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Highly selective Lewis acid sites in desilicated MFI zeolites for dihydroxyacetone isomerization to lactic acid

Pierre Y. Dapsens, Cecilia Mondelli*, and Javier Pérez-Ramírez*

This study demonstrates that desilication of commercial MFI-type zeolites in solutions of alkali metal hydroxides generates highly selective catalysts for the aqueous-phase isomerization of biobased dihydroxyacetone to lactic acid (LA). The best hierarchical ZSM-5 sample attains a LA selectivity exceeding 90%, comparable to that of the state-of-the-art catalyst (Sn-beta) and is recyclable for 3 runs. The Lewis acid sites created by desilication simultaneously with the introduction of mesoporosity are proved to play a crucial role in the formation of the desired product and cannot be mimicked by other post-synthetic methods such as steaming or impregnation of Al species. Desilication of other metallosilicates such as Ga-MFI also leads to high LA selectivity. In the presence of a soluble Al source (aluminum nitrate), alkaline-assisted alumination can introduce these unique centers in all-silica MFI (silicalite-1). These findings further highlight the potential of zeolites in the field of biomass-to-chemicals and expand the applicability of desilication from improving accessibility to the generation of selective catalytic centers. Enhancing the stability of these selective hierarchical zeolites under the acidic and high-temperature reaction conditions represents the challenge to be met in view of their future practical use.

Introduction

Scientists are increasingly exploring the possibility to generate high added-value chemicals through the chemocatalytic transformation of biobased compounds as a means to build a more sustainable chemical industry.[1] In this context, the preparation of lactic acid (LA) has been the focus of considerable attention, owing to the major drawbacks that characterize the current synthetic biocatalytic route and to the industrial relevance of the products that can be derived.[2] With regards to the latter point, particularly important are polyactic acid, propylene glycol, and acrylic acid and its ester and amide derivatives. The preferred chemocatalytic pathway to LA is the aqueous-phase acid-catalyzed isomerization of dihydroxyacetone (DHA) or glyceraldehyde, compounds that can be obtained from glycerol or fructose (Scheme 1). Remarkably, by simply replacing water by an alcoholic solvent, the same route also leads to a variety of valuable alkyl lactates. Tin-containing zeolites, such as Sn-beta[3] and Sn-silicalite,[4] have shown outstanding performance in this reaction, attaining full conversion and 90% LA selectivity. Tin functionalization has also been applied to mesoporous materials, e.g. MCM-41, SBA-15,[5] and a silica-carbon composite,[6] but the performance of Sn-beta remained unsurpassed. The drawbacks of tin-based materials are the typically complex and lengthy syntheses and the scarce worldwide availability of tin, which may hamper their large-scale utilization. Therefore, commercially available zeolites have also been investigated.[7] The LA selectivity ranged from 22% for H-ZSM-5 (Si/Al = 25) to 71% for H-USY (Si/Al = 6), thus being inferior with respect to tin-based catalysts. Interestingly, by comparing the performances of H-USY zeolites with different Si/Al ratios, West et al.[7a] have found that those containing more Lewis acid sites (probed by infrared of adsorbed pyridine) led to higher LA selectivity. Furthermore, a clear direct proportionality between the yield of ethyl lactate attained with the zeolites NH4-Y and USY, H-beta, and H-ZSM-5 and the amount of extraframework aluminum (EFAI) that these materials contain (determined by 29Si MAS NMR) has been shown by Pescarmona et al.[8] These findings indicate that a better performing zeolite catalyst can be obtained by tailoring its

Scheme 1. Proposed reaction mechanism of the acid-catalyzed conversion of dihydroxyacetone and glyceraldehyde to lactic acid and alkyl lactates. Adapted from ref. 7.

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Supporting information for this article is available on the WWW under http://www.chemsuschem.org or from the authors.
acidity and possibly its porosity. Among the different strategies available for these purposes, turning conventional zeolites into their hierarchical form seems appealing. In fact, mesoporous zeolites display enhanced accessibility, due to the presence of a secondary network of mesopores interconnected with the native micropores. Post-synthesis modification constitutes an effective, versatile, and scalable approach to attain these materials. Demetallation essentially comprises basic (desilication) and acid (dealumination) treatments that can be separately or sequentially applied depending on the original zeolite features and on the porous and acid properties desired. In particular, treatments in alkaline solutions (typically NaOH) enable to generate hierarchical zeolites possessing increased Lewis acidity compared to their purely microporous counterparts. In fact, while silicon is preferentially extracted under these conditions, the residual aluminum redistributes on the surface, possibly being partially reincorporated into the zeolite framework. This phenomenon is referred to as re alumination. Mesoporous zeolites have already demonstrated improved catalytic performance in a number of classical reactions. Although their use in the conversion of bioderived molecules is still fairly limited, the perspectives of a wider successful application are bright.

Herein, we show that alkaline treatment of MFI-type zeolites generates hierarchical zeolites affording high activity and selectivity in the isomerization of DHA to LA. By decoupling the effect of the introduced mesoporosity and acidity, it is demonstrated that LA selectivity is related to the generation of unique Lewis acid sites, which cannot be easily reproduced by other post-synthetic treatments. The role of the initial Si/Al ratio and the nature of these active sites are discussed and the strategy developed is successfully extrapolated to other post-synthetic treatments. The role of the initial Si/Al ratio and the nature of these active sites are discussed and the strategy developed is successfully extrapolated to other metallosilicates that can give rise to Lewis acidity, i.e. Ga-MFI. Furthermore, we evidence that these sites can be introduced in all-silica MFI by conducting the alkaline treatment in the presence of an aluminum source. We also show that hydroxides of other alkali metals than sodium are effective in producing selective catalysts too. Finally, we explore the reusability of the best materials, providing insights into their deactivation mechanism and underlining the existing challenges in view of a practical application of these hierarchical zeolites.

**Results and Discussion**

**Characterization of the alkaline-treated samples**

The effect of the alkaline treatment on the porous, acid, and catalytic properties of a commercial H-ZSM-5 (Si/Al = 40) sample, denoted hereafter as Z40-P, was explored. For this purpose, characterization and catalytic data were collected for Z40-P and for hierarchical Z40 samples obtained by desilication using NaOH solutions of different concentration (0.1-0.7 M). The reason for selecting Z40 was threefold: (i) it contains negligible amounts of EFAl (vide infra), (ii) its degree of modification has been reported to sensibly depend on the strength of the alkaline solutions used, and (iii) ZSM-5 zeolites with Si/Al = 15-40 are proved to be stable in hot liquid water. The treatment conditions and textural properties of the parent and modified Z40 samples are summarized in Table 1 (entries 1-6.8). According to the X-ray diffraction (XRD) analysis (Fig. S11a), the major reflections specific to the MFI structure were retained upon alkaline treatment for NaOH concentrations up to 0.5 M, indicating that the zeolitic structure was substantially preserved, in line with previous evidences from our group. Still, the gradual broadening and depletion of their intensity imply a decrease of the crystallinity, as expected from the introduction of mesopores and partial amorphization of the surface. The shape of the N2 sorption isotherms evolved from type I of the purely microporous Z40-P to type II, thus confirming the development of mesoporosity (Fig. S11b). The external surface area (S\text{meso}) of the parent zeolite (79 m² g⁻¹) progressively augmented, reaching a plateau value of 400 m² g⁻¹ for Z40-AT5. Contrarily, the micropore volume (V\text{micro}) decreased, finally reaching a third of its initial value for Z40-AT5. The partial occlusion of the V\text{micro} is a direct consequence of the redistribution of aluminum species upon desilication. The use of a higher concentration in hydroxyl ions, i.e. 0.7 M, did not enable to attain a larger external surface area. On the opposite, Z40-AT7 presented a S\text{meso} of 292 m² g⁻¹, associated with the

**Table 1. Preparation conditions and characterization data of the MFI-type zeolites.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst[a]</th>
<th>Si/M[b]</th>
<th>[NaOH] (M)</th>
<th>S\text{meso} [c]</th>
<th>( V\text{micro} ) [d]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Z40-P</td>
<td>41</td>
<td>–</td>
<td>473</td>
<td>79</td>
</tr>
<tr>
<td>2</td>
<td>Z40-AT1</td>
<td>36</td>
<td>0.1</td>
<td>484</td>
<td>141</td>
</tr>
<tr>
<td>3</td>
<td>Z40-AT2</td>
<td>34</td>
<td>0.2</td>
<td>570</td>
<td>280</td>
</tr>
<tr>
<td>4</td>
<td>Z40-AT3</td>
<td>24</td>
<td>0.3</td>
<td>598</td>
<td>370</td>
</tr>
<tr>
<td>5</td>
<td>Z40-AT4</td>
<td>17</td>
<td>0.4</td>
<td>577</td>
<td>390</td>
</tr>
<tr>
<td>6</td>
<td>Z40-AT5</td>
<td>10</td>
<td>0.5</td>
<td>617</td>
<td>400</td>
</tr>
<tr>
<td>7</td>
<td>Z40-AT5-AW</td>
<td>36</td>
<td>0.5</td>
<td>664</td>
<td>405</td>
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<tr>
<td>8</td>
<td>Z40-AT7</td>
<td>5</td>
<td>0.7</td>
<td>349</td>
<td>292</td>
</tr>
<tr>
<td>9</td>
<td>Z40-STm</td>
<td>43</td>
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<td>Z40-STs</td>
<td>47</td>
<td>–</td>
<td>450</td>
<td>131</td>
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<tr>
<td>11</td>
<td>Z15-P</td>
<td>15</td>
<td>–</td>
<td>537</td>
<td>75</td>
</tr>
<tr>
<td>12</td>
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<td>11</td>
<td>0.6</td>
<td>520</td>
<td>125</td>
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<tr>
<td>13</td>
<td>Z15-STm</td>
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<td>–</td>
<td>442</td>
<td>84</td>
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<tr>
<td>14</td>
<td>Z1000-P</td>
<td>961</td>
<td>–</td>
<td>395</td>
<td>53</td>
</tr>
<tr>
<td>15</td>
<td>Z1000-AT2TPABr</td>
<td>–</td>
<td>0.2</td>
<td>531</td>
<td>213</td>
</tr>
<tr>
<td>16</td>
<td>Z1000-AT2Al</td>
<td>70</td>
<td>0.2</td>
<td>515</td>
<td>137</td>
</tr>
<tr>
<td>17</td>
<td>Z1000-AT2TPABr-DI</td>
<td>617</td>
<td>0.2</td>
<td>572</td>
<td>220</td>
</tr>
<tr>
<td>18</td>
<td>Ga-MFI-P</td>
<td>20</td>
<td>–</td>
<td>378</td>
<td>59</td>
</tr>
<tr>
<td>19</td>
<td>Ga-MFI-AT2</td>
<td>17</td>
<td>0.2</td>
<td>371</td>
<td>116</td>
</tr>
<tr>
<td>20</td>
<td>Ga-MFI-AT2-AW</td>
<td>19</td>
<td>0.2</td>
<td>441</td>
<td>102</td>
</tr>
</tbody>
</table>

[a] P = parent, AT1-7 = alkaline treatment with 0.1-0.7 M NaOH, AW = acid washing with 0.1 M HCl, ST = steaming, AT2TPABr = NaOH treatment in the presence of Al(NO₃)₃ or tetrapropylammonium bromide, DI = dry impregnation with Al(NO₃)₃. [b] M stands for Al (entries 1-17) or Ga (entries 18-20), [c] Determined by the BET method. [d] Determined by the t-plot method.
Formic acid, acetic acid, and pyruvaldehyde have been identified as the main by-products beside LA. The DHA conversion increased, though to limited extent, upon application of alkaline solutions of higher concentration in the post-synthesis treatment. The changes in LA selectivity were more marked. The parent material presented a selectivity of 22%, which matches reported data. The LA selectivity progressively increased for the desilicated materials following the strength of the alkaline treatment and finally reaching a maximum of 80% for Z40-AT5. The latter is about four times the initial value and surpasses that attained with H-USY (Si/Al = 6) under similar conditions. Interestingly, a parallel can be drawn between the evolution of the selectivity to the desired product, the development of the \( S_{\text{meso}} \), and the amount of Lewis acid sites. On the other hand, this interdependence does not enable the clear identification of the parameter playing the dominant role in the control of the selectivity. Lewis acidity is expected to be relevant, but the introduction of mesoporosity, leading to a shorter diffusion paths to the micropores, could also affect the course of the reaction.

In order to decouple these two parameters, acid washing was applied to the best performing desilicated zeolite, Z40-AT5. Indeed, this treatment was demonstrated to preferentially remove the aluminum species located on the external surface of zeolites, while preserving their porous properties. Accordingly, \( S_{\text{meso}} \) and \( V_{\text{micro}} \) were retained (Table 1, entries 6,7) and the concentration of Lewis acid sites was significantly depleted (Fig. 1). This sample exhibited a moderately reduced DHA conversion, explained by the decrease in the total amount of acid sites, and, more remarkably, a strong depletion of the LA selectivity (32%) (Fig. 2). This unequivocally demonstrates that the formation of the LA product is driven by the Lewis acidity.

### Selective character of Lewis acid sites generated by alkaline treatment

Among the other post-synthesis treatments commonly used to tailor zeolites, steaming is extensively practiced in industry. This method generates EFAI species possessing a Lewis acid character, which appear to be active for the DHA isomerization to LA, as exemplified by the case of H-USY. Herein, we evaluated the performance of steamed H-ZSM-5 and compared it to that of alkaline-treated H-ZSM-5, ultimately aiming at elucidating the relationship between structure and activity of Lewis acid sites generated by means of these two treatments. Steaming at 873 K produced a material, Z40-STm, displaying a
different performances, the nature of the aluminum species is Z40-AT5 and even to Z40-P. Thus, as both the steamed and conversion over Z40-STm and Z40-STs was inferior compared to alkaline-treated sample was not matched. Furthermore, the DHA enhanced LA selectivity (60%). Still, the performance of the best introduction of EFAl, but significantly lower than the value this sample attained a LA selectivity of 36%, which is the moderately higher than for the parent zeolite, in consistency with with the aluminum incorporated species on the basis of NMR characterization remains introduction of EFAI, but significantly lower than the value disputable and debating the various hypotheses lies beyond the scope of this study. Nevertheless, these results clearly point out that the nature of realuminated species created during alkaline treatment and steaming is not equivalent, which result in a better performance for the former. Recent literature studies seem to shed some light on the actual nature of the Lewis acid centers formed by desilication. Holm et al.\textsuperscript{20} have indicated, based on an infrared study of adsorbed CO on alkaline-treated ZSM-5, that at least two distinct species are produced in the realumination process, of which one probably comprises a dimeric (Al(OH)\textsubscript{3})\textsubscript{2} species. DFT calculations by Ohshima et al.\textsuperscript{26} on the conversion mechanism of glyxolal to glycolic acid, reaction that proceeds through a 1,2-hydride shift as the DHA to LA conversion,\textsuperscript{6,7} suggested that protonated monomeric Al(OH)\textsubscript{3} species could efficiently catalyze this reaction. Since the nature, amount, or distribution of the Lewis acid sites created by the post-synthesis methods might be affected by the initial content of Al in the zeolite, the same experimental program was applied to H-ZSM-5 with Si/Al = 15 (Z15-P). As for the Z40 series, steaming of Z15-P did not appreciably increase its mesoporous area, while alkaline treatment determined a more consistent introduction of mesoporosity (Table 1, entries 11-13). It is worth noting that the crystallinity of Z15 was preserved to much larger extent upon desilication compared to Z40 (Figs. SI1-3). The higher stability of zeolites with lower Si/Al ratio in alkaline solutions of similar strength has already been highlighted.\textsuperscript{19} The catalytic trend of the Z15 family appeared substantially similar to that of the Z40 family (Fig. 3b). Still, the DHA conversion level for the parent zeolite already reached ca. 90% and, thus, less relevant variations were observed for the modified samples. Concerning the LA selectivity, the absolute values were overall higher: 55% for Z15-P, likely associated to an intrinsic content of EFAI, 81% for Z15-ST, and 92% for Z15-AT6. The latter LA selectivity is the highest attained in this study and it is comparable to the state-of-the-art catalyst (Sn-beta). In this respect, it has to be stressed that the catalytic tests in this work have been performed at a higher temperature than usually applied for tin-containing materials.

### Catalyst stability and recyclability

Stability and recyclability were investigated for our best zeolites. The XRD pattern of Z15-AT6 after the first catalytic run did not show any peak broadening, shift, or decrease in intensity, indicating remarkable stability. This is in contrast with the strong structural deterioration observed for USY-6 under comparable conditions.\textsuperscript{7a} The originally white catalyst powder turned black due to coke formation (ca. 8 wt.%, as determined by elemental analysis), which led to a partial blockage of the microporous volume and decrease in S\textsubscript{meso}. Still, upon removal of the carbonaceous deposits by calcination at 823 K for 5 h, the pristine porous properties were fully recovered. The DHA conversion (92%) and LA selectivity (92%) over this regenerated material were identical to those attained over the fresh zeolite (Fig. 5a). Upon a third run, the values dropped by ca. 20 and 10%, respectively, and further slightly decreased upon a fourth run. N\textsubscript{2} sorption and XRD analyses of the sample collected after the third cycle evidenced that the textural and structural properties were towards lower chemical shifts. These evidences are claimed to originate from the presence of distorted tetrahedral aluminum species.\textsuperscript{25} Furthermore, the generation of penta-coordinated aluminum, usually giving rise to a signal at around 30 ppm, cannot be excluded.\textsuperscript{25} Determining the exact nature of the aluminum species on the basis of NMR characterization remains unsolved, and the scope of this study. Nevertheless, these results clearly point out that the nature of realuminated species created during alkaline treatment and steaming is not equivalent, which result in a better performance for the former. Recent literature studies seem to suggest that the crystallinity of Z15 was preserved to much larger extent upon desilication compared to Z40 (Figs. SI1-3). The higher stability of zeolites with lower Si/Al ratio in alkaline solution has already been highlighted.\textsuperscript{19} The catalytic trend of the Z15 family appeared substantially similar to that of the Z40 family (Fig. 3b). Still, the DHA conversion level for the parent zeolite already reached ca. 90% and, thus, less relevant variations were observed for the modified samples. Concerning the LA selectivity, the absolute values were overall higher: 55% for Z15-P, likely associated to an intrinsic content of EFAI, 81% for Z15-ST, and 92% for Z15-AT6. The latter LA selectivity is the highest attained in this study and it is comparable to the state-of-the-art catalyst (Sn-beta). In this respect, it has to be stressed that the catalytic tests in this work have been performed at a higher temperature than usually applied for tin-containing materials.

![Figure 4](image-url)

**Figure 4.** (a) NH\textsubscript{3}-TPD profiles and (b) \(^{27}\text{Al MAS NMR spectra of Z40-P, Z40-AT5, and Z40-ST.}**
still retained, while IR studies of adsorbed pyridine indicated depletion in the concentration of Lewis acid sites by about one third with respect to the fresh Z15-AT6 zeolite (Fig. S14). It is likely that the rather strong acidity of the reaction product ($pK_a = 3.85$, pH of the mixture at the end of the run = 3) causes Al leaching. Owing to its efficacy in selectively removing Al species, an acidic treatment was indeed applied to Z40 as a means to prove the crucial role of Lewis acidity in this isomerization reaction. In order to enhance the stability of Z15-AT6, a 20 K lower reaction temperature was applied (393 K). The catalyst amount was simultaneously doubled to compensate for the expected decrease in activity. Under these conditions, the performance remained unaltered in 3 consecutive runs (Fig. 5b). Remarkably, the LA selectivity was identical to that observed in the tests at higher temperature and still relevant DHA conversion levels were attained (60-70%).

Reusability tests on Z40-AT5 led to a very similar trend to Z15-AT6 (Fig. 5c) and a comparable drop in Lewis acidity was detected for this zeolite. Accordingly, the deactivation process seems independent of the original Si/Al ratio of the zeolite.

Desilication by hydroxides of other alkali metals

The kinetics of dissolution of silica in alkaline media has been reported to increase in the order LiOH < NaOH < KOH, likely due to the fact that the charge density and, thus, the effective cationic diameter of the alkali metal decrease.\cite{30,31} Indeed, smaller cations better interact with the leached anionic silicon species. Application of these bases in the desilication of ZSM-5 with Si/Al = 35 also led to introduction of mesoporosity to different extents.\cite{32} Based on these results, we decided to investigate the effect of hydroxides of Group 1 metals on the generation of our selective Lewis sites. For this purpose, Z40-P was alternatively treated with 0.2 M solutions of LiOH, KOH, as well as CsOH. A higher $S_{\text{meso}}$ was obtained in the order with CsOH > KOH > LiOH (Table 2). The mesoporosity developed with NaOH is intermediate between KOH and LiOH (Table 1, entry 3). As expected, the LA selectivity over these materials was found to linearly scale with the $S_{\text{meso}}$ (Fig. 6). The value reached with Z40-AT2Cs (78%) is comparable to that obtained with Z40-AT5. As the amount of hierarchical zeolite recovered after the alkaline treatment in the former case is about twice as in the latter (54 versus 29%), CsOH could represent a more efficient alternative base for the introduction of the selective Lewis centers by desilication.

### Table 2. Characterization data of Z40 samples treated with MOH (M = Li, K, Cs) 0.02 M.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Si/Al</th>
<th>$S_{\text{BET}}$ [^{\text{a}}] (m(^2) g(^{-1}))</th>
<th>$S_{\text{meso}}$ [^{\text{b}}] (m(^2) g(^{-1}))</th>
<th>$V_{\text{micro}}$ [^{\text{c}}] (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Z40-AT2Li</td>
<td>33</td>
<td>519</td>
<td>205</td>
<td>0.14</td>
</tr>
<tr>
<td>2</td>
<td>Z40-AT2K</td>
<td>29</td>
<td>570</td>
<td>301</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>Z40-AT2Cs</td>
<td>28</td>
<td>565</td>
<td>360</td>
<td>0.10</td>
</tr>
</tbody>
</table>

[^{a}]: Determined by ICP-OES.  [^{b}]: Determined by the BET method.  [^{c}]: Determined by the t-plot method.

Alkaline-assisted alumination of silicalite-1

The presence of aluminum or gallium in the zeolite framework is known to control the mesopores formation during the desilication process.\cite{33} Alkaline treatment of highly siliceous ZSM-5 zeolites, such as silicalite-1, is not effective in generating mesoporosity.
achieved by realumination upon PDA-free desilication. We thus decided to investigate the potential of this treatment in the generation of performing catalysts for LA production. Z1000-P featured a mesoporous area of 53 m²g⁻¹ (Table 1, entry 14). Alkaline treatment with a 0.2 M NaOH solution did not determine any increase of the S_{meso} or change in the N₂ sorption isotherms (Fig. SI6a), as expected. On the contrary, desilication in the presence of tetrapropylammonium bromide or aluminum nitrate (0.006 M) as pore directing agent was effective in rendering a hierarchical material (Table 1, entries 15,16; Fig. SI6a). Still, due to the diverse propensity of the two cations to bind to the zeolite surface and drive the desilication process, the extent of mesopore formation was different. All samples lacking of aluminum, either microporous or hierarchical, did not produce any LA, while Z1000-AT2Al retained a LA selectivity of 50%. Upon raising the concentration of Al(NO₃)₃ in the alkaline solution up to 0.012 M, the LA selectivity increased to 72%. Higher molarities of the salt led to comparable values. At the same time, the S_{meso} steadily dropped (Fig. 7). These observations further substantiate the essential role of the Lewis acid centers and the less relevant effect of S_{meso} in LA production by DHA isomerization. The DHA conversion rose from 68 to 82% upon increasing the concentration of the Al salt, reaching comparable levels to those obtained with desilicated Z40 zeolites.

Upon reusing Z1000-AT2Al prepared in the presence of 0.012 M Al(NO₃)₃ in a second cycle, the selectivity was only ca. two thirds of the original value. The Si/Al ratio of the material after the first run decreased from 45 to 99, indicating substantial Al leaching. The lower stability of aluminated species with respect to the aluminum-substituted counterparts also suggests that the LA selectivity is retained. These findings further highlight the potential of post-synthesis modified zeolites for application to chemocatalytic conversion of bioderived dihydroxyacetone.

Extrapolation to Ga-MFI

The isomorphous substitution of aluminum with gallium has been shown to enhance the catalytic performance of H-ZSM-5 in several industrially-relevant processes such as the dehydrogenation-aromatization of light alkanes and alkenes to aromatics. Compared to their aluminum-containing analogues, gallium-substituted MFI zeolites feature a lower Bronsted-acid strength and have a high propensity to generate extraframework gallium species, which can be formed already upon calcination of the freshly prepared material. Li et al. have recently shown that also gallium-substituted MCM-41 attains superior selectivity in the production of ethyl lactate, at equal Si replacement, compared to the aluminum-substituted counterpart. These premises make it attractive to test Ga-MFI in the DHA to LA conversion.

The gallosilicate was successfully synthesized in the lab, as confirmed by XRD analysis (Fig. SI7), and its mesoporous form was proven to be active (Table 1, entries 18,19). Upon testing under the same reaction conditions as applied to the Z40 and the Z15 samples, the parent Ga-MFI attained a LA selectivity of 69%. This value is significantly higher than a H-ZSM-5 zeolite of comparable Si/Al ratio would be expected to provide, indicating that a considerable amount of extraframework gallium species was already present in the parent material. The alkaline-treated zeolite attained a LA selectivity of 87%. This suggests that desilication induced further gallium redistribution and/or modified the chemical nature of the existing extraframework species rendering them more selective. This value is close to that of our best aluminosilicate. Acid washing was again applied to prove the crucial role of the extraframework Lewis species. In order to retain the porous and structural characteristics of this more fragile material, the treatment was performed under milder conditions than for Z40-AT5. Still, the LA selectivity dropped to some extent (81%). Overall, these results indicate that also Lewis acid gallium sites can selectively drive the DHA isomerization and that, compared to an aluminosilicate, an equally performing gallosilicate can be obtained from a parent MFI zeolite with a higher initial Si/M ratio.

Figure 7. LA selectivity (dark grey bars) and S_{meso} (white bars) versus the concentration of Al³⁺ used in the alkaline treatment of Z1000-P.

Conclusion

In this study, desilication was demonstrated as a tool to modify the intrinsic acidity characteristics of MFI-type zeolites and, thus, confer improved catalytic performance in the production of lactic acid by isomerization of bioderived dihydroxyacetone. The realumination phenomena taking place during alkaline treatment were proved to afford Lewis acid sites which appear very selective for this transformation and cannot be attained by use of other common post-synthesis treatments such as steaming or impregnation of aluminum ions. Our optimized hierarchical material reaches the selectivity of the best performer for this reaction, Sn-beta, and can be reused in three consecutive runs. These findings further highlight the potential of post-synthesis modified zeolites for application to chemocatalytic conversion of
biorenewable resources. Furthermore, they uncover a new facet of the desilicitation process: the intrinsically generated aluminum-rich species formed simultaneously with the generation of intracrystalline mesopores can constitute catalytic centers with exceptional properties. In view of a practical application, future research efforts will be devoted to identify effective means to enhance the stability of these highly selective alkaline-treated zeolites.

**Experimental Section**

**Catalysts**

Three commercially available MFI-type zeolites have been used throughout this study: Z15 (CBV3024E, Zeolyst international), Z40 (CBV 8014, Zeolyst International), and Z1000 (HSZ-890H04A, Tosoh Corporation). The number in the Zx code indicates the nominal Si/Al ratio, according to the manufacturers’ specifications. Prior to their utilization, the zeolites were converted into the protonic form by calcination in static air at 823 K (5 K min\(^{-1}\)) for 10 h. Ga-MFI with a Si/Ga ratio of 20, was synthesized following to the protocol described by Mentzel et al.\(^{[25]}\) Thus, 26.52 g of tetrapropylammonium bromide (40 wt. %) were drop-wise added to a solution containing 2.108 g of NaOH in 68 g of H\(_2\)O. Separately, 1.674 g of Ga(NO\(_3\))\(_3\).H\(_2\)O were dissolved in 17 g of H\(_2\)O. The two solutions were simultaneously and drop-wise added to 68 g of tetraethylorthosilicate. The final mixture was stirred for 2 h. The obtained gel was transferred into a Teflon lined autoclave, placed in an oven, and heated to 453 K for 72 h. The product was filtered off, washed with deionized water, and dried overnight at room temperature (RT). The template was removed by calcination in static air at 823 K (5 K min\(^{-1}\)) for 10 h. Finally, the solid was converted into the protonic form by three consecutive ion exchanges in an aqueous NH\(_4\)NO\(_3\) solution (0.1 M, RT, 6 h, 100 cm\(^3\) per gram of zeolite) and calcined under the conditions indicated above.

These commercial and lab-prepared zeolites, referred to as parent (suffix P), were modified by various post-synthetic treatments. Alkaline-treated zeolites were obtained by treatment in an aqueous solution of NaOH (0.1-0.7 M, 30 cm\(^3\) per gram of zeolite) at 338 K for 30 min using an Easymax\(^{[11]}\) 102 reactor system (Mettler Toledo). Prior to the catalytic tests, the alkaline-treated samples were converted into their protonic form by three consecutive ion exchanges in an aqueous NH\(_4\)NO\(_3\) solution (0.1 M, 298 K, 12 h, 100 cm\(^3\) per gram of zeolite), followed by the above-described calcination step. Alkaline-treated samples are denoted by the suffix ATx, where x represents the first digit after the comma of the NaOH concentration used for the modification. Z1000 was also base-leached in the presence of tetrapropylammonium bromide (TPABr) or aluminum nitrate as pore directing agents, which were added in an amount corresponding to 0.006 M to the NaOH solution. When TPABr was used, an additional calcination step was required prior to conversion to the protonic form by ion exchange. Aluminum incorporation in this latter sample was achieved by means of subsequent dry impregnation with a 0.006 M aqueous Al(NO\(_3\))\(_3\) solution, followed by calcination in static air at 823 K (5 K min\(^{-1}\)) for 10 h. Accordingly, the Z1000-ATx codes were extended by TPABr, Al, or TPABr-DI. Selected alkaline-treated samples were subsequently acid-washed with an aqueous 0.1 M HCl solution at 338 K during 6 h. In the case of Ga-MFI-AT, the acid washing was performed at RT. The resulting zeolites are denoted by the suffix ATx-AW. Alkaline treatments were performed in 0.02 M solutions of other alkali bases, namely LiOH, KOH, and CsOH. The samples derived are indicated with the suffix AT2M, where M indicates the alkali cation. Steaming was carried out in a fixed-bed reactor (9 mm i.d.) with a shallow bed of zeolite powder at ambient pressure. The zeolite was treated in a flow of water vapor and N\(_2\) (30 cm\(^3\) min\(^{-1}\) N\(_2\), H\(_2\)O partial pressure 300 mbar) during 5 h at 873 or 1073 K. The steamed zeolites are denoted by the suffixes STm (mild) and STs (severe), respectively.

**Characterization methods**

The concentrations of Si, Al, and Ga in the samples were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) in a Horiba Ultra 2 instrument equipped with a photomultiplier tube detector. Nitrogen sorption at 77 K was performed in a Quantachrome Quadrasorb-Si gas adsorption analyzer. Prior to the measurements, samples were degassed in vacuum at 573 K for 3 h. Powder X-ray diffraction (XRD) was conducted in a PANalytical X’Pert PRO-MPD diffractometer. Data were recorded in the 3-60° 2θ range with an angular step size of 0.05° and a counting time of 8 s per step. Infrared spectroscopy measurements of adsorbed pyridine were performed in a Bruker IFS 66 spectrometer equipped with a liquid N\(_2\)-cooled MCT detector. Self-supporting zeolite wafers (5 tons cm\(^{-2}\), 20 mg, 1 cm\(^3\)) were evacuated under reduced pressure for 4 h at 693 K. After cooling down to RT, the samples were saturated by pyridine vapor and then evacuated at 473 K for 30 min. Spectra were recorded in the 4000-650 cm\(^{-1}\) range at 4 cm\(^{-1}\) resolution, by co-addition of 32 scans. Temperature-programmed desorption of ammonia (NH\(_3\)-TPD) was carried out in a Thermo TPDRO 1100 unit equipped with a thermal conductivity detector. The zeolite powder was pre-treated at 823 K in He flow (20 cm\(^3\) min\(^{-1}\)) for 2 h. Afterwards, 10 vol.% NH\(_3\) in He (20 cm\(^3\) min\(^{-1}\)) was adsorbed at 473 K for 30 min, followed by He purging at the same temperature for 1 h. This procedure was repeated three times. Desorption of NH\(_3\) was monitored in the range of 473-973 K using a heating rate of 10 K min\(^{-1}\).\(^{[25]}\) Al MAS NMR spectra were recorded at a spinning speed of 12 kHz in a Bruker AVANCE 400 NMR spectrometer equipped with a 4 mm probe head and 4 mm Z\(_2\)O rotors at 104.3 MHz. Spectra were measured using 4096 accumulations, 1 µs pulses, a recycle delay of 0.5 s, and (NH\(_3\))Al(SO\(_4\))\(_3\)·12H\(_2\)O as reference.

**Catalytic tests**

Catalytic tests were carried out batch-wise in 15-ml thick-walled glass vials (Ace\(^{6}\), pressure tubes, front seal) dipped in an oil bath at 413 K under autogenous pressure. The vials were loaded with 120 mg of dihydroxycetone (Sigma-Aldrich, 97%, dimer), 80 mg of catalyst, and 4 g of deionized water and the mixture was vigorously stirred for 6 h. After this time, the reaction was quenched in an ice bath and the catalyst removed by means of a Chromatik Xtra 0.45 μm syringe filter. The components of the reaction mixture were separated by high-performance liquid chromatography (HPLC) in a Merck LaChrom system equipped with a HPX-87H column heated at 308 K, using an eluent of aqueous 0.005 M H\(_2\)SO\(_4\) flowing at 0.6 mL min\(^{-1}\). Dihydroxycetone and lactic acid were quantified by means of a multi-wavelength diode-array UV/Vis detector, following the absorbances at 272 nm and 200 nm, respectively. The conversion of DHA was calculated as the moles of DHA reacted per moles of DHA fed, while the yield of LA as the moles of LA formed per moles of DHA fed. The selectivity to LA was determined as the ratio between the yield of LA and the conversion of DHA. Recyclability tests were performed over Z15-AT6 and Z40-AT5 under the same conditions described above. For the former catalyst, cycles were also carried out at a lower reaction temperature (393 K) with double the catalyst amount (160 mg). Prior to every reuse, the catalysts were calcined in static air at 823 K (5 K min\(^{-1}\)) for 5 h.

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**Keywords:** Biobased chemicals · Hierarchical zeolites · Isomerization · Lactic acid · Lewis acidity
Making the right site: Lewis acid centers generated upon desilication of commercial MFI zeolites in alkaline media catalyze the isomerization of dihydroxyacetone to lactic acid, competing with tin-containing zeotypes. This opens exciting perspectives for the use of hierarchical zeolites with tailored porous and acidic properties in biomass-to-chemicals conversions.
Figure S11. a) X-ray diffraction patterns and b) N$_2$ isotherms of Z40 in parent form and after different post-synthesis treatments.
**Figure S12.** Amount of Brønsted acid sites (probed by infrared of adsorbed pyridine) versus the mesoporous surface area of parent and NaOH-treated Z40 zeolites.

**Figure S13.** X-ray diffraction patterns of a) parent and steamed Z40 samples and b) parent, alkaline-treated, and steamed Z15 samples.
Figure S14. a) N₂ isotherms, b) X-ray diffractograms, and c) normalized IR spectra of adsorbed pyridine for Z15-AT6 in fresh form and after use in 3 consecutive catalytic runs.
**Figure S15.** X-ray diffractograms of Z40 after alkaline treatment with 0.2 M LiOH, KOH, and CsOH at 338 K for 30 minutes.

![X-ray diffractograms of Z40](image)

**Figure S16.** a) N\textsubscript{2} isotherms of Z1000 in parent form and after different post-synthesis treatments and b) X-ray diffractograms of Z1000 in parent form and alkaline-treated with a 0.2 M NaOH solution in the presence of 0.012 M Al(NO\textsubscript{3})\textsubscript{3}.

![Nitrogen isotherms and X-ray diffractograms of Z1000](image)
Figure SI7. X-ray diffractograms of parent and alkaline-treated Ga-MFI.
**Figure SI1.** a) X-ray diffraction patterns and b) N\textsubscript{2} isotherms of Z40 in parent form and after different post-synthetic treatments.
Figure SI2. Amount of Brønsted acid sites probed by infrared of adsorbed pyridine versus the mesoporous surface area of parent and NaOH-treated Z40 zeolites.

Figure SI3. X-ray diffraction patterns of a) parent and steamed Z40 samples and b) parent, alkaline-treated, and steamed Z15 samples.
Figure SI4. a) N₂ isotherms, b) X-ray diffractograms, and c) normalized IR spectra of adsorbed pyridine for Z15-AT6 in fresh form and after use in 3 consecutive catalytic runs.
Figure S15. X-ray diffractograms of Z40 after alkaline treatment with 0.2 M LiOH, KOH, and CsOH at 338 K for 30 min.

Figure S16. a) N$_2$ isotherms of Z1000 in parent form and after different post-synthetic treatments and b) X-ray diffractograms of Z1000 in parent form and alkaline-treated in aqueous 0.2 M NaOH in the presence of 0.012 M Al(NO$_3$)$_3$. 
Figure SI7. X-ray diffraction patterns of parent and alkaline-treated Ga-MFI.