Effects of co-adsorbed water on different bond cleavages of oxygenates on Pd (111)

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ABSTRACT

Experimental studies have shown that co-adsorbates and solvents affect both activity and selectivity of heterogeneous catalysts but how it affects different bond cleavages and network of parallel reactions is not well understood. Here we present a density functional theory (DFT) theory calculation of how co-adsorbed water affects different bond cleavages of oxygenates on metal surface, using decomposition of acetic acid over Pd (111) as a model system for oxygenates, with application in biomass conversion. The presence of co-adsorbed water generally enhances O-H bond cleavage while generally inhibits the OC-O, C-C, and OC-OH bond cleavage. The influence of co-adsorbed water on C-H bond cleavage varies the most and depends on the nature of the transition state and how co-adsorbed water stabilizes the initial and final state. Although these are trends are useful as general guidance, they are not sufficient to predict the effect on a complex reaction networks such as acetic acid decomposition which has several parallel reaction paths. In the absence of co-adsorbed water, the two lowest energy pathways are decarboxylation and decarbonylation pathways through a common CH₂COO intermediate. But through

an inhibition of OC-O bond cleavage but enhancement of C-C bond cleavage of CH₂COO, one of three exceptions to the general trend of C-C inhibition in the presence of water, the two lowest free energy pathways are decarboxylation forming CO₂ in the presence of water. This illustrates how a single reaction step can affect a complex reaction network with many parallel, energetically similar paths. This suggests that the presence of co-adsorbed water makes acetic acid decarboxylation (formation of carbon dioxide) more favorable than acetic acid decarbonylation (formation of carbon monoxide) over Pd (111).



Figure 0: TOC Graphics

KEYWORDS: Acetic acid, Density Functional Theory, Solvent effects, Effects of co-adsorbed water on different bond-cleavages, decarboxylation, decarbonylation, Pd (111).

1 INTRODUCTION

Numerous chemical processes, such as biomass conversion to biofuels, rely on heterogeneous catalytic reactions in solvents. Bio-oils contains 25% oxygenates and 10-30% water,^{1, 2} making acetic acid decomposition in the presence of co-adsorbed water, a good model system to study how co-adsorbed

water affects different bond cleavages of oxygenates found in biomass conversion. This study provides atomic-level understanding of how water affects OC-O, OC-OH, OCO-H, C-C and C-H bond cleavages which can enable design of more efficient catalyst system.

Experimental and theoretical studies have shown that solvents affect the selectivity and rate of heterogeneous catalytic reactions.³⁻¹⁰ These includes water promotion of Fisher-Tropsch reaction on Ru by increasing the selectivity of C₅ products,¹⁰ increased reaction rate for hydrogenation of 2-butanone to 2-butanol on Ru in presence of water,¹¹ and water reducing the selectivity towards C₁₇ products during catalytic deoxygenation of oleic acid over Pd/C.¹² Significant advancement has been made in atomic-level understanding of solvent effects on oxygenates in heterogeneous catalysis through recent computational studies.^{8, 13-24} These studies focused on how co-adsorbed water affects different bond cleavages in a particular pathway but here we investigate how it affects all the different pathways in a reaction network including parallel pathways. Our study focuses on how co-adsorbed water affects different bond cleavages and hence the competition between different reaction pathways in a complex reaction network of acetic acid decomposition on Pd (111).

Modeling of surface reactions in complex environment is challenging. These challenges include computational cost, capturing the solvent/solute interaction (e.g. hydrogen bonding), entropic effects beyond harmonic approximation, and those from the bulk solvent during bond cleavages.^{9, 25} Many methods have been proposed for modeling the effects of solvents on heterogeneous catalytic reaction including implicit solvation.²⁶⁻³¹ Although implicit solvation is computational inexpensive, it does not capture hydrogen bonding which plays an important role in some elementary reaction steps³² and can influence the activation barrier and the reaction energy of an elementary reaction step through stabilization/destabilization of the transition, final, or initial states and by opening a new minimum energy pathway (MEP) through hydrogen shuttling.^{10, 11, 21, 25, 33} Quantum mechanical/molecular mechanical (QM/MM) and ab-initio molecular dynamics (AIMD) methods captures the hydrogen bonding or hydrogen shuttling effects and have been employed in metal-water interfaces studies,^{14, 34} and bond cleavages at water-metal interfaces³⁵⁻³⁷ but are computationally expensive for larger reaction networks.³⁸ Microsolvation is a combined approach in which one or two solvent molecules are explicitly included with or without implicit solvation.^{19, 25, 39} Microsolvation captures the hydrogen bonding/hydrogen shuttling effect and is computational tractable for the study of different bond cleavages in large reaction network. Here we focus on capturing the effect of hydrogen bonding/hydrogen shuttling on the different bond cleavages by explicitly including the effect of coadsorbed water and how that changes the overall reaction path of acetic acid decomposition. Previous studies have observed that elementary steps for C=O bond cleavage have significantly higher barrier and reaction energies than C-O, C-C and C-H bond scission,^{40, 41} therefore these elementary steps are not included herein.

2. METHODS

Density functional theory calculations were done using the Vienna Ab-initio Simulation Package (VASP).⁴²⁻⁴⁴ A plane-wave basis set were used to solve the Kohn-Sham equations and the projected augmented wave (PAW) method were used to describe the core electrons.⁴⁵ Electron exchange and correlation were described within the PW91 (Perdew-Wang 91) generalized gradient approximation (GGA).⁴⁶⁻⁴⁸ Spin polarization and cutoff energy of 400 eV was used for all calculations. A 4 × 4 × 1 Monkhorst-Pack grid of Brilliouin zone integration were used for all calculations.

The optimized Pd lattice constant was 3.96 Å in reasonable agreement with experimental results of 3.89 Å.⁴⁹ The Pd (111) surface was constructed by a four-atomic layer slab of (3×4) surface atoms and a 17 Å thick vacuum region was used to separate the surface from its periodic images in the z-direction. The last two bottom Pd layers were fixed, and remaining layers and adsorbates were allowed to relax.

The interaction energy (ΔE_{int}) was calculated to determine the interactions between the adsorbate (A) and the co-adsorbed water.

 $\Delta E_{int} = E_{Pd + A+ H_2O} + E_{Pd} - E_{Pd + A} - E_{Pd + H_2O}$

where $E_{Pd + A + H_2O}$ is the total energy of the system with reaction intermediate (A) and water adsorbed, E_{Pd} is the total energy of the Pd (111) slab, $E_{Pd + A}$ is the total energy of A adsorbed on Pd (111), and $E_{Pd + H_2O}$ is the total energy of adsorbed water on Pd (111). A more negative interaction energy equates an attractive interaction while positive interaction energy equates a repulsive interaction. The reaction energy (ΔE_{rxn}) is defined as the energy difference between the reactants ($E_{Pd + AB + H_2O}$) and the products ($E_{Pd + A + B + H_2O}$). Dissociation of water is not considered herein.

The minimum energy path for different elementary reaction steps were calculated with the climbing image nudged elastic band (CI-NEB)⁵⁰⁻⁵³ and the dimer method.⁵⁴⁻⁵⁶ All transition states were confirmed by vibrational analysis to have only one imaginary frequency. The convergence criteria for the maximum residual force for adsorbate and CI-NEB calculations were 0.03 and 0.05 eV/Å, respectively. Standard statistical mechanics approach was used to calculate Gibbs free energy of reaction and activation at 300 K.²⁰

Co-adsorbed water was represented by a single water molecule interacting with the adsorbate, to verify this approach we calculated the effect of an additional water molecule on each of elementary reaction steps involved in the three lowest energy pathways. The presence of two co-adsorbed water molecules does not change any of the trends observed with single co-adsorbed water (see Figure S6 in SI). The free energies of reaction and activation with and without co-adsorbed water, along with the overall energy landscape are included in the supporting information (SI).

3. RESULTS AND DISCUSSIONS

Co-adsorbed water can affect the activation energy by stabilizing or destabilizing the initial, final, or transition states or through changes in the reaction path. The forward activation barriers and reaction

energies for the different elementary steps, in the presence and absence of co-adsorbed water, along with the interaction energy between the co-adsorbed water and the reactant/products are summarized in Table 1. The activation barriers and reaction energies in absence of co-adsorbed water were published previously and are also included here for comparison.⁵⁷ Snapshots of all initial and transition states with co-adsorbed water for all elementary reaction steps are in the SI, Figure S3, S4 and S5.

Table 1. Reaction energies and activation barriers of elementary reaction steps in the presence (E_{rxn_HzO} and E_{a_HzO}) and absence (E_{rxn} and E_a) of co-adsorbed water as well as interaction energy of co-adsorbed water with the initial and final states (ΔE_{int}). The energies do not include zero-point energy correction. See Table S2 for free energy of reaction and activation energy at 300 K.

| step | surface reactions | Erxn_H20[eV] | Ea_H2O[eV] | E _{rxn} [eV] | E _a [eV] | ∆E _{int} initial state [eV] | ∆E _{int} final state[eV] |
|------|--|--------------|------------|-----------------------|---------------------|--|--------------------------------------|
| 1 | $CH_3COOH^* + * + H_2O^* \rightarrow CH_3^* + COOH^* + H_2O^*$ | 0.53 | 2.33 | 0.66 | 1.90 | -0.14 | -0.27 |
| 2 | $CH_3COOH^* + {}^* + H_2O^* \rightarrow CH_3COO^* + H^* + H_2O^*$ | -0.15 | 0.55 | -0.07 | 0.69 | -0.14 | -0.22 |
| 3 | $CH_3COOH^* + {}^* + H_2O^* \rightarrow CH_3CO^* + OH^* + H_2O^*$ | 0.84 | 1.30 | 0.83 | 1.23 | -0.14 | -0.13 |
| 4 | $CH_{3}COOH^{*} + {}^{*} + H_{2}O^{*} \rightarrow CH_{2}COOH^{*} + H^{*} + H_{2}O^{*}$ | 0.22 | 1.09 | 0.30 | 1.07 | -0.14 | -0.22 |
| 5 | $CH_{3}COO^{*} + {}^{*} + H_{2}O^{*} \rightarrow CH_{2}COO^{*} + H^{*} + H_{2}O^{*}$ | 0.54 | 1.40 | 0.77 | 1.37 | -0.21 | -0.44 |
| 6 | $CH_3COO^* + * + H_2O^* \rightarrow CH_3^* + CO_2^* + H_2O^*$ | 0.53 | 2.11 | 0.36 | 1.92 | -0.21 | -0.04 |
| 7 | $CH_3COO^* + * + H_2O^* \rightarrow CH_3CO^* + O^* + H_2O^*$ | 1.09 | 1.78 | 1.02 | 1.56 | -0.21 | -0.14 |
| 8 | $CH_2COOH^* + * + H_2O^* \rightarrow CH_2^* + COOH^* + H_2O^*$ | 0.42 | 1.47 | 0.44 | 1.33 | -0.22 | -0.24 |
| 9 | $CH_2COOH^* + {}^* + H_2O^* \rightarrow CH_2CO^* + OH^* + H_2O^*$ | 0.73 | 1.17 | 0.71 | 1.19 | -0.22 | -0.20 |
| 10 | $CH_2COOH^* + * + H_2O^* \rightarrow CHCOOH^* + H^* + H_2O^*$ | 0.27 | 1.03 | 0.13 | 0.91 | -0.22 | -0.08 |
| 11 | $CH_2COOH^* + * + H_2O^* \rightarrow CH_2COO^* + H^* + H_2O^*$ | 0.21 | 0.97 | 0.45 | 1.33 | -0.22 | -0.44 |
| 12 | $CHCOOH^* + ^* + H_2O^* \rightarrow CHCO^* + OH^* + H_2O^*$ | 0.61 | 1.59 | 0.73 | 1.68 | -0.07 | -0.19 |
| 13 | $CHCOOH^* + ^* + H_2O^* \rightarrow CCOOH^* + H^* + H_2O^*$ | -0.39 | 0.36 | -0.20 | 0.64 | -0.07 | -0.26 |
| 14 | $CHCOOH^* + {}^* + H_2O^* \rightarrow CH^* + COOH^* + H_2O^*$ | -0.27 | 1.09 | -0.09 | 1.00 | -0.07 | -0.25 |
| 15 | $CHCOOH^* + ^* + H_2O^* \rightarrow CHCOO^* + H^* + H_2O^*$ | 0.19 | 1.25 | 0.51 | 1.57 | -0.07 | -0.39 |
| 16 | $CH_2COO^* + * + H_2O^* \rightarrow CH_2^* + CO_2^* + H_2O^*$ | 0.18 | 1.12 | -0.27 | 1.36 | -0.40 | 0.05 |
| 17 | $CH_2COO^* + * + H_2O^* \rightarrow CH_2CO^* + O^* + H_2O^*$ | 0.60 | 1.54 | 0.36 | 0.99 | -0.40 | -0.16 |
| 18 | $CH_2COO^* + {}^* + H_2O^* \rightarrow CHCOO^* + H^* + H_2O^*$ | 0.20 | 0.97 | 0.17 | 0.95 | -0.40 | -0.37 |
| 19 | $CHCOO^* + {}^* + H_2O^* \rightarrow CCOO^* + H^* + H_2O^*$ | -0.01 | 0.94 | -0.08 | 0.79 | -0.38 | -0.30 |
| 20 | $CHCOO^* + * + H_2O^* \rightarrow CH^* + CO_2^* + H_2O^*$ | -0.53 | 0.74 | -0.90 | 0.61 | -0.38 | -0.01 |
| 21 | $CHCOO^* + {}^* + H_2O^* \rightarrow CHCO^* + O^* + H_2O^*$ | 0.36 | 1.37 | 0.20 | 1.21 | -0.38 | -0.22 |
| 22 | $CH_3CO^* + * + H_2O^* \rightarrow CH_2CO^* + H^* + H_2O^*$ | 0.11 | 0.89 | 0.29 | 1.08 | -0.01 | -0.19 |

| 23 | $CH_3CO^* + * + H_2O^* \rightarrow CH_3^* + CO^* + H_2O^*$ | -0.57 | 1.14 | -0.52 | 1.15 | -0.01 | -0.06 |
|----|---|-------|------|-------|------|-------|-------|
| 24 | $CH_2CO^* + * + H_2O^* \rightarrow CH_2^* + CO^* + H_2O^*$ | -0.49 | 1.36 | -0.65 | 1.03 | -0.21 | -0.05 |
| 25 | $CH_2CO^* + * + H_2O^* \rightarrow CHCO^* + H^* + H_2O^*$ | -0.17 | 0.84 | -0.14 | 0.83 | -0.21 | -0.24 |
| 26 | $CHCO^* + * + H_2O^* \rightarrow CH^* + CO^* + H_2O^*$ | -0.90 | 0.65 | -1.04 | 0.52 | -0.19 | -0.05 |
| 27 | $CHCO^* + {}^* + H_2O^* \rightarrow CCO^* + H^* + H_2O^*$ | 0.22 | 1.22 | -0.06 | 1.07 | -0.19 | 0.09 |
| 28 | $CCOOH^* + {}^* + H_2O^* \rightarrow C^* + COOH^* + H_2O^*$ | 0.59 | 1.63 | 0.51 | 1.79 | -0.29 | -0.21 |
| 29 | $CCOOH^* + {}^* + H_2O^* \rightarrow CCOO^* + H^* + H_2O^*$ | 0.63 | 1.27 | 0.63 | 1.25 | -0.29 | -0.29 |
| 30 | $CCOOH^* + {}^* + H_2O^* \rightarrow CCO^* + OH^* + H_2O^*$ | 1.19 | 1.68 | 0.99 | 1.42 | -0.29 | -0.09 |
| 31 | $COOH^* + {}^* + H_2O^* \rightarrow CO^* + OH^* + H_2O^*$ | -0.28 | 0.72 | -0.31 | 0.66 | -0.22 | -0.19 |
| 32 | $COOH^* + * + H_2O^* \rightarrow CO_2^* + H^* + H_2O^*$ | -0.20 | 0.57 | -0.34 | 0.74 | -0.22 | -0.08 |
| 33 | $CCOO^* + * + H_2O^* \rightarrow CO_2^* + C^* + H_2O^*$ | -0.17 | 0.26 | -0.46 | 0.31 | -0.32 | -0.03 |
| 34 | $CCOO^* + {}^* + H_2O^* \rightarrow CCO^* + O^* + H_2O^*$ | 0.68 | 1.75 | 0.44 | 1.03 | -0.32 | -0.08 |
| 35 | $CCO^* + {}^* + H_2O^* \rightarrow CO^* + C^* + H_2O^*$ | -0.79 | 0.84 | -0.64 | 0.90 | 0.07 | -0.08 |
| 36 | $CO_2^* + * + H_2O^* \rightarrow CO^* + O^* + H_2O^*$ | 0.03 | 1.44 | -0.03 | 1.63 | -0.06 | -0.12 |

Although there are exceptions, for the most part, co-adsorbed water increases the reaction and activation energy for C-C, OC-OH, and OC-O bond cleavage but decreases them for O-H bond cleavage in agreement with previous studies.^{10, 14, 58} The effect on the C-H bond cleavage varies the most for the reactions studied herein due to the weak interactions between the C-H bond and co-adsorbed water.

3.1 Co-adsorbed water can change the minimum energy path of a reaction.

Co-adsorbed water can change the minimum energy path (MEP) through two different processes; by opening a new reaction path involving H-shuttling or by strong hydrogen bonding, which hinder rotations/reorientation before bond cleavage as is the case for OC-O bond cleavage of CH₂COO as shown in Figure 1.



Figure 1. (a) MEP for OC-O bond cleavage of CH₂COO in absence of co-adsorbed water and snapshot of the initial (i), after rotation (iv), transition (v) and final (vi) state configurations. (b) MEP for OC-O bond cleavage of CH₂COO in presence of co-adsorbed water and snapshot of the initial (i), intermediate (ii), transition (iv) and final (viii) state configurations. The lowest energy path involves OC-O bond cleavage of the C-O interacting with the co-adsorbed water, the activation energy for the other OC-O bond cleavage is even higher (2.0 eV) (see Figure S7 for the NEB plot).

At the initial state, CH₂COO is adsorbed on the top site through the two oxygen atoms both with and without co-adsorbed water. Before the OC-O bond cleavage without co-adsorbed water, the CH₂COO rotates up on the side so that one of the oxygen atoms sits above a bridge site but at the transition state, the (dissociating) oxygen atom sits above the nearest hollow site. With co-adsorbed water, hydrogen bonding between the co-adsorbed water and the CH₂COO stabilizes the initial state by 0.40 eV but also hinders the rotation before the OC-O bond cleavage. The molecule lies flat in the transition state, maintaining an interaction with the co-adsorbed water forming a H-O----H-O-R complex leading to an increase in the activation barrier relative to the no co-adsorbed water case. This is a common effect for OC-O bond cleavage, see Figure S1 for OC-O bond cleavage of CH₃COO.

The MEP can also change through hydrogen shuttling during O-H bond cleavage in the presence of coadsorbed water as shown in Figure 2 and S2. Unlike OC-O bond cleavage, hydrogen shuttling reduces the activation barrier for the O-H bond cleavage, in agreement with previous studies.^{10, 17, 21, 59} This is the case for COOH, in which the oxygen of the co-adsorbed water is interacting with hydrogen of the adsorbates, but not for other O-H bond cleavage (e.g. CH₃COOH, CHCOOH and CCOOH) because the most stable initial state involves the interaction between the hydrogen of co-adsorbed water and the oxygen of the adsorbate instead of the OH group.



Figure 2. Energy diagram of O-H bond cleavage of CH₂COOH with and without co-adsorbed water and snapshot of the initial (a, d), transition (b, e) and final (c, f) stage configurations. The two initial states are shown at the same relative energy for easier comparison of the activation energies, but the co-adsorbed water stabilizes the initial state by 0.22 eV.

3.2 How co-adsorbed water affects elementary steps depends on the nature of the transition state.

The nature of the transition state is also important when determining how co-adsorbed water affects the activation barrier of an elementary reaction step. For an early transition state, where the electronic structure of the transition state is more like the initial state, the effect of co-adsorbed water interactions is comparable for the initial and the transition state. Hence the co-adsorbed water interactions have little effect on the energy difference between the initial and the transitions state or the forward activation barriers. But co-adsorbed water can affect the reaction energy by stabilizing/destabilizing the final state relative to the initial state. For instance, for the C-C bond cleavage of CCOO (see Figure 3), coadsorbed water stabilizes the initial state more than the final state (by 0.29 eV) while the interaction energy with the initial and transition state differs by only 0.05 eV. Therefore, in the presence of coadsorbed water, this elementary step is more endothermic by 0.29 eV, but the change in forward activation energy is small (Δ 0.05 eV).



Figure 3. Energy diagram of C-C bond cleavage of CCOO with and without co-adsorbed water and snapshot of the initial (a, d), transition (b, e) and final (c, f) stage configurations. The two initial states are shown at the same relative energy for easier comparison of the activation energies, but the co-adsorbed water stabilizes the initial state by 0.32 eV.

However, for late transition states, the interaction energy of the co-adsorbed water with the final and transition state are comparable. In this case, the change in reaction and forward activation energy is comparable. For example, for C-C bond scissoring of CHCO (see Figure 4), co-adsorbed water stabilizes the initial state by 0.19 eV but has little effect on the final state (-0.05 eV). Consequently, in the presence of co-adsorbed water, the reaction energy becomes more endothermic by 0.14 eV and the initial state is stabilized more than the transition state by 0.14 eV, increasing the forward activation energy for this elementary step from 0.51 eV to 0.65 eV. This is a common effect for most of the C-C

and C-H bond cleavage, in which their transition states are largely late transition state based on BEP relationship.⁵⁷



Figure 4. Snapshot of the different images in the C-C bond cleavage of CHCO with and without coadsorbed water and snapshot of the initial (a, d), transition (b, e) and final (c, f) stage configurations. The two initial states are shown at the same relative energy for easier comparison of the activation energies, but the co-adsorbed water stabilizes the initial state by 0.19 eV.

3.3 The effects of co-adsorbed water on OC-O, OCO-H and OC-OH bond cleavage.

The effect of co-adsorbed water on OC-OH/OCO-H bond cleavage of CH_xCOOH and COOH, and OC-O bond cleavage of CH_xCOO is shown in Figure 5. Generally, co-adsorbed water increases the activation barrier and endothermicity for OC-O bond cleavages of CH_xCOO (see Figure 5a) through stabilization of the initial state and hinderance of rotation in the transition state. The weaker interaction between the co-adsorbed water and the products (O* + CH_xCO^*) compared to the initial state, increases the endothermicity of this reaction step.



Figure 5. (a) Change in activation barriers (blue) and reaction energies (red) for OC-O bond cleavages in presence of co-adsorbed water for different CH_xCOO intermediates. (b) Change in activation barriers and reaction energies for OCO-H (red) and OC-OH (blue) bond cleavages of (CH_xCOOH and COOH) intermediates in presence of co-adsorbed water (compared to the same reaction without co-adsorbed water). Negative and positive change indicates decrease and increase in the activation and reaction energy in the presence of co-adsorbed water. The activation barriers/reaction energies (in eV) for each reactant, without co-adsorbed water, are included on the x-axis.

Previous studies have suggested that water enhances O-H bond cleavage but inhibits C-OH bond cleavages.¹⁴ Here we see similar enhancement of O-H bond cleavage for CH_xCOOH (x=1-3) and COOH while the effect on C-OH bond cleavage is generally smaller in magnitude and less consistent (Figure 5b). The lower barrier for O-H bond cleavages in presence of co-adsorbed water is due to a combination of hydrogen shuttling (CH₂COOH and COOH) and stronger interactions of the co-adsorbed water with the final state compared to the initial state (CH₃COOH and CHCOOH). The increased reaction energy for OCO-H bond cleavage of COOH is primarily due to weak interaction of co-adsorbed water with the CO₂ product.

3.4 The effects of co-adsorbed water on C-C bond cleavage.

Co-adsorbed water generally increases the barrier and decreases the reaction energy for C-C bond cleavage (CH_xCOOH), except for C-C bond cleavage of CCOOH as shown in Figure 6a. The strong interaction between the COOH product and the co-adsorbed water, compared to the initial state, stabilizes the final state relative to the initial state, hence decreasing the reaction energy of the elementary reaction step. Co-adsorbed water has similar effect on the activation energy of C-C bond cleavage of the CH_xCO intermediates but increases the reaction energy, the exception being CH₃CO as shown in Figure 6b. The weak interaction of co-adsorbed water with CO (final state) compared to the initial state leads to an increase in reaction energy and activation barrier for most of the elementary reaction steps.



Figure 6. (a) Change in activation barriers and reaction energies for C-C bond cleavages of the CH_xCOOH intermediates in presence of co-adsorbed water. (b) Change in activation barriers and reaction energies for C-C bond cleavages of the CH_xCO intermediates in presence of co-adsorbed water. (c) Change in the activation barriers and reaction energies for C-C (red) and OC-O (blue) bond cleavages of CH_xCOO intermediates in presence of co-adsorbed water. Negative and positive change indicates decrease and increase in the activation and reaction energy in the presence of co-adsorbed water. The activation barriers/reaction energies (in eV) for each reactant, without co-adsorbed water, are included on the x-axis.

The reaction energy of C-C and OC-O bond cleavage increases (making them more endothermic or less exothermic) when co-adsorbed water is included but the effect on the C-C bond cleavage is generally larger suggesting that C-C bond cleavage become less thermodynamically favorable (see Figure 6c). On the other hand, co-adsorbed water increases the activation barrier for OC-O bond cleavage more than it does for C-C bond cleavages, suggesting that OC-O bond cleavage is less kinetically favorable in the presence of co-adsorbed water.

Figure 7 summaries the effects of co-adsorbed water on reaction intermediates leading to the formation of CO and CO₂. The barriers for OC-O and OC-OH bond cleavage increase (shown in red) with co-adsorbed water while the barrier for OCO-H bond cleavage decreases (shown in light blue), making it harder to make CH_xCO intermediates which breaks down to form CO (see Figure 7). The barriers for C-C bond cleavages either increase or the effect is negligible (shown in black) Additionally, the dehydroxylation of COOH is less favorable, suggesting that the formation of CO is harder in the presence of co-adsorbed water.



Figure 7. Reaction network for the decarboxylation and decarbonylation pathway. The intermediates important for the formation of CO are inside the purple dash-line boxes. Red lines indicate increase in activation barrier

with co-adsorbed water, light blue lines indicate a decrease in activation barrier and black lines indicate that co-adsorbed water has negligible effect on the activation barrier. Water does not decrease the barrier for any of the routes leading to CO formation.

3.5 The effect of co-adsorbed water on C-H bond cleavage.

The weak electronegativity of carbon compared to oxygen leads to very weak or no interaction between water and the C-H bond,⁶⁰ therefore co-adsorbed water has no or insignificant effect on the MEP for C-H bond cleavage, in agreement with previous study.⁶¹ The influence of co-adsorbed water on the activation barrier for C-H bond cleavage, therefore, depends on the nature of the transition state and on how water stabilizes/destabilizes the initial/final states. For example, the interaction energy of water with the initial state and final state of (CH₃CO* + * \rightarrow CH₂CO* + H*) are -0.01 eV and -0.19 eV respectively, and the change in the activation energy ($\Delta E_a = 0.19eV$) is the same as the change in reaction energy due to the product like transition state, as shown in Figure 8. Similarly, for CH₂CO* + * \rightarrow CHCO* + H*, the interaction energy of co-adsorbed water with the initial state (ΔE_{int} = -0.17eV) and final state (ΔE_{fin} = -0.14eV) are comparable, so the activation energy of the elementary reaction step is unchanged.



Figure 8. Snapshot of the different images in the C-H bond cleavage of CH₃CO with and without coadsorbed water and snapshot of the initial (a, d), transition (b, e) and final (c, f) stage configurations for C-H bond cleavage of CH₃CO. The two initial states are shown at the same relative energy here for easier comparison of the activation energies, but the co-adsorbed water stabilizes the initial state by 0.01 eV.

Generally, the effect of co-adsorbed water on the transition state of C-H bond cleavages depends on how much co-adsorbed water stabilize the initial/final state.

3.6 Effects of co-adsorbed water on the three lowest energy pathways for acetic acid decomposition on Pd (111).

Many chemical reactions, including acetic acid decomposition, are a combination of C-O, O-H and C-C bond cleavages and how co-adsorbed water affects the overall reaction is therefore an interplay between the effects on different elementary reaction steps. The free energy diagram for the three lowest energy pathways for acetic acid decomposition on Pd (111) through decarbonylation (DCN) and decarboxylation (DCX) in the presence and absence of co-adsorbed water is shown in Figure 9. The first and second overall lowest energy routes for acetic decomposition over Pd (111) in the absence of co-adsorbed water have been established previously.⁵⁷



Figure 9. (a) A free energy diagram for the three lowest energy pathways for acetic acid DCN (red) and DCX (blue and black) on Pd (111) in vacuum (solid lines) and in presence of co-adsorbed water (dash-dotted line) at 300 K. Without co-adsorbed water, the two lowest energy routes are a DCN (red) and DCX (black) routes but in the presence of co-adsorbed water the two lowest energy routes are both DCX routes (black and blue) (b) Network schematic of the three lowest energy pathways for acetic acid DCX and DCN on Pd (111) in the presence of co-adsorbed water.

Co-adsorbed water affects the reaction energy and activation barriers for most of the steps in this reaction network. Without co-adsorbed water, the first and second overall lowest energy routes are the

DCX and DCN routes, respectively, as shown in Figure 9. The first two elementary reaction steps for these two pathways are the same. The third elementary reaction step, the one that separates these two paths, is the deoxygenation of CH₂COO and dehydrogenation of CH₂COO, which have free energy of activation of 0.91 and 0.78 eV respectively, without co-adsorbed water at 300 K. In the presence of co-adsorbed water, both the free energy of activation and reaction for the deoxygenation of CH₂COO were increased to 1.41 eV and 0.43 eV, respectively, while the free energy of activation and reaction is unaffected for dehydrogenation of CH₂COO, making the dehydrogenation of CH₂COO lower in energy than deoxygenation (see Figure 9a).

The presence of co-adsorbed water increases the activation barrier for the OC-O bond cleavage of CH₂COO and decreases the activation barrier for the C-C bond cleavage of CH₂COO (see Table 1). Consequently, in the presence of co-adsorbed water, the first and second overall lowest energy route are both DCX pathways. The second lowest energy route goes through the C-C bond cleavage of CH₂COO and the lowest energy DCN pathway becomes the overall third lowest energy route in presence of co-adsorbed water. (The reaction paths for the three lowest energy routes with and without co-adsorbed water are listed in Scheme S1 and S2 in the SI). This suggests that the DCX pathway would be more favorable than the DCN pathway in the presence of co-adsorbed water. In this case, the hindrance of OC-O bond cleavage, the decrease in the barrier for C-C bond cleavage and negligible change in the C-H barrier of CH₂COO is what leads to the overall change in the lowest energy routes.

Only the three lowest energy paths are shown here to highlight the change from competition between DCN and DCX route to two DCX routes in the presence of co-adsorbed water. The whole reaction network has 33 reaction routes, many with similar energy landscape, these reaction routes, and the effect of co-adsorbed water on these routes are shown in Figure S9-S13.

4. CONCLUSION

We used DFT to investigate how co-adsorbed water influences different bond cleavages of small oxygenates, using acetic acid on Pd (111) as a model system. The presence of co-adsorbed water generally favors OCO-H bond cleavage over OC-OH bond cleavage and hinders OC-O bond cleavage of CH_xCOO, which is an important elementary reaction step in the formation of CO. The presence of coadsorbed water also generally inhibits C-C bond cleavage, but the effect varies for C-H bond cleavage. Although these are the general trends observed, there are exceptions for individual reaction steps which can have important implications for reaction networks with many parallel reaction paths.

For acetic acid decomposition on Pd (111), the two lowest free energy routes are DCX route (leading to CO₂ formation) and DCN route (leading to CO formation) through a common CH₂COO intermediate. In the presence of co-adsorbed water, the C-C bond cleavage of a second DCX route from the same intermediate is enhanced while the OC-O bond cleavage in the DCN is hindered, leading to two DCX routes to become the lowest free energy routes. Although C-C bond cleavage is generally hindered by water, we found three exceptions, which are the C-C bond cleavage of the CH₂COO, CCOOH and CCO intermediates, but the CH₂COO plays a key role in the reaction network studied here, illustrating the complexity of these systems.

This study gives insight on how water can affect different bond cleavages and how that translates into changes in the overall favorability of different reaction pathways as well as providing fundamental insights on how the presence of water can influence the decomposition of oxygenates on metal surfaces.

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7. SUPPORTING INFORMATION

The supporting information contains the equations for the calculations of the interaction energy and reaction energy in the presence of two co-adsorbed water; the table for the free energy of activation and reaction for key elementary reaction steps involved in the three lowest energy pathways; snapshots for the initial and transition states of all elementary reaction steps in the presence of co-adsorbed water; and the reaction scheme for the three lowest energy pathway and all pathways for acetic acid decarboxylation and decarbonylation on Pd (111); and the energy diagram for all pathways for acetic acid acid decarboxylation and decarbonylation on Pd (111) in the absence and presence of co-adsorbed water.

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