

Theoretical Investigation of the Hydrodeoxygenation of Methyl Propionate over Pd (111) Model Surfaces

Supporting Information

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1. Adsorbate-Adsorbate Interactions

It is well known that the adsorption energy of CO on Pd (111) decreases dramatically at higher CO coverages.¹⁻³ Our DFT calculations for CO adsorption on Pd (111) at different CO coverages show the same trend. At high CO coverage, lateral interactions between adsorbed CO molecules destabilize the binding strength of the CO molecules with the Pd surface. For instance, the adsorption energy of CO at 1/12 ML coverage is calculated to be -2.03 eV while it is -0.94 eV at 1 ML coverage. Therefore lateral interactions should be taken into account to compute approximate differential adsorption energies. Co-adsorption effects of several different species complicate the situation.

Preliminary results of our microkinetic model showed that CO, H and CH₃C are the three most abundant surface intermediates. To improve the accuracy of our microkinetic model, we therefore employed a method similar to the one proposed by Grabow *et al.*⁴ to determine coverage dependent adsorption energies of CO, H, and CH₃C.

From adsorption energy calculations of CO at various coverages ($\theta_{\text{CO}}=1/4$ ML, $2/4$ ML, $3/4$ ML, $4/4$ ML), we determined a differential adsorption energy of CO as a function of θ_{CO} , $E_{\text{CO}}(\theta_{\text{CO}})$ shown in Eq. (1).

$$E_{\text{CO}}(\theta_{\text{CO}}) = -2.031 + 2 * 1.559 * (\theta_{\text{CO}} - 0.164) \quad (1)$$

Similarly, for the reaction $0.5\text{H}_{2(\text{gas})}^{+*} \rightarrow \text{H}^*$, we determined the adsorbed H energy at various coverages ($\theta_{\text{H}}=1/4$ ML, $2/4$ ML, $3/4$ ML, $4/4$ ML) to determine the differential adsorption energy as a function of θ_{H} , $E_{\text{H}}(\theta_{\text{H}})$ shown in Eq. (2).

$$E_{\text{H}}(\theta_{\text{H}}) = -0.598 + 2 * 0.084 * (\theta_{\text{H}} - 0.220) \quad (2)$$

For the coverage dependent adsorption energy of CH₃C ($\theta_{\text{CH}_3\text{C}}=1/4$ ML, $2/4$ ML, $3/4$ ML, $4/4$ ML) we found the differential adsorption energy of CH₃C as a function of $\theta_{\text{CH}_3\text{C}}$, $E_{\text{CH}_3\text{C}}(\theta_{\text{CH}_3\text{C}})$ shown in Eq. (3).

$$E_{\text{CH}_3\text{C}}(\theta_{\text{CH}_3\text{C}}) = -5.767 + 2 * 4.076 * (\theta_{\text{CH}_3\text{C}} - 0.170) \quad (3)$$

Next, coadsorption of CO and H at various coverages ($\theta_{\text{CO}}=1/4$ ML, $\theta_{\text{H}}=1/4$ ML; $\theta_{\text{CO}}=2/4$ ML, $\theta_{\text{H}}=1/4$ ML; $\theta_{\text{CO}}=1/4$ ML, $\theta_{\text{H}}=2/4$ ML; $\theta_{\text{CO}}=1/4$ ML, $\theta_{\text{H}}=3/4$ ML; $\theta_{\text{CO}}=2/4$ ML, $\theta_{\text{H}}=2/4$ ML; $\theta_{\text{CO}}=3/4$ ML, $\theta_{\text{H}}=1/4$ ML) leads to $E_{\text{CO}}(\theta_{\text{CO}}, \theta_{\text{H}})$ and $E_{\text{H}}(\theta_{\text{CO}}, \theta_{\text{H}})$ shown in Eq. (4) and Eq. (5), respectively.

$$E_{\text{CO}}(\theta_{\text{CO}}, \theta_{\text{H}}) = -2.031 + 2 * 1.559 * (\theta_{\text{CO}} - 0.164) + 0.190\theta_{\text{H}} + 1.5 * 0.984 * \theta_{\text{H}}(\theta_{\text{CO}}\theta_{\text{H}})^{0.5} \quad (4)$$

$$E_{\text{H}}(\theta_{\text{CO}}, \theta_{\text{H}}) = -0.598 + 2 * 0.084 * (\theta_{\text{H}} - 0.220) + 0.190\theta_{\text{CO}} + 1.5 * 0.984 * \theta_{\text{CO}}(\theta_{\text{CO}}\theta_{\text{H}})^{0.5} \quad (5)$$

Coadsorption of CO and CH₃C at various coverages ($\theta_{\text{CO}}=1/4$ ML, $\theta_{\text{CH}_3\text{C}}=1/4$ ML; $\theta_{\text{CO}}=2/4$ ML, $\theta_{\text{CH}_3\text{C}}=1/4$ ML; $\theta_{\text{CO}}=1/4$ ML, $\theta_{\text{CH}_3\text{C}}=2/4$ ML; $\theta_{\text{CO}}=1/4$ ML, $\theta_{\text{CH}_3\text{C}}=3/4$ ML; $\theta_{\text{CO}}=2/4$ ML, $\theta_{\text{CH}_3\text{C}}=2/4$ ML; $\theta_{\text{CO}}=3/4$ ML, $\theta_{\text{CH}_3\text{C}}=1/4$ ML) gives $E_{\text{CO}}(\theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}})$ and $E_{\text{CH}_3\text{C}}(\theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}})$ shown in Eq. (6) and Eq. (7), respectively.

$$E_{\text{CO}}(\theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}}) = -2.031 + 2 * 1.559 * (\theta_{\text{CO}} - 0.164) + 2.375\theta_{\text{CH}_3\text{C}} + 1.5 * 3.342 * \theta_{\text{CH}_3\text{C}}(\theta_{\text{CO}}\theta_{\text{CH}_3\text{C}})^{0.5} \quad (6)$$

$$E_{\text{CH}_3\text{C}}(\theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}}) = -5.767 + 2 * 4.076 * (\theta_{\text{CH}_3\text{C}} - 0.170) + 2.375\theta_{\text{CO}} + 1.5 * 3.342 * \theta_{\text{CO}}(\theta_{\text{CO}}\theta_{\text{CH}_3\text{C}})^{0.5} \quad (7)$$

And, coadsorption of H and CH₃C at various coverages ($\theta_{\text{H}}=1/4$ ML, $\theta_{\text{CH}_3\text{C}}=1/4$ ML; $\theta_{\text{H}}=2/4$ ML, $\theta_{\text{CH}_3\text{C}}=1/4$ ML; $\theta_{\text{H}}=1/4$ ML, $\theta_{\text{CH}_3\text{C}}=2/4$ ML; $\theta_{\text{H}}=1/4$ ML, $\theta_{\text{CH}_3\text{C}}=3/4$ ML; $\theta_{\text{H}}=2/4$ ML, $\theta_{\text{CH}_3\text{C}}=2/4$ ML; $\theta_{\text{H}}=3/4$ ML, $\theta_{\text{CH}_3\text{C}}=1/4$ ML) leads to $E_{\text{H}}(\theta_{\text{H}}, \theta_{\text{CH}_3\text{C}})$ and $E_{\text{CH}_3\text{C}}(\theta_{\text{H}}, \theta_{\text{CH}_3\text{C}})$ in Eq. (8) and Eq. (9), respectively.

$$E_{\text{H}}(\theta_{\text{H}}, \theta_{\text{CH}_3\text{C}}) = -0.598 + 2 * 0.084 * (\theta_{\text{H}} - 0.220) + 0.382\theta_{\text{CH}_3\text{C}} + 1.5 * 1.485 * \theta_{\text{CH}_3\text{C}}(\theta_{\text{CH}_3\text{C}}\theta_{\text{H}})^{0.5} \quad (8)$$

$$E_{\text{CH}_3\text{C}}(\theta_{\text{H}}, \theta_{\text{CH}_3\text{C}}) = -5.767 + 2 * 4.076 * (\theta_{\text{CH}_3\text{C}} - 0.170) + 0.382\theta_{\text{H}} + 1.5 * 1.485 * \theta_{\text{H}}(\theta_{\text{CH}_3\text{C}}\theta_{\text{H}})^{0.5} \quad (9)$$

Finally, we conclude for the coverage dependent CO and H adsorption energies

$$E_{\text{CO}}(\theta_{\text{H}}, \theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}}) = -2.031 + 2 * 1.559 * (\theta_{\text{CO}} - 0.164) + 0.190\theta_{\text{H}} + 1.5 * 0.984 * \theta_{\text{H}}(\theta_{\text{CO}}\theta_{\text{H}})^{0.5} + 2.375\theta_{\text{CH}_3\text{C}} + 1.5 * 3.342 * \theta_{\text{CH}_3\text{C}}(\theta_{\text{CO}}\theta_{\text{CH}_3\text{C}})^{0.5} \quad (10)$$

$$E_{\text{H}}(\theta_{\text{H}}, \theta_{\text{CO}}, \theta_{\text{CH}_3\text{C}}) = -0.598 + 2 * 0.084 * (\theta_{\text{H}} - 0.220) + 0.190\theta_{\text{CO}} + 1.5 * 0.984 * \theta_{\text{CO}}(\theta_{\text{CO}}\theta_{\text{H}})^{0.5} + 0.382\theta_{\text{CH}_3\text{C}} + 1.5 * 1.485 * \theta_{\text{CH}_3\text{C}}(\theta_{\text{CH}_3\text{C}}\theta_{\text{H}})^{0.5} \quad (11)$$

These two equations have been implemented into our microkinetic model to approximately include the effects of lateral interactions.

2. BEP relationships

In our effort to provide correlations for predicting activation barriers without having to perform expensive transition state searches and also to better understand the accuracy of these correlations, we show in Figure S1 Brønsted-Evans-Polanyi (BEP) relations that aim at linearly correlating the activation barrier of all C-H, C-C, and C-O bond dissociations to their reaction energies on Pd (111).^{5,6} The obtained BEP relation for C-H dissociation is $E_{\text{act}} = 0.43 \times \Delta E_0 + 0.76$. The mean absolute error (MAE) of this relation is 0.10 eV and the largest error in all the data is 0.27 eV which originates from CH₂O dissociation to CHO and H. Next, the BEP relation for all C-C bond cleavage steps is $E_{\text{act}} = 0.26 \times \Delta E_0 + 1.03$ with a MAE of 0.11 eV and a maximum error of 0.23 eV. The dissociation of CH₃CCO to CH₃C and CO has the maximum absolute error among all C-C bond cleavage steps. Finally, the C-O bond dissociation data points can be fitted to

$E_{\text{act}}=0.42\times\Delta E_0+0.58$ with a MAE of 0.12 eV. The largest error is 0.29 eV which comes from the dissociation of $\text{CH}_3\text{CH}_2\text{COOCH}_2$ to $\text{CH}_3\text{CH}_2\text{CO}$ and OCH_2 .

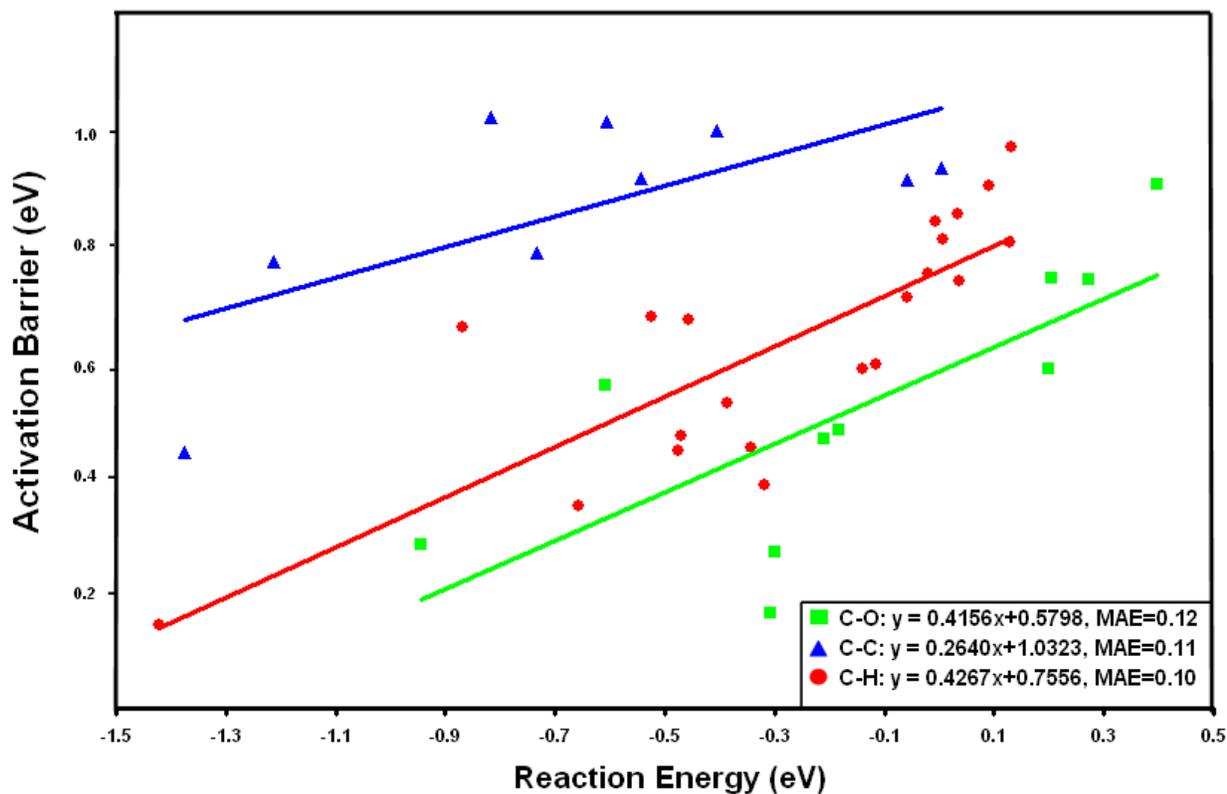


Figure S1. Brønsted-Evans-Polanyi (BEP) correlation for C-O (green line), C-C (blue line) and C-H (red line) bond dissociations. The zero-point energy corrected activation barriers of the investigated reactions have been plotted vs. zero-point energy corrected reaction energies.

3. References

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