Reaction mechanism of aqueous-phase conversion of γ -valerolactone (GVL) over a Ru/C catalyst

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Abstract

The present work explores the reaction pathways of γ -valerolactone (GVL) over a supported ruthenium catalyst. The conversion of GVL in aqueous phase over a 5% Ru/C catalyst was investigated in a batch reactor operating at 463K under 500-1000 psi of H_2 . The main reaction products obtained under these conditions were 2-butanol (2-BuOH), 1,4-pentanediol (1,4-PDO), 2-methyltetrahydrofuran (2-MTHF) and 2-pentanol (2-PeOH). A complete reaction network was developed, identifying the primary and/or secondary products. In this reaction network, production of 2-BuOH via decarbonylation of a ring-opened surface intermediate $CH_3CH(O^*)-(CH_2)_2-CO^*$ is clearly the dominant pathway. From the evolution of products as a function of reaction time and theoretical (DFT) calculations, a mechanism for the formation of intermediates and products is proposed. The high sensitivity of 2-BuOH production to the presence of CO, compared to a much lower effect on the production of the other products indicates that the sites responsible for decarbonylation are particularly prone to CO adsorption and poisoning. Also, since the decarbonylation rate is not affected by the H_2 pressure it is concluded that the direct decarbonylation path of the $CH_3CH(O^*)-(CH_2)_2-CO^*$ intermediate does not required a previous dehydrogenation step, as is the case in decarbonylation of short alcohols.

1. Introduction

A wide variety of processing strategies that allow the conversion of lignocellulosic biomass into targeted platform chemicals have been investigated in recent years [1–7]. Hydrolysis, solvolysis and other liquefaction approaches are particularly attractive, since they can produce energetically denser streams and allow for the production of a wide range of platform chemicals [8]. For instance, hydrolysis of the cellulose portion of the lignocellulose leads to the formation of sugars that via dehydration/hydrolysis steps may be converted to levulinic acid (LA) [9], which, in the presence of stoichiometrically formed formic acid as an in situ source of hydrogen, can be further upgraded to yield γ -valerolactone (GVL) [10]. Ruthenium-based catalysts have been successfully employed in the selective hydrogenation and hydrogenolysis of a variety of carboxylic acids and esters [11–13]. Particularly, it has been proven to be suitable for the hydrogenation of LA into GVL [14]. Alternatively, Bui et al. [15] have recently proposed an integrated process for direct production of GVL from furfural through a sequence of reactions catalyzed by zeolites with Brønsted and Lewis acid sites. This alternative is particularly attractive since there already exist well-established methods for the production of furfural from hemicellulose [16]. Therefore, GVL has been identified as a strategic renewable platform chemical with a wide range of potential applications, including its direct use as a low-toxicity solvent or as an intermediate in the production of fuels and chemicals [17–19]. Upon hydrogenation on a metal based-catalyst, GVL can be converted to 1,4-pentanediol (1,4-PDO) [20], which along with other biogenic diols, can be building blocks for biodegradable polyesters and other polymers [21]. It can also produce 1,4-PDO which, in turn, can be dehydrated to form 2-methyltetrahydrofuran (2-MTHF) [22,23], which can potentially be blended in gasoline as an

additive [24]. Al-Shaal et al. [4] have reported the formation of 2-butanol (2-BuOH) and 2-pentanol (2-PeOH) along with the 1,4-PDO and 2-MTHF when using Ru/C as a catalyst.

The conversion of GVL on Ru-based catalysts has been studied in a variety of solvents and in solvent-free environments [4,25,26]. However, the reaction mechanisms and their kinetics remain largely unexplored. This study aims to generate a fundamental understanding of the reaction pathways and explore potential mechanisms of the ring-opening via catalyzed hydrogenation with a Ru/C catalyst in aqueous phase. By identifying the primary and secondary products and analyzing the evolution of products with the extent of reaction, we have been able to establish a complete reaction network, which along with a theoretical analysis has lead to the proposal of a reaction mechanism.

2. Experimental

2.1. Catalytic materials

A 5 wt % Ru/C catalyst was prepared by incipient wetness impregnation of a carbon support (Norit by Sigma-Aldrich) with a Ruthenium (II) nitrosyl nitrate solution in dilute nitric acid (Aldrich) of appropriate concentration to obtain a nominal 5 wt% Ru loading in the final catalyst. Following the impregnation, the catalyst was dried overnight at 373 K and calcined for 4 h in a H₂ flow of 150 mL/min at 673 K. The exact Ru content on the calcined sample was 4.6 wt%, as quantified by ICP analysis (Galbraith Laboratories, Inc.). A commercial 5 wt% Ru/C catalyst (Alfa Aesar, Type 619) was also used on some experiments. γ -Valerolactone (GVL) (Sigma-Aldrich, 99%), 1,4-Pentanediol (1,4-PDO) (Aldrich, 99%) and 2-Methyltetrahydrofuran (2-MTHF) (Sigma-Aldrich, $\geq 99\%$) were used as received. Deionized water was used as a solvent.

Transmission Electron Microscopy (TEM) images of the catalyst were obtained in a JEOL 2000 fx system. The samples were prepared dispersing the catalyst powder in isopropanol, and sonicating for 10 min at 25% amplitude (Cole-Palmer horn sonicator). The sample was placed on holey carbon coated Cu grids for analysis. Images were processed with ImageJ software to obtain the particle size distribution and average particle size. Dynamic CO chemisorption was carried out in a pulse reactor system in order to estimate metal dispersion. 0.05 g of catalyst were loaded to a quartz tubular reactor, and held in place by two plugs of quartz wool. First, the sample was reduced in H₂ at 473 K for 1 h, and subsequently purged with He (Airgas) for 30 min and cooled to room temperature. A 5% CO/He gas mixture (Airgas) was fed to the catalyst bed in consecutive pulses with a 0.1 mL loop size, at room temperature. The CO content in the outlet stream was quantified with an on-line GC-MS (Cirrux LM99 by MKS Spectra Products). The experiment was concluded when the size of the CO peaks no longer increased, indicating saturation of the surface of the solid.

2.2. Catalytic reaction measurements

The GVL conversion was studied in the aqueous phase in a 160 mL batch reactor (Parr Instrument Company), at 500-1000 psi of total pressure (in H₂) and 473 K. The total volume was kept at 100 mL, with a reactant initial concentration of 0.1 M. In each experiment, 50–100 mg of catalyst was loaded into the reactor along with 84 mL of deionized water. Prior to injection of the reactant, the catalyst was reduced for 3 h in H₂ (Airgas, ultra-high purity) at a total pressure of 1000 psi and 503 K. Once the catalyst was fully reduced, the 16 mL reactant mixture was injected through a feeding cylinder. After the injection, the temperature and pressure were adjusted to the desired operating values, keeping the stirring speed at 500 rpm. After completing

the desired reaction time, the reactor was quickly quenched in a cold water bath. Finally, the reaction mixture was filtered and sent for analysis.

The filtered reaction mixture was analyzed in a GC-FID (Agilent 7890B with a Phenomenex ZB-WaxPlus high-polarity wax column) for product quantification, using 1-propanol (Sigma-Aldrich, $\geq 99\%$) as internal standard. Products were identified in a GC-MS (Shimadzu GC-2010 with a Phenomenex ZB-1701 mid-polarity column).

On selected experiments additional amounts of CO were incorporated in the feed to the reaction medium by two different methods. In the first method, a gas mixture of H_2 and CO (Airgas, $H_2:CO = 4:1$) was fed to the reactor after the catalyst reduction. In the second method, the addition of CO was accomplished by including varying amounts of methanol (MeOH) (Sigma-Aldrich, 99.8%) in the reactant mixture in the range of 0.25–0.75 M of initial concentration. It is well known that CH_3OH readily decomposes on Ru surfaces at 473 K, only producing CO and H_2 in equimolar quantities [27].

2.3. Density functional theory calculations

The density functional theory (DFT) calculations were carried out using periodic plane-wave based methods implemented in VASP [28]. The plane-waves were constructed with an energy cutoff of 400 eV using projected augmented-wave (PAW) potentials [29]. The PBE form of the generalized gradient approximation (GGA) was used to determine corrections for the exchange and correlation energies [30]. DFT-D3 method was used for the correction of van der Waals (vdW) interactions [31].

The close-packed 4×4 Ru (0001) surface with four metal layers and 15 Å of vacuum separating the slabs in the z -direction were used to model the Ru catalyst. The top two metal

layers were allowed to relax during the calculations, whereas the bottom two layers were fixed in their bulk positions. The wave functions were converged to within 10^{-6} eV and the force on unconstrained atoms was converged to below 0.01 eV/Å. The first Brillouin zone was sampled using a Monkhorst-pack scheme with the k-point mesh of $3\times3\times1$ [32]. The energies of the adsorbates in vacuum were calculated spin-polarized using an $18\times18\times18$ Å unit cell with the Γ only k-point mesh. Transition states were located using the dimer method [33] with the initial guesses for the transition state structure and the reaction trajectory obtained through the nudged elastic band (NEB) method [34].

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the TEM images obtained on a fresh 5%Ru/C catalyst. The dark spots in the images correspond to Ru particles, as previously reported [35]. The images show fine, well dispersed Ru particles with an average particle size of about 2.3 nm, as estimated from measurements of over 50 particles. This result is in line with previous findings on similar catalysts [35]. From the CO chemisorption experiment, the fraction of Ru exposed was calculated to be 0.38.

Figure 1. TEM images of a 5%Ru/C catalyst and Ru particle size distribution.

Figure 2. Evolution of selectivity with overall γ -valerolactone (GVL) conversion in a batch reactor (0.1 M GVL in water, 473 K and 1000 psi H_2).

Figure 3. Evolution of selectivity with addition of MeOH during γ -valerolactone (GVL) conversion in a batch reactor (0.1 M GVL in water, 473 K and 1000 psi H_2).

3.2. Catalytic measurements

The results of the catalytic runs conducted with the GVL feed are shown in Table 1, which includes mass of catalyst used, reaction time, and product yields. The products identified in the reaction mixture are 1,4 pentanediol (1,4-PDO), 2-butanol (2-BuOH), 2-methyl tetrahydrofuran

(2-MTHF), and 2-pentanol (2-PeOH). Similar products have been reported in previous studies, but in different proportions. For example, working with an analogous catalyst under similar conditions to ours, but using ethanol as a solvent instead of water, Du et al. [36] obtained no detectable amounts of 2-MTHF or 1,4-PDO. On the other hand, in a similar experiment, but under solvent-free conditions, Al-Shaal et al. [14] obtained 2-MTHF as the most abundant product.

Table 1. Yields of products in batch reactor at varying reaction time and catalyst mass (Feed of 0.1 M γ -valerolactone (GVL) in water, 473 K and 1000 psi of H_2).

Run No.	m_{cat} (mg)	Time (h)	GVL	Yields (%)			
			Conversion (%)	1,4 PDO	2- BuOH	2- MTHF	2-PeOH
1	15	0.5	0.7	0.45	0.2	0	0.05
2	35	0.25	1	0.6	0.3	0	0.1
3	53	0.25	4.5	1.5	2.4	0.46	0.1
4	51	0.5	5.3	1.9	2.8	0.5	0.11
5	52	1	8.6	2.2	5.3	0.95	0.2
6	53	1.5	15	2.5	9.9	2.1	0.4
7	103	1	29	2.7	22.3	3.5	0.6

From an initial analysis of the observed products, one can conceive possible reaction pathways. First, the presence of the 1,4-PDO diol, along with the corresponding mono-alcohols, suggests that a major path may be the opening of the GVL ring at the C–O bond next to the carbonyl, involving the carbonyl C (C1) and the ring oxygen (O1), rather than the other C–O bond that involves the tertiary carbon (C4) and O1, since pentanoic acid was not observed. This result is further analyzed when discussing the DFT calculations (see Fig. 4).

Figure 4. DFT optimized adsorption geometry of GVL on Ru(0001) and its possible C–O breaking reaction paths.

Figure 5. DFT calculated decarbonylation, hydrogenation and deoxygenation reactions of the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2\text{CO}^*$ intermediate.

Figure 6. DFT calculated decarbonylation of the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2\text{CO}^*$ intermediate via the dehydrogenation and C–C breaking path.

If 1,4-PDO is an intermediate product, the ring-opening step should be followed by hydrogenolysis or decarbonylation to yield as secondary products 2-PeOH or 2-BuOH, respectively. Alternatively, as discussed below, one can consider the direct conversion of GVL to 1,4-PDO, 2-BuOH, and 2-PeOH in parallel paths derived from the same surface intermediate, in this case, all three compounds would be obtained as primary products.

To determine which of these pathways are dominant, we conducted runs at varying reaction times and with different amounts of catalyst to identify primary and secondary products. Runs 3–6 in Table 1 show the evolution of products with increasing reaction times. By adding a

larger amount of catalyst in run 7, we reached near 30% conversion. At this high conversion, 2-BuOH is the dominant product. At the lowest conversions, 1,4-PDO and 2-BuOH are the most abundant products, while 2-PeOH and 2-MTHF are only obtained in small quantities. Even lower conversions were obtained by loading smaller amounts of catalyst, resulting in the data listed as runs 1 and 2. Interestingly, no 2-MTHF was obtained in these stages, leading us to conclude that 2-MTHF is a secondary product, forming strictly via dehydration of 1,4-PDO, in line with previous conclusions of other researchers [37,38]. As discussed below, DFT calculations demonstrate that the oxophilicity of the Ru surface is enough to cause a strong structural tension between the two O atoms in the GVL molecule, facilitating the opening of the ring. Additionally, the abundance of water in the reaction medium confirms that the dehydration of 1,4-PDO is not limited by equilibrium and is an irreversible reaction.

Both, 2-BuOH and 2-PeOH seem to be primary products, since they are detected at very early stages of the reaction. However, they can also be obtained as secondary products as demonstrated in Table 2. As shown in the results of run 8, when using 1,4-PDO as a feed not only the dehydration product (2-MTHF) was observed as a product, as expected, but also the two mono-alcohols (2-BuOH and 2-PeOH) were obtained in significant amounts. This finding confirms that at least some of the 2-BuOH produced in high yields when feeding GVL as a reactant is due to decarbonylation of 1,4-PDO. Here, again, 2-BuOH is obtained in greater amounts than 2-MTHF and 2-PeOH. One can expect that both GVL and 1,4-PDO can produce the same surface intermediate that undergoes decarbonylation and C-O hydrogenolysis to produce 2-BuOH and 2-PeOH, respectively. Fig. 2 shows the variation of selectivity with GVL conversion and clearly demonstrates that the only product with zero selectivity at zero conversion is MTHF. At the same time, it is clearly seen that the selectivity to 2-BuOH

increases with conversion as the selectivity to 1,4-PDO decreases, which indicates that 1,4-PDO converts to 2-BuOH in a secondary reaction.

Table 2. Yields of products from intermediate products in batch reactor at varying reaction time and catalyst mass (Feed of 0.1 M 1,4-PDO or 2-MTHF in water, 473 K and 1000 psi of H₂).

Run No.	m_{cat} (mg)	Time (h)	Feed	Yields (%)			
				1,4 PDO	2-BuOH	2-MTHF	2-PeOH
8	53	1	1,4-PDO	feed	5.3	3.7	0.13
9	34	1.5	2-MTHF	0	0	feed	0.47

In Run 9, 2-MTHF was used as a reactant and it yielded 2-PeOH as its only product. Hence, it is demonstrated that ring-opening and hydrogenation of 2-MTHF is possible under the conditions investigated, and this path is responsible for at least some of the formation of 2-

PeOH. Other authors have also detected 2-PeOH among their products when reacting 2-MTHF on a Cu-Ru/C catalyst [39].

Since decarbonylation seems to play an important role in the reaction pathway and it is well known that the presence of CO strongly inhibits the decarbonylation rate [40], we incorporated varying amounts of CO from external sources, in addition to that produced by the reaction. In the first experiment (run 10, Table 3), a 1:2 gas mixture of CO and H₂ was fed to the reactor for the first 10 min of reaction, after which the reaction was brought to room temperature and depressurized. Once at room temperature and atmospheric pressure, the H₂ was replenished to the operating pressure and the temperature brought back to the reaction set point, and the reaction was carried out in normal conditions for another 50 min. It is worth mentioning that running this reaction under the high CO-concentration mixture resulted in complete inhibition of the catalyst activity and no products were detected. After removal of the CO from the gas phase, the activity was lower than that observed without added CO (see run 5 in Table 1) at comparable catalyst mass and reaction conditions. More importantly, it is observed that the product most strongly affected is 2-BuOH, indicating that decarbonylation is much more sensitive to CO poisoning than hydrogenation, hydrogenolysis, or ring-opening.

Table 3. Effect of CO addition to the reaction mixture (Feed of 0.1 M γ -valerolactone (GVL) in water with added CO as indicated in the Table. Reaction time 1 h, 473 K and 1000 psi of H_2).

Run No.	m_{cat} (mg)	Method of CO addition	Feed	Yields (%)			
				1,4-PDO	2-BuOH	2-MTHF	2-PeOH
10	53.2	CO/ H_2	GVL	1.13	1.32	0.28	0.16
11	53.0	MeOH 0.25 M	GVL	1.35	1.82	0.72	0.07
12	53.5	MeOH 0.5 M	GVL	1.31	1.15	0.63	0.06
13	53.0	MeOH 0.75 M	GVL	1.12	0.73	0.41	0.03
14	52.4	MeOH 0.5 M	1,4-PDO	feed	3.89	3.39	0.12

In a different set of experiments, increasing amounts of methanol (MeOH) were injected with the reactant mixture (in the range of 0.25–0.75 M of initial concentration), expecting that the methanol decomposition incorporates increasing amounts of CO into the reaction vessel. Table 3 shows that incorporation of CO in the reaction medium clearly has a detrimental effect in the product yield, since all of the products' concentrations diminish by a significant amount when compared to the case of no CO addition. Runs 11–13 show that increasing amounts of CO have a greater effect on 2-BuOH than on the rest of the products, which stay constant or decrease very little. 2-BuOH experiences the greatest drop when CO is externally added to the reaction medium. The same result is obtained when 1,4-PO is fed as a reactant with (run 14) or without addition of CO (run 8). This is evidence that the site in which the decarbonylation takes place is also most prone to adsorb CO and be poisoned. And this active site is not necessarily the most active one for hydrogenation reactions.

The influence of H₂ pressure on activity and product distribution was also investigated at 473 K, but running the reaction at two different H₂ pressure values. The results are shown in Table 4. Interestingly, while the overall conversion decreases when the H₂ pressure is reduced in half, there is little change in the yield of 2-BuOH, the decarbonylation product. By contrast, 1,4-PDO, formed by hydrogenation of the ring-opening intermediate is the most highly inhibited product when the H₂ pressure decreases.

Table 4. Effect of H₂ pressure on GVL conversion (Feed of 0.1 M γ -valerolactone (GVL) in water, temperature 473 K and pressure 1000–500 psi H₂).

Run No.	Pressure (psi)	GVL conversion (%)	Yield (%)			
			2-MTHF	2-BuOH	2-PeOH	1,4-PDO
14	1000	10.3	0.64	4.95	0.08	4.63
15	500	6.58	0.48	4.19	0.07	1.84

An interesting comparison can be made with the CO- and H₂-dependences reported by Gürbüz et al. [40] for the decarbonylation of the propanol-derived intermediate on Ir, Pt and Ru catalysts. First, similar to the results reported here, they observed that decarbonylation was strongly inhibited by chemisorbed CO. Also, they found a 100-fold decrease in the decarbonylation/hydrogenolysis ratio as the metal cluster size increased and explained this

changes proposing that decarbonylation occurs preferentially on low-coordination sites. More interesting, a significant difference in behavior was observed by these authors on the H₂-dependence of decarbonylation. While here, the effect of H₂ on decarbonylation is practically negligible (or positive), in their study, Gürbüz et al. [40] found the decarbonylation rate to be strongly inhibited by H₂. They explained this H₂ inhibition by proposing that the decarbonylation is preceded by the formation of a partially dehydrogenated species, formed in sequential quasi-equilibrated dehydrogenation steps. It is interesting to analyze the possibility that in the case of GVL conversion, direct decarbonylation is possible, without requiring previous dehydrogenation steps, thus reducing the inhibition by H₂. To help interpreting these results, we have conducted DFT calculations that have allowed us to determine the nature of reaction intermediates, transition states, and ultimately propose a reaction mechanism.

3.3. *Density functional theory calculations*

First, we determined the most probable structure of the adsorbed GVL on a Ru(0001) surface. As shown in Figure 4, GVL adsorbs on this Ru surface via the carbonyl carbon (C1), carbonyl oxygen (O2) as well as the ring oxygen (O1) atop three Ru atoms with the C1-Ru, O1-Ru and O2-Ru distance of 2.13 Å, 2.07 Å and 2.25 Å respectively. The adsorption energy was calculated to be -141 kJ/mol, which shows a strong adsorption of the reactant. Next, we considered the reaction steps that the adsorbed GVL can undergo toward different products. That is, as illustrated in Figure 4, it could break the C1–O1 bond forming the CH₃CH(O*)-(CH₂)₂-CO* intermediate, which can further go through decarbonylation, hydrogenation or hydrogenolysis to form 2-BuOH, 1,4-PDO or 2-POH, respectively as the final (primary) observable products. In fact, the energy barrier for the breaking of C1–O1 bond of adsorbed GVL is very low (7 kJ/mol) with a significant exothermicity (-74 kJ/mol). The extreme low barrier and the strong exothermic

reaction energy indicate that this reaction will readily occur. In comparison, the breaking of the C4–O1 bond is more difficult with the energy barrier of 122 kJ/mol. This is in agreement with the experimental observation that no pentanoic acid or its derivatives such as butane (formed by decarboxylation) was formed in the conversion of GVL over the Ru/C catalyst. The breaking of the carbonyl C1–O2 bond is also more difficult than the C1–O1 bond breaking with the energy barrier of 84 kJ/mol, this also agrees with the above experiments; MTHF was not formed at low GVL conversions, which indicates that it is not formed directly from GVL, but rather as a secondary products from 1,4-PDO. Thus, among all the possible C–O bond breaking reactions of GVL, the C1–O1 bond breaking is dominant to form the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ intermediate. The extremely low barrier for this reaction also suggests that the ring opening of GVL is not likely to be the rate limiting step in the overall conversion path.

After the surface intermediate, $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$, is formed by ring opening of adsorbed GVL, it can go through decarbonylation, hydrogenation or hydrogenolysis reaction to form different products. These parallel alternative steps are illustrated in Figure 5. In the decarbonylation step, the C–CO bond in $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ is cleaved, releasing CO with an energy barrier of 96 kJ/mol.

In the work by Gürbüz et al. [40], it was reported that the pre-removal of H atoms at the α -C can facilitate the decarboxylation of aldehydes. We have also analyzed the effect of H removal on the decarbonylation of the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ intermediate via dehydrogenation and C–C breaking path as shown in Figure 6. We see that indeed, after removal of one α -C hydrogen, the energy barrier for the C–CO* breaking decreases significantly to 14 kJ/mol. However, the dehydrogenation at the α -C of $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ in the case of GVL is exceedingly difficult, 149 kJ/mol, and even higher than the barrier for the direct

decarbonylation reaction (96 kJ/mol). The higher barrier for the dehydrogenation at the α -C is probably due to the steric effects that the binding of O* at the C4 position constrained the carbon chain. Thus, the direct decarbonylation path is still favorable for the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ intermediate. After decarbonylation, the formed $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2^*$ intermediate will continue to hydrogenate to form 2-butanol.

As shown in Figure 4, the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ intermediate can also hydrogenate the $-\text{CO}^*$ group to form aldehyde and further the di-alcohol 1,4-PDO. The hydrogenation of $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ to form $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{COH}$ and the energy barrier was calculated to be 89 kJ/mol, which is slightly lower than the decarbonylation reaction, suggesting that it is slightly more favorable. The deoxygenation reaction of the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ intermediate to form $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$, which can subsequently hydrogenate to form 2-POH was also shown in Figure 4. The energy barrier is calculated to be 106 kJ/mol. This is higher than the barriers for either decarbonylation or hydrogenation, suggesting that this path is the least favorable among the three.

According to the analysis of the DFT calculations, the major products 2-BuOH, 1,4-PDO, and 2-POH can all be formed as primary products from the $\text{CH}_3\text{CH}(\text{O}^*)-(\text{CH}_2)_2-\text{CO}^*$ intermediate, which is readily formed by ring opening of GVL. This is in agreement with the experiments that all these three products are formed at low conversion of GVL. However, it is important to point out that as conversion increases, 2-BuOH and 2-POH can also be formed as secondary products from the re-adsorption and reaction of 1,4-POH, as shown in the experiments.

3.4. Reaction mechanism

Based on the analysis of the observed intermediates and products, a mechanism for the GVL conversion on Ru/C can be proposed in Figure 7. Ru surface strongly interacts with the oxygen atoms of the GVL molecule, causing the ring to strain and eventually break, forming the acyl species (1) [41,42]. At this point, different pathways are available, leading to the formation of all the experimentally observed products. Under the reaction conditions of this study, the acyl preferentially decarbonylates and undergoes hydrogenation to form 2-BuOH (2). Analysis of the gas phase showed the presence of CO, which confirms the decarbonylation route. The acyl can also be hydrogenated to η -2 complex (3), which can then undergo a series of hydrogenation steps and yield 1,4-PDO (4). Alternatively, hydrogenolysis of the η -2 complex and further hydrogenation can yield 2-PeOH (5). The steps leading to the formation of 1,4-PDO are proposed to be reversible, since 2-BuOH as well as 2-PeOH were shown to be secondary products of 1,4-PDO, which in turn can also dehydrate and cyclize to form 2-MTHF (6), which can in turn undergo hydrogenolysis forming 2-PeOH (7).

Figure 7. Summarized mechanism of the conversion of GVL over Ru catalyst.

4. Conclusions

The combination of experimental and theoretical studies has allowed us to identify the reaction pathways and reaction intermediates in the aqueous-phase conversion of γ -valerolactone (GVL) over a supported Ru catalyst. At 473 K, and in the presence of 500–1000 psi H_2 the reaction starts with a ring-opening step that forms a surface intermediate, $CH_3CH(O^*)-(CH_2)_2-CO^*$. This intermediate can take any of the following three parallel paths:

- (a) Decarbonylation that leads to 2-butanol
- (b) Hydrogenation that leads to 1,4-pentanediol
- (c) C–O hydrogenolysis that leads to 2-pentanol

All three paths are reversible and the products can undergo secondary reactions. Under the conditions of the study, at high GVL conversions the dominant product is 2-butanol.

Decarbonylation is strongly inhibited by CO, but not affected by H_2 pressure. The other two paths are less affected by CO and enhanced by H_2 . It is concluded that the direct decarbonylation path of the $CH_3CH(O^*)-(CH_2)_2-CO^*$ intermediate does not require a previous dehydrogenation step, as previously proposed for decarbonylation of short alcohols.

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Graphical abstract

The conversion of γ -valerolactone on ruthenium, aqueous phase (473 K, 1000 psi H₂) proceeds via a common surface intermediate $\text{CH}_3\text{CH}(\text{O}^*)\text{-(CH}_2)_2\text{CO}^*$ that subsequently can undergo decarbonylation, hydrogenation, or deoxygenation to yield 2-butanol, pentanediol, or 2-pentanol, respectively.