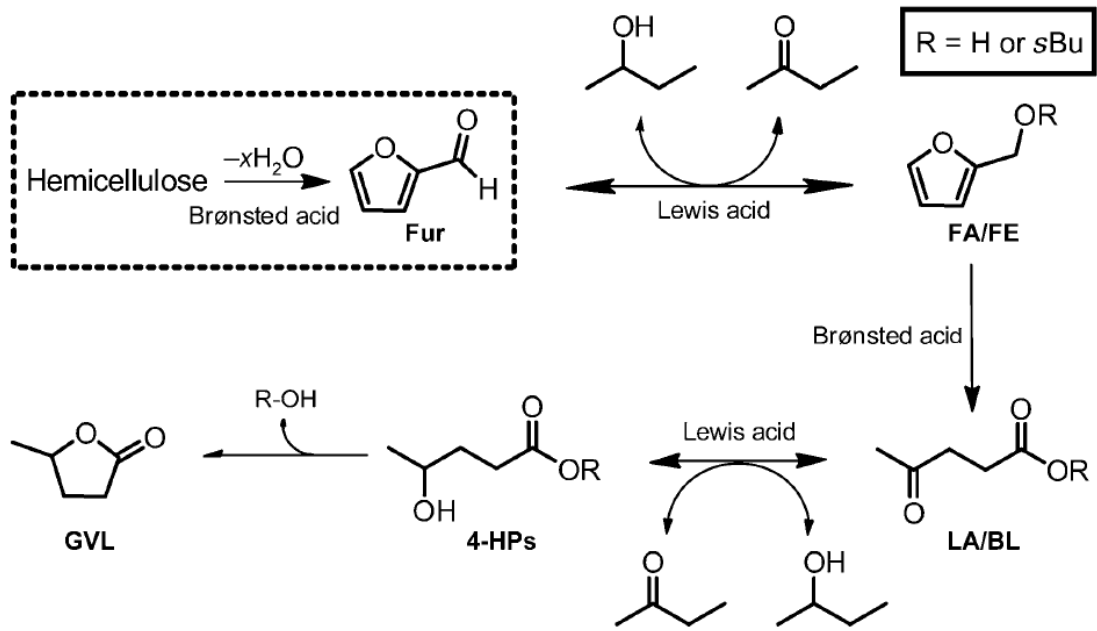
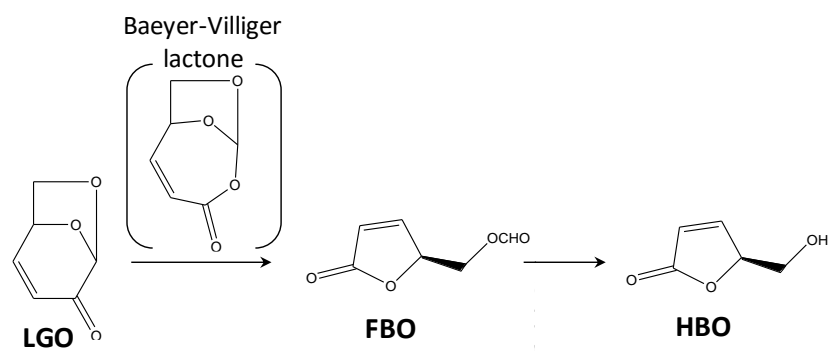




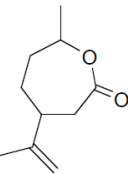
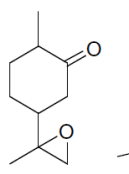
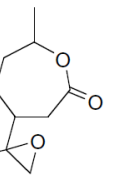

Figure 11: Domino reaction for the production of GVL from furfural. Reproduced from <sup>65</sup>



**Figure 12: Reaction pathway for the selective oxidation of levoglucosenone to unsaturated  $\gamma$ -lactone HBO. Reproduced from <sup>69</sup>**



**Table 1: Baeyer-Villiger oxidation of dihydrocarvone using different oxidation systems. Reproduced from <sup>17</sup>**

Oxidant	Reactant conversion (%)	Product selectivity (%)			
					
Sn-zeolite beta H <sub>2</sub> O <sub>2</sub>	68	100	0	0	
mCPBA†	85	11	71	18	
Ti-zeolite beta/H <sub>2</sub> O <sub>2</sub>	48	0	79*	0	

The same conditions as for adamantanone (see Table 1) were employed.

\* Rest missing to 100% were opening products of the epoxide.

† *m*-chloroperbenzoic acid.

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