Decarboxylation of Lactones over Zn/ZSM-5: Elucidation of the Structure of the Active Site and Molecular Interactions

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Abstract: Herein, we report the catalytic decarboxylation of γ-valerolactone (GVL) over Zn/ZSM-5 to butene, followed by aromatization at high yield with co-feeding of water. An evaluation of the catalytic performance after prolonged periods of time showed that a water molecule is essential to maintain the decarboxylation and aromatization activities and avoid rapid catalyst deactivation. Synchrotron X-ray powder diffraction and Rietveld refinement were then used to elucidate the structures of adsorbed GVL and immobilized Zn species in combination with EXAFS and NMR spectroscopy. A new route for the cooperative hydrolysis of GVL by framework Zn–OH and Brønsted acidic sites to butene and then to aromatic compounds has thus been demonstrated. The structures and fundamental pathways for the nucleophilic attack of terminal Zn–OH sites are comparable to those of Zn-containing enzymes in biological systems.

Currently, fuels and chemicals are mainly produced from non-renewable oil, coal, and gas. However, their depleting supplies, geographically uneven distributions, and associated CO2 emissions are of significant concern. As a result, identifying an alternative sustainable carbon source for the production of fuels and chemicals is of key importance for industry. In fact, biomass has long been regarded as a potential alternative to mitigate these problems. The currently low oil prices, as opposed to the high cost of processing biomass, do not yet offer immediate economic incentives. As a result, vigorous research activities are currently lacking. Lactones, such as γ-valerolactone (GVL), can be favourably produced from lignocellulosic biomass. However, only few catalytic studies on the conversion of lactones into useful products have been reported. By making use of the Brønsted acidic sites of SiO2-Al2O3, aqueous GVL can undergo ring opening and decarboxylation to form butene. After separation from water, butene gas can be processed into heavier alkenes (for fuels) with Amberlyst in a second catalyst bed. Following this work, the direct conversion of GVL into aromatic compounds as platform chemicals via butene without water has also been briefly studied over the Brønsted acidic sites in zeolites. However, the low liquid product yield and rapid catalyst deactivation posed technical problems. Furthermore, it would be advantageous to carry out the catalysis without the need for water separation (see the Supporting Information).

Here, we report that aromatic compounds can be produced in high yield from a GVL/steam mixture via butene at 450 °C by feeding an aqueous solution of GVL directly over Zn-modified ZSM-5. This process remains stable for at least 310 h. While we realized the interesting potential of this new chemical conversion process, we noted that Zn incorporation into H-ZSM-5 gives much superior catalytic activity compared to pure H-ZSM-5. We were thus interested in finding out how the Zn/ZSM-5 structure provides for such efficient conversion. It is interesting to note that nature also selects the element Zn to catalyze acid–base hydrolysis reactions in cellular and extra-cellular environments. This is due its high effective nuclear charge (Zeff) compared to the other transition metals, rapid water exchange, and no complications from the redox properties. For example, carbonic anhydrase (CA) enzymes containing Zn2+ are used to catalyze the reversible hydration of CO2. Similarly, Zn2+-containing β-lactamase (BL) enzymes can rapidly hydrolyze the lactam groups in penicillins. With the specific Zn structure in these enzymes, their turnover frequency can reach 103–105 s−1 (the diffusion rate limit of water), making them the most “active” and kinetically “perfect” of all enzymes.

Owing to the intrinsic shape and size selectivity as well as the single-site confinement, zeolite catalysts have long been regarded as “solid enzymes”. In addition, two or more catalytically active sites may work in a cooperative manner, giving rise to unusual properties. The introduction of Lewis metal ion sites into zeolites containing an excess of Brønsted acidic sites may create a synergistic effect in catalysis. In the present case, GVL contains a reactive lactone group with a carboxyl moiety that could be susceptible to ring opening as the first step in hydrolysis at these sites. To understand this new process, information on the structure of the active Zn sites with respect to the Brønsted acidic sites and their interactions with GVL in Zn/ZSM-5 is crucial.

Recently, the significant advancement of modern diffraction facilities with bright synchrotron radiation has provided chemists with a powerful tool for studying porous but
We have recently also reported the use of SXRD combined with 8teld refinement to elucidate the structures of organic adsorbates in zeolites. The alteration of the scattering parameters of the modified framework atoms by the molecules enables the probing of adsorption geometries and interactions with the Brønsted acidic sites in terms of atomic distances and angles. Thus the Zn environment and the adsorption geometry of GVL were elucidated by SXRD in combination with EXAFS and 1H MAS NMR spectroscopy. The obtained structures were compared to that of the “perfect” CAII enzyme with a view of rationalizing this unique catalytic process and providing insight for further improvement.

The Brønsted acidic sites in H-ZSM-5 may further catalyze the transformation of butene into aromatic compounds. Thus some pure and metal-modified ZSM-5 catalysts were tested with a flow reactor at SINOPEC (SRIFT) by feeding a continuous liquid flow of 40 wt% GVL/H2O with a weight hourly space velocity (WHSV) of 1.0 h⁻¹ to a catalyst zone at 450°C (with a preheated zone) under industrially applicable conditions. As seen in Figure 1a, the catalytic performances of some ZSM-5-based catalysts were compared (see also the Supporting Information, Section S2). The GVL conversions were generally found to be greater than 99% (complete conversion) within 12 h of reaction time for all of the catalysts studied (Figure S1b). For the unmodified H-ZSM-5 sample, the total selectivity for aromatic compounds (benzene, toluene, xylene (BTX) and higher-alkyl aromatic compounds) is about 62% with the light alkane/alkene selectivity reaching 38%. As stated, GVL can undergo ring opening and decarboxylation to initially form butene, but H-ZSM-5 alone appears to be insufficient to generate aromatic compounds with high selectivity. The addition of particularly Sn, Ga, and Zn can significantly increase the selectivity towards aromatic compounds at the expense of light alkanes/alkenes, presumably owing to the introduction of other active sites through the metal ion doping. Among the screened samples, Zn/ZSM-5 gave the highest selectivity towards aromatic compounds of 91.4%, which is about 30% higher than that of unmodified H-ZSM-5. The carbon balance was found to be 99 ± 1% while coke and gaseous products accounted for 2.4% and 7.2%, respectively, of the total carbon amount detected. The major gas-phase product was found to be 1-butene (4.8%; see Section S2).

Figure 1b shows the long-term evaluation of the catalytic performance of the Zn/ZSM-5 catalyst. There is a small but progressive decrease in GVL conversion over 310 h owing to “carbon” deposition but with a marginal change in the total selectivity towards aromatic compounds. Feeding the same amount of GVL in nitrogen without water results in a much lower yield for the aromatic compounds (ca. 50%). It also shows an extremely fast deactivation, indicating the important role of water in this catalyzed decarboxylation/aromatization reaction. As such an effect has not been reported in previous studies. Further investigations were conducted. The evaluation of the Zn/ZSM-5 catalyst under repeated, accelerated deactivation and reactivation steps (replacing the nitrogen carrier with air and calcining the sample at 600°C for 1 h) shows that the activity of Zn/ZSM-5 was totally restored (Figure S2). The high catalytic activity, good lifetime, and recyclability of Zn/ZSM-5 make it a promising candidate for the decarboxylation of lactones such as GVL in water in future bioprocessing applications. Perhaps there are a number of key questions that remain to be answered: Why does Zn²⁺ modification give the best activity for the formation of aromatic compounds via butene from GVL/H2O over the tested catalysts? How does the active site interact with GVL? Why does H2O appear to be essential for the catalysis? How do the structure and catalytic mechanism of the decarboxylation reaction by this Zn-containing zeolite differ from those of Zn enzymes in nature?

The structure of enzymatic catalysts and their pathways can be elucidated by growing single crystals of the corresponding enzyme structure and the substrate–enzyme complex. However, this process is not applicable to industrial powder zeolite-based catalysts even though they are regarded as “solid enzymes”. On the other hand, the structure of Zn/ZSM-5 and the substrate–active site interaction in the zeolite could provide important insight into the catalytic activity. As a result, SXRD combined with Rietveld refinement was used, for the first time, to monitor the coordination environment of the Zn species in the zeolite. The Zn environment reflects the nature of the interaction between Zn, the GVL molecule, and...
water during the first step of the aromatization over the Zn/ZSM-5 catalyst. All data were refined by the Rietveld method using TOPAS Academic Refinement Software (Bruker AXS, version 5; see Section S3).

First, upon comparing the SXRD patterns of fresh, unmodified H-ZSM-5 with and without Zn incorporation, it was observed that the relative intensities of the peaks were different for the two samples but there was no peak broadening or formation of other ZnO crystalline peaks (Figure S3). As mentioned in the Supporting Information, more than 4000 independent hkl reflections were used for the refinement calculations, which allowed for a greater number of structural variables to be refined in satisfactory manner. The quality of the Rietveld refinements of the SXRD data was confirmed by low R-weighted pattern (Rwp) values and goodness-of-fit factors (Tables S1–S5). The structural details and Brønsted acidic sites (at the framework T6 sites) of our H-ZSM-5 catalyst had already been characterized in our previous work.¹⁴ ¹⁵

Figure 2a (see also Figure S6) and the refinement result clearly show that the space group of fresh and regenerated Zn/ZSM-5 (after 310 h upon air treatment) was Pnma as for a typical H-ZSM-5. Two isolated Zn species with electron-rich regions were identified within the zeolite cavities. One Zn$^{2+}$ ion (named Zn-1) is located at the intersection of the sinusoidal and straight channels.

By including a hexaaqua Zn-1 species into the Rietveld refinement, a good fit with the experimental data was achieved. This entrapped Zn-1 with six equivalent non-framework O atoms as typical hexaaqua Zn$^{2+}$ gives rise to an average Zn–OH$_2$ distance of 2.12(3) Å (Table S6; see the Supporting Information for details). Its location in the porous cavity of Zn/ZSM-5 is likely ensured by the surrounding negatively charged framework oxygen atoms through electrostatic interactions by ion exchange with the Brønsted acidic sites. The site occupancy factor (SOF) of Zn-1 is 0.104(2). Taking the symmetry of the Pnma space group into account, there are 0.104 × 4 = 0.42 Zn-1 ions per unit cell of Zn/ZSM-5. Interestingly, a tetrahedrally coordinated Zn (Zn-2) attached to the five-membered ring of ZSM-5 through the wall oxygen atoms next to Al(T6) was also identified. The SOF of Zn-2 is 0.071(3), which corresponds to 0.071 × 8 = 0.57 Zn-2 per unit cell. Thus a total value of 0.99 Zn ions per unit cell is obtained, which is in agreement with the value derived from ICP-MS of 0.97 Zn per unit cell. The k$^*$-weighted Fourier-transformed EXAFS data of fresh Zn/ZSM-5 were measured at the Zn K-edge, using ZnO as a standard (Table 1 and Figure S7). A k$^*$/k$^3$/k$^5$ fitting procedure in k- and R-space was carried out to identify the presence of any Zn-O or Zn-Zn interactions in the first shell and Zn-O interactions in the second shell. The fitting result gives the averaged bond length and coordination number (CN) of Zn/ZSM-5. It is clear that the average bond length of 2.07(1) Å is related to the backscattering from oxygen atoms to directly bonded Zn. There is no evidence for the possible Zn–Zn nearest bond distance of 2.3 Å or second-shell Zn–O distances of 3.0 Å in the ZnO lattice in the Zn/ZSM-5 EXAFS spectrum. This result undoubtedly indicates that the Zn species in Zn/ZSM-5 are isolated without any ZnO aggregates or clusters, which is consistent with the SXRD result. The average CN of 5.2(2) from the EXAFS data matches the calculated average CN of 4.8(2) derived from 57% four-coordinate Zn (Zn-2) and 42% six-coordinate Zn (Zn-1) ions, according to the SOFs of the SXRD refinement. In addition, the derived Zn–O distance of 2.07(1) Å or 2.06(1) Å from the EXAFS data is close to the average bond length of 2.11(2) Å of the two Zn species from the SXRD data (Tables S2–S6).

According to the refined structure of the tetrahedral Zn-2 site surrounded by four oxygen atoms (Figure 2a), it is clear that this Zn$^{2+}$ is directly immobilized by the framework oxygen atoms O6, O18, and O9 following the ion exchange and subsequent calcination of Zn/ZSM-5. The derived bond lengths of Zn-2–O6, Zn-2–O18, and Zn-2–O9 are 1.92(2), 1.95(2), and 2.19(3) Å, respectively, from the SXRD and refinement. Although H atoms cannot be located by SXRD

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Table 1: Comparison of the refined structural models from SXRD and best-fit EXAFS
data.¹⁴

| Zn/ZSM-5 catalyst | CN$_{\text{SXRD}}$ | CN$_{\text{EXAFS}}$ | R$_{\text{EXAFS}}$ | Debye–Waller | E$_{\text{ref}}$ | eV |
|-------------------|------------------|-------------------|---------------|--------------|-------------|
| fresh Zn–O        | 5.2(2)           | 5.0(1)            | 2.11(2)       | 2.06(1)      | 0.009(1)    | 4.6|
| regenerated Zn–O  | 4.8(2)           | 5.2(2)            | 2.11(2)       | 2.07(1)      | 0.007(1)    | 3.4|

[a] Statistical errors given in parentheses. CN = coordination number, R = derived atomic distance (see Section S4).
owing to their low electron density, the remaining non-framework oxygen atom at a distance of 2.32(5) Å to Zn was identified to be in the form of Zn–2–O(H) by 1H NMR and Raman spectroscopy (see below). Thus the hydrated Zn$^{2+}$ ion loses some of its coordinated water molecules after ion exchange and calcination and is then immobilized onto the framework oxygen atoms. The formation of the terminal Zn–OH in its immobilized form initially looks puzzling as Zn$^{2+}$ itself cannot activate water molecules at moderate temperatures.

Nevertheless, if formed, the strong nucleophilicity of terminal Zn–OH$^{2-}$ (i.e., the new active site) can result in attack at the carbonyl group of GVL. Through ring opening, CO$_2$, butene, and water are then produced. This offers an alternative to the simple acid hydrolysis route by the Brønsted acidic sites (framework or extra-framework), which equally leads to the generation of butene and CO$_2$. We observed higher rates and selectivities for GVL conversion into aromatic compounds via butene over Zn/ZSM-5 than over H-ZSM-5 (Figure 1). This finding clearly suggests that Zn–OH species are more active and selective for such processes. However, we cannot exclude the possibility that the interaction of GVL with Zn-1 (presumably via one of its coordinated saturated H$_2$O ligands) may also contribute to the overall catalytic activity. This is due to the fact that our approach cannot detect non-crystalline GVL-Zn-1 and hence cannot rule out their existence. It is however envisaged that despite the polarization by Zn$^{2+}$, the non-dissociated H$_2$O molecule is a weaker nucleophile than Zn$^{2+}$–OH$^-$ for the rapid GVL attack. Similarly, without the presence of Zn$^{2+}$, the Brønsted acidic sites (BAS) are also unable to polarize a water molecule to OH$^-$ and H$^+$. The key question is how these Zn–OH sites can be regenerated during the catalysis with water co-feeding. It should be noted that the terminal Zn–OH groups are located adjacent to the original Brønsted acidic sites in other unsymmetric units (T6). Previous DFT calculations indicated that one of the coordinated water molecules on divalent metal cations such as Zn$^{2+}$ can dissociate when they are introduced into the framework of H-ZSM-5 by ion exchange. This water dissociation is energetically favored, resulting in the formation of a hydroxy group bonded to the metal cation and a regenerated proton residing on a nearby ionized Brønsted acidic site (see the Supporting Information for further information). Thus a cooperative dissociative activation of a water molecule that regenerates Zn–OH with a deprotonated Brønsted acid site to complete the catalytic cycle is plausible, based on our structural findings.

Figure 2b depicts the crystal structure of GVL adsorbed on Zn/ZSM-5 determined by SXRD and Rietveld refinement. Despite the fact that there are two Zn species (i.e., Zn-1 and Zn-2) in our Zn/ZSM-5 catalyst, the carbonyl group of a GVL molecule only aligns itself to the terminal hydroxy group of Zn-2. A closer inspection of the adsorption geometry (Figure 2c) suggests the formation of a strong dative bond between the GVL and Zn–OH with a short O–C$_{\text{carbonyl}}$ distance of 1.82(4) Å. In contrast, no interaction of GVL with Zn-1 species was found in this structure. We also note that the Zn–OH at the Zn-2 site in Zn/ZSM-5 is structurally comparable to the active site of the CA II enzyme (Figure S4d, PDB No. 1CA2). The active Zn$^{2+}$ site is similarly tetrahedrally coordinated, but with three histidine groups and a terminal O(H). During biocatalysis, the hydroxy group of the amino acid at site 199 near the Zn$^{2+}$ is known to activate the incoming water molecules. Hence, terminal Zn–O(H) and H$^+$ are formed through hydrogen bonding interactions. They have an analogous proton-accepting role as our ionized T6 site in a similar atomic spatial position in Zn/ZSM-5, as previously discussed. The nucleophilic OH$^-$ can then attack CO$_2$ to form a Zn hydrogen carbonate species. Thus this enzymatic Zn$^{2+}$ catalyzes the conversion of CO$_2$ and H$_2$O into HCO$_3^-$ and H$^+$ with extremely high TOFs.

Figure 2d shows the published crystal structure of the T199A CAII enzyme–CO$_2$ complex from the crystal database of the National Center for Biotechnology Information. Interestingly, the adsorption geometry of GVL in the zeolite by the terminal Zn–OH as shown in Figure 2c and the configuration of the Zn-containing enzyme–CO$_2$ complex are alike. Scheme S2 (Section S8) shows the proposed mechanism for butene production by cooperative ring opening and hydrolytic decarboxylation of GVL and water activation over Zn/ZSM-5, followed by regeneration of Zn–OH and Brønsted acidic sites. As seen in the proposed mechanism (Sections S8–S10), a water molecule directly participates in the hydrolysis for the decarboxylation of GVL, in a similar manner to that seen in the “perfect” Zn enzymes. This mechanism is consistent with our labeling experiment showing the formation of C$_{14}$H$_{16}$O$_2$ when H$_2$O was used (Section S5). Thus water is not only required to reduce “carbon” deposition, but also acts as a catalyst to produce CO$_2$ and butene from GVL over the Zn–OH and Brønsted acidic sites in a cooperative manner. Butene, once formed, is known to undergo aromatization over H-ZSM-5-based materials to give aromatic compounds; this has been well studied and will not be further discussed.

As mentioned, the Zn/ZSM-5 catalyst is a typical micro-porous acidic zeolite. It exhibits slow but progressive deactivation over 310 h of on-stream testing. However, the deactivated Zn/ZSM-5 catalyst can be fully regenerated through calcination in air at 600°C for 1 h. The same concentration of Zn (0.99 Zn per unit cell) was obtained, by adding up the SOFs of Zn-1 and Zn-2 (Table S5). Similarly, the derived coordination numbers and corresponding Zn–O distances from SXRD refinement and EXAFS (Table 1 and Table S6) of the regenerated sample also clearly indicate the structural integrity of the active sites in Zn/ZSM-5 after prolonged testing (see Sections S6 and S7 and Figure S9). The structure and ability for nucleophilic attack of Zn/ZSM-5 and Zn-containing enzymes resemble each other. This suggests that immobilized tetravalent Zn$^{2+}$ ions with terminal hydroxy groups are the common active sites.

However, they should not be taken for a direct like-for-like comparison in terms of the mechanism. The initial step of nucleophilic attack at GVL by Zn–OH during hydrolysis requires a bond cleavage with a higher activation barrier than that of the dehydration/hydration of the more labile CO$_2$ in the enzymatic reaction without bond cleavage. In addition, the Zn$^{2+}$ is immobilized by the “O” ligands (Si–O–Si) of the
rigid zeolite framework. It is hence electronically and structurally different from those supported by the flexible prosthetic hydrophobic protein chain in the case of Zn-containing enzymes. We understand that even if this heterogeneous catalyst contains sites that are geometrically akin to enzymes, the reaction temperature, conditions, interactions with the framework, and adsorption and desorption processes still make this system significantly different. Nevertheless, the tetrahedral structure of Zn-2 with a terminal nucleophilic Zn–OH for hydrolysis and its regeneration by a neighboring H+ acceptor site, which activates a water molecule in a cooperative manner, is clearly comparable in both cases. It is also noted that the nucleophilicity of M–OH over our tested catalysts follows the order of Zn > Ga > Sn. This trend can be rationalized by the order of their electronegativities: Zn(1.65) < Ga(1.81) < Sn(1.96). Hence, the electron density of the "O" atom of the M–OH group follows the trend Zn–OH > Ga–OH > Sn–OH.[5a] As the regenerative formation of nucleophilic Zn–OH by GVL and water in this enzyme-mimetic Zn/ZSM-5 is a key feature, it is crucial to experimentally confirm the existence of the Zn–OH active site. Figure 3a shows five resolved 1H MAS NMR resonances of fresh Zn/ZSM-5 at 1.21, 1.88, 2.66, 4.15, and 5.61 ppm, which were assigned to Zn–OH, Si–OH, Al–OH, H+ of Brønsted acidic sites, and the H atoms of H2O adsorbed on Brønsted acidic sites, respectively. The latter four resonances have been previously detected in various aluminosilicate-based zeolites[22] but the former peak is due to the characteristic Zn–OH in Zn/ZSM-5.[23] Raman spectroscopy was also employed to study the structure of GVL adsorbed on Zn/ZSM-5. Figure 3b shows a much larger and broader peak with Raman frequencies of 1100–2240 cm⁻¹, which encompasses the C=O vibration of GVL at about 1600 cm⁻¹ and symmetric O–C–O stretches at 1360 cm⁻¹ upon GVL adsorption on Zn/ZSM-5. In addition, the A₁(TO) mode of Zn–O at 374 cm⁻¹[25] is clearly visible upon adsorption of GVL on terminal Zn–OH in Zn/ZSM-5.

In conclusion, by combining SXRD with Rietveld refinement, we were able to show that the Zn–OH motifs in Zn/ZSM-5 can adsorb GVL via a strong Lewis acid–base interaction. The regenerative Zn–OH sites and neighboring Brønsted acidic sites in H-ZSM-5 work in a cooperative manner by dissociative adsorption of water molecules. They provide new catalytically active sites for a cascade of reactions to form aromatic compounds via butene. The structure and mechanism for the nucleophilic attack of the active Zn–OH site are comparable to that of the CA II enzyme. Hence, the Zn/ZSM-5 catalyst can be regarded as an efficient "solid enzyme" for this reaction. Thus the immobilized Zn²⁺ ions may provide inspiration to the chemical industry as to how to harness biomass to produce useful products.

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**Conflict of interest**

The authors declare no conflict of interest.

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