

Theoretical Insights into the Conversion of γ -Valerolactone to Butene Over γ -Alumina

A Thesis

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Master of Science

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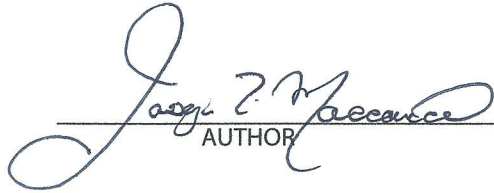
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Abstract

The catalytic conversion of γ -valerolactone (GVL) over γ -alumina which is comprised of Lewis acid sites results in the formation of 1-butene with a high initial selectivity but drops as a function of residence time and due to the formation of 2-butene. First principle density functional theory (DFT) calculations were carried out to examine the nature of the active sites on the (100) surface of γ -alumina, specifically the tri-coordinated or tetrahedral aluminum atoms and the elementary steps involved in the general reaction pathways. The reaction mechanism is thought to follow a sequence of Lewis acid catalyzed elementary steps involving the adsorption and ring opening of GVL to form a γ -carbenium intermediate and subsequent deprotonation to form adsorbed 3-pentenoic acid. The reprotonation of the bound 3-pentenoic acid at the γ -carbon leads to the formation a stable β -carbenium intermediate. The β -carbenium ion intermediate can readily undergo decarboxylation via retro-Diels-Alder (rDA) reaction to form 1-butene. The reaction proceeds with a very high selectivity to form 1-butene. This is due to high selectivity of activating GVL to form adsorbed 3-pentenoic acid over that of the 4- or 2-pentenoic intermediates which would result in the formation of 4-pentenoic acid and 2-pentenoic acid intermediates as well as to the elimination of olefin isomerization over γ - Al_2O_3 in the presence of water.

Introduction

γ -Valerolactone (GVL) can be sustainably produced by the conversion of waste biomass to levulinic acid and the subsequent reduction of levulinic acid over supported Ru catalysts with yields of GVL of greater than 95%.^[1] GVL can be used directly as a solvent or a gasoline blending agent or converted to a range of other products including acrylic polymers, dimethyl adipate and methyl tetrahydrofuran. As such GVL is an important platform chemical intermediate.^[2] Recent experiments have shown that GVL can be converted to 1-butene with high selectivity over γ -alumina. At longer residence times, however, the selectivity to 1-butene is significantly reduced due to the subsequent reactions of 1-butene to 2-butene and by retroaldol reactions that convert GVL to 2-butene as along with acetic acid and propanal, respectively.^[3] For reactions carried out over $\text{SiO}_2\text{-Al}_2\text{O}_3$, which is comprised of both Brønsted and Lewis acid sites, the overall butene yield is ~90% but the selectivity to the 1-butene product is only ~25%. While the overall yield of butene over γ -alumina comprised of Lewis acid sites is lower at ~42%, the selectivity to 1-butene is ~90% which is significantly higher than that on $\text{SiO}_2\text{-Al}_2\text{O}_3$. The high selectivity of GVL to 1-butene over $\gamma\text{-Al}_2\text{O}_3$ demonstrated by Dumesic et al.^[4] may prove to be a valuable route for the production of α -olefins.

The higher conversions and low selectivity over $\text{SiO}_2\text{-Al}_2\text{O}_3$ along with the high selectivity and lower yields over γ -alumina suggests that Brønsted acid sites can readily ring open GVL but are unable to control isomerization and other pathways that ultimately yield much lower product selectivity. The lower yields and high selectivity for the reaction carried out over γ -alumina indicate that Lewis acid sites are less active but

provide much stricter control of the subsequent reactions and thus higher product selectivity to 1-butene versus unsaturated acid byproducts such as 2-, 3-, and 4-pentenoic acid.

The conversion of GVL to butene is thought to proceed by the adsorption of GVL to the Lewis acid Al center followed by the activation of the C γ -O bond and ring opening. Bond et al. proposed that ring opening results in the formation of an unsaturated carboxylic acid intermediate that can desorb or further react on the surface.^[5] β , γ unsaturated acids are known to readily undergo decarboxylation thus resulting in the formation of the corresponding α -olefin as the primary product.^[6, 7] Chia et al. showed that the location of the double bond at the 3-4 or β - γ position in the unsaturated carboxylic acid is important for decarboxylation and the high selectivity to form the α -olefin.^[8] Despite our general understanding of the possible reaction paths, little is known about how these reactions proceed and the role of Lewis acid sites.

Density functional theory (DFT) calculations were carried out herein along with kinetic analyses to examine the general reaction paths and reaction mechanisms. The reaction is thought to proceed via three general steps that include the ring opening of GVL, the decarboxylation of intermediates and the isomerization steps. The balance of these paths control the selectivity to different products. The results suggest that the activation and ring opening of GVL ultimately results in the formation of a β -carbenium ion intermediate that is critical in controlling the selectivity to the 1-butene product.

Recent Experimental Results

Recent experiments carried out by the Dumesic group at the University of Wisconsin (Madison) demonstrated that the conversion of GVL over γ -alumina results in ~90% selectivity to 1-butene as is shown in Figure 2. The yield and selectivity for this reaction at different reactor residence times carried out over $\text{SiO}_2\text{-Al}_2\text{O}_3$ as well as γ -alumina are also summarized in Figure 2. The reactions were carried in a fixed bed heated to 375 °C with a 30 wt% GVL in water feed stream. They reported experimental butene yields of over 40% and selectivities of 1-butene at 92% at a weight hourly space velocity of 0.18 h^{-1} without any optimization of the γ -alumina catalyst.^[4]

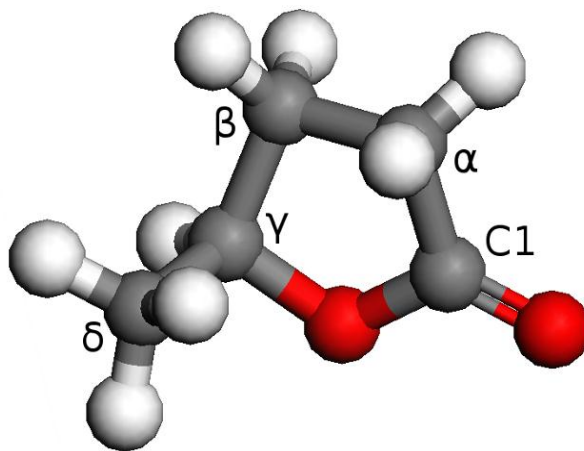


Figure 1: γ -valerolactone with carbon atoms labelled. Carbon atoms are gray, oxygen atoms red, and hydrogen atoms white.

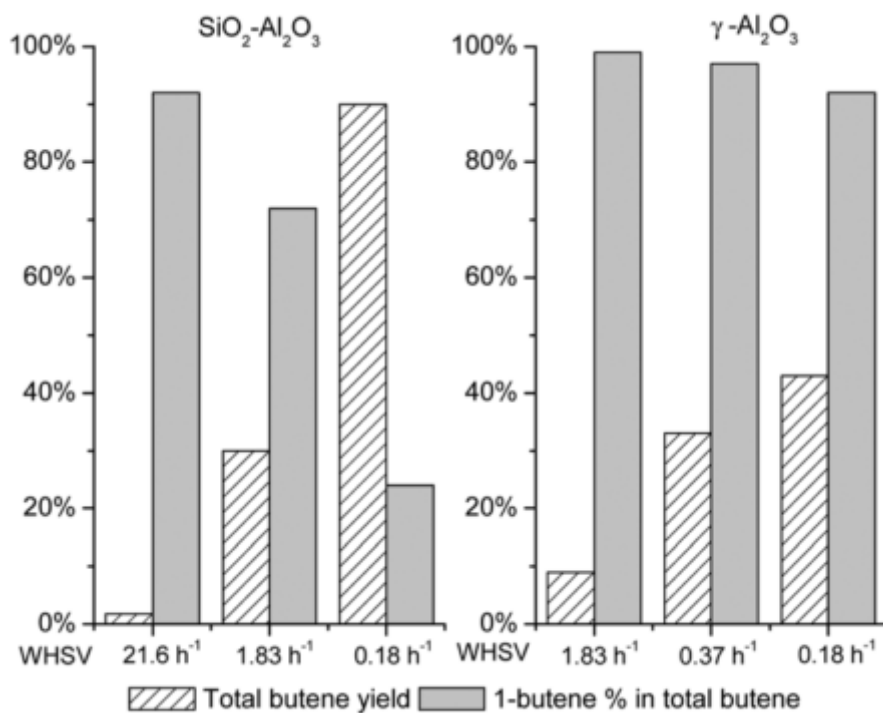


Figure 2: Experimental butene yield and 1-butene selectivity results of reacting GVL over both $\text{SiO}_2\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3$.^[4]

Potential Reaction Pathways

A series of elementary paths were suggested to help explain the resulting products that formed. Wang et al. proposed that the reaction proceeds by the adsorption and ring-opening of GVL to form 3- or 4-pentenoic acid which subsequently isomerizes to form 2-pentenoic acid. The 2-pentenoic acid can then decarboxylate via the formation of a β -carbenium ion intermediate to form 1-butene and carbon dioxide.^[4] This path is illustrated in Figure 3.

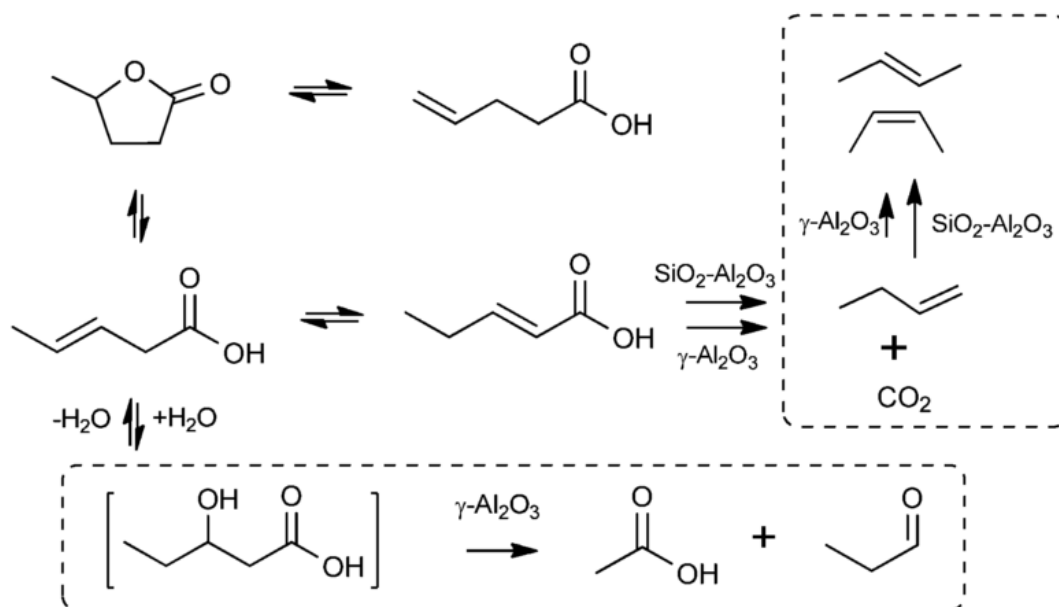


Figure 3: Wang *et al.* proposed reaction pathway.^[4]

A second path for the acid catalyzed ring opening and decarboxylation of GVL was suggested by Bond *et al.* This path proceeds via the adsorption and ring opening of GVL ring opening to form the γ -carbenium ion intermediate that subsequently deprotonates to form 3-pentenoic acid. The 3-pentenoic acid can then be reprotonated to form the β -carbenium which readily decarboxylates to form 1-butene and carbon dioxide as is illustrated in Figure 4 (Pathway 1).

Bond, *et al.* proposed a third path which involves the acid catalyzed ring opening of GVL to form the γ -carbenium followed by a hydride shift to form the β -carbenium. The β -carbenium ion intermediate can then readily decarboxylate to form 1-butene and carbon dioxide^[5] as is illustrated in path 2 Figure 4.

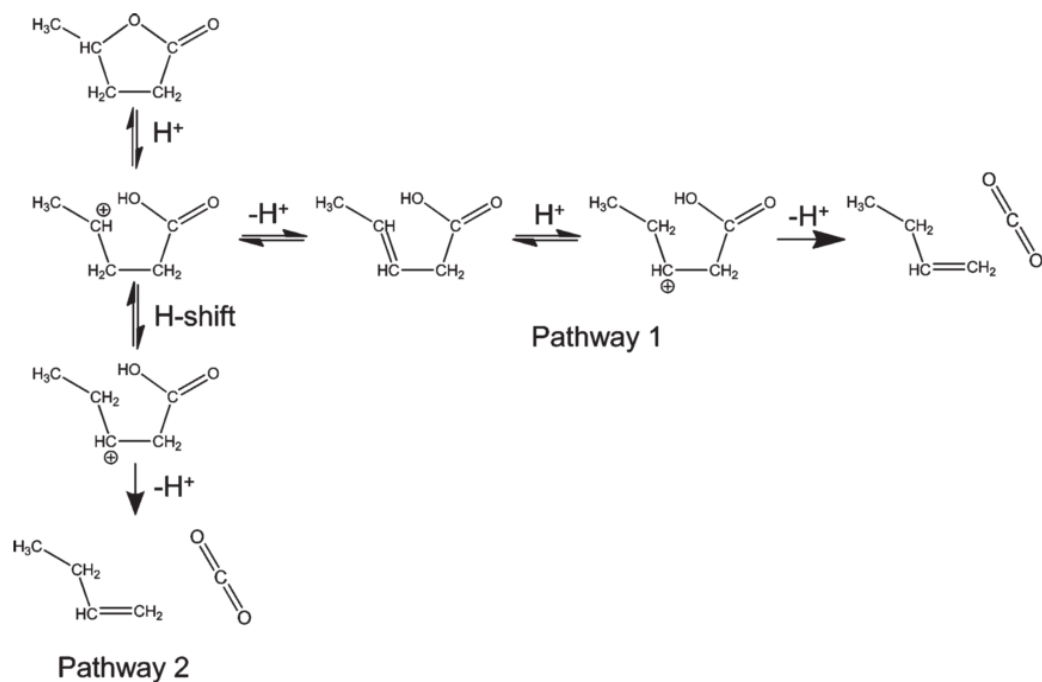


Figure 4: Additional reaction pathways proposed by Bond et al.^[5]

While each of these paths results in the formation of 1-butene, the lowest energy path is unknown. Experimental evidence for the ring opening and decarboxylation of β -lactones suggests a mechanism involving a zwitterion or β -carbenium intermediate.^[9,10]

In this work we use first principle density functional theory (DFT) calculations to examine different plausible elementary reaction steps potentially involved in the conversion of GVL to 1-butene over γ -alumina, possible reaction mechanisms and the role of specific sites on the surface for carrying out catalysis. The work was carried out in collaboration with experimental efforts from Professor James Dumesic's group at the University of Wisconsin. While the experiments are carried out with GVL in water,^[4] the calculations presented here do not include explicit water molecules or their influence on the reaction mechanism. This is forthcoming and part of future work. A discussion on

the potential role of water on the activity and selectivity is included in the conclusions and future work portion of this document.

Surface of γ -Alumina

The bulk structure of γ -alumina does not have a well ordered crystal structure. It is heterogeneous in nature and as such is not strictly periodic.^[11] The structure often contains defects and inclusions and disorder which are difficult to fully capture. More simplified periodic structures, however, have been developed to begin to simulate important structural aspects of γ -Al₂O₃. A simplified model that simulated the dehydration of alumina salt solution was developed by Krokidis, et al.^[11] and further refined by Digne to simulate different properties of the γ -Al₂O₃ surface.^[12] We use the same approach here to simulate the catalytic properties on the alumina surface.

The Al₂O₃ cell structure was established by simulating the dehydration of an aluminum oxide mother solution into boehmite and then further carrying out the dehydration of boehmite, along with the collapse of its matrix, via calcination as illustrated in Figure 5 to achieve a representation of the spinel-like periodic unit cell of γ -alumina. The table of values in Figure 6 lists the resulting locations of the atoms within the cell along with the cell geometry and symmetries. The structure represented in Figure 6 is the result of programming this structure into the Material Studio software code. While the model does not treat different defects, inclusions or the amorphous nature of the structure, it appears to capture the local structure of γ -Al₂O₃ and provides good agreement between experimental and calculated data^[11,12] thus making it useful in probing trends in the catalytic reactivity on the surface of γ -alumina and the effects of

changes in structure and surface composition. The resulting rhombohedral particle crystals of γ -alumina upon calcination of boehmite are formed with the (110), (100), and (111) surfaces exposed with the (110) surface making up the majority of particle surface area.

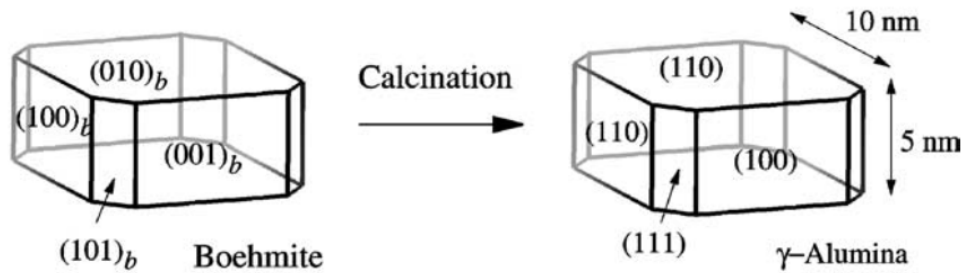


Figure 5: Calcination of boehmite to γ -alumina resulting in (111), (100), and (110) exposed faces.^[12]

Table of Values		
Crystallographic Structure of bulk γ -alumina [9]		
Space Group	P21/m	
a(Å)	5.587	
b(Å)	8.413	
c(Å)	8.068	
β (°)	90.59	
Atom	Position	(x,y,z)
Al	2e	(0.377,0.750, 0.126)
Al	2e	(0.868,0.250,0.498)
Al	2e	(0.875,0.750,0.125)
Al	2e	(0.615,0.750,0.745)
Al	4f	(0.367,0.075,0.612)
Al	4f	(0.116,0.579,0.862)
O	2e	(0.881,0.750,0.874)
O	2e	(0.614,0.250,0.640)
O	2e	(0.364,0.750,0.889)
O	2e	(0.132,0.250,0.627)
O	4f	(0.889,0.406,0.899)
O	4f	(0.605,0.917,0.614)
O	4f	(0.357,0.406,0.853)
O	4f	(0.138,0.916,0.637)

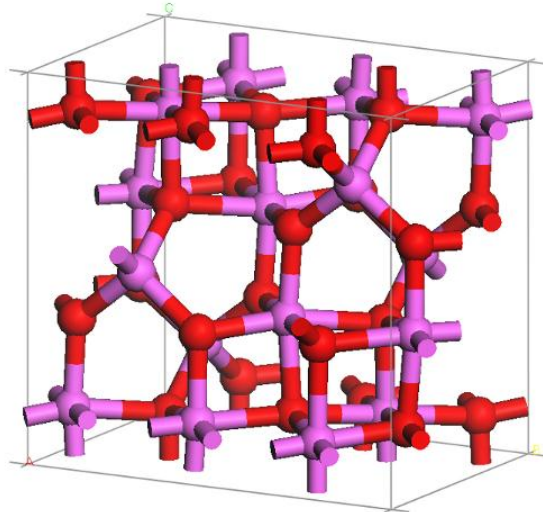


Figure 6: Table^[12] of the crystallographic structure and the atomic coordinates for the model γ -alumina periodic cell used for computational simulation. Red atoms are oxygen, violet atoms are aluminum.

With a unit cell and the Miller indices of the exposed surfaces defined, the local atomic structures of the surfaces were modeled using VASP to optimize (relax) each surface structure of interest upon cleaving the cell to produce the indicated surfaces. The calculated Miller indices and the optimized structure for the bulk γ - Al_2O_3 were used to build models for the different exposed surfaces.

The optimized bulk γ -Al₂O₃ structure was cleaved along different planes and exposed to vacuum to provide models of different single crystal surface of γ -Al₂O₃. The structures of these surfaces were then optimized using periodic density functional theory methods discussed below. These surfaces provided model Lewis acid and Lewis base sites that were used to examine the different pathways involved in the conversion of GVL.

In this work we specifically examine the reactivity of GVL on the low energy γ -Al₂O₃ (110) and (100) surfaces. The (111) surface was not examined as it terminates with a non-reactive oxygen layer that cannot contribute to the chemistry. In addition the surface area of the (111) surface makes up only a very small percentage of the total exposed surface area of a γ -alumina particle.

Computational Methods

First principle density functional theory calculations were carried out herein to provide insight into the elementary steps and the plausible mechanisms for the conversion of GVL to 1-butene over the model catalytic γ -alumina surfaces. The calculations performed were roughly divided into two sets. The initial set of calculations was used to determine the active sites on the surface of γ -alumina by analyzing the properties of the stable Lewis acid/base pairs that are present on the surface. The remaining calculations were focused on modeling the chemistry of the reaction on the surface of the periodic cell at the most stable surface sites identified in the initial set of calculations. While we do not examine the detailed reaction chemistry at each site on the model γ -alumina, this two-step approach provides a useful strategy to examine the low energy paths from GVL to 1-butene and carbon dioxide on the most probable sites on the γ -Al₂O₃ surface.

Surface/Site Determination and Adsorption Energies

All of the calculations reported here were carried out using periodic plane wave density functional theory calculations as implemented in VASP by Kresse and Hafner.^[13] The calculations were carried out using the projector augmented-wave (PAW) method as a pseudopotential^[14] to economically simulate electronic potential and the Perdew-Wang-91 (PW91) functional for consistency with previous work and as an approximation to model the corrections to the exchange and correlation energies.^[15] The wavefunctions were constructed from periodic plane-wave expansions out to a kinetic energy cutoff of 396 eV. A single gamma-point was used to sample the first Brillouin zone. The wavefunctions were converged to a tolerance of 1×10^{-6} eV, while the geometric structures were optimized until forces on each atom were < 0.05 eV \AA^{-1} .

The first set of DFT calculations was used to model the structure of γ -alumina to facilitate determination of the most active surface and the sites where reactions can proceed. The (100) and (110) surfaces were cleaved from the bulk γ - Al_2O_3 unit cell and a 15 \AA vacuum region was placed between these surface slabs. The surfaces were then optimized for the (100) surface. A periodic surface cell with lattice dimensions ($a \times b \times c$) 10.099 $\text{\AA} \times 8.068 \text{\AA} \times 22.422 \text{\AA}$ and angles measuring (α, β, γ) 90.0°, 90.0°, and 90.3° resulted. For the (110) surface, a periodic surface cell with the dimensions ($a \times b \times c$) 8.413 $\text{\AA} \times 8.068 \text{\AA} \times 22.1682 \text{\AA}$ and angles measuring (α, β, γ) 90°, 90°, and 90° resulted. Any atoms with a fractional z dimension less than 0.16 were frozen so that they were not allowed to move during computations, more accurately simulating a crystal with structure extending below the simulated periodic cell.

The optimized γ -Al₂O₃ surfaces were subsequently used to examine the adsorption of GVL to different sites on the surface. GVL preferentially adsorbs via its oxygen to exposed Lewis acid sites on the surface where there is strong stabilization of the negative charge on the oxygen and the positive charge on the Al cation. The adsorption energy of GVL at each of the different exposed Al sites in the surface is calculated via equation 1:

$$\Delta E_{\text{ads}} = E_{\text{gas+surface}} - (E_{\text{gas}} + E_{\text{surface}}) \quad (1)$$

where $E_{\text{gas+surface}}$, E_{gas} and E_{surface} refer to the energies for the adsorbed species on the γ -Al₂O₃ surface, the gas phase adsorbate, and the γ -Al₂O₃, respectively.

The Al sites with the lowest adsorption energies were considered the most stable adducts and species most likely to undergo ring opening. As such these sites were chosen to carry out the full series of reaction simulations.

Surface Model

Our initial simulations indicate that the (100) surface is less stable than the (110) surface and contributes to only a small fraction of the overall surface. The (110) surface on the other hand provides active sites and is the predominant phase present at the surface of γ -Al₂O₃ particles. The (110) surface was modeled by cleaving the γ -Al₂O₃ bulk unit cell described in Figure 6 and inserting a 15 Å vacuum over the cleaved surface slab,

generating a three dimensional periodic surface cell with the dimensions ($a \times b \times c$) $8.413 \text{ \AA} \times 8.068 \text{ \AA} \times 22.5548 \text{ \AA}$ and angles measuring (α, β, γ) $90^\circ, 90^\circ,$ and 90° . All atoms at the bottom of the $\gamma\text{-Al}_2\text{O}_3$ surface ($z < 0.07$) were frozen during the simulations as is shown in Figure 7, to more accurately simulate the single crystal with structure extending below the simulated periodic cell. The exposed Al and O sites at this surface were subsequently used to examine the reactants, intermediates and products and to simulate the conversion of GVL to different products.

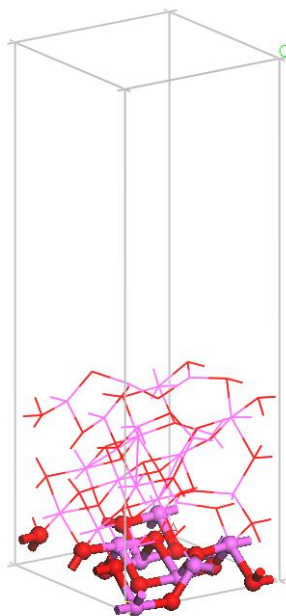


Figure 7: The $8.413 \text{ \AA} \times 8.068 \text{ \AA} \times 22.5548 \text{ \AA}$ with angles measuring (α, β, γ) $90^\circ, 90^\circ,$ and 90° periodic unit cell of the $\gamma\text{-Al}_2\text{O}_3$ (110) surface. A 15 \AA vacuum is used to separate the different slabs. The bottom layers of the slab are held fixed to mimic the single crystal $\gamma\text{-Al}_2\text{O}_3$ (110) surface. The Al and O atoms are depicted in purple and red, respectively.

The γ -Al₂O₃ (110) surface was simulated using a 2x2x1 gamma-point mesh to model the first Brillion zone. All of the structures were optimized until the structures converged to within a tolerance of 1e-6 eV. The transition states were isolated using the nudged elastic band (NEB) method to find the minimum energy reaction pathway and refined through utilization of the dimer method.^[16] A set of from eight to sixteen images between the known initial and final states were supplied to the NEB subroutine included with VASP which minimized the energies of each image allowing it to adjust perpendicularly to the reaction coordinate. While the NEB method is able to roughly discern the minimum energy pathway (MEP), it can only provide an initial guess of the saddle point corresponding to the transition state of the reaction step. The dimer algorithm within VASP was used to more faithfully determine the MEP and saddle point configuration. The NEB approach can examine in detail a number of images between which the transition state to establish a first guess at the transition state and to calculates the corresponding saddle point configuration.

The γ -Al₂O₃ surface structures used in this work are simplified models of the different low energy surfaces of amorphous γ -alumina particles used to gain insights into the plausible mechanism and may not be able to provide quantitative information concerning the rates. The effects of temperature, reaction conditions and water are not considered nor is the presence of hydroxyl groups, protons, defect sites or coordinatively unsaturated edge or corner sites. These are all important topics for future work.

Results

Surface/Site Determination and Adsorption Energies

We used the adsorption of GVL to probe the reactivity of the exposed Al sites on the (110) and (100) surfaces (see Figure 8). The results indicate that the γ -Al₂O₃ (110) surface binds GVL much more strongly than the (100) surface and as such is considerably more active than the (100) surface in activating C-O, C-H, O-H and C-C bonds. The results shown in Table 1 are consistent with previous theoretical studies by Wischert et al., which report higher adsorption energies and lower activation barriers on the (110) surface over the (100) surface of γ -Al₂O₃.^[17]

The adsorption strength of GVL to the Al sites provides a measure of the Lewis acidity of the Al site to which it is bound. As such the adsorption energy was used to probe the strengths of the acid sites on the (100) and (110) surface of γ -Al₂O₃. The results which are reported in Table 1 indicate stronger adsorption energies at the more coordinatively-unsaturated Al sites. These sites are likely more active than those at the coordinatively saturated sites. The barriers to activate GVL at these weaker acid sites would likely be significantly higher and as such we do not examine the reactivity on the (100) surface.

GVL binds most strongly on the tri-coordinated aluminum centers (Al^{III}) on the (110) surface with energies of ~140 kJ/mol as they are the most electrophilic sites on either surface. These sites are thought to be the most active in the ring opening of GVL and its conversion to 1-butene.

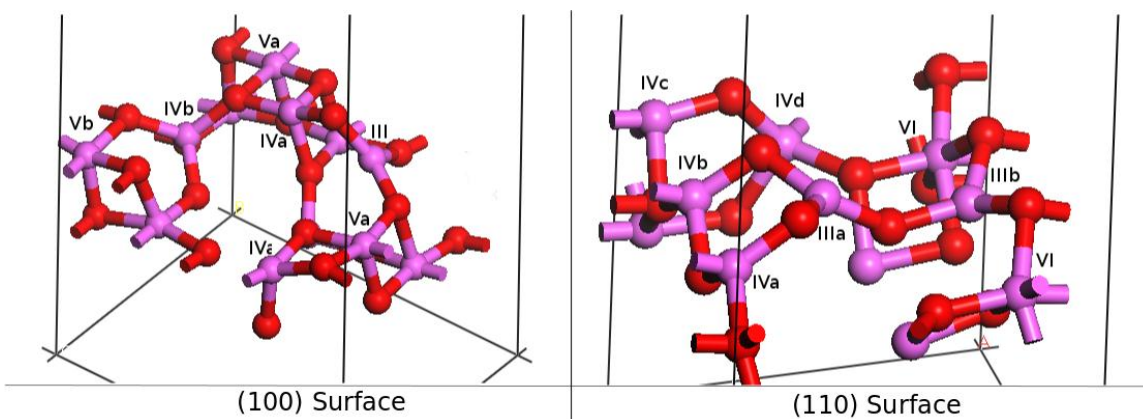


Figure 8: Adsorption sites examined on the (100) and (110) surfaces of γ -alumina. Only the uppermost layers are shown for clarity.

Table 1: GVL adsorption energies (adduct formation) to each of the acidic sites on the (110) and (100) surfaces of γ -alumina reported kJ/mol.

Site	Adsorption Energy [kJ/mol]
	(110)
IIIa_IIIb	-140
IVb	-81
IVb_IVc	-80
IIIa	-142
	(100)
Va_IVa	-61
III	-88
IVa	-37
IVa_Va	-99
Va	-64

Reaction Energies

Multiple reaction pathways were examined for the ring opening of GVL and its subsequent reactions to form different pentenoic acid isomers and butene products at the active Al Lewis sites on the γ -Al₂O₃ (110) surface. All of these paths proceed via the adsorption of GVL to a 3-coordinate Al³⁺ Lewis acid site to form the GVL-Al adduct. GVL subsequently undergoes C_γ-O bond activation to form the γ -pentenate carbenium ion intermediate that can readily undergo a hydride shift from the β position to form the β -carbenium ion intermediate or a proton transfer from the β position to the O bound to Al to form 3-pentenoic acid. The hydride transfer from the γ -pentenate intermediate to the δ -position would result in the formation of δ -pentenate, a highly unstable primary carbenium ion intermediate which was not considered. The β -carbenium ion intermediate can subsequently undergo a C_α-O or C_γ-O hydride transfer to form the 2-pentenoic acid or 3-pentenoic acid. The β -carbenium ion can also readily undergo direct decarboxylation via an rDA reaction to form 1-butene and adsorbed CO₂. These pathways are illustrated in Figure 9.

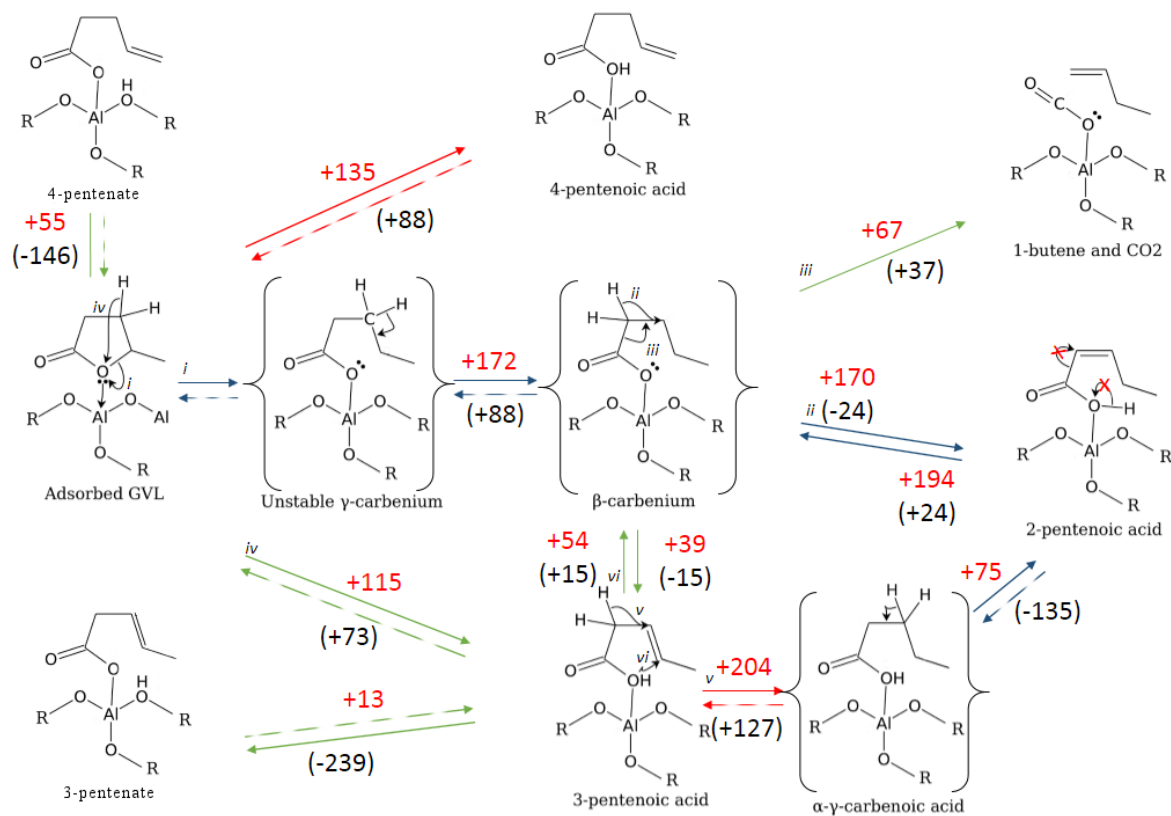


Figure 9: Reaction pathways studied. The red and blue reaction arrows show alternate mechanisms. Reaction energies not reported for dashed arrows. Brackets represent unstable intermediates. Reaction energies are of solid reaction arrows.

GVL adsorbs onto the tri-coordinated Al centers on the (110) surface to form the GVL-Al adduct with an adsorption energy of \sim -140 kJ/mol. The energy of the GVL-Al adduct that forms will be used as the basis to calculate the subsequent reaction energies and activation barriers.

GVL to 1-Butene via 2-Pentenoic Acid

The work by Bond^[3,5] and Wang^[4] et al. suggest that GVL reacts to form 2-pentenoic acid which can subsequently decarboxylate to form butene. There are two potential paths by which GVL can react to form 2-pentenoic acid. The first proceeds via the ring opening of GVL to form the γ -carbenium intermediate (pathway *i* in Figure 9) which subsequently reacts to form a β -carbenium ion intermediate. The second is via the formation of 3-pentenoic acid (pathway *iv* in Figure 9). Both of these paths are examined below in detail.

Pathway 1

The first route to convert the γ -carbenium ion intermediate to 2-pentenoic acid proceeds via a single concerted step involving the transfer of a proton from the α -carbon to the carboxylate oxygen bound to the Al center together with the simultaneous transfer of a proton from the β -carbon to the γ -carbenium. A detailed transition state search showed that the reaction cannot proceed via a concerted mechanism but proceeds instead in a sequential manner involving the transfer of a hydride from the β -carbon to the γ -carbenium ion upon ring opening followed by a proton transfer from the α -carbon to the bound oxygen of the carboxylate to form 2-pentenoic acid as is illustrated in Figure 9.

The reaction energy and activation energy for the hydride transfer from the β -carbon to the γ -carbenium center were calculated to be +88 kJ/mol and 172 kJ/mol respectively. The optimized reactant, transition and product states for this reaction are reported in Figure 10.

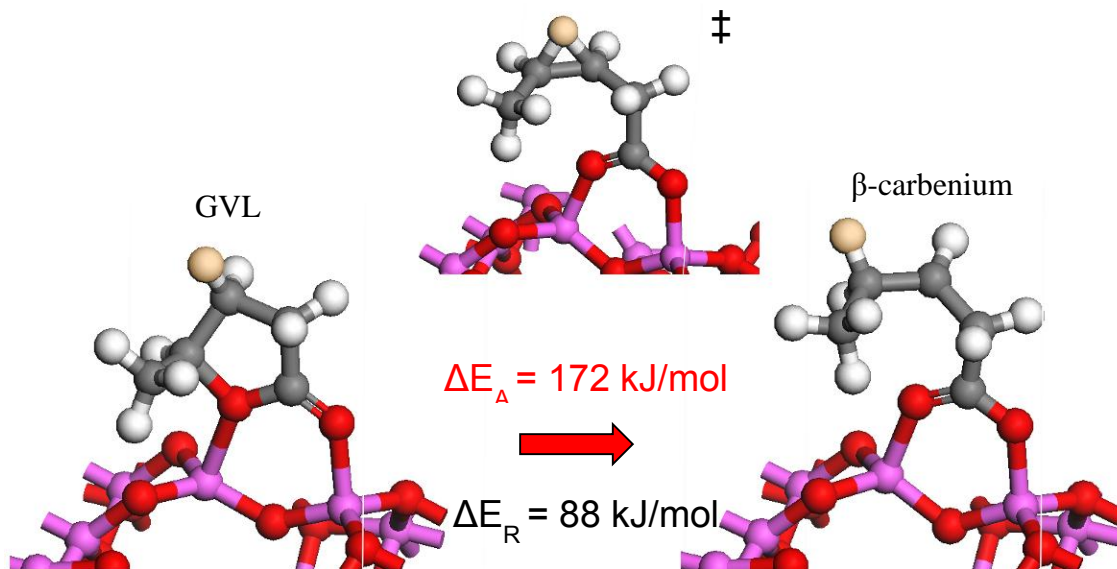


Figure 10: Concerted deprotonation and reprotonation (hydrogen shift) of GVL to form β -carbenium.

The β -carbenium ion subsequently reacts via a proton transfer from the α -carbon to the carboxyl group to form 2-pentenoic acid (pathway *ii* in Figure 9). The deprotonation of the α -carbon to form 2-pentenoic acid resulted in a calculated reaction energy of -24 kJ/mol and an activation barrier of 170 kJ/mol. The reactant, transition and product states for this step are shown in Figure 11.

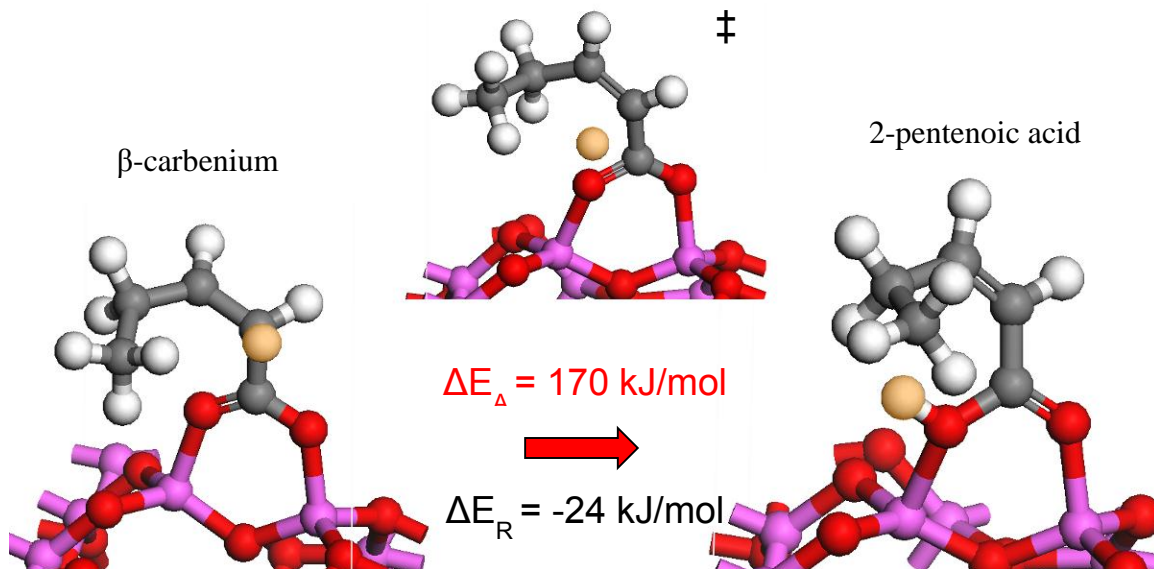


Figure 11: Deprotonation of α -carbon to produce 2-pentenoic acid.

2-pentenoic acid can subsequently decarboxylate to form 1-butene and adsorbed carbon dioxide via the simultaneous activation of the C_{α} - C_{β} bond and reprotonation of the α -carbon. We were unable to isolate a direct path involving the simultaneous decarboxylation and reprotonation. As such, decarboxylation does not appear to proceed via the 2-pentenoic acid directly but instead via the β -carbenium ion intermediate. 2-pentenoic acid can reprotonate the α -carbon to reform the β -carbenium intermediate. This is simply the reverse step of the deprotonation step to form 2-pentenoic acid illustrated in Figure 11. The overall reaction energy for this reverse reaction step is +24 kJ/mol and the activation barrier is 194 kJ/mol.

The β -carbenium ion intermediate whether it is formed directly via ring opening of GVL or by the reprotonation of the α -carbon of the 2-pentenoic acid can readily decarboxylate via an rDA reaction which involves the activation C_{α} - C_{β} bond and direct

formation of 1-butene and adsorbed CO₂ (pathway *iii* in Figure 9). The reaction energy and activation barriers for this step were calculated to be +37 kJ/mol and +67 kJ/mol, respectively. The reactant, transition and product states are shown in Figure 12. While this pathway is viable, the activation energies required to form the β -carbenium ion intermediate directly or via 2-pentenoic acid are higher than the other paths that will be discussed.

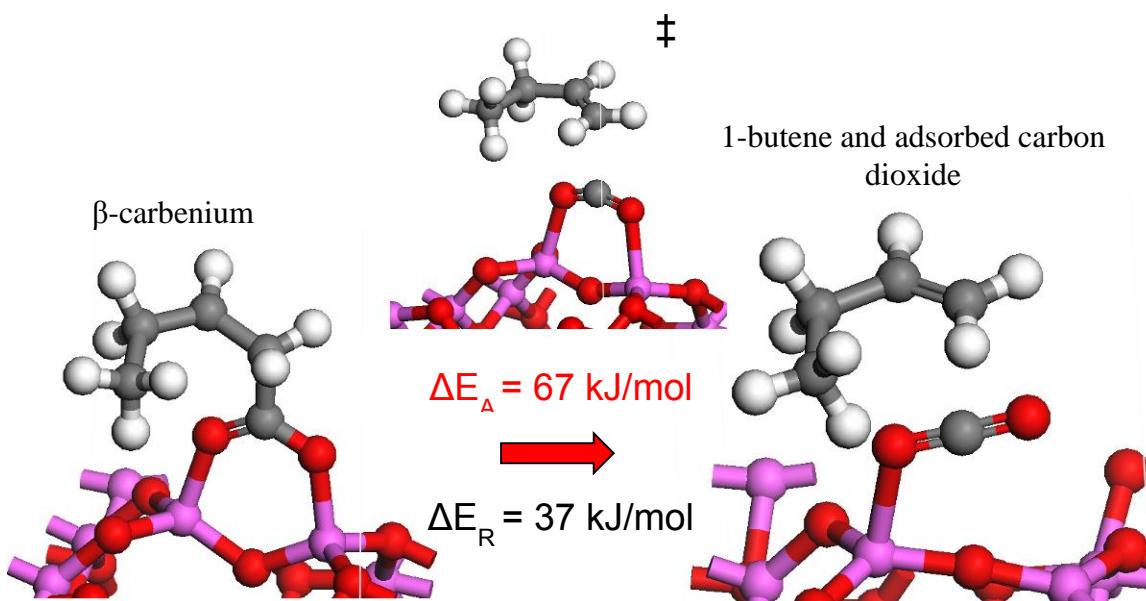


Figure 12: The direct decarboxylation of the β -carbenium intermediate to form 1-butene and adsorbed carbon dioxide.

The results here indicate that decarboxylation does not proceed directly from 2-pentenoic acid.

Pathway 2

The second path to form 2-pentenoic acid from GVL proceeds via the formation of 3-pentenoic acid which is subsequently converted via a secondary path to 2-pentenoic acid. 3-pentenoic acid can be formed via a sequence of steps involving the ring opening of GVL to the γ -carbenium ion intermediate, hydride transfer from the β -carbon to the γ -carbon to form the β -carbenium ion intermediate and the subsequent proton transfer from the α -carbon to the oxygen on the carboxylate. This last step has a barrier of 54 kJ/mol and an overall reaction energy of +15 kJ/mol.

There is also a direct concerted route (pathway *iv* in Figure 9) to go from GVL to 3-pentenoic acid which involves a direct proton transfer from the β -carbon to the bound oxygen of the carboxylate upon ring opening. The concerted route avoids the high energy paths that proceed via the unstable γ and β carbenium ion thus lowering the activation barrier. The activation barrier and overall reaction energy for the conversion of GVL to 3-pentenoic acid were calculated to be +115 and 73 kJ/mol, respectively. The reactant, transition and product states for this reaction are shown in Figure 13.

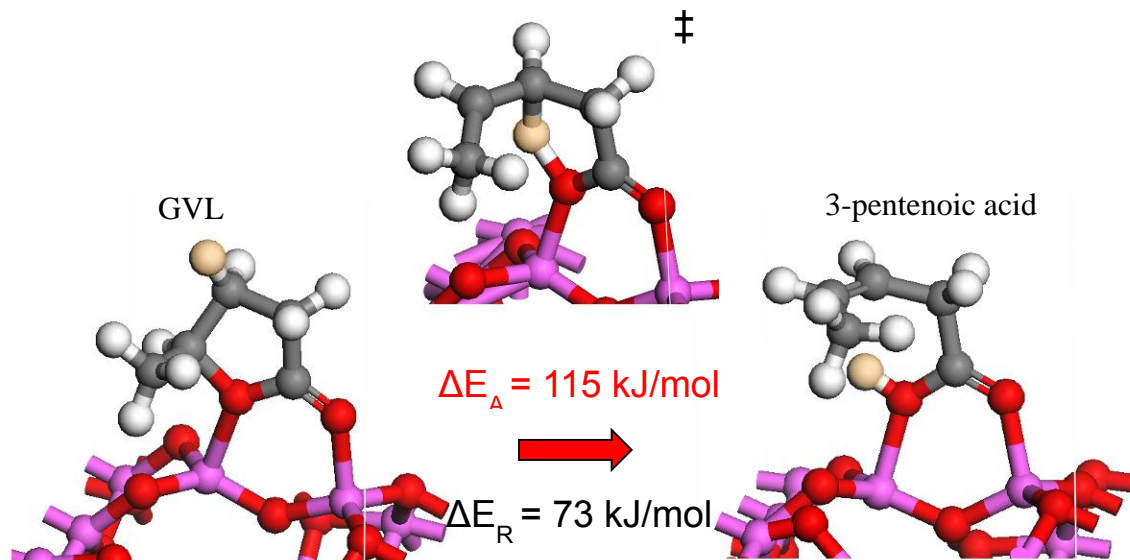


Figure 13: Direct deprotonation of GVL to form 3-pentenoic acid and associated transition state.

The adsorbed 3-pentenoic acid that forms can subsequently isomerize to form 2-pentenoic acid either through the formation of the α - γ -carbenium ion intermediate (pathway *v* in Figure 9) or via the β -carbenium intermediate (pathway *vi* in Figure 9). The reactant, transition and product states for the reaction via the α - γ -carbenium ion are illustrated in Figure 14.

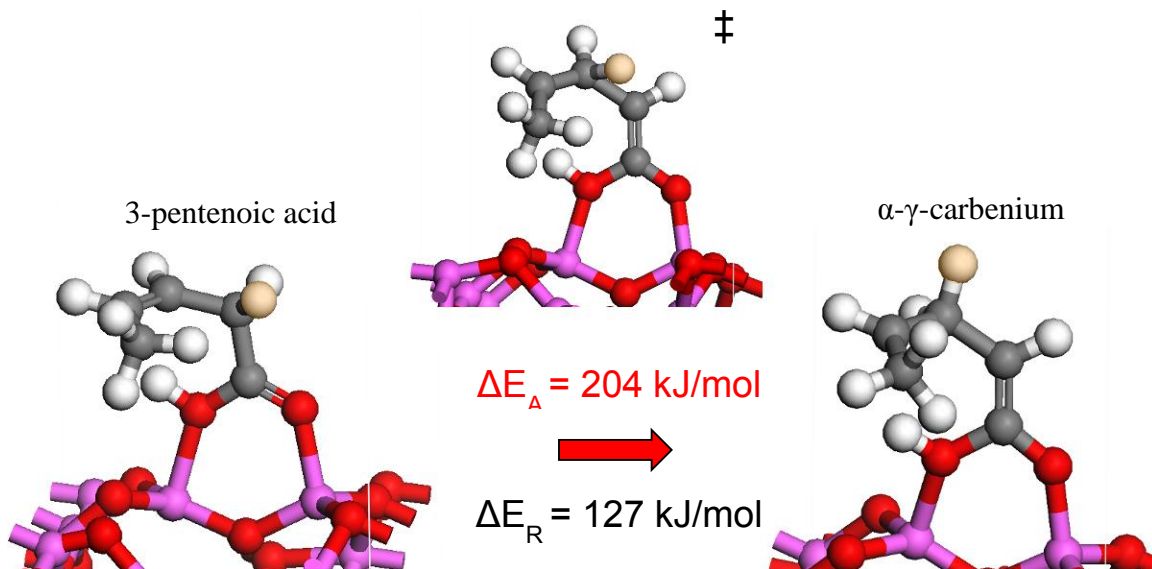


Figure 14: 3-pentenoic acid to α - γ -carbenium and the associated transition state.

The α - γ -carbenic acid intermediate can then react to form 2-pentenoic acid via the hydride shift from the C_β to the C_α resulting in an overall reaction energy of -135 kJ/mol and an activation barrier of 75 kJ/mol. The reactant, transition and product states for this reaction are illustrated in Figure 15. Once 2-pentenoic acid is formed, the path to form 1-butene is identical to that described in the previous section by forming the β -carbenium ion and subsequent decarboxylation.

The very high barrier for the formation of the α - γ carbenic acid for this path is due to the formation two carbenium ion centers located at the α and γ position. This is a highly unlikely and unstable intermediate and as such this path is highly unlikely.

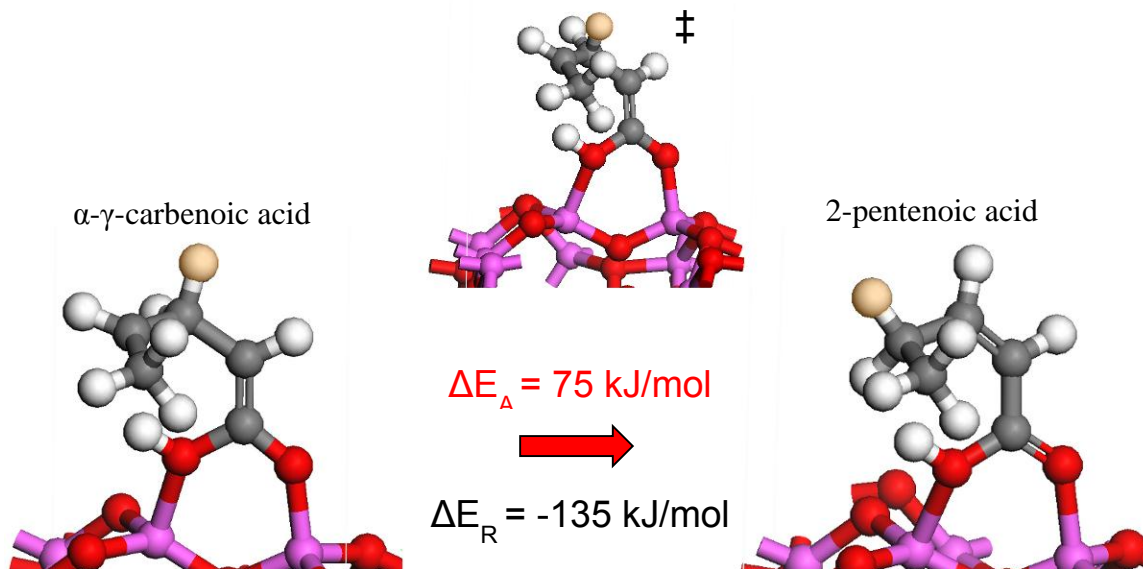


Figure 15: α - γ -carbenoic acid to 2-pentenoic acid and associated transition state.

The reaction of 3-pentenoic acid to 2-pentenoic acid would more likely proceed instead via formation of the β -carbenium ion intermediate. This step is simply the microscopic reverse of the reaction involved in forming 3-pentenoic acid from the β -carbenium ion. The reaction proceeds quite readily as the overall reaction energy and activation barrier for the conversion of 3-pentenoic acid to the β -carbenium ion intermediate were calculated to be +15 kJ/mol and 54 kJ/mol, respectively. The reactant, transition and product states for this reaction are shown in Figure 16.

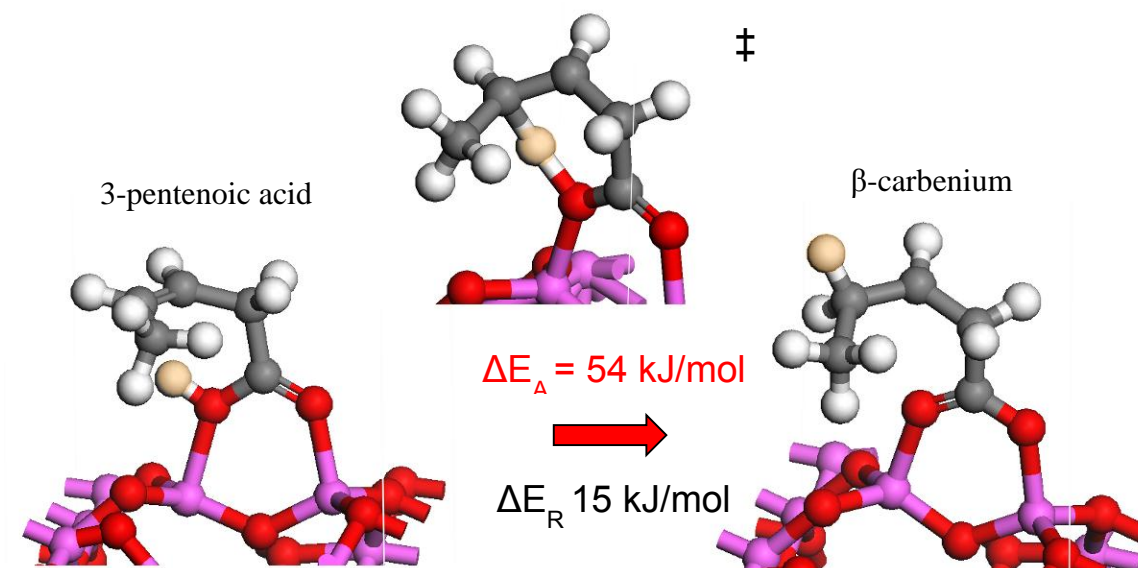


Figure 16: Repronation from 3-pentenoic acid to form β -carbenium and associated transition state.

The results discussed here suggest that 2-pentenoic acid is likely formed as a secondary product rather than as a primary product and that decarboxylation does not appear to occur via a direct path from 2-pentenoic acid.

GVL to 1-Butene via 3-Pentenoic Acid

The conversion of GVL to 3-pentenoic acid provides a second viable route for the production of 1-butene. The conversion of GVL to 3-pentenoic acid proceeds through the ring opening of GVL and formation of a β -carbenium ion intermediate which requires the ability to overcome the activation energy of +115 kJ/mol as discussed for the path via 2-pentenoic acid and illustrated in Figure 13. The subsequent activation of 3-pentenoic acid readily proceeds via the repronation of C_β to form the β -carbenium ion which

occurs with a barrier of only +39 kJ/mol as was presented in the previous section for the conversion of 3-pentenoic acid to 2-pentenoic acid. The final step in this path involves the decarboxylation of the β -carbenium species via an rDA reaction as was discussed in the decarboxylation of 2-pentenoic acid requiring a barrier of only 67 kJ/mol.

A comparison of the results for the decarboxylation of 2-pentenoic acid and 3-pentenoic acid indicate that both proceed via the formation of the β -carbenium ion intermediate. This path is relatively easy for 3-pentenoic acid as the barrier is only +39 kJ/mol as it involves a direct transfer of a proton from the terminal OH to the adjacent C_γ site. The reaction for 2-pentenoic acid, however, is much more difficult as it involves a more distant and constrained proton transfer from the terminal OH to the C_β carbon resulting in a barrier is over three times higher (+146 kJ/mol) than that for the conversion of the 3-pentenoic acid.

GVL to 4-Pentenoic Acid

The conversion of GVL to 1-butene can also proceed via the formation of 4-pentenoic acid. GVL can be converted to 4-pentenoic acid in a single step involving the concerted C_γ -O activation together with a direct proton transfer from the C_β to the oxygen on the carboxylate bound to the Al as is shown in the path depicted in Figure 17. The activation barrier and overall reaction energy for the concerted ring opening and proton transfer to form 4-pentenoic acid were calculated to be +135 and +88 kJ/mol, respectively. The barrier as well as the overall reaction energy for the concerted ring opening and proton transfer to form 4-pentenoic acid were found to be +20 kJ/mol and

+15 kJ/mol higher than those for the same steps to form 3-pentenoic acid. This is due to the better stabilization of the carbenium ion character that forms in transferring the proton from the primary (terminal) carbon in 4-pentenoic acid versus a secondary carbon in 3-pentenoic acid.

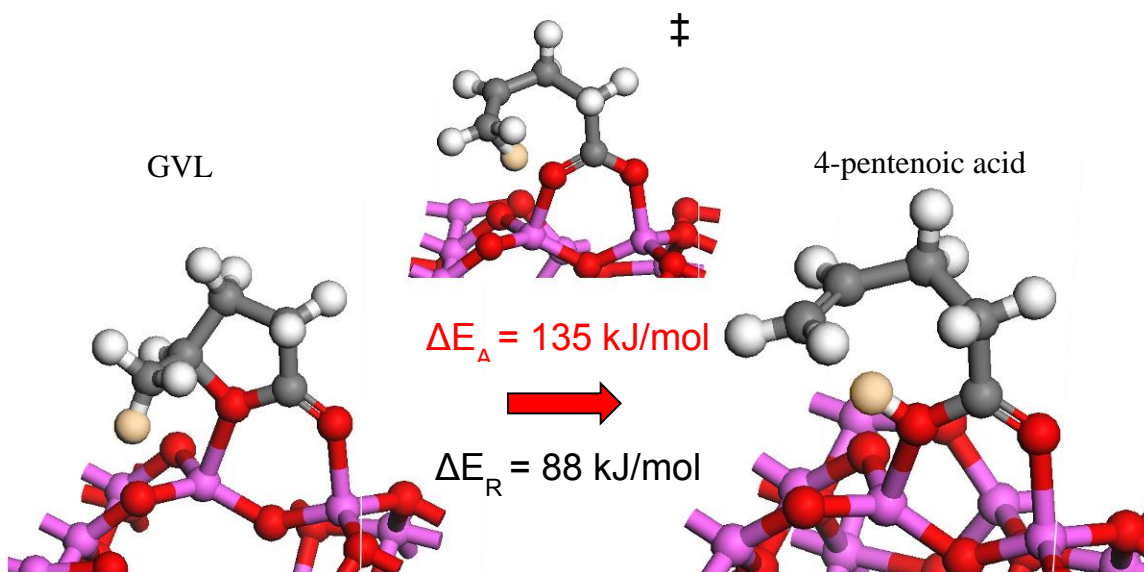


Figure 17: Deprotonation of GVL to form 4-pentenoic acid and associated transition state.

The conversion of the 4-pentenoic acid to 1-butene would require either reprotonating the terminal (δ -carbon) carbon to form the secondary γ -carbenium intermediate or the secondary (γ -carbon) to form the primary δ -carbenium ion intermediate. The former would subsequently proceed via the same path as that for the 3-pentenoic acid, whereas the latter step is unlikely due to the high energy cost of forming a primary carbenium ion. As such we did not examine the latter path.

GVL to 1-Butene via Hydrogen Shift

GVL can be converted to 1-butene without having to form the 2-, 3- or 4-pentenoic acid isomers by the direct ring opening of GVL to the γ -carbenium ion intermediate which undergoes a hydride shift to form the β -carbenium ion which subsequently decarboxylates to form 1-butene and CO_2 as shown in Figure 12. This same path was already discussed in the mechanism for 2-pentenoic acid. The final decarboxylation of the β -carbenium ion is involved in the conversion of all three pentenoic acid isomers.

GVL to Adsorbed Pentenate (Deprotonation to Surface)

To this point we have only analyzed the conversion of the GVL, 2-, 3- and 4-pentenoic acids to 1-butene via intramolecular hydrogen transfer and C-C activation paths. The sole role of the surface has been to supply the Lewis acid Al site to activate the $\text{C}_\gamma\text{-O}$ bond of GVL and to stabilize the $\text{H}_x\text{C}_5\text{O}_2\text{H}_x$ hydrocarbon intermediate without the direct participation of the weak basic oxygen sites. These sites however can play a role in assisting the proton transfer steps outlined in Figure 9. We analyze here the paths from GVL to 1-butene that proceed via proton transfer to the surface oxygens.

Depending on the proton that is transferred, the species that forms is either adsorbed 3-pentenate or adsorbed 4-pentenate. Calculations were performed to probe the energies associated with deprotonation to the surface of the catalyst forming both species.

The GVL ring opening reaction to form a γ -carbenium ion state can proceed together with a concerted proton from the vicinal β -carbon or the δ -to a surface O to form

the 3-pentenate or 4-pentenate, respectively. The concerted proton transfer from the β -C-H to the surface to form the 3-pentenate would be very sterically hindered transition state as schematically illustrated in Figure 18 thus resulting in a high activation barrier.

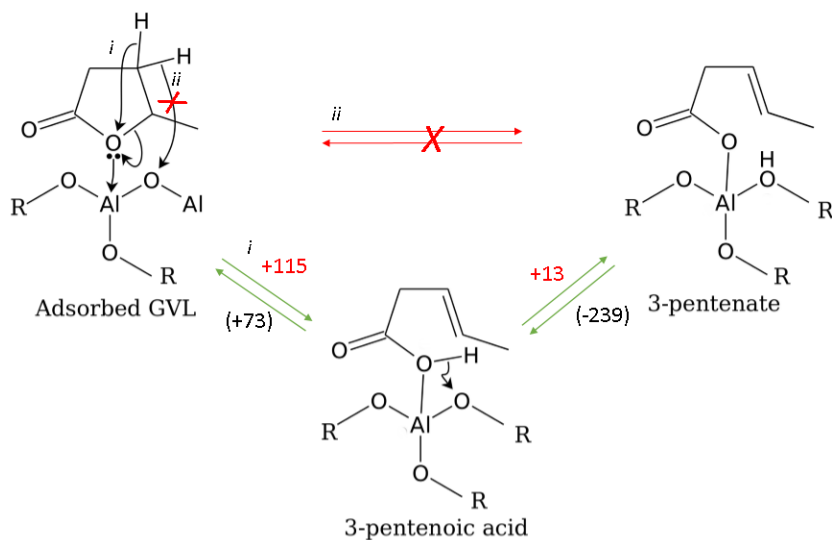


Figure 18: Sterically hindered transition of GVL directly to 3-pentenate. Alternate path via 3-pentenoic acid also shown.

It is more likely that the proton transfers to one of the carboxyl oxygen atoms first to produce 3-pentenoic acid. Once 3-pentenoic acid is formed, the proton can then readily transfer to the surface to produce 3-pentenate. The first elementary step of ring opening and deprotonation of the GVL molecule to produce 3-pentenoic acid is the same as that which was previously described and illustrated in Figure 13 requiring a barrier of 115 kJ/mol. The subsequent proton transfer from the 3-pentenoic acid to the surface resulted in an activation barrier of only 13 kJ/mol and overall reaction energy of -239 kJ/mol. The reactant, transition and product states are shown in Figure 19.

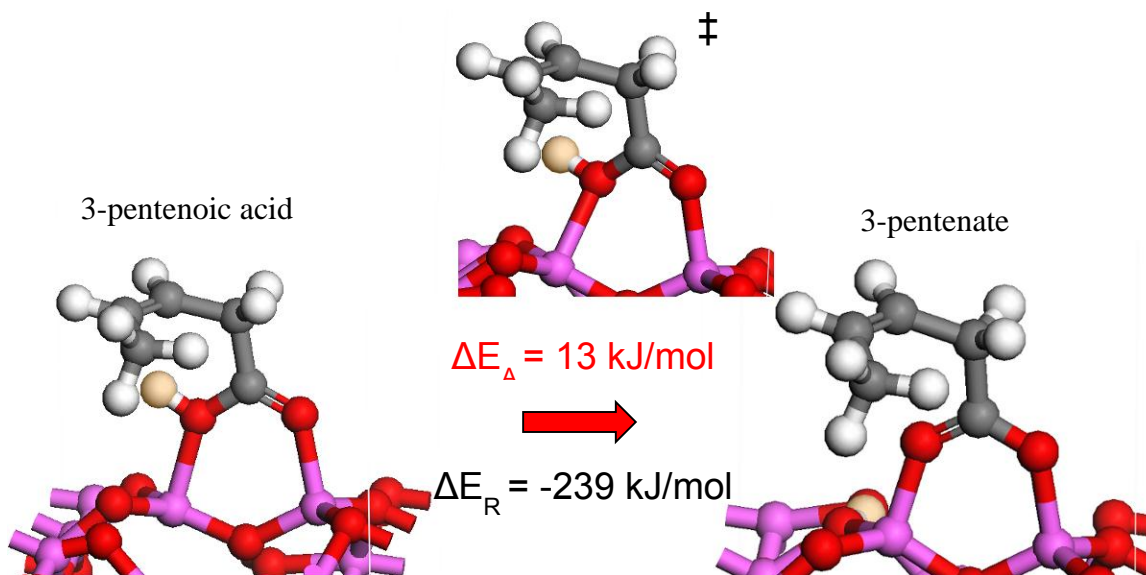


Figure 19: 3-pentenoic acid to 3-pentenate and associated transition state.

The activation of the δ -C-H bond upon the ring opening of GVL can also proceed via the assistance of the surface oxygen. In this case there are not steric constraints and as such the C_{γ} -O and the C_{δ} -H bonds can be activated concertedly to form 4-pentenate directly from GVL. The activation barrier and overall reaction energy for this step were calculated to be +55 and -146 kJ/mol, respectively. The reactant, transition and product states are shown in Figure 20.

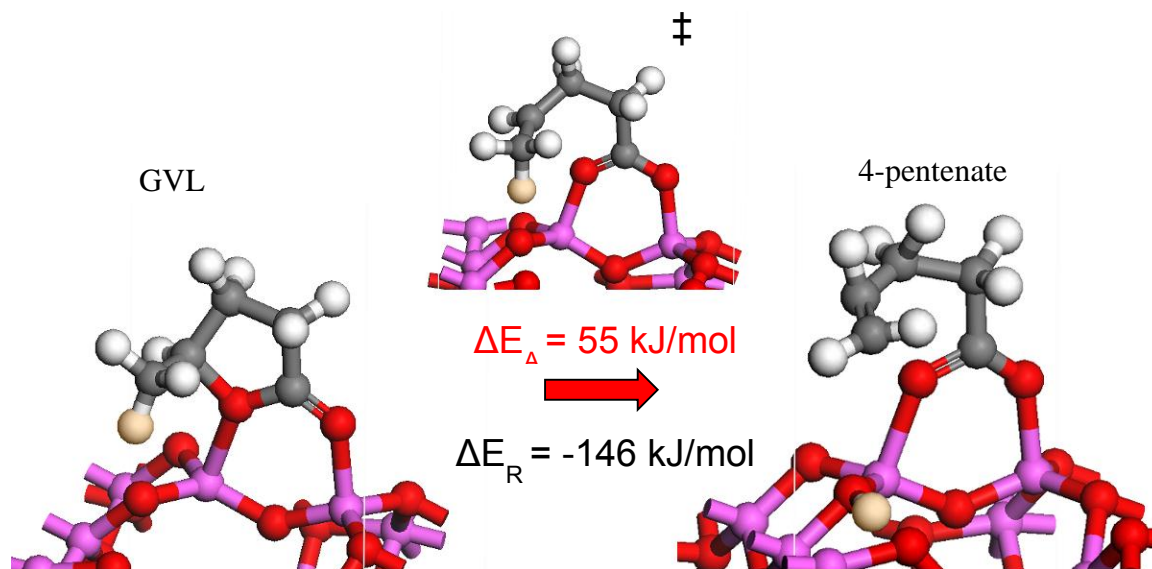


Figure 20: GVL deprotonation to form 4-pentenate and associated transition state.

Reaction Energies Summarized

The calculations and surface model used here indicate that the conversion of GVL to 1-butene occurs via a Lewis acid catalyzed ring opening and decarboxylation mechanism that is rather similar to the mechanism for the Brønsted acid catalyzed ring opening and decarboxylation of pyrones proposed by Chia et al. The reaction proceeds via the adsorption, concerted ring-opening and deprotonation of GVL to form an unsaturated carboxylic acid which subsequently reprotonates to form the β -carbenium ion intermediate that then reacts via a retro Diels Alder decarboxylation reaction to form 1-butene and carbon dioxide which desorb from the surface. The intrinsic activation and reaction energies for the elementary steps involved in the pathways studied were used to construct the reaction energy diagrams reported in Figure 21 and to compare different plausible reaction paths. The most favored lowest energy path in this figure is the one

shown in green which involves the direct formation of 3-pentenoic acid and its decarboxylation to form 1-butene and CO₂.

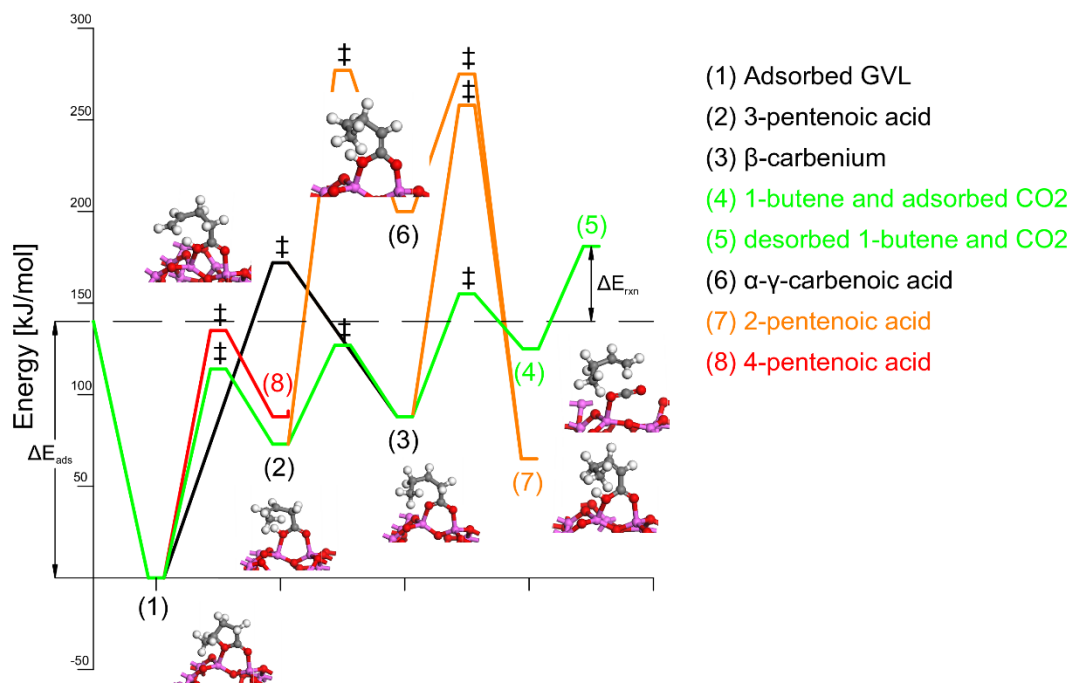


Figure 21: Summary of calculated energy values of reaction intermediates and transition states. Green line is the preferred pathway from GVL to 1-butene via 3-pentenoic acid. The orange line displays the pathways via 2-pentenoic acid. The red line is the pathway to 4-pentenoic acid. The black line represents a hydrogen shift to directly form β -carbenium upon ring opening.

Discussion

All of the reaction paths appear to follow a general sequence of elementary steps involving ring opening, deprotonation, reprotonation, and ultimately decarboxylation to form 1-butene. All of the reactions tend to proceed via the formation of a β -carbenium

ion intermediate that can readily undergo decarboxylation to form 1-butene and carbon dioxide. The differences in these pathways are determined by the hydrogen transfer steps and specific sites on the molecule where hydrogen atoms are being transferred to or from the β -carbenium species.

Surface Model

The calculations reported within this work indicate that the energetically most favorable sites for the adsorption and activation of GVL are the tri-coordinate Al^{2+} centers on the (110) surface of γ -alumina. Wischert et al.¹⁷ suggested that these sites and their reactivity can be influenced by the presence of pre-existing protons and hydroxyl groups on the alumina surface. Investigation of the effect of any pre-existing species on the surface will be an important part of future efforts.

GVL to 1-Butene via 2-Pentenoic Acid

The conversion of GVL to 1-butene could also proceed via the formation and subsequent conversion of 2-pentenoic acid. There are two general paths by which 2-pentenoic acid can be formed. The first path involves the adsorption and ring opening of GVL to form the γ -carbenium species, which can undergo a hydrogen shift from the β -carbon to the γ -carbon to form the more stable β -carbenium ion. The β -carbenium intermediate then undergoes deprotonation to form 2-pentenoic acid. The relatively high activation energy barrier of 258 kJ/mol (relative to adsorbed GVL) associated with conversion to 2-pentenoic acid would prevent this route from occurring. The high apparent barrier is due to the large endothermicity for the concerted ring opening and

hydride shift reaction to form the β -carbenium ion as well as the high intrinsic (+170 kJ/mol) for the deprotonation of the β -carbenium ion to form 2-pentenoic acid.

The second path to 2-pentenoic acid proceeds similarly to form the β -carbenium ion via a concerted ring-opening and hydride shift. The β -carbenium, however, does not undergo the energetically costly activation of the α -C-H bond but instead activates the γ -C-H bond to form 3-pentenoic acid (which has an activation barrier which is 131 kJ/mol lower than that to form 2-pentenoic acid) followed by the isomerization of 3-pentenoic acid to 2-pentenoic acid through the α - γ -carbenoic acid intermediate.

The energy barrier to form 2-pentenoic acid from GVL via β -carbenium is significantly higher than the path to form 3-pentenoic acid directly. Isomerization of 3-pentenoic acid to 2-pentenoic acid, however, also presents a high energy barrier (> 277 kJ/mol relative to the adsorbed GVL) as it requires the formation of the unstable α - γ -carbenoic acid. The apparent barrier for the subsequent conversion of the α - γ -carbenoic acid to form 2-pentenoic acid is also very high at 274 kJ/mol (relative to adsorbed GVL). The high apparent barriers for both path 1 as well as path 2 indicate that these pathways are not preferred due to the double bond in 2-pentenoic acid not being correctly positioned to allow for conversion to 1-butene without either isomerization of 2-pentenoic acid back to 3-pentenoic acid or the reaction of 2-pentenoic acid through the β -carbenium.

GVL to 1-Butene via 3-Pentenoic Acid

Ring Opening and Deprotonation

The conversion of GVL to 1-butene via 3-pentenoic acid proceeds by the adsorption and concerted ring opening of GVL and proton transfer from the unstable γ -C-H bond and the negatively charged oxygen on the carboxylate bound to the Al center to form 3-pentenoic acid directly. This concerted path only requires overcoming an apparent barrier of 115 kJ/mol (relative to adsorbed GVL) to form 3-pentenoic acid.

Reprotonation

Reprotonation of the 3-pentenoic acid involves the transfer of the proton from the carboxylic group to the γ -carbon of the acid thus resulting in the transformation from the pentenoic acid intermediate into the β -carbenium intermediate. The barrier for this step to overcome is 54 kJ/mol (127 kJ/mol relative to adsorbed GVL).

Decarboxylation

Decarboxylation appears to preferentially proceed via the formation of a β -carbenium ion intermediate that results from the bond scission that occurs between the C1 and α carbons, to form 1-butene which is free to diffuse from the catalyst surface. A barrier of 155 kJ/mol (relative to adsorbed GVL) is required to proceed and is similar to the acid catalyzed thermal decarboxylation of an unsaturated acid as described by Arnold, et al. through a cyclic transition state, which bears similarity to the rDA mechanism. This cyclic transition state precedes the formation of a β -carbenium intermediate which undergoes elimination of the carbon dioxide portion of the complex, resulting in

exclusive production of 1-butene. Upon desorption of the remaining carbon dioxide molecule from the active site, the catalytic cycle is complete.

GVL to 1 Butene via 4-Pentenoic Acid

Ring Opening and Deprotonation

The route to 1-butene through the 4-pentenoic acid species can proceed via the ring opening of GVL to form the γ -carbenium ion intermediate which can facilitate the deprotonation of the γ -C-H bond and proton transfer to the oxygen of the carboxylate group bound to the Al center to form the stable 4-pentenoic acid intermediate. This step, however, must overcome a barrier of 135 kJ/mol (relative to adsorbed GVL), which is 20 kJ/mol higher than activation barrier to form the 3-pentenoic acid intermediate.

Decarboxylation

Since the double bond of the 4-pentenoic acid is not at the β - γ position, it cannot carry out the direct decarboxylation via a low energy rDA path. Instead it preferentially isomerizes to form 3-pentenoic acid rather than undergoing direct decarboxylation

GVL to 1-Butene via Hydrogen Shift

Deprotonation/Reprotonation

The γ -carbenium ion intermediate that forms via the ring opening of GVL potentially allows the α -hydride on the β -carbon to shift to the γ -carbon thus transferring the positive charge to the β -carbon and providing a potential path for the decarboxylation and 1-butene formation directly from the ring opening of the GVL. The hydrogen shift

involves a combination of both deprotonation and reprotonation steps. While the resulting intermediate from the shifted hydrogen atom reduces the number of elementary steps to form the β -carbenium intermediate which should facilitate the subsequent decarboxylation, the barrier to carry out this hydrogen transfer is still relatively high at 172 kJ/mol (relative to adsorbed GVL) as compared to the calculated barriers leading to β -carbenium through 3-pentenoic acid, so it is unlikely that the reaction would follow this path.

GVL to 1 Butene via x -Pentenates (Deprotonation to the Surface)

The unstable γ -carbenium ion intermediate that forms upon the ring opening of GVL can undergo direct deprotonation via reaction with the weak Lewis base oxygen sites on the γ -Al₂O₃ surface to form either the 3-pentenate or 4-pentenate intermediates. The weakly basic surface oxygen centers can aid in lowering the barriers to activate weakly acidic C-H and O-H bond of GVL and other surface intermediates. While these sites can lower the activation barriers, it is not clear, however, that such sites are exposed under reaction conditions. In the presence of water, it is likely that the active sites may be terminated with OH groups.

We examined the concerted ring opening and β or δ C-H bond activation of GVL by the Lewis acid Al – Lewis base O site pair on the Al₂O₃ surface to form 3- and 4-pentenate, respectively. Conformational restrictions prevented the involvement of the surface O in the concerted GVL ring opening and C $_{\beta}$ -H activation to 3-pentenate. The reaction proceeds instead in a sequential route which involves the concerted GVL ring opening and C-H deprotonation by the oxygen of the carboxylate group (as opposed to

the oxygen in the lattice) to form 3-pentenoic acid as was shown in Figure 13 resulting in an activation energy of 115 kJ/mol. The 3-pentenoic acid can then readily be deprotonated by a vicinal surface O to form 3-pentenate. The barrier for the second step involving the conversion of 3-pentenoic acid to 3-pentenate was calculated to be only 13 kJ/mol and is found to be rather exothermic at -239 kJ/mol (relative to adsorbed GVL state).

GVL can react concertedly to form the 4-pentenate as there are no significant conformational restrictions. Ring opening can proceed in a concerted manner with the direct deprotonation of the δ C-H bond by a weakly basic vicinal surface O site to form the 4-pentenate and a surface OH in a single step. The activation barrier for this reaction is 55 kJ/mol (relative to adsorbed GVL) and results in an overall reaction energy of -146 kJ/mol (relative to adsorbed GVL).

The very high exothermicities that result from the involvement of the surface oxygen sites suggest that these sites would not remain vacant under reaction conditions and would more likely be present instead as hydroxyl surface intermediates. As such these sites are likely not involved in the conversion of GVL. Future work would need to carry out a more detailed study of the degree of hydration of the working γ -Al₂O₃ surface under reaction conditions to determine the nature of the exposed oxygen sites and their role in aiding the chemistry. Herein we have focused predominantly on the role of the Lewis acid Al sites.

Reaction Pathways/Mechanism

The early experimental studies proposed three possible reaction paths by which the reaction proceeds. The first suggest that the reaction proceeds via a hydrogen shift mechanism which involves the Lewis acid catalyzed ring opening of GVL to form a reactive γ -carbenium ion intermediate, followed by a hydrogen transfer from the vicinal β -carbon to the γ -carbenium ion center to form the β -carbenium intermediate that readily decarboxylates to 1-butene and carbon dioxide.

The second proposed path involved the ring opening of GVL to form 3-pentenoic acid. The 3-pentenoic acid can then isomerize to form 2-pentenoic acid which decarboxylates to liberate 1-butene and carbon dioxide. This path would require a proton transfer from the O on the carboxylic acid group of 3-pentenoic acid to its α -carbon to form the β -carbenium ion intermediate. The activation barrier of this step is rather high at 193 kJ/mol (relative to adsorbed GVL) which would suggest that this path is not viable.

The third path that was proposed involves the concerted ring opening of the GVL ring to and intramolecular proton transfer from the β -carbon to the Al bound O of the carboxylate to form 3-pentenoic acid. The 3-pentenoic acid can subsequently undergo a proton transfer from the acid CO₂H to the γ -carbon forming the active β -carbenium intermediate which readily decarboxylates via an rDA step to form 1-butene and carbon dioxide with rather high selectivity. This was calculated to be the lowest energy path of all of those studied in this work and is considered to be the preferred path to 1-butene.

The theoretical results reported here indicate that the β -carbenium ion intermediate is the key to the decarboxylation and formation of 1-butene. This can

effectively proceed by the formation of 3-pentenoic acid. The formation of 1-butene from 2-pentenoic acid cannot proceed directly and instead occurs via the conversion of 2-pentenoic acid via the β -carbenium ion intermediate.

All of the paths reported here proceed via ring opening and deprotonation to a basic oxygen. Reprotonation of the saturated 3-pentenoic acid is the preferred path to form the β -carbenium intermediate, enabling decarboxylation. As is prevalent in literature, elimination of carbon dioxide is then a viable and irreversible consequence of β -carbenium formation, solely resulting in the α -olefin product.

Conclusions and Future Work

First-principle quantum chemical calculations were used to provide insights into the sites, reaction paths and mechanisms into the Lewis acid catalyzed conversion of γ -valerolactone to form 1-butene and different isomers of pentenoic acid. The results suggest that the tri-coordinated aluminum sites on the (110) surface of γ -alumina are the most favorable sites for the adsorption of GVL and likely the most active sites. The Lewis acidity of the aluminum aids in the adsorption and subsequent activation of the GVL molecule. The adsorption of GVL to the Al site results in the stabilization of the negative charge on the oxygen and the positive change on the metal. There is an electron transfer to the Al center as the C-O bond length increases along the reaction coordinate which aids in the stabilization of the transition state and the formation of the γ -carbenium intermediate. The γ -carbenium intermediate can subsequently or simultaneously undergo a hydrogen transfer from the β -carbon to the oxygen of the carboxyl group bound to Al to form 3-pentenoic acid. The location of the double bond within 3-pentenoic acid is key to

allowing for reprotonation of the γ -carbon, the formation of a stable β -carbenium intermediate and the subsequent decarboxylation at high selectivity to 1-butene. β carboxylic acids are unique compared to other substituted acids in that they can readily decarboxylate in the presence of acids or upon heating. The mechanism proceeds through an rDA reaction.

The unique reactivity of the β position would help to explain the very high initial selectivities for ring-opening and decarboxylation leading to the α -olefin product. This would also indicate that the 3-pentenoic acid would be the primary intermediate that leads to decarboxylation and that the 2-pentenoic and 4-pentenoic acids likely proceed via isomerization to 3-pentenoic acid and subsequent elimination through the β -carbenium ion intermediate. The results reported here were recently corroborated by more detailed experimental studies which indicate 3-pentenoic acid is the primary and key intermediate in the decarboxylation of GVL.

Experimental evidence shows that when water is co-fed to the flow reactor the selectivity of the reaction with regard to 1-butene increases versus isomerization of the product to undesirable by-products. The activity of γ -alumina to promote decarboxylation of the acid species may be heightened by the presence of water or alternatively the activity of the catalyst to promote isomerization may be reduced. Wischert reports a similar result when activating methane.^[17, 18] Another possibility is that water limits side reactions by poisoning basic sites on the catalyst surface that can lead to isomerized side products.

Future investigation should include work to answer whether the presence of water limits the potential paths open to isomerization or promotes basicity of the oxygen atom

of the carboxylic acid, allowing it to either promote deprotonation or alternatively demotes basicity where decarboxylation is promoted. Another potential impact worthy of investigation of vicinal water is its potential to stabilize the reactant states, causing a lower overall activation energy barrier or altered reaction kinetics. Additionally, future work should investigate alternative sites for activity. Wischert reports that tetrahedral aluminum atoms are reactively competitive with the tri-coordinated aluminum atoms in the presence of surface bound protons and hydroxyl groups.

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