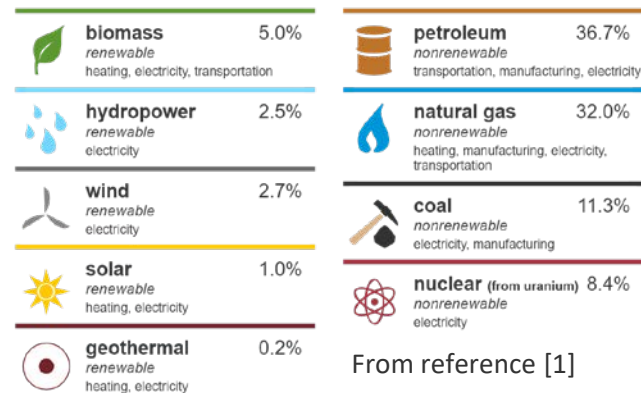# Assessing the role of the support in acetic acid hydrodeoxygenation selectivity on Pt/TiO$_2$
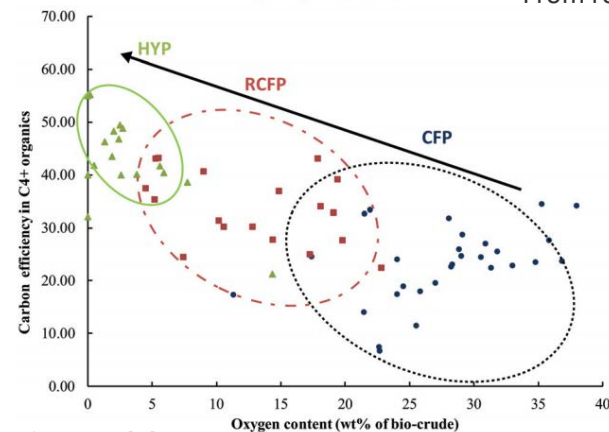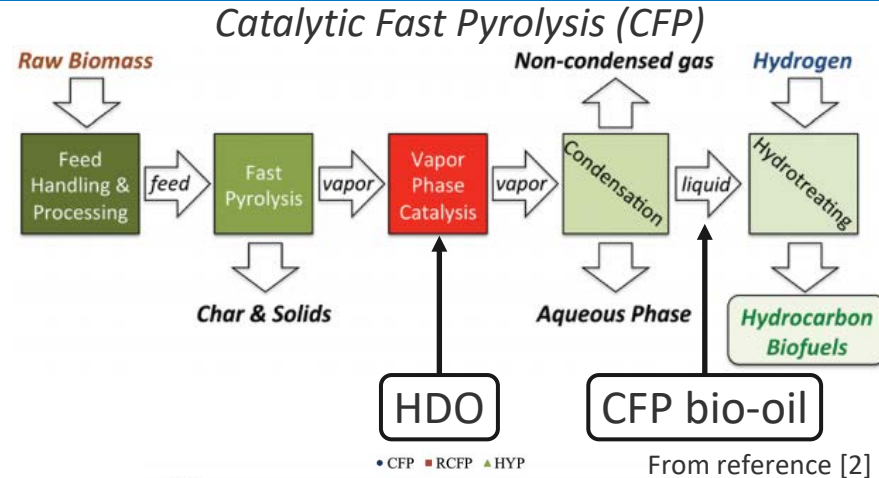
Sean A. Tacey, Matthew M. Yung, Michael B. Griffin, Carrie A. Farberow
ACS Fall 2021 Meeting
August 25th, 2021

Bioenergy - CFP vapors upgraded through HDO reactions

U.S. energy consumption by source, 2019

biomass *renewable* heating, electricity, transportation	5.0%	petroleum *nonrenewable* transportation, manufacturing, electricity	36.7%	
hydropower *renewable* electricity	2.5%	natural gas *nonrenewable* heating, manufacturing, electricity, transportation	32.0%	
wind *renewable* electricity	2.7%	coal *nonrenewable* electricity, manufacturing	11.3%	
solar *renewable* heating, electricity	1.0%	nuclear (from uranium) *nonrenewable* electricity	8.4%	
geothermal *renewable* heating, electricity	0.2%			

From reference [1]

Focus on renewable energy from **biomass sources**.

Catalytic Fast Pyrolysis (CFP)

HDO   CFP bio-oil

From reference [2]

- Bifunctional metal-acid catalysts are **key** for hydrodeoxygenation (HDO) reactions.[4]

- Promising materials include:[4]

  - Noble-metals (Pt, Pd, Ru) supported on reducible metal oxides (TiO_2, ZrO_2)

  - Molybdenum carbide (Mo_2C)

1. https://www.eia.gov/energyexplained/what-is-energy/sources-of-energy.php
2. D.A. Ruddy, et al. *Green Chem.*, **16** (2014) 454.
3. M.B. Griffin, et al. *Energy Environ. Sci.*, **11** (2018) 2904.
4. K. Wang, D.C. Dayton, J.E. Peters, and O.D. Mante. *Green Chem.*, **19** (2017) 3243.

From reference [3]

Model compound studies

Previous **experimental + theoretical** model-compound HDO studies have focused on aromatics to understand how the interface influences the deoxygenation mechanism.
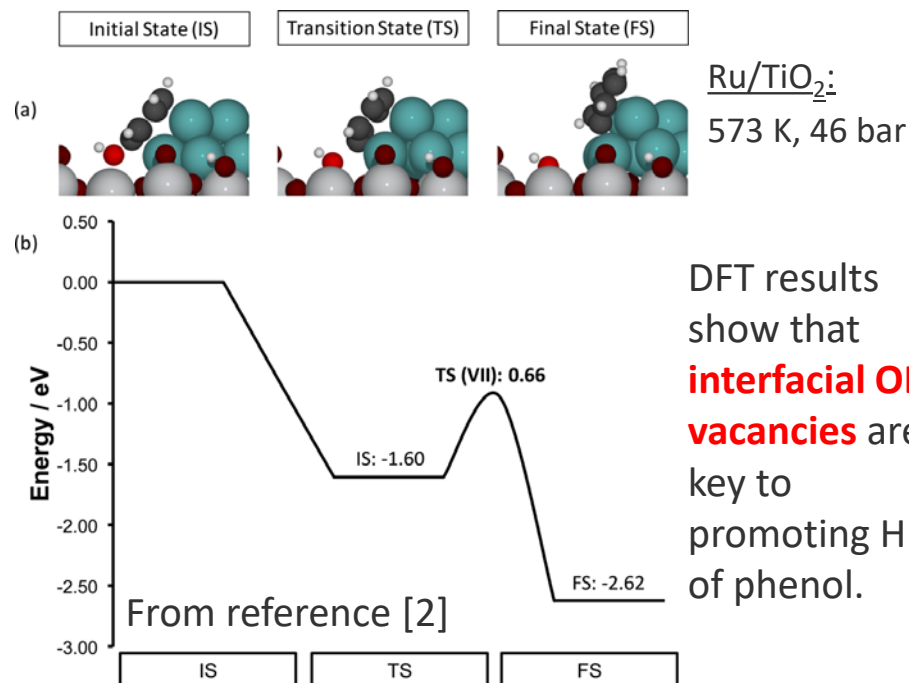
m-Cresol HDO
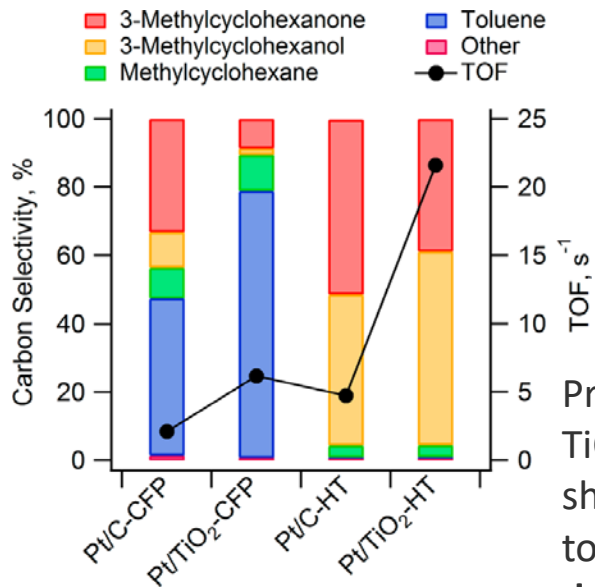
From reference [1]

Pt/C and Pt/TiO$_2$:
523 K, 2.0 MPa

Presence of Pt-TiO$_2$ interface shifts selectivity toward **deoxygenated products**.

Phenol HDO

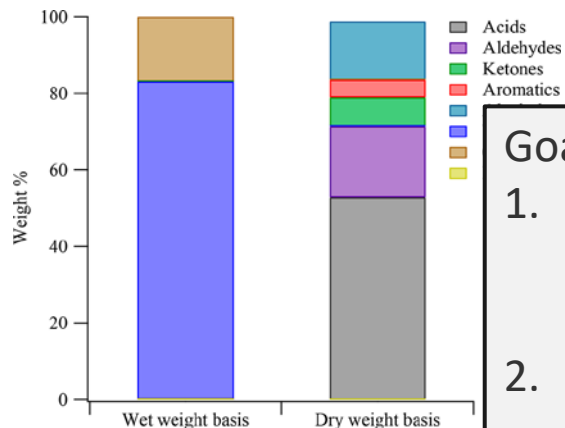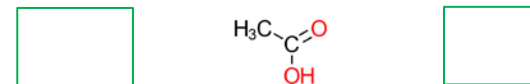From reference [2]

Ru/TiO$_2$:
573 K, 46 bar

DFT results show that **interfacial OH vacancies** are key to promoting HDO of phenol.

1. M.B. Griffin, et al. *ACS Catal.*, **6** (2016) 2715.
2. R.C. Nelson, et al. *ACS Catal.*, **5** (2015) 6509.

Model compound studies

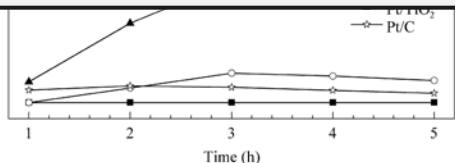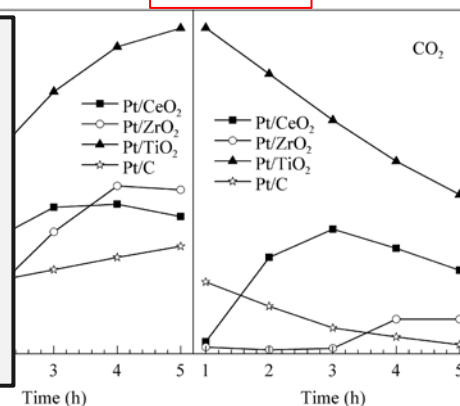However, carboxylic acids are another predominant class of compounds present in the CFP bio-oil.

H_3C—C O / OH

Acetic acid HDO: 300 °C, 4 MPa.

From reference [1]

Goals of this project:
1. Develop fundamental insights into the role of **Pt-metal** and **interface sites** in acetic acid HDO.
2. Assess the role of **interfacial vacancies** in the HDO reaction pathway.

From reference [2]

- Pt/TiO_2 shows selectivity toward **deoxygenation products**.
- However, limited fundamental studies on HDO of carboxylic acids.

1. A.K. Starace, et al. *ACS Sustain. Chem. Eng.*, **5** (2017)
2. Z. He and X. Wang. *J. Energy Chem.*, **22** (2013) 883.
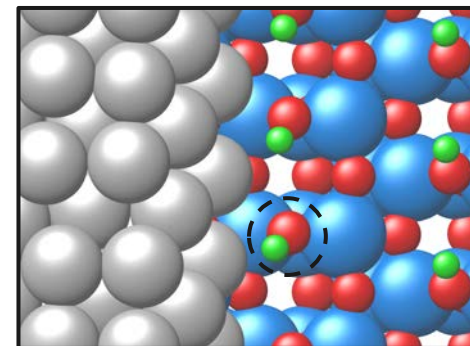
Computational methods

- VASP[1,2]

- PBE[3]-D3[4]

- Pt(111): 3x3x4, bottom 2 layers fixed

- Anatase-supported Pt-nanowire to capture interface[5,6]

- +U corrections for TiO$_2$ support[7]

  U_{eff} = 2.5 eV for Ti cations[8]

- CI-NEB calculations for elementary-step activation barriers[9,10]
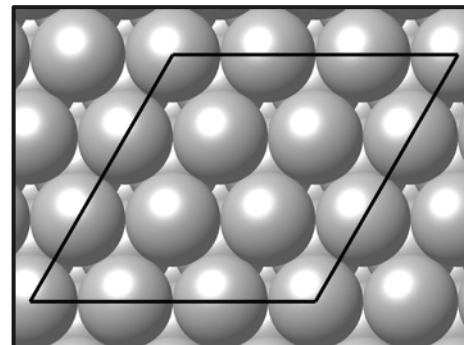
Pt(111)
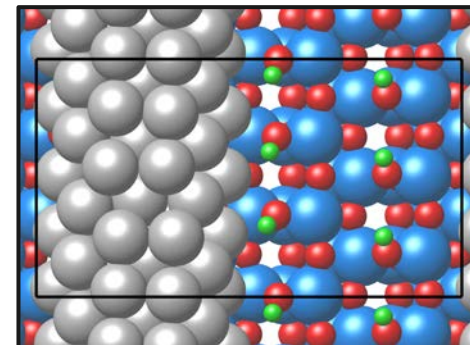
Pt$_{NW}$/OH-aTiO$_2$(101)


Pt$_{NW}$/OH(vac)-aTiO$_2$(101)

1. G. Kresse and J. Furthmüller. *Comput. Mater. Sci.*, **6** (1996) 15.
2. G. Kresse and J. Furthmüller. *Phys. Rev. B*, **54** (1996) 11169.
3. J.P. Perdew, K. Burke, and M. Ernzerhof. *Phys. Rev. Lett.*, **77** (1996) 3865.
4. S. Grimme, J. Antony, S. Ehrlich, and S. Krieg. *J. Chem. Phys.*, **132** (2010) 154104.
5. P. Ghanekar, et al. *Top. Catal.*, **63** (2020) 673.
6. Z.-J. Zhao, et al. *J. Catal.*, **345** (2017) 157.
7. S.L. Dudarev, G.A. Botton, S.Y. Savrasov, C.J. Humphreys, and A.P. Sutton. *Phys. Rev. B*, **57** (1998) 1505.
8. M.B. Griffin, et al. *ACS Catal.*, **6** (2016) 2715.
9. G. Henkelman and H. Jónsson. *J. Chem. Phys.*, **113** (2000) 9978.
10. G. Henkelman, B.P. Uberuaga, and H. Jónsson. *J. Chem. Phys.*, **113** (2000) 9901.

Acetic acid HDO reaction pathway

Black – C, Red – O, Green – H
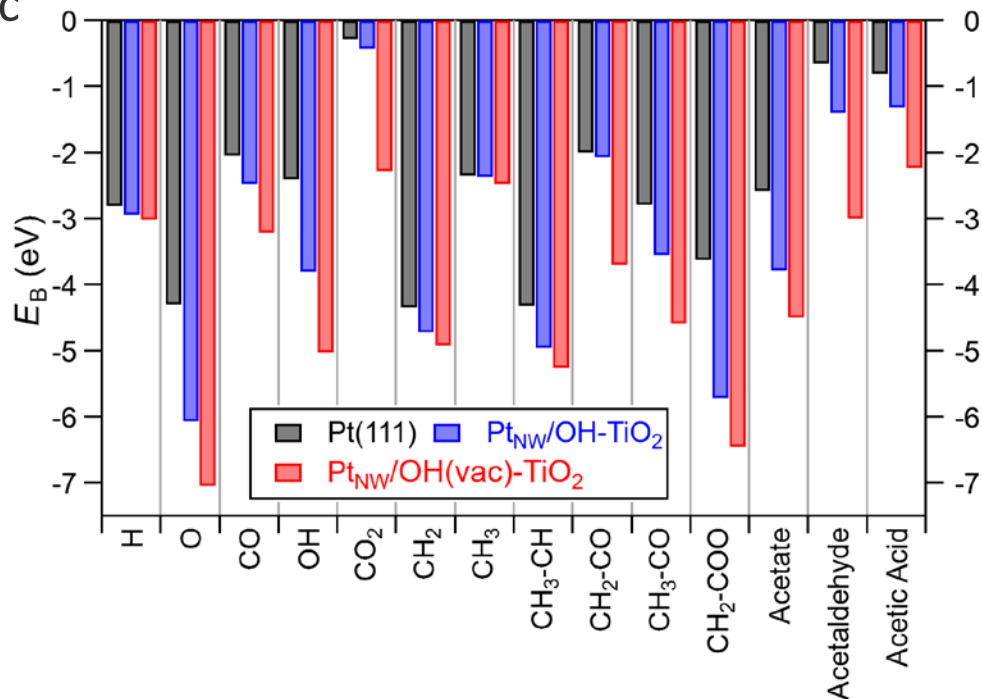
Adsorption of surface intermediates

Calculated adsorption energetics for relevant surface intermediates in acetic acid HDO:
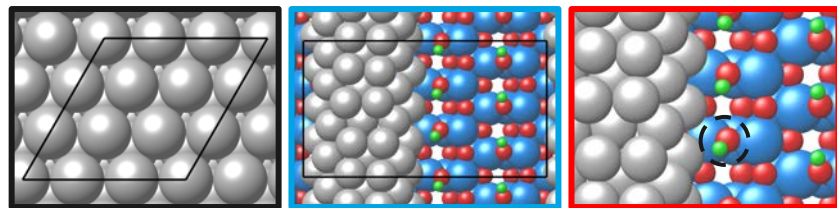
Relative to **Pt(111)**, interface stabilizes adsorption on average by:
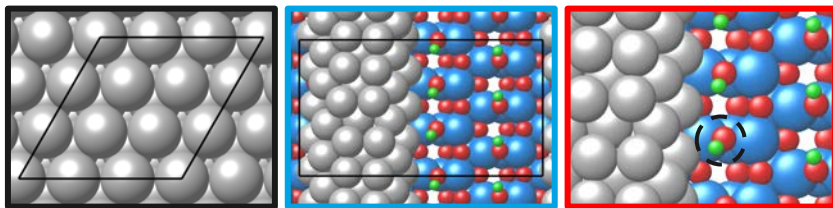Pt_{NW}/OH-TiO_2: **0.73 eV**
Pt_{NW}/OH(vac)-TiO_2: **1.60 eV**

*Grey − Pt, **Blue − Ti**, **Red − O**, **Green − H***

Reaction energies for elementary steps

1 eV = 96.5 kJ/mol

Next, calculated reaction energies for studied acetic acid HDO elementary steps:

Surface	<ΔE> (eV)		
	C-C	**C-O**	**(de)H**
Pt(111)	−0.34	+0.44	+0.37
Pt$_{NW}$/OH-TiO$_2$(101)	+0.22	−0.68	−0.04
Pt$_{NW}$/OH(vac)-TiO$_2$(101)	−0.21	−1.72	−0.13

Desired **+** **−**

Grey − Pt, *Blue − Ti*, *Red − O*, *Green − H*

C-C bond cleavage   C-O bond cleavage   (de)hydrogenation

All energies in eV
1 eV = 96.5 kJ/mol
Reaction energy in parentheses

E_a (ΔE)
0.57 (−0.04)
−H

1.01 (+0.54)
−H

1.25
(−0.46)

0.91
(+0.60)
−OH

Decarbonylation/decarboxylation products **energetically preferred** on Pt(111).

(+0.12)

−O

+H

+/−H

−O

C-C bond cleavage ➡
C-O bond cleavage ➡
(de)hydrogenation ➡

Black – C, Red – O, Green – H, Grey – Pt

All energies in eV
1 eV = 96.5 kJ/mol

E_a (ΔE)
0.24 (−0.86)
−H

0.78 (−0.50)
−H

1.99 (+1.13)

0.98 (−1.06) −OH

+H

−O

While following a different pathway, **decarbonylation/decarboxylation products** are still **energetically preferred** at the Pt$_{NW}$/OH-aTiO$_2$(101) interface.

Need to assess the role of **OH vacancies** on the reaction pathway.

1.30 (−0.55)

0.86 (−1.05)

C-C bond cleavage →
C-O bond cleavage →
(de)hydrogenation →

Black − C, Red − O, Green − H, Grey − Pt, Blue − Ti

Reaction pathway: Pt$_{NW}$/OH(vac)-aTiO$_2$(101)

All energies in eV
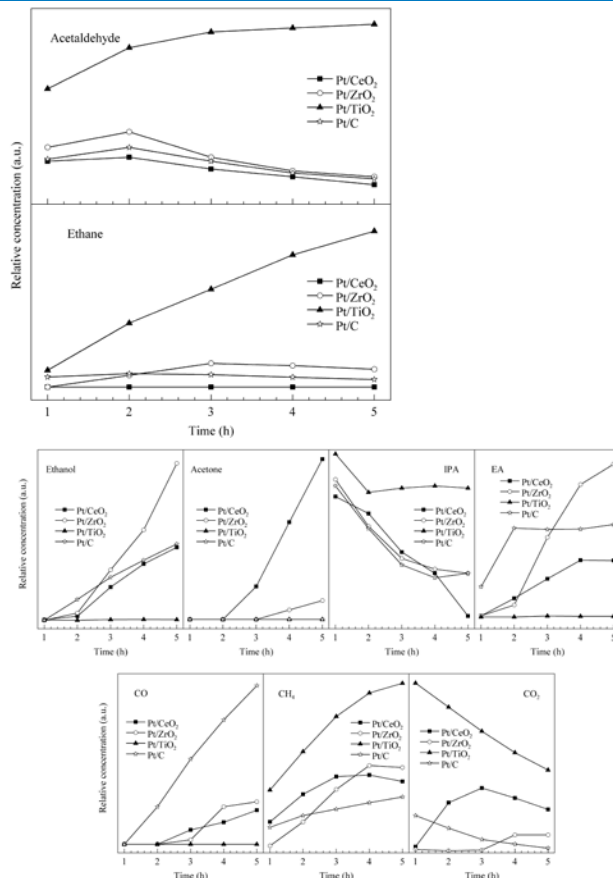*1 eV = 96.5 kJ/mol*
Reaction energy in parentheses

E_a (ΔE)

0.24 (−0.72) −H

0.65 (−0.59) −H

1.57 (−0.18)

0.79 (−2.39) −OH

0.82 (−1.98)

1.58

Desorb (+2.99)

0.66 (+0.66) +H
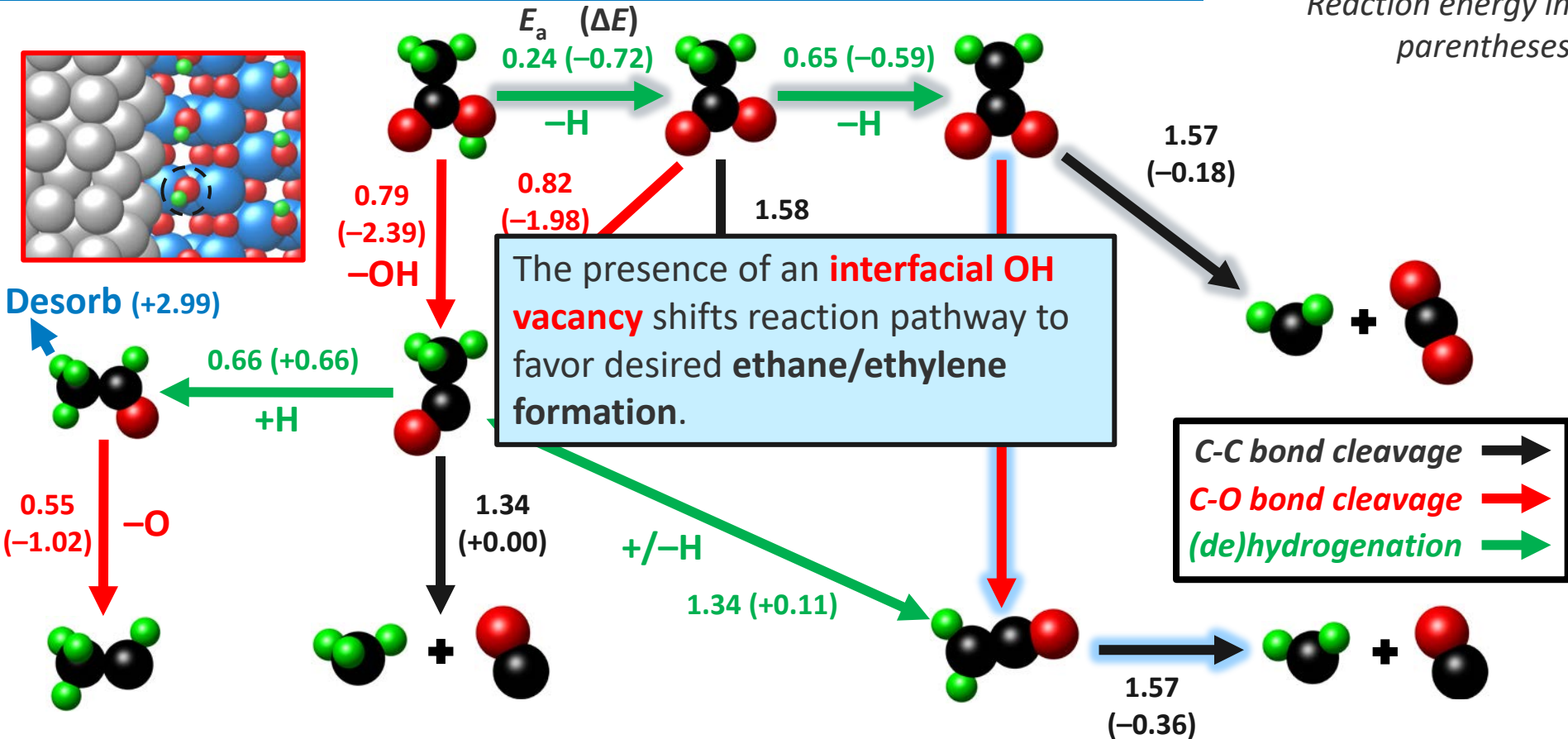
The presence of an **interfacial OH vacancy** shifts reaction pathway to favor desired **ethane/ethylene formation**.

0.55 (−1.02) −O

1.34 (+0.00)

+/−H

1.34 (+0.11)

1.57 (−0.36)

C-C bond cleavage →
C-O bond cleavage →
(de)hydrogenation →

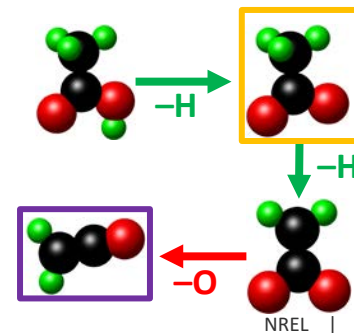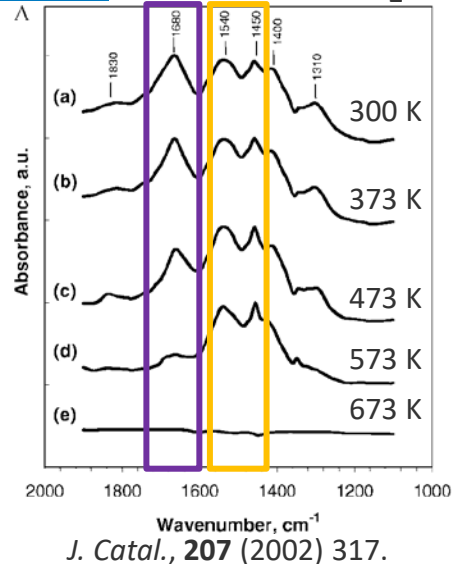**Black − C, Red − O, Green − H, Grey − Pt, Blue − Ti**

Connections with experiments

These results agree with previous experimental measurements:

- **Pt(111)** preferentially forms undesired C-C bond-dissociation products.

- With an **interfacial-OH vacancy**, the formation of desired deoxygenation products is preferred, primarily ethane/ethylene.

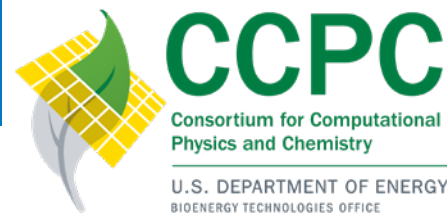- Acetate and acyl species have been observed in AA-HDO using in situ DRIFTS measurements.
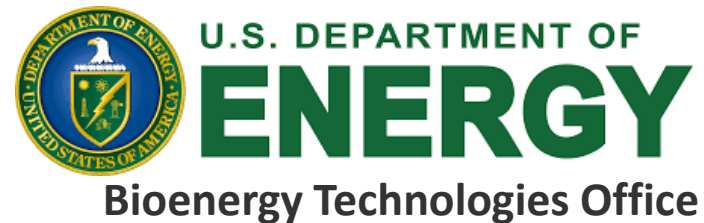
Black – C, Red – O, Green – H

J. Energy Chem., **22** (2013) 883.

DRIFTS: Pt/TiO$_2$

J. Catal., **207** (2002) 317.

Future steps

All energies in eV
1 eV = 96.5 kJ/mol
Reaction energy in parentheses

- However, acetaldehyde is a primary product in Pt/TiO$_2$-catalyzed AA-HDO.

- In the Pt/TiO$_2$ surface models, CH$_2$-CO is the main branch point.
  - We have only studied two elementary steps involving CH$_2$-CO:
    1. **CH$_2$-CO + H → CH$_3$-CO**
    2. **CH$_2$-CO → CH$_2$ + CO**
  - Plan to study additional elementary steps involving CH$_2$-CO and species formed from CH$_2$-CO on all three surface models:
    1. **CH$_2$-CO + H → CH$_2$-CHO**
    2. **CH$_2$-CHO + H → CH$_3$-CHO** (could further hydrogenate to ethanol)
    3. **CH$_2$-CHO → CH$_2$-CH + O** (further hydrogenate to ethane/ethylene)

- Interfacial water can notably lower the barrier for C-OH bond dissociation.[1]

- Plan to study role of interfacial water on AA activation:

  CH$_3$-COOH + H$_2$O$_{int}$ → CH$_3$-CO + OH$_{int}$ + H$_2$O

Black – C, Red – O, Green – H, Grey – Pt, Blue – Ti

Desorb (+2.99)   **Desorb (+1.39)**

0.55 (−1.02) **−O**   **1.34 (−1.33)** **−O**

−H

−H

−O

1. *ACS Catal.*, **5** (2015) 6509.

Acknowledgements

Catalytic Carbon Transformation & Scale-Up Center

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Webpage – https://www.nrel.gov/research/staff/sean-tacey.html