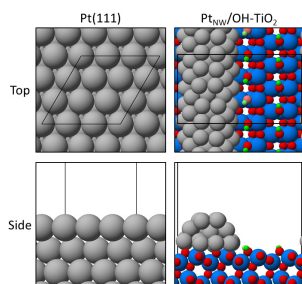


Introduction

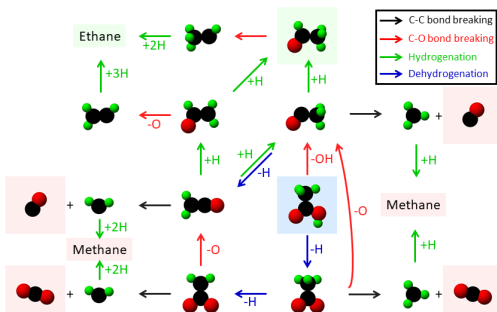
- Hydrodeoxygenation (HDO) reactions are needed to create more-stable bio-oil product following catalytic fast pyrolysis (CFP) of raw biomass.¹
- Noble metals supported on reducible metal oxides (e.g., Pt/TiO₂) are promising catalysts for HDO.²
- Model-compound studies of phenols show interfacial vacancies are required to promote desired deoxygenation steps.³
- Carboxylic acids (e.g., acetic acid) are an important class of compounds in biomass pyrolysis vapors.⁴
- Fundamental insights into the role of metal, interface, and vacancy sites are lacking for carboxylic acid HDO.
- We therefore used density functional theory (DFT) to probe the role of metal, interface, and interfacial-vacancy sites in acetic acid HDO (AA-HDO) reaction pathways.

Computational details

- VASP^{5,6}
- PBE exchange-correlation functional⁷ with D3 dispersion corrections⁸
- Transition states identified using climbing-image nudged elastic band method^{9,10}
- Pt-metal sites: Pt(111)
- Interface/interfacial-vacancy sites: lattice-matching code^{11,12} used to construct anatase(101)-supported Pt-nanowire model (Pt_{NW}/OH-TiO₂)



Reaction mechanism

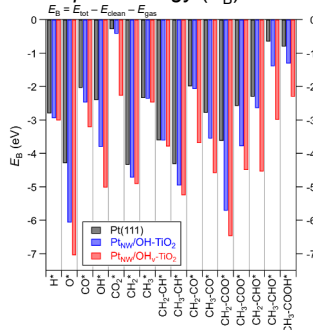


Based on previous experimental work,^{13,14} elementary steps for AA-HDO included steps involving the formation of:

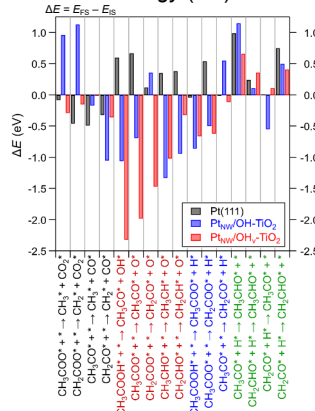
- Acetate and acyl surface intermediates.
- Desired C-O bond-breaking products, **acetaldehyde and ethane**.
- Undesired C-C bond-breaking products, **CO, CO₂, and CH₄**.

Adsorption and reaction energetics

Adsorption energy (E_B)



Reaction energy (ΔE)



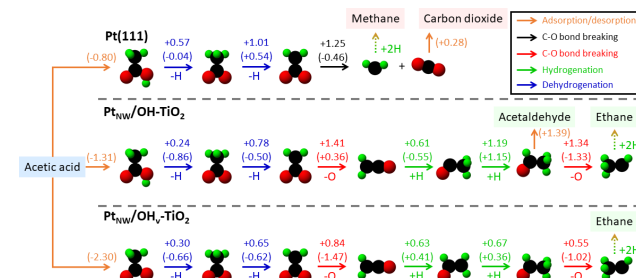
Adsorption Energy Relative to Pt(111)

- Interface stabilizes all adsorbates on average by:
 - Pt_{NW}/OH-TiO₂ **0.67 eV**
 - Pt_{NW}/OH-TiO₂-**1.56 eV**
- Interfacial vacancy notably stabilizes oxygen-containing surface intermediates.

Reaction Energy Relative to Pt(111)

- C-C bond breaking step reaction energies differ at the interface, though not systematically (i.e., some are more endothermic, others more exothermic).
- C-O bond-breaking steps mostly shift from endothermic on Pt(111) to notably exothermic at the interface, particularly with an **interfacial vacancy**.

Minimum energy pathways



- Based on the lowest activation barrier for each step, minimum energy pathway (MEP) constructed for AA-HDO on each active-site model system.
- Pt(111) MEP leads to undesired decarboxylation products, **CH₄ and CO₂**.
- Both interface model systems form **desired deoxygenation products, acetaldehyde and ethane**.
- Interfacial vacancy may accelerate the **C-O bond-breaking step** for CH₂COO (**0.81 eV with vs. 1.41 eV without vacancy**).
- Model systems illustrate surface chemistry underlying experimental observation that Pt/C and Pt/TiO₂ preferentially form C-C bond-breaking and C-O bond-breaking products, respectively.¹³

Conclusions

- Pt-TiO₂ interface stabilizes all studied surface intermediates in AA-HDO pathway relative to Pt.
- The addition of the TiO₂ support results in a Pt-TiO₂ active site that is more favorable toward **desired deoxygenation steps**, which lead to the formation of **acetaldehyde and ethane**.
- Interfacial vacancies** may facilitate the **first C-O bond-breaking step**, the predicted rate-limiting step without an interfacial vacancy; however, vacancy formation is highly activated (1.76 eV).
- Future catalyst development for HDO could target smaller catalyst particles that expose higher concentrations of metal-metal oxide interface sites.

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