Theoretical Investigation of the Decarboxylation and Decarbonylation Mechanism of Propanoic Acid over a Ru(0001) Model Surface

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Abstract

The hydrodeoxygenation of organic acids is often found to be a rate-controlling process during upgrading of biomass feedstocks into fuels. We developed a microkinetic model based on data obtained from density functional theory calculations for the decarboxylation and decarbonylation mechanisms of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) over a Ru(0001) model surface. The model predicts that the decarbonylation mechanism is two orders of magnitude faster than the decarboxylation mechanism. The most favorable decarbonylation pathway proceeds via removal of the acid -OH group to produce propanoyl ($\text{CH}_3\text{CH}_2\text{CO}$) followed by C-CO bond scission of propanoyl to produce CH_3CH_2 and CO. Finally, CH_3CH_2 is hydrogenated to CH_3CH_3 . Dehydrogenation reactions that have been observed to be important over Pd catalysts play no role over Ru(0001) and a sensitivity analysis indicates that removal of the acid -OH group is the rate controlling step in the deoxygenation. Overall, our results suggest that to improve the Ru catalyst performance for the decarbonylation of organic acids the free site coverage needs to be increased by, e.g., adding a catalyst promoter that decreases the hydrogen and CO adsorption strength (without significantly affecting the C-OH bond scission rate), or by raising the reaction temperature and operating at relatively low CO and H_2 partial pressures.

Keywords: ruthenium; density functional theory; microkinetic model; deoxygenation; hydrodeoxygenation; organic acid

1. Introduction

Increased consumption of non-renewable fossil fuels in the last couple of decades has led to growing concerns over the environmental impact of fossil fuel utilization. Liquid fuels derived from renewable raw materials such as biomass have thus gained more and more attention and are increasingly being developed. Intensive research is currently being conducted on the catalytic hydrodeoxygenation (HDO) of triglycerides (a major constituent of vegetable oil and animal fats) and fatty/carboxylic acids over transition metal surfaces.[1-9] During the HDO of triglycerides, carboxylic acids have often been found to be reaction intermediates and the HDO of organic acids is often the rate controlling process.[10] Three reaction mechanisms – decarbonylation (DCN), decarboxylation (DCX), and reductive deoxygenation without C-C bond cleavage (RDO) – have been proposed to be the dominant deoxygenation pathways for organic acids. Considering that the first two reaction mechanisms require less hydrogen which is likely constrained in a future biorefinery, there is a desire to design more active and selective decarbonylation/decarboxylation catalysts.

In our recent papers[11, 12], we have studied the DCN and DCX mechanisms of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) to C_2 hydrocarbons on Pd(111) surface models and found that the DCN is favored over the DCX. To gain more insights into the DCN and DCX mechanisms of organic acids (such as propanoic acid) on transition metal surfaces and to possibly design novel metal catalysts, it is necessary to study multiple metal surfaces. Ruthenium is more oxophilic than Palladium and has experimentally been found to be an active catalyst for the conversion of organic acids to hydrocarbon molecules.[2, 13-15] Experiments on the HDO of propanoic acid over Ru/C by Chen *et*

al.[13] and the HDO of acetic acid over Ru/C by Olcay *et al.*[14] show that at high H₂ partial pressure (> 20 bar) and at temperatures of around 400 K, Ru/C has a high selectivity to propanol and ethanol, respectively. On the other hand, it has been shown that when flowing acetic acid over Ru/C at a low H₂ partial pressure (< 1 bar),[14] mostly methane (~70% selectivity) and only small amounts of ethanol are produced (~6% selectivity). Experiments on propanoic acid on Ru/SiO₂ at low H₂ partial pressure (< 1 bar) by Lugo-Jose *et al.*[15] showed that the selectivity to C₂ hydrocarbons increases with increasing temperature in the range of 473 K – 573 K and that the deoxygenation mechanism proceeds by decarbonylation.

In this paper, we report a microkinetic modeling study based on data obtained from density functional theory (DFT) calculations for the DCN and DCX mechanisms of propanoic acid over Ru(0001) terrace sites. We aim at determining the preferred reaction mechanism and identifying possible descriptors relevant for the selectivity of the DCN and DCX at low H₂ partial pressure where the alcohol production selectivity is low and can to a first approximation be neglected. Also, we will compare our Ru(0001) results with those obtained from Pd(111).[12]

2. Methods

We have employed the Vienna Ab Initio Simulation Package (VASP),[16, 17] a periodic plane wave based density functional theory program, to calculate all adsorption energies and vibrational properties. The electron-ion interactions are described by the projector-augmented wave method (PAW), which is a frozen core all-electron method which uses the exact shape of the valence wave functions instead of pseudo-wave

functions.[18] The exchange correlation energy has been calculated within the generalized gradient approximation by the Perdew and Wang 1991 formulation (GGA-PW91).[19, 20] The kinetic energy cutoff of the plane-wave basis set was fixed to 400 eV in all calculations. To approximately consider dispersion interactions for adsorption and desorption processes of hydrocarbon species, we also performed selected calculations using the PBE-D3 method[30]. Further details about these calculations can be found in Section 3.3.2.

Using the PW91 functional, the total energy of hcp-Ru bulk approaches a minimum when its lattice constants are $a=2.7264 \text{ \AA}$ and $c=4.3134 \text{ \AA}$, which are in reasonable agreement with the experimental values ($a=2.7059 \text{ \AA}$ and $c=4.2815 \text{ \AA}$ [21]). The Ru(0001) surface was built as a periodic slab with four Ru layers separated by a vacuum layer of $15 \text{ \AA}$ in order to diminish lateral interactions between the slab and its periodic images. Each Ru layer has 12 Ru atoms with a $(3 \times 2\sqrt{3})$ periodicity, allowing for adsorbate coverages as low as $1/12 \text{ ML}$. For all calculations the bottom two Ru layers were fixed to their bulk positions to represent the semi-infinite substrate while the top two layers were allowed to relax in all directions. The adsorbates were free to relax in all directions, too. Coordinates of the adsorbates and the Ru atoms in the relaxed layers were optimized to a force less than $0.03 \text{ eV/\AA}$ on each atom. All self-consistent field (SCF) calculations were converged to $1 \times 10^{-3} \text{ kJ/mol}$. Brillouin zone integration was performed using a $4 \times 4 \times 1$ Monkhorst-Pack grid and a Methfessel-Paxton smearing of 0.2 eV .

Adsorption energies, E_{ads} , of all surface intermediates were calculated in their most stable adsorption modes using equation 1

$$E_{\text{ads}} = E_{\text{slab+adsorbate}} - E_{\text{slab}} - E_{\text{adsorbate(gas)}} \quad (1)$$

where $E_{\text{slab+adsorbate}}$ is the total energy of the Ru slab with an adsorbate binding on to it, E_{slab} is the total energy of the clean slab, and $E_{\text{adsorbate(gas)}}$ is the total energy of the adsorbate in the gas phase.

Transition states of elementary reactions were located by a combination of the nudged elastic band (NEB) method[22] and the dimer method.[23-25] In the NEB method, an interpolated chain of configurations/images between the initial and final states were relaxed simultaneously. The image of the NEB calculation which is closest to a likely transition state structure was then employed as an initial guess structure for the dimer method. All adsorption energies and activation barriers reported in this study have been zero-point energy corrected (ΔZPE).

In our microkinetic model development, we used the same methodology as described in our latest publication [12]. For adsorption processes, we used collision theory with a sticking coefficient of 1 to calculate the reaction rate constant. For the calculation of surface reaction rate constants, harmonic transition state theory has been used. Frequencies below 100 cm^{-1} are shifted to 100 cm^{-1} during the partition function calculations to minimize the errors of the harmonic approximation for small frequencies [12]. All reverse reaction rate constants are determined by the equilibrium and forward rate constants. The nonlinear steady state surface species equations have finally been solved using the BzzMath library developed by G. Buzzi-Ferraris [26].

3. Results and discussion

Figure 1 illustrates the reaction pathways investigated for the DCN and DCX of propanoic acid to C₂ alkanes over Ru(0001). This scheme does not include reactions that lead to C₁ or C₃ products. C₁ hydrocarbons are experimentally not observed and while C₃ products are possibly important at high hydrogen partial pressure, we decided to focus this study on the relevant mechanisms at low hydrogen partial pressure. The reductive deoxygenation (RDO) mechanism leading to C₃ products is currently under investigation in the context of a high hydrogen partial pressure environment.

In the following, we will discuss the adsorbed intermediates in section 3.1. Then, we will investigate the potential energy surface of various reaction pathways in sections 3.2. Finally, we will develop a microkinetic model, compute turnover frequencies and compare our results to experimental observations in section 3.3.

(Figure 1 here)

3.1. Adsorbed intermediates

Figure 2 shows adsorption geometries of the reactants, products and possible reaction intermediates involved in both DCN and DCX mechanisms. There are 10 surface intermediates on Ru(0001) which have a different (most stable) adsorption configuration from their counterparts on Pd(111).[11] The propanoic acid molecule adsorbs in an orientation in which both the carbonyl O and the hydroxyl H bind to Ru atoms while on Pd(111) only the carbonyl O binds strongly to the Pd atop site. Similarly, both the hydroxyl O of CH₃CHCOOH and the carbonyl O of CH₃CHCO bind to Ru atoms in atop position, while they do not bind to Pd atoms on Pd(111). Also, CO and the carbonyl C of CH₃CH₂CO bind to an atop site on Ru(0001) while they bind to fcc hollow

and bridge sites on Pd(111), respectively. Next, one C atom in CH₂CH₂ and the C in COOH bind to bridge sites on Ru(0001) while they bind to atop sites on Pd(111). Finally, CHCH, CH₃C, and OH bind to hcp hollow sites on Ru(0001) while they prefer fcc hollow sites on Pd(111).

Table 1 lists the binding modes, adsorption energies and zero point energy corrections of all intermediates. We have employed the nomenclature $\eta i \mu j$ to designate that i atoms of the adsorbate are binding to j atoms of the Ru surface. We observe that saturated intermediates, such as propanoic acid ($E_{\text{ads}}=-0.71$ eV), ethane (-0.07 eV), water (-0.43 eV), and carbon dioxide (-0.20 eV) are relatively weakly adsorbed to the surface. These relatively weak bonds are formed either by interactions between the lone pair electrons on the hydroxyl oxygen with the surface or by weak π -bonded interactions of the C=O group with the surface.[27] Meanwhile, open-shell intermediates strongly adsorb onto the Ru(0001) surface with adsorption energies ranging from -1.02 eV to -5.95 eV. Especially, the CH₃C species binds very strongly to the surface with an adsorption energy of -5.95 eV. Carbon atoms tend to satisfy their tetrahedral bonding geometry on the surface[8] and a deeper dehydrogenation results in stronger adsorption. For example, CH₃CH₃ adsorbs very weakly on Ru(0001). The first dehydrogenation product CH₃CH₂ forms a significantly stronger bond with the surface ($E_{\text{ads}}=-1.76$ eV), CH₃CH adsorbs about twice as strong as CH₃CH₂ ($E_{\text{ads}}=-4.23$ eV), and the third dehydrogenation product CH₃C adsorbs about three times as strong as CH₃CH₂ ($E_{\text{ads}}=-5.95$ eV) such that to a good approximation each dehydrogenation leads to an increase in adsorption strength of 1.6 – 2.0 eV. All intermediates, except ethane, have a stronger

adsorption energy on Ru(0001) than on Pd(111) which can be explained by the higher oxophilicity of Ru.

(Figure 2 here)

3.2. Potential energy surface of various reaction pathways

The pathways shown in Figure 1 can be classified into decarbonylation (DCN) or decarboxylation (DCX) pathways. Both DCN and DCX pathways can be further distinguished into direct decomposition pathways and pathways involving dehydrogenation steps. Snapshots of all transition states involved are shown in Figures 3 and 4 and the activation barriers, reaction energies, and rate parameters at four characteristic reaction temperatures are listed in Table 2.

(Figures 3 and 4 here)

3.2.1 Reaction pathways for the DCN mechanism

The direct decomposition DCN pathway starts with -OH removal of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) to produce $\text{CH}_3\text{CH}_2\text{CO}$ and OH surface intermediates (step 1). This reaction is rather facile with an activation barrier of only 0.49 eV and a reaction energy of -0.36 eV. $\text{CH}_3\text{CH}_2\text{CO}$ can decarbonylate into CH_3CH_2 and CO (step 4) which has an activation barrier of 0.84 eV and a reaction energy of -0.41 eV.

DCN pathways involving dehydrogenation steps can be divided into two groups. One group starts with α -carbon dehydrogenation of $\text{CH}_3\text{CH}_2\text{CO}$ to yield CH_3CHCO (step 5); in the following, we call these pathways CH_3CHCO -derived reaction pathways. The other group starts with α -carbon dehydrogenation of the acid to yield CH_3CHCOOH (step

2) and we will call these pathways CH_3CHCOOH -derived reaction pathways. The former group might be viable since step 5 (dehydrogenation of $\text{CH}_3\text{CH}_2\text{CO}$) has a low activation barrier of 0.32 eV and a reaction energy of -0.37 eV. The later pathway might be viable based on an activation barrier of 0.56 eV which is only slightly larger than the barrier for the direct C–OH bond cleavage (step 1).

In the CH_3CHCO -derived DCN pathways, CH_3CHCO can decompose by decarbonylation (step 15), α -carbon dehydrogenation (step 16), or β -carbon dehydrogenation (step 17). Among these pathways step 16 is preferred with an activation barrier of 0.66 eV and a reaction energy of -0.43 eV. Step 17 has a similar reaction energy of -0.44 eV but possesses a slightly larger activation barrier of 0.78 eV. Finally, decarbonylation of CH_3CHCO to CH_3CH (step 15) is the most difficult step with an activation barrier of 0.85 eV and a reaction energy of -0.66 eV.

The CH_3CHCOOH -derived DCN pathways can proceed either by initial –OH removal to produce CH_3CHCO (step 6) or by β -carbon dehydrogenation to CH_2CHCOOH (step 7). We find step 7 to be slightly preferred ($E_a = 0.52$ eV, $\Delta E_0 = -0.51$ eV) over step 6 ($E_a = 0.61$ eV, $\Delta E_0 = -0.44$ eV) that merges here with the CH_3CHCO -derived pathways. Adsorbed CH_2CHCOOH can decompose either by initial –OH removal to CH_2CHCO (step 18), decarbonylation to CH_2CH (step 26), or by further β -carbon dehydrogenation to CHCHCOOH (step 20) followed by –OH removal (step 28) and decarbonylation to CHCH (step 32). Note that we also considered –COOH removal steps, i.e., step 10 ($\text{CH}_3\text{CHCOOH} \rightarrow \text{CH}_3\text{CH} + \text{COOH}$) and 27 ($\text{CH}_2\text{CHCOOH} \rightarrow \text{CH}_2\text{CH} + \text{COOH}$), however, both steps have activation barriers of 0.89 eV (step 10) and 0.98 eV (step 26) that are much higher than other competitive reaction steps.

3.2.2 Reaction pathways for the DCX mechanism

The DCX mechanisms investigated can also be classified into direct decomposition pathways and pathways involving dehydrogenation steps. The direct decomposition pathway starts with initial O-H bond scission of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) to produce $\text{CH}_3\text{CH}_2\text{COO}$ (step 3), which is a facile and exothermic step ($E_a = 0.21 \text{ eV}$, $\Delta E_0 = -1.02 \text{ eV}$), followed by decarboxylation of $\text{CH}_3\text{CH}_2\text{COO}$ to CH_3CH_2 and CO_2 (step 12). Step 12 has a high activation barrier of 1.71 eV and is endothermic by 0.95 eV . Considering the high reaction barrier, it becomes apparent that the DCN pathways are likely preferred to this DCX mechanism.

Next, other DCX pathways involving dehydrogenation steps can be divided into CH_3CHCOO -derived pathways that start with α -carbon dehydrogenation steps of $\text{CH}_3\text{CH}_2\text{COO}$ (step 11) and CH_3CHCOOH -derived pathways that start with dehydrogenation step 2. CH_3CHCOO can either be decarboxylated to CH_3CH (step 23) or go through further dehydrogenation steps to CH_3CCOO (step 22), followed by decarboxylation to CH_3C (step 29). Both steps 22 and 23 possess large barriers of 0.94 and 1.18 eV , respectively.

CH_3CHCOOH -derived pathways follow either an O-H bond scission of CH_3CHCOOH to produce CH_3CHCOO (step 9) or a full α -carbon dehydrogenation to CH_3CCOOH (step 8), followed by O-H bond scission to CH_3CCOO (step 21). Step 9 is facile with an activation barrier of 0.39 eV and a reaction energy of -0.68 eV . Also, step 8 is relatively facile with an activation barrier of 0.62 eV and a reaction energy of -0.48 eV . In contrast, the thermoneutral step 21 is slow with an activation barrier of 1.17 eV .

Overall, it is difficult to identify the preferred reaction mechanism from the activation and reaction energies under relevant reaction conditions. As a result, we developed a microkinetic model based on parameters obtained from first principles and harmonic transition state theory.

3.3. Microkinetic modeling

3.3.1 Lateral interaction effects

Mean-field microkinetic models that do not consider lateral interactions at least approximately often predict non-physically low turnover frequencies due to an exceedingly low free site coverage. This is a particular challenge for reactions involving gas phase CO whose lateral interaction can be very strong. As a result, we used a method similar to the one proposed by Grabow *et al.*[28] and previously applied by us[12] to take lateral interaction effects for those surface intermediates into account that a preliminary study identified to have significant surface coverages, i.e., H, CO and CH₃C (linear parameterization of differential adsorption energies). We note that this approximate procedure for considering lateral interactions does not change surface reaction rate constants but only changes (reduces) the surface coverages of the most dominant surface species. While lateral interactions can also change elementary surface reaction rate constants, the determination of coverage dependent rate constants is beyond the scope of this work. The data used to fit the coverage dependent adsorption energies can be found in the supporting information.

From adsorption of H atoms at various coverages ($\theta_H=1/4$ ML, $2/4$ ML, $3/4$ ML, $4/4$ ML), the differential adsorption energy of H as a function of its coverage θ_H , $E_H(\theta_H)$ is calculated to be:

$$E_H(\theta_H) = -2.906 + 0.168 * (\theta_H - 0.139) \quad (2)$$

Similarly, the differential adsorption energy of CO as a function of its coverage θ_{CO} , $E_{CO}(\theta_{CO})$ is calculated to be:

$$E_{CO}(\theta_{CO}) = -1.955 + 1.748 * (\theta_{CO} - 0.087) \quad (3)$$

For the differential adsorption energy of CH_3C , $E_{CH_3C}(\theta_{CH_3C})$, we found

$$E_{CH_3C}(\theta_{CH_3C}) = -6.101 + 6.062 * (\theta_{CH_3C} - 0.192) \quad (4)$$

From coadsorption of H and CO at various coverages, we get $E_H(\theta_H, \theta_{CO})$ and $E_{CO}(\theta_H, \theta_{CO})$ as follows:

$$E_H(\theta_H, \theta_{CO}) = -2.906 + 0.168 * (\theta_H - 0.139) + 0.622 * \theta_{CO} - 0.609 * \theta_{CO} (\theta_H \theta_{CO})^{0.5} \quad (5)$$

$$E_{CO}(\theta_H, \theta_{CO}) = -1.955 + 1.748 * (\theta_{CO} - 0.087) + 0.622 * \theta_H - 0.609 * \theta_H (\theta_H \theta_{CO})^{0.5} \quad (6)$$

Similarly, from coadsorption of H and CH_3C at various coverages, we get $E_H(\theta_H, \theta_{CH_3C})$ and $E_{CH_3C}(\theta_H, \theta_{CH_3C})$ as follows:

$$E_H(\theta_H, \theta_{CH_3C}) = -2.906 + 0.168 * (\theta_H - 0.139) + 1.049 * \theta_{CH_3C} - 2.096 * \theta_{CH_3C} (\theta_H \theta_{CH_3C})^{0.5} \quad (7)$$

$$E_{CH_3C}(\theta_H, \theta_{CH_3C}) = -6.101 + 6.062 * (\theta_{CH_3C} - 0.192) + 1.049 * \theta_H - 2.096 * \theta_H (\theta_H \theta_{CH_3C})^{0.5} \quad (8)$$

Next, from coadsorption of CO and CH_3C at various coverages, we get $E_{CO}(\theta_{CO}, \theta_{CH_3C})$ and $E_{CH_3C}(\theta_{CO}, \theta_{CH_3C})$ as follows:

$$E_{CO}(\theta_{CO}, \theta_{CH_3C}) = -1.955 + 1.748 * (\theta_{CO} - 0.087) - 0.800 * \theta_{CH_3C} + 8.105 * \theta_{CH_3C} (\theta_{CO} \theta_{CH_3C})^{0.5} \quad (9)$$

$$E_{\text{CH}_3\text{C}}(\theta_{\text{H}}, \theta_{\text{CH}_3\text{C}}) = -6.101 + 6.062 * (\theta_{\text{CH}_3\text{C}} - 0.192) - 0.800 * \theta_{\text{CO}} + 8.105 * \theta_{\text{CO}} (\theta_{\text{CO}} \theta_{\text{CH}_3\text{C}})^{0.5} \quad (10)$$

Finally, we get the coverage dependent adsorption energy of H and CO, $E_{\text{H}}(\theta_{\text{H}}, \theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}})$ and $E_{\text{CO}}(\theta_{\text{H}}, \theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}})$ as follows:

$$\begin{aligned} E_{\text{H}}(\theta_{\text{H}}, \theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}}) = & -2.906 + 0.168 * (\theta_{\text{H}} - 0.139) \\ & + 0.622 * \theta_{\text{CO}} - 0.609 * \theta_{\text{CO}} (\theta_{\text{H}} \theta_{\text{CO}})^{0.5} \\ & + 1.049 * \theta_{\text{CH}_3\text{C}} - 2.096 * \theta_{\text{CH}_3\text{C}} (\theta_{\text{H}} \theta_{\text{CH}_3\text{C}})^{0.5} \end{aligned} \quad (11)$$

$$\begin{aligned} E_{\text{CO}}(\theta_{\text{H}}, \theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}}) = & -1.955 + 1.748 * (\theta_{\text{CO}} - 0.087) \\ & + 0.622 * \theta_{\text{H}} - 0.609 * \theta_{\text{H}} (\theta_{\text{H}} \theta_{\text{CO}})^{0.5} \\ & - 0.800 * \theta_{\text{CH}_3\text{C}} + 8.105 * \theta_{\text{CH}_3\text{C}} (\theta_{\text{CO}} \theta_{\text{CH}_3\text{C}})^{0.5} \end{aligned} \quad (12)$$

Equations 11 and 12 have been implemented into our microkinetic model to include lateral interaction effects on the hydrogen and CO surface coverages.

3.3.2 Dispersion interaction corrections

Dispersion interactions are potentially relevant for all adsorption and desorption processes of hydrocarbon species in the reaction mechanism of the HDO of propanoic acid over Ru(0001). Unfortunately, these interactions are not included in the PW91 functional such that adsorption energies computed by PW91 are likely lower estimates. For example, it has experimentally been shown that methanol with 1/9 ML coverage on Pt(111) has an adsorption energy of -58.6 ± 0.8 kJ/mol.[29] But the PW91 functional predicts an adsorption energy of only -27.2 kJ/mol from our calculations with a 1/12 ML coverage. Empirical dispersion corrections to DFT can to a large extent resolve this problem. For instance, we have used the PBE-D3 method[30] to calculate the adsorption energy of methanol with 1/16 ML coverage and obtained -66.2 kJ/mol, which is slightly

larger than, but quite close to, the experimental value. To investigate the effect of dispersion interactions on our microkinetic model, we report in the next subsection both microkinetic modeling results with parameters obtained with PW91 functional and microkinetic modeling results in which the PBE-D3 functional is used to compute the adsorption and desorption energetics of $\text{CH}_3\text{CH}_2\text{COOH}$, H_2 , CO , CO_2 , H_2O , CH_2CH_2 , CH_3CH_3 . The PBE-D3 results are reported in [] brackets and Table 3 lists the zero-point energy corrected adsorption energies computed with both PW91 and PBE-D3. The computational setup for the PBE-D3 calculations is identical to the one for the PW91 calculations except that the equilibrium lattice constants of the Ru bulk unit cell are calculated to be $a=2.7022 \text{ \AA}$ and $c=4.2736 \text{ \AA}$ with PBE-D3 functional which are slightly smaller than the PW91 result and very close to the experimental values.

3.3.3 Turnover frequencies

The reaction temperature in our microkinetic model is 473 K and the reactant gas phase pressures of propanoic acid and H_2 are 0.01 bar and 1 bar, respectively, which are typical values in laboratory scale experiments. Assuming a small conversion of approximately 10%, we set the product partial pressures of CO , CO_2 , H_2O , CH_2CH_2 , CH_3CH_3 to 10^{-3} bar. We note that our model does not contain a water-gas shift model such that we had to approximate the product/ CO partial pressures. Fortunately, we find that our results are not very sensitive to the product/ CO partial pressures (see below). Under these conditions, we find that ethane is the preferred reaction product.

Our model predicts the dominant surface intermediates to be H (57.2%, [33.3%]), CO (41.1%, [50.9%]), CH_3C (1.2%, [2.2%]), and $\text{CH}_3\text{CH}_2\text{COO}$ (0.14%, [6.8%]). The

free site coverage is 0.16% [0.04%], i.e., the catalyst surface is crowded with intermediates. We note that dispersion interactions significantly increase the $\text{CH}_3\text{CH}_2\text{COO}$ coverage and decrease the free site coverage. Figure 5 illustrates the turnover frequencies of various reaction pathways in our microkinetic model.

(Figure 5 here)

It is apparent that the direct DCN pathway is dominant (independent of inclusion of dispersion interactions). It proceeds by initial $-\text{OH}$ removal of propanoic acid to $\text{CH}_3\text{CH}_2\text{CO}$ (step 1), followed by decarbonylation to CH_3CH_2 (step 4) and hydrogenation to ethane (step 13). It has a TOF of $2.4 \times 10^{-7} \text{ s}^{-1}$ [$6.5 \times 10^{-6} \text{ s}^{-1}$] which is 2 orders of magnitude faster than the direct DCX pathway ($2.8 \times 10^{-9} \text{ s}^{-1}$, [$9.8 \times 10^{-8} \text{ s}^{-1}$]), steps 3, 12, and 13, such that we conclude that the DCN mechanism is the dominant reaction pathway. We note that the microkinetic model with dispersion-corrected adsorption/desorption energies predicts a one order of magnitude higher TOF than the model without dispersion corrections. Nevertheless, the predicted TOF is quite small which could mean that the Ru(0001) surface is not active. However, it is noted that the free site coverage is very small in our models (0.16% [0.04%]), and considering the approximate nature of our lateral interaction model, an increase in the free site surface coverage of 1-2 orders of magnitude is conceivable which would increase the TOF by 2-4 orders of magnitude (since we will show below that the rate controlling step involves 2 free surface sites). In other words, very realistic TOFs are conceivable on the Ru(0001) surface.

Next, the preference of the DCN over the DCX has previously also been reported by us for the HDO of propanoic acid over Pd(111). The noticeable difference between these two surface models is that on Ru(0001) none of the key reaction pathways involves

dehydrogenation steps that we found to be essential over Pd(111), particularly at low hydrogen partial pressures. For example, the pathways starting with α -carbon dehydrogenation of the acid (step 2) have a low TOF of $3.0 \times 10^{-12} \text{ s}^{-1}$ [$1.9 \times 10^{-11} \text{ s}^{-1}$] and are 5 orders of magnitude slower than the direct decomposition DCN pathway. The pathways starting with α -carbon dehydrogenation of $\text{CH}_3\text{CH}_2\text{CO}$ and $\text{CH}_3\text{CH}_2\text{COO}$ are also much slower. This observation can be explained with Ru(0001) being a good C-O bond cleavage catalyst and a poor dehydrogenation catalyst, while Pd(111) is worse at cleaving C-O bonds but quite good at dehydrogenation.[12] In other words, Pd catalyzes the HDO of propanoic acid by starting with α - and β -carbon dehydrogenation of the acid to activate the acid group carbon before the C-OH bond can be cleaved and propanoic acid can be decarbonylated. These dehydrogenation steps are not necessary on the more oxophilic Ru surface that is primarily limited by its low free site coverage.

Our predictions from this microkinetic model agree well with experimental observations by Olcay *et al.*[14] and Lugo-Jose *et al.*[15] Olcay *et al.* studied the hydrodeoxygenation of acetic acid (CH_3COOH) over Ru/C catalysts and found that at 458 K and low H_2 partial pressure, methane production has a selectivity of $\sim 70\%$, following a decarbonylation mechanism. With increasing H_2 partial pressure, the selectivity to methane decreases linearly while the selectivity to ethanol increases linearly. At the highest H_2 partial pressure (corresponding to 1.4 mol/L in water), the selectivity to methane decreases to 40% while it is 55% to ethanol. We will discuss the change in mechanism to a reductive deoxygenation at high hydrogen partial pressure in a separate paper. Next, Lugo-Jose *et al.* investigated the hydrodeoxygenation of propanoic acid over Ru/SiO₂ catalysts at low H_2 partial pressures and found that in a temperature range

of 473K-573K the selectivity to C₂ hydrocarbons increases with increasing temperature and generally follows a decarbonylation mechanism.

3.3.4 Degree of rate control

We have used Campbell's degree of rate control,[31, 32] X_{RC} , to perform a sensitivity analysis and to determine the rate-controlling steps in our mechanism at 473 K. The degree of rate control is defined as:

$$X_{RC,n} = \frac{1}{r} \left(\frac{\partial r}{\partial \left(\frac{-G_n^{TS}}{RT} \right)} \right)_{G_{m \neq n}^0, G_i^{0,ads}} \quad (13)$$

where r is the overall rate of reaction and G_n^{TS} is the free energy of the transition state for elementary step n . Rate-controlling steps are identified by nonzero X_{RC} values. In the following, we only report rate-control values that deviate from zero. Our microkinetic model predicts that the reaction $\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{**} + \text{OH}^*$ (step 1) has an X_{RC} of 0.99 [0.98] and $\text{CH}_3\text{CH}_2\text{COO}^{**} \rightarrow \text{CH}_3\text{CH}_2^* + \text{CO}_2^*$ (step 12) has an X_{RC} of 0.01 [0.02], i.e., the C-OH bond scission is rate controlling. These results agree with observations on the HDO of acetic acid where it has been reported that the $\text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{CO} + \text{OH}$ step is also rate controlling.[10, 27] Considering furthermore that two free sites are involved in step 1 and no free sites are involved in step 12, we conclude that increasing the free site coverage will increase the DCN rate while it will have no effect on the rate controlling DCX step.

3.3.5 Degree of thermodynamic rate control

We have used the degree of thermodynamic rate control[33-35], X_{TRC} , to perform a sensitivity analysis and to determine the key surface intermediates at 473K:

$$X_{\text{TRC},n} = \frac{1}{r} \left(\frac{\partial r}{\partial \left(\frac{-G_n^0}{RT} \right)} \right)_{G_{m \neq n}^0, G_i^{0,\text{TS}}} \quad (14)$$

where G_n^0 is the free energy of adsorbate n . Rate-controlling intermediates are identified by nonzero X_{TRC} values. In the following, we only report thermodynamic rate-control values that deviate from zero. Negative values signify that reducing the adsorption strength will increase the overall rate, while positive values signify that increasing the adsorption strength will increase the overall reaction rate. Our model predicts that adsorbed $\text{CH}_3\text{CH}_2\text{COO}$, CO , H and the free site are the surface intermediates with a significant degree of thermodynamic control. Our model predicts that $\text{CH}_3\text{CH}_2\text{COO}$ has an X_{TRC} of -0.10 [-0.82], CO has an X_{TRC} of -0.37 [-0.14], H has an X_{TRC} of -2.40 [-0.03], and the free site has an X_{TRC} of 1.88 [0.65]. In other words, our model without considering dispersion interactions for adsorption predicts that destabilizing the adsorption of H and to a lesser degree destabilizing the adsorption of CO will increase the overall rate, while our model that considers (and possibly overestimates) dispersion interactions for adsorption finds that destabilizing $\text{CH}_3\text{CH}_2\text{COO}$ and to a smaller degree CO will increase the overall rate. Finally, the large positive X_{TRC} value for the free site suggests that increasing the free site coverage of the Ru surface will dramatically increase the TOF.

3.3.6 Apparent activation energy and reaction orders

To understand the sensitivity of our modeling results with regards to temperature and partial pressure, we have calculated the apparent activation energy (E_{app}) and reaction orders (α_i),

$$E_{\text{app}} = RT^2 \left(\frac{\partial \ln(r)}{\partial T} \right)_{P, p_i} \quad (15)$$

$$\alpha_i = \left(\frac{\partial \ln(r)}{\partial \ln(p_i)} \right)_{T, p_j} \quad (16)$$

Our model predicts a large apparent activation energy (E_{app}) of 2.27 eV [1.67 eV] in the temperature range of 433-473 K which can be explained by the free energy barrier of C-OH bond cleavage relative to the clean surface and the low free site coverage in the low temperature range. As for the reaction orders at 473 K, the model predicts that the order with respect to propanoic acid is 0.35 [0.06] in the acid partial pressure range of 0.01-0.33 bar, illustrating that increasing the propanoic acid chemical potential does not increase the TOF significantly due to a lack of free sites. The order with respect to H_2 is -0.97 [-0.25] in the H_2 partial pressure range of 0.5-2.0 bar, indicating again the high hydrogen surface coverage and the need for more free sites. Finally, the reaction order with respect to CO is -0.22 [-0.16] in the CO partial pressure range of 10^{-5} - 10^{-3} bar, illustrating that CO only slightly diminishes the reaction rate and that our results and conclusions are likely valid over a large CO pressure range.

4. Conclusions

The decarbonylation and decarboxylation mechanisms of propanoic acid ($\text{CH}_3\text{CH}_2\text{COOH}$) to C_2 hydrocarbons has been studied over Ru(0001) by mean-field microkinetic modeling based on data obtained from density functional theory and

transition state theory. Our model predicts that at low H_2 partial pressures the decarbonylation mechanism is preferred over the decarboxylation mechanism. The most favorable decarbonylation pathway proceeds by direct removal of the acid -OH group to produce propanoyl (CH_3CH_2CO), followed by C-C bond scission of CH_3CH_2CO to CH_3CH_2 and CO, and finally hydrogenation to ethane. Dehydrogenation pathways that have been found to be relevant over Pd catalysts do not play any role over Ru(0001). The rate controlling step is the removal of the acid -OH group and the creation of a sufficient number of free sites since the Ru(0001) surface is almost fully covered by H, CO, CH_3C and CH_3CH_2COO . To improve the Ru(0001) catalyst for the decarbonylation of organic acids, the free site coverage needs to be increased by, e.g., adding a catalyst promoter that decreases the hydrogen and CO adsorption strength without significantly affecting the C-OH bond scission rate, or by raising the reaction temperature and operating at relatively low CO and H_2 partial pressures. Finally, we note that this investigation did not include reactions that lead to C_3 products such as propanol that are relevant at high hydrogen partial pressures. The reductive deoxygenation (RDO) mechanism leading to C_3 products is currently under investigation in the context of a high hydrogen partial pressure environment.

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TABLE 1: Binding modes, zero-point energy corrected adsorption energies (E_{ads} , in eV), and zero point energy corrections (ΔZPE , in eV) of reaction intermediates calculated from DFT.

Species	Stoichiometry	Binding mode	E_{ads} (eV)	ΔZPE (eV)
Propanoic acid	$\text{CH}_3\text{CH}_2\text{COOH}$	$\eta 1\mu 1$ (O)	-0.64	0.04
Ethylidene-1-ol-1-olate	CH_3CHCOOH	$\eta 3\mu 3$ (C,O,O)	-1.94	0.05
Ethylidyne-1-ol-1-olate	CH_3CCOOH	$\eta 2\mu 3$ (C,O)	-4.13	0.11
Propanoyl	$\text{CH}_3\text{CH}_2\text{CO}$	$\eta 2\mu 2$ (C,O)	-2.74	0.08
Carbonylethylidene	CH_3CHCO	$\eta 2\mu 3$ (C,O)	-1.80	0.04
Carbonylethylidyne	CH_3CCO	$\eta 2\mu 4$ (C,C)	-3.61	0.00
Vinyl-1-ol-1-olate	CH_2CHCOOH	$\eta 3\mu 3$ (C,C,O)	-1.56	-0.02
Carbonylvinyl	CH_2CHCO	$\eta 4\mu 4$ (C,C,C,O)	-2.99	0.07
Ethyne-1-ol-1-olate	CHCHCOOH	$\eta 3\mu 3$ (C,C,O)	-3.88	0.08
Carbonylethyne	CHCHCO	$\eta 4\mu 4$ (C,C,C,O)	-4.65	0.05
Propanoate	$\text{CH}_3\text{CH}_2\text{COO}$	$\eta 2\mu 2$ (O,O)	-3.57	0.08
Carboxylethylidene	CH_3CHCOO	$\eta 3\mu 3$ (C,O,O)	-2.62	0.01
Carboxylethylidyne	CH_3CCOO	$\eta 2\mu 3$ (C,O)	-2.66	0.04
Carboxylic	COOH	$\eta 2\mu 3$ (C,O)	-2.62	0.07
Ethyne	CHCH	$\eta 2\mu 3$ (C,C)	-2.59	0.07
Vinyl	CH_2CH	$\eta 2\mu 3$ (C,C)	-3.38	0.10
Ethene	CH_2CH_2	$\eta 2\mu 2$ (C,C)	-1.00	0.10
Ethylidyne	CH_3C	$\eta 1\mu 3$ (C)	-5.92	0.18
Ethylidene	CH_3CH	$\eta 1\mu 2$ (C)	-4.20	0.08
Ethyl	CH_3CH_2	$\eta 1\mu 2$ (C)	-1.76	0.08
Ethane	CH_3CH_3	$\eta 1\mu 1$ (H)	-0.03	-0.01
Hydrogen	H	$\eta 1\mu 3$ (H)	-2.74	0.17
Hydroxyl	OH	$\eta 1\mu 3$ (O)	-3.53	0.11
Water	H_2O	$\eta 1\mu 1$ (O)	-0.40	0.08
Carbon monoxide	CO	$\eta 1\mu 1$ (C)	-1.88	0.08
Carbon dioxide	CO_2	$\eta 2\mu 2$ (C,O)	-0.17	-0.01

TABLE 2. ZPE-corrected reaction energies (ΔE), activation barriers ($E^\ddagger$), equilibrium constants (K) and forward rate constants (k^+) at various temperatures in the decarbonylation and decarboxylation of propanoic acid to ethane over Ru(0001).

Step	Reaction	constant	473 K	523 K	573 K	623 K
0	$\text{CH}_3\text{CH}_2\text{COOH} + * \rightarrow \text{CH}_3\text{CH}_2\text{COOH}^*$ $\Delta E_0 = -0.63 \text{ eV}$	K_0 $k_0^+, \text{s}^{-1}\text{bar}^{-1}$	2.11×10^{-4} 9.06×10^7	5.24×10^{-5} 8.61×10^7	1.73×10^{-5} 8.23×10^7	6.83×10^{-6} 7.89×10^7
1	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{**} + \text{OH}^*$ $\Delta E_1 = -0.36 \text{ eV}, E_1^\ddagger = 0.49 \text{ eV}$	K_1 k_1^+, s^{-1}	4.09×10^3 1.45×10^7	1.89×10^3 4.95×10^7	1.07×10^2 1.38×10^8	5.99×10^2 3.28×10^8
2	$\text{CH}_3\text{CH}_2\text{COOH}^* + 3* \rightarrow \text{CH}_3\text{CHCOOH}^{***} + \text{H}^*$ $\Delta E_2 = -0.30 \text{ eV}, E_2^\ddagger = 0.56 \text{ eV}$	K_2 k_2^+, s^{-1}	3.48×10^2 3.74×10^6	1.77×10^2 1.54×10^7	1.03×10^2 5.01×10^7	6.54×10^1 1.36×10^8
3	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2* \rightarrow \text{CH}_3\text{CH}_2\text{COO}^{**} + \text{H}^*$ $\Delta E_3 = -1.02 \text{ eV}, E_3^\ddagger = 0.21 \text{ eV}$	K_3 k_3^+, s^{-1}	1.56×10^{10} 1.12×10^{10}	1.40×10^9 2.00×10^{10}	1.92×10^8 3.26×10^{10}	3.64×10^7 4.95×10^{10}
4	$\text{CH}_3\text{CH}_2\text{CO}^{**} \rightarrow \text{CH}_3\text{CH}_2^* + \text{CO}^*$ $\Delta E_4 = -0.41 \text{ eV}, E_4^\ddagger = 0.84 \text{ eV}$	K_4 k_4^+, s^{-1}	5.84×10^4 9.82×10^3	2.45×10^4 7.95×10^4	1.20×10^4 4.50×10^5	6.66×10^3 1.94×10^6
5	$\text{CH}_3\text{CH}_2\text{CO}^{**} + 2* \rightarrow \text{CH}_3\text{CHCO}^{***} + \text{H}^*$ $\Delta E_5 = -0.37 \text{ eV}, E_5^\ddagger = 0.32 \text{ eV}$	K_5 k_5^+, s^{-1}	4.66×10^3 2.29×10^9	1.98×10^3 5.27×10^9	9.82×10^2 1.06×10^{10}	5.50×10^2 1.92×10^{10}
6	$\text{CH}_3\text{CHCOOH}^{***} + * \rightarrow \text{CH}_3\text{CHCO}^{***} + \text{OH}^*$ $\Delta E_6 = -0.44 \text{ eV}, E_6^\ddagger = 0.61 \text{ eV}$	K_6 k_6^+, s^{-1}	5.48×10^4 1.38×10^6	2.11×10^4 6.00×10^6	9.64×10^3 2.02×10^7	5.03×10^3 5.57×10^7
7	$\text{CH}_3\text{CHCOOH}^{***} + * \rightarrow \text{CH}_2\text{CHCOOH}^{***} + \text{H}^*$ $\Delta E_7 = -0.51 \text{ eV}, E_7^\ddagger = 0.52 \text{ eV}$	K_7 k_7^+, s^{-1}	1.03×10^5 2.99×10^7	2.98×10^4 1.12×10^8	1.08×10^4 3.34×10^8	4.61×10^3 8.45×10^8
8	$\text{CH}_3\text{CHCOOH}^{***} + * \rightarrow \text{CH}_3\text{CCOOH}^{***} + \text{H}^*$ $\Delta E_8 = -0.48 \text{ eV}, E_8^\ddagger = 0.62 \text{ eV}$	K_8 k_8^+, s^{-1}	3.07×10^4 2.39×10^6	9.73×10^3 1.14×10^7	3.79×10^3 4.15×10^7	1.72×10^3 1.24×10^8
9	$\text{CH}_3\text{CHCOOH}^{**} + * \rightarrow \text{CH}_3\text{CHCOO}^{**} + \text{H}^*$ $\Delta E_9 = -0.68 \text{ eV}, E_9^\ddagger = 0.39 \text{ eV}$	K_9 k_9^+, s^{-1}	5.14×10^6 2.67×10^8	9.93×10^5 7.01×10^8	2.56×10^5 1.57×10^9	8.25×10^4 3.10×10^9
10	$\text{CH}_3\text{CHCOOH}^{***} + 2* \rightarrow \text{CH}_3\text{CH}^{***} + \text{COOH}^{**}$ $\Delta E_{10} = -0.21 \text{ eV}, E_{10}^\ddagger = 0.89 \text{ eV}$	K_{10} k_{10}^+, s^{-1}	2.54×10^2 1.75×10^3	1.63×10^2 1.54×10^4	1.13×10^2 9.26×10^4	8.34×10^1 4.20×10^5
11	$\text{CH}_3\text{CH}_2\text{COO}^{**} + 2* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$ $\Delta E_{11} = 0.05 \text{ eV}, E_{11}^\ddagger = 0.75 \text{ eV}$	K_{11} k_{11}^+, s^{-1}	3.97×10^{-2} 2.09×10^4	4.36×10^{-2} 1.31×10^5	4.75×10^{-2} 6.00×10^5	5.15×10^{-2} 2.18×10^6
12	$\text{CH}_3\text{CH}_2\text{COO}^{**} \rightarrow \text{CH}_3\text{CH}_2^* + \text{CO}_2^*$ $\Delta E_{12} = 0.95 \text{ eV}, E_{12}^\ddagger = 1.71 \text{ eV}$	K_{12} k_{12}^+, s^{-1}	1.83×10^{-10} 1.44×10^{-6}	1.90×10^{-9} 8.63×10^{-5}	1.32×10^{-8} 2.56×10^{-3}	6.76×10^{-8} 4.45×10^{-2}
13	$\text{CH}_3\text{CH}_2^* + \text{H}^* \rightarrow \text{CH}_3\text{CH}_3^* + *$ $\Delta E_{13} = 0.26 \text{ eV}, E_{13}^\ddagger = 0.84 \text{ eV}$	K_{13} k_{13}^+, s^{-1}	1.79×10^{-2} 4.48×10^4	3.41×10^{-2} 3.60×10^5	5.76×10^{-2} 2.01×10^6	8.89×10^{-2} 8.53×10^6
14	$\text{CH}_3\text{CH}^{***} + \text{H}^* \rightarrow \text{CH}_3\text{CH}_2^* + 3*$ $\Delta E_{14} = 0.63 \text{ eV}, E_{14}^\ddagger = 0.70 \text{ eV}$	K_{14} k_{14}^+, s^{-1}	3.27×10^{-7} 2.82×10^5	1.42×10^{-6} 1.54×10^6	4.73×10^{-6} 6.28×10^6	1.29×10^{-5} 2.04×10^7
15	$\text{CH}_3\text{CHCO}^{***} + * \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}^*$ $\Delta E_{15} = -0.66 \text{ eV}, E_{15}^\ddagger = 0.85 \text{ eV}$	K_{15} k_{15}^+, s^{-1}	3.83×10^7 2.34×10^4	8.73×10^6 1.94×10^5	2.59×10^6 1.12×10^5	9.36×10^5 4.88×10^6
16	$\text{CH}_3\text{CHCO}^{***} + 2* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$ $\Delta E_{16} = -0.43 \text{ eV}, E_{16}^\ddagger = 0.66 \text{ eV}$	K_{16} k_{16}^+, s^{-1}	7.07×10^4 1.94×10^6	2.71×10^4 1.02×10^7	1.24×10^4 4.06×10^7	6.43×10^3 1.30×10^8
17	$\text{CH}_3\text{CHCO}^{***} + 2* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{H}^*$ $\Delta E_{17} = -0.44 \text{ eV}, E_{17}^\ddagger = 0.78 \text{ eV}$	K_{17} k_{17}^+, s^{-1}	8.87×10^3 4.82×10^4	3.04×10^3 3.35×10^5	1.26×10^3 1.67×10^6	6.07×10^2 6.51×10^6
18	$\text{CH}_2\text{CHCOOH}^{***} + 2* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{OH}^*$ $\Delta E_{18} = -0.37 \text{ eV}, E_{18}^\ddagger = 0.99 \text{ eV}$	K_{18} k_{18}^+, s^{-1}	4.73×10^3 3.85×10^2	2.15×10^3 4.53×10^3	1.13×10^3 3.51×10^4	6.63×10^2 1.97×10^5
19	$\text{CH}_2\text{CHCOOH}^{***} + 2* \rightarrow \text{CH}_2\text{CH}^{***} + \text{COOH}^{**}$ $\Delta E_{19} = -0.09 \text{ eV}, E_{19}^\ddagger = 0.94 \text{ eV}$	K_{19} k_{19}^+, s^{-1}	8.48 4.31×10^2	7.34 4.26×10^3	6.56 2.84×10^4	5.99 1.40×10^5
20	$\text{CH}_2\text{CHCOOH}^{***} + * \rightarrow \text{CHCHCOOH}^{***} + \text{H}^*$ $\Delta E_{20} = -0.35 \text{ eV}, E_{20}^\ddagger = 0.27 \text{ eV}$	K_{20} k_{20}^+, s^{-1}	3.08×10^3 1.09×10^{10}	1.35×10^3 2.25×10^{10}	6.86×10^2 4.10×10^{10}	3.90×10^2 6.81×10^{10}

Table 2 (continued)

Step	Reaction	constant	473 K	523 K	573 K	623 K
21	$\text{CH}_3\text{CCOOH}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$ $\Delta E_{21} = 0.01 \text{ eV}, E_{21}^\ddagger = 1.17 \text{ eV}$	K_{21} k_{21}^+, s^{-1}	2.01 5.64	2.13 1.02×10^2	2.24 1.12×10^3	2.34 8.48×10^3
22	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$ $\Delta E_{22} = 0.22 \text{ eV}, E_{22}^\ddagger = 0.94 \text{ eV}$	K_{22} k_{22}^+, s^{-1}	1.20×10^{-2} 1.74×10^3	2.08×10^{-2} 1.83×10^4	3.31×10^{-2} 1.29×10^5	4.91×10^{-2} 6.66×10^5
23	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}_2^*$ $\Delta E_{23} = 0.22 \text{ eV}, E_{23}^\ddagger = 1.18 \text{ eV}$	K_{23} k_{23}^+, s^{-1}	2.76×10^{-2} 1.43×10^1	5.33×10^{-2} 2.61×10^2	9.26×10^{-2} 2.88×10^3	1.49×10^{-1} 2.18×10^4
24	$\text{CH}_3\text{C}^* + \text{H}^* + * \rightarrow \text{CH}_3\text{CH}^{***}$ $\Delta E_{24} = 0.75 \text{ eV}, E_{24}^\ddagger = 0.90 \text{ eV}$	K_{24} k_{24}^+, s^{-1}	1.01×10^{-8} 2.45×10^3	5.79×10^{-8} 2.22×10^4	2.43×10^{-7} 1.37×10^5	8.09×10^{-7} 6.31×10^5
25	$\text{CH}_3\text{CCO}^{****} \rightarrow \text{CH}_3\text{C}^* + \text{CO}^* + 2^*$ $\Delta E_{25} = -0.98 \text{ eV}, E_{25}^\ddagger = 0.36 \text{ eV}$	K_{25} k_{25}^+, s^{-1}	5.35×10^{10} 1.98×10^9	5.57×10^9 5.08×10^9	8.61×10^8 1.11×10^{10}	1.80×10^8 2.13×10^{10}
26	$\text{CH}_2\text{CHCO}^{****} \rightarrow \text{CH}_2\text{CH}^{***} + \text{CO}^*$ $\Delta E_{26} = -0.61 \text{ eV}, E_{26}^\ddagger = 0.98 \text{ eV}$	K_{26} k_{26}^+, s^{-1}	1.48×10^7 9.32×10^2	3.87×10^6 1.08×10^4	1.28×10^6 8.20×10^4	5.10×10^5 4.52×10^5
27	$\text{CH}_2\text{CHCO}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{H}^*$ $\Delta E_{27} = -0.48 \text{ eV}, E_{27}^\ddagger = 0.51 \text{ eV}$	K_{27} k_{27}^+, s^{-1}	1.02×10^5 2.78×10^7	3.34×10^4 1.02×10^8	1.34×10^4 3.02×10^8	6.27×10^3 7.56×10^8
28	$\text{CHCHCOOH}^{***} + 2^* \rightarrow \text{CHCHCO}^{****} + \text{OH}^*$ $\Delta E_{28} = -0.35 \text{ eV}, E_{28}^\ddagger = 1.43 \text{ eV}$	K_{28} k_{28}^+, s^{-1}	4.24×10^3 9.86×10^{-3}	2.04×10^3 3.37×10^{-1}	1.13×10^3 6.31×10^0	6.89×10^2 7.45×10^1
29	$\text{CH}_3\text{CCOO}^{***} \rightarrow \text{CH}_3\text{C}^* + \text{CO}_2^* + *$ $\Delta E_{29} = -0.69 \text{ eV}, E_{29}^\ddagger = 0.44 \text{ eV}$	K_{29} k_{29}^+, s^{-1}	1.32×10^8 2.08×10^8	2.89×10^7 6.36×10^8	8.28×10^6 1.61×10^9	2.90×10^6 3.51×10^9
30	$\text{CH}_2\text{CH}^{***} + \text{H}^* \rightarrow \text{CH}_2\text{CH}_2^{**} + 2^*$ $\Delta E_{30} = 0.42 \text{ eV}, E_{30}^\ddagger = 0.75 \text{ eV}$	K_{30} k_{30}^+, s^{-1}	4.30×10^{-5} 1.31×10^5	1.15×10^{-4} 8.33×10^5	2.56×10^{-4} 3.84×10^6	5.00×10^{-4} 1.38×10^7
31	$\text{CHCH}^{***} + \text{H}^* \rightarrow \text{CH}_2\text{CH}^{***} + *$ $\Delta E_{31} = 0.58 \text{ eV}, E_{31}^\ddagger = 0.95 \text{ eV}$	K_{30} k_{30}^+, s^{-1}	9.44×10^{-7} 8.89×10^2	3.64×10^{-6} 8.69×10^3	1.10×10^{-5} 5.70×10^4	2.77×10^{-5} 2.76×10^5
32	$\text{CHCHCO}^{****} \rightarrow \text{CHCH}^{***} + \text{CO}^*$ $\Delta E_{32} = -0.71 \text{ eV}, E_{32}^\ddagger = 0.99 \text{ eV}$	K_{32} k_{32}^+, s^{-1}	1.54×10^8 5.09×10^2	3.18×10^7 5.91×10^3	8.70×10^6 4.50×10^4	2.94×10^6 2.49×10^5
33	$\text{CH}_3\text{CH}_2^* + 2^* \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$ $\Delta E_{33} = -0.59 \text{ eV}, E_{33}^\ddagger = 0.06 \text{ eV}$	K_{33} k_{33}^+, s^{-1}	4.51×10^5 9.05×10^{11}	3.28×10^4 1.10×10^{12}	9.45×10^3 1.30×10^{12}	3.32×10^3 1.51×10^{12}
34	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$ $\Delta E_{34} = -0.20 \text{ eV}, E_{34}^\ddagger = 0.68 \text{ eV}$	K_{34} k_{34}^+, s^{-1}	3.22×10^2 7.09×10^5	2.12×10^2 3.92×10^6	1.51×10^2 1.63×10^7	1.14×10^2 5.42×10^7
35	$\text{COOH}^{**} \rightarrow \text{CO}^* + \text{OH}^*$ $\Delta E_{35} = -0.89 \text{ eV}, E_{35}^\ddagger = 0.34 \text{ eV}$	K_{35} k_{35}^+, s^{-1}	8.25×10^9 5.46×10^9	1.13×10^9 1.39×10^{10}	2.21×10^8 3.02×10^{10}	5.64×10^7 5.82×10^{10}
36	$\text{OH}^* + \text{H}^* \rightarrow \text{H}_2\text{O}^* + *$ $\Delta E_{36} = 0.61 \text{ eV}, E_{36}^\ddagger = 1.22 \text{ eV}$	K_{36} k_{36}^+, s^{-1}	2.47×10^{-6} 2.12	1.08×10^{-5} 4.13×10^1	3.66×10^{-5} 4.81×10^2	1.01×10^{-4} 3.80×10^3
37	$\text{H}_2\text{O}^* \rightarrow \text{H}_2\text{O} + *$ $\Delta E_{37} = 0.41 \text{ eV}$	K_{37} k_{37}^+, s^{-1}	4.92×10^2 9.03×10^{10}	1.26×10^3 2.20×10^{11}	2.74×10^3 4.57×10^{11}	5.10×10^3 8.16×10^{11}
38	$\text{CH}_3\text{CH}_3^* \rightarrow \text{CH}_3\text{CH}_3 + *$ $\Delta E_{38} = 0.07 \text{ eV}$	K_{38} k_{38}^+, s^{-1}	4.04×10^6 5.75×10^{14}	4.24×10^6 5.74×10^{14}	4.33×10^6 5.60×10^{14}	4.38×10^6 5.43×10^{14}
39	$\text{CH}_2\text{CH}_2^* \rightarrow \text{CH}_2\text{CH}_2 + *$ $\Delta E_{39} = 1.01 \text{ eV}$	K_{39} k_{39}^+, s^{-1}	3.10×10^{-2} 4.56×10^6	3.56×10^{-1} 4.99×10^7	2.67×10^0 3.57×10^8	1.46×10^1 1.88×10^9
40	$\text{CO}_2^* \rightarrow \text{CO}_2 + *$ $\Delta E_{40} = 0.20 \text{ eV}$	K_{40} k_{40}^+, s^{-1}	3.84×10^5 4.74×10^{13}	5.56×10^5 6.52×10^{13}	7.40×10^5 8.29×10^{13}	9.30×10^5 9.99×10^{13}
41	$\text{CO}^* \rightarrow \text{CO} + *$ $\Delta E_{41} = 1.88 \text{ eV}$	K_{41} k_{41}^+, s^{-1}	9.43×10^{-12} 1.39×10^{-3}	1.14×10^{-9} 1.60×10^{-1}	6.24×10^{-8} 8.35×10^0	1.86×10^{-6} 2.39×10^2
42	$0.5\text{H}_2(\text{g}) + * \rightarrow \text{H}^*$ $\Delta E_{42} = -0.60 \text{ eV}$	K_{42} k_{42}^+, s^{-1}	2.20×10^3 7.80×10^8	4.57×10^2 7.41×10^8	1.23×10^2 7.08×10^8	4.03×10^1 6.79×10^8

TABLE 3. ZPE-corrected adsorption energies (E_{ads} , in eV) in eV of all stable gas phase species in the decarbonylation and decarboxylation of propanoic acid to ethane on Ru(0001) computed using the PW91 functional and the PBE-D3 method.

E_{ads} (eV)	PW91	PBE-D3
$\text{H}_2(\text{g}) + 2^* \rightarrow 2\text{H}^*$	-1.26	-1.27
$\text{CH}_3\text{CH}_2\text{COOH}$	-0.64	-0.93
CH_3CH_3	-0.03	-0.38
CH_2CH_2	-1.00	-1.37
H_2O	-0.40	-0.56
CO	-1.88	-2.05
CO_2	-0.17	-0.40

Figure 1. Reaction scheme of various decarbonylation and decarboxylation pathways of propanoic acid to C₂ hydrocarbons over Ru(0001).

Figure 2. Side (upper panel) and top view (lower panel) of preferred adsorption structure of various surface intermediates in the reaction network of decarbonylation and decarboxylation of propanoic acid over Ru(0001).

Figure 3. Snapshots of transition states of steps 1 to 18 on the Ru(0001) surface. Upper panels are for side views and lower ones for top views.

Figure 4. Snapshots of transition states of steps 19 to 36 on the Ru(0001) surface. Upper panels are for side views and lower ones for top views.

Figure 5. Turnover frequencies (s⁻¹) of all elementary reactions steps at 473 K. Numbers in brackets are from the microkinetic model with dispersion corrected adsorption/desorption energies. The red and green numbered pathways correspond to the preferred decarbonylation and decarboxylation pathways, respectively.

Graphical abstract

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Graphical abstract

References

- [1] B. Donnis, R.G. Egeberg, P. Blom, K.G. Knudsen, *Top. Catal.* 52 (2009) 229-240.
- [2] M. Snare, I. Kubickova, P. Maki-Arvela, K. Eranen, D.Y. Murzin, *Ind. Eng. Chem. Res.* 45 (2006) 5708-5715.
- [3] I.L. Simakova, O.A. Simakova, P. Maki-Arvela, A. Simakov, M. Estrada, D.Y. Murzin, *Appl. Catal. A-Gen.* 355 (2009) 100-108.
- [4] J.G. Immer, H.H. Lamb, *Energy Fuels* 24 (2010) 5291-5299.
- [5] J. Fu, X. Lu, P.E. Savage, *Energy Environ. Sci.* 3 (2010) 311-317.
- [6] E.W. Ping, R. Wallace, J. Pierson, T.F. Fuller, C.W. Jones, *Microporous Mesoporous Mater.* 132 (2010) 174-180.
- [7] L. Boda, G. Onyestyak, H. Solt, F. Lonyi, J. Valyon, A. Thernes, *Appl. Catal. A-Gen.* 374 (2010) 158-169.
- [8] L. Xu, Y. Xu, *Surf. Sci.* 604 (2010) 887-892.
- [9] B. Rozmyslowicz, P. Maki-Arvela, A. Tokarev, A.-R. Leino, K. Eranen, D.Y. Murzin, *Ind. Eng. Chem. Res.* 51 (2012) 8922-8927.
- [10] H. Olcay, L. Xu, Y. Xu, G.W. Huber, *ChemCatChem* 2 (2010) 1420-1424.
- [11] J.M. Lu, S. Behtash, A. Heyden, *J. Phys. Chem. C* 116 (2011) 14328-14341.
- [12] J.M. Lu, S. Behtash, M. Faheem, A. Heyden, *J. Catal.* 305 (2013) 56-66.
- [13] Y. Chen, D.J. Miller, J.E. Jackson, *Ind. Eng. Chem. Res.* 46 (2007) 3334-3340.
- [14] H. Olcay, Y. Xu, G.W. Huber, *Green Chem.* 16 (2014) 911-924.
- [15] Y.K. Lugo-Jose, J.R. Monnier, C.T. Williams, *Appl. Catal. A-Gen.* 469 (2014) 410-418.
- [16] G. Kresse, J. Hafner, *Phys. Rev. B* 47 (1993) 558-561.
- [17] G. Kresse, J. Furthmuller, *Comput. Mater. Sci.* 6 (1996) 15-50.
- [18] G. Kresse, D. Joubert, *Phys. Rev. B* 59 (1999) 1758-1775.
- [19] J.P. Perdew, Y. Wang, *Phys. Rev. B* 33 (1986) 8800-8802.
- [20] J.P. Perdew, Y. Wang, *Phys. Rev. B* 45 (1992) 13244-13249.
- [21] V.A. Finkel, G.P. Kovtun, M.I. Palatnik, *Phys. Met. Metallogr.* 32 (1971) 231-235.
- [22] G. Henkelman, B.P. Uberuaga, H. Jonsson, *J. Chem. Phys.* 113 (2000) 9901-9904.
- [23] G. Henkelman, H. Jonsson, *J. Chem. Phys.* 111 (1999) 7010-7022.
- [24] R.A. Olsen, G.J. Kroes, G. Henkelman, A. Arnaldsson, H. Jonsson, *J. Chem. Phys.* 121 (2004) 9776-9792.
- [25] A. Heyden, A.T. Bell, F.J. Keil, *J. Chem. Phys.* 123 (2005) 224101.
- [26] G. Buzzi-Ferraris, "BzzMath: Numerical libraries in C++", Politecnico di Milano: www.chem.polimi.it/homes/gbuzzi.
- [27] V. Pallassana, M. Neurock, *J. Catal.* 209 (2002) 289-305.
- [28] L.C. Grabow, B. Hovlbak, J.K. Norskov, *Top. Catal.* 53 (2010) 298-310.
- [29] E.M. Karp, T.L. Silbaugh, M.C. Crowe, C.T. Campbell, *J. Am. Chem. Soc.* 134 (2012) 20388-20395.
- [30] S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* 132 (2010) 154104.
- [31] C.T. Campbell, *Top. Catal.* 1 (1994) 353-366.
- [32] C.T. Campbell, *J. Catal.* 204 (2001) 520-524.
- [33] S. Kozuch, S. Shaik, *Journal of the American Chemical Society* 128 (2006) 3355-3365.
- [34] S. Kozuch, S. Shaik, *The Journal of Physical Chemistry A* 112 (2008) 6032-6041.

[35] C. Stegelmann, A. Andreasen, C.T. Campbell, Journal of the American Chemical Society 131 (2009) 8077-8082.