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Transforming ENERGY

Assessing the Role of Interfacial and Metal Sites in Pt/TiO2-Catalyzed Acetic Acid Hydrodeoxygenation

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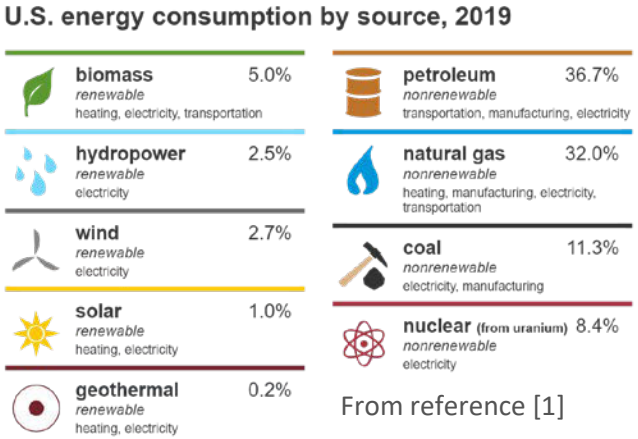
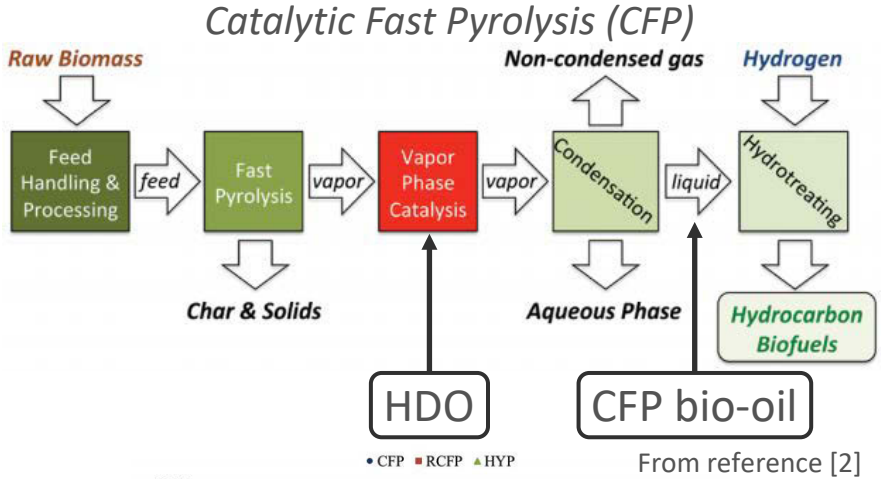
Bioenergy - CFP vapors upgraded through HDO reactions



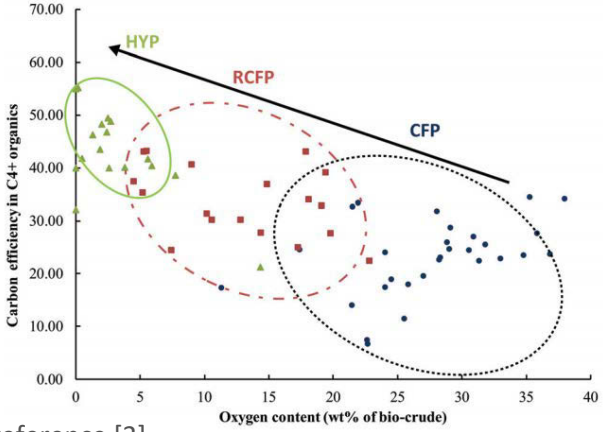
From reference [1]

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



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)



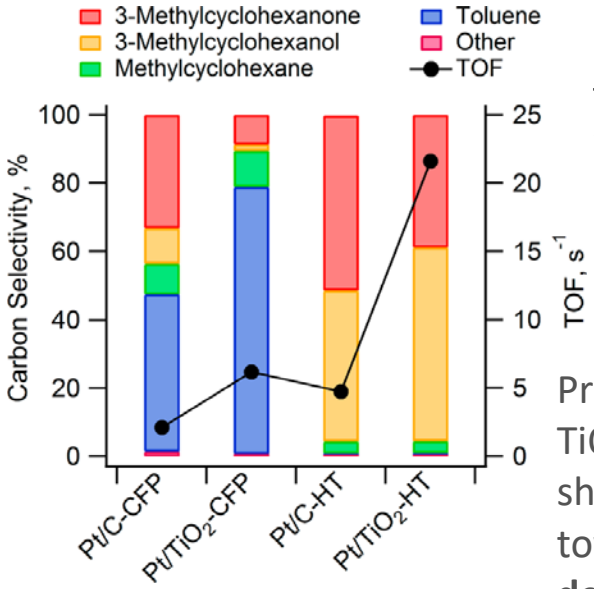
From reference [3]

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.

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

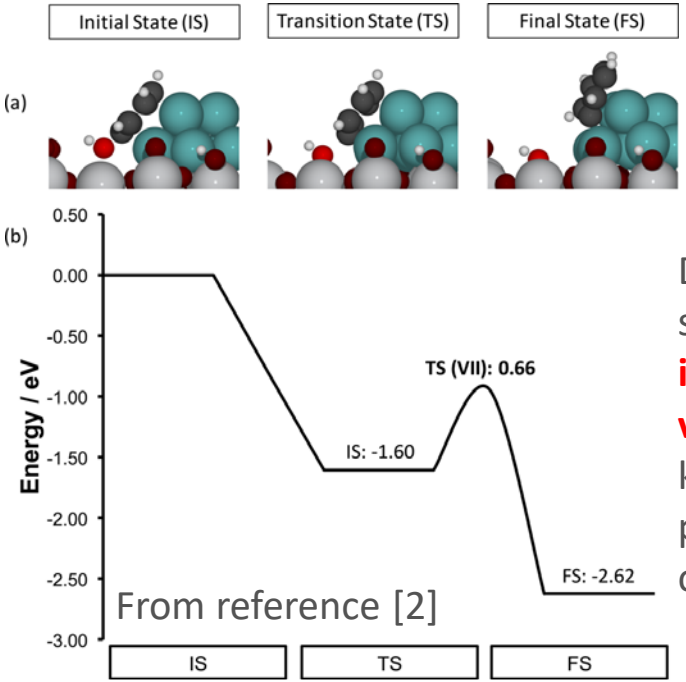


From reference [1]

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]

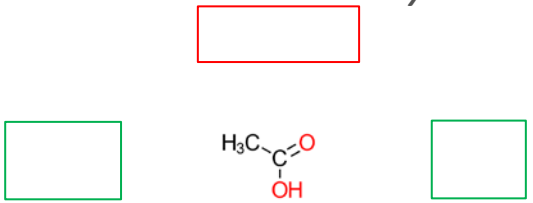
Ru/TiO_2:
573 K, 46 bar

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

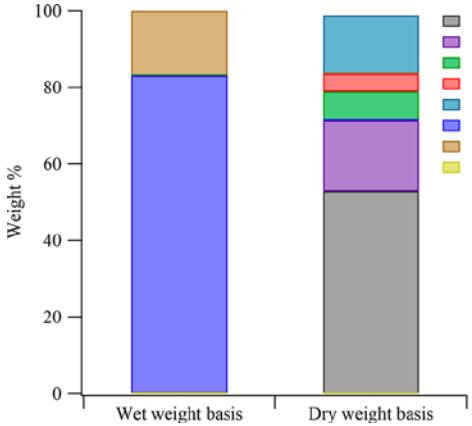
1. M.B. Griffin, et al. *ACS Catal.*, **6** (2016) 2715.
2. R.C. Nelson, et al. *ACS Catal.*, **5** (2015) 6509.

Model compound studies

Reaction Pathways



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

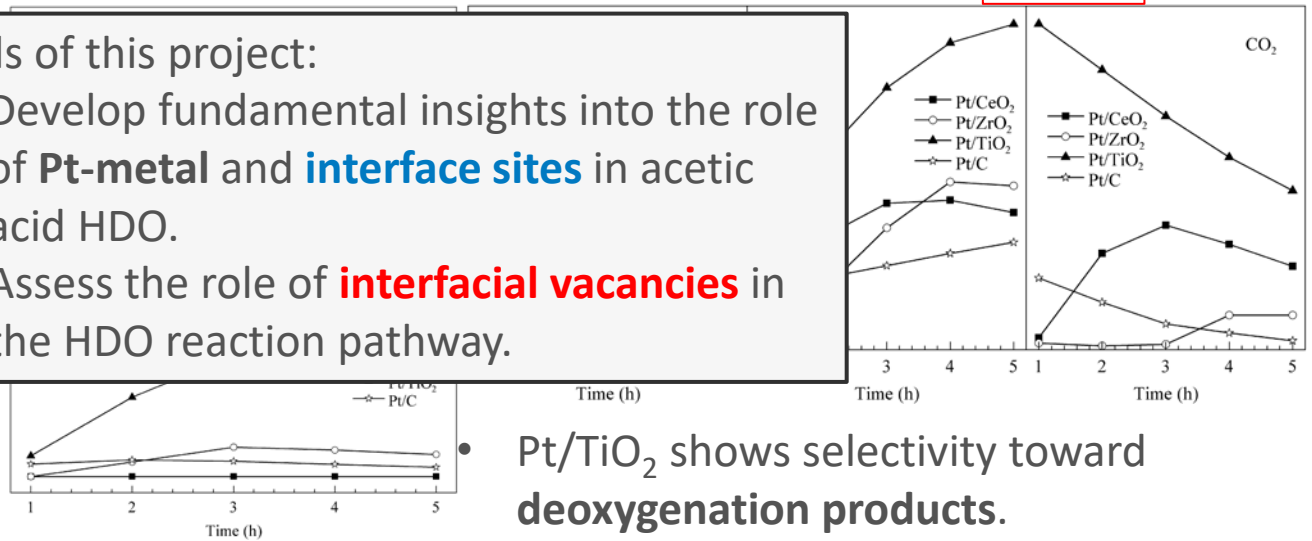


From reference [1]

Acetic acid HDO: 300 °C, 4 MPa.

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.

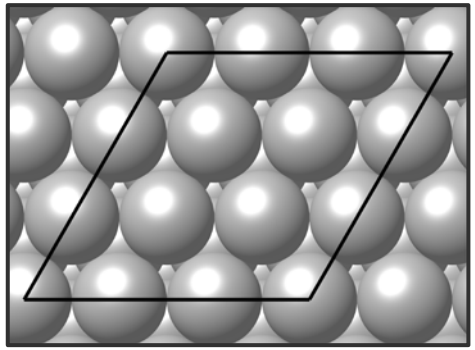
1. A.K. Starace, et al. *ACS Sustain. Chem. Eng.*, **5** (2017)
2. Z. He and X. Wang. *J. Energy Chem.*, **22** (2013) 883.

Computational methods

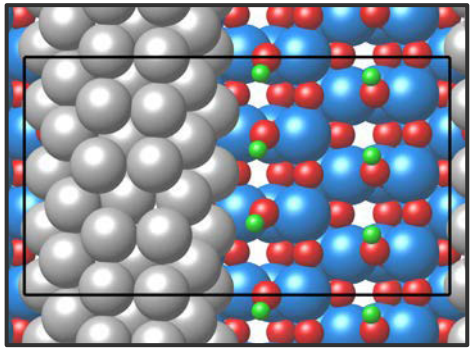
Grey – Pt, ***Blue – Ti***,
Red – O, ***Green – H***

- 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]

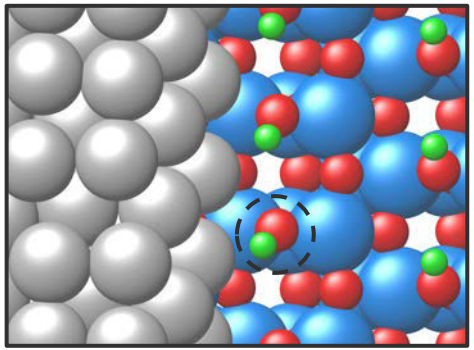
  U_{eff} = 2.5 eV for Ti cations[8]
- CI-NEB calculations for elementary-step activation barriers[9,10]



Pt(111)



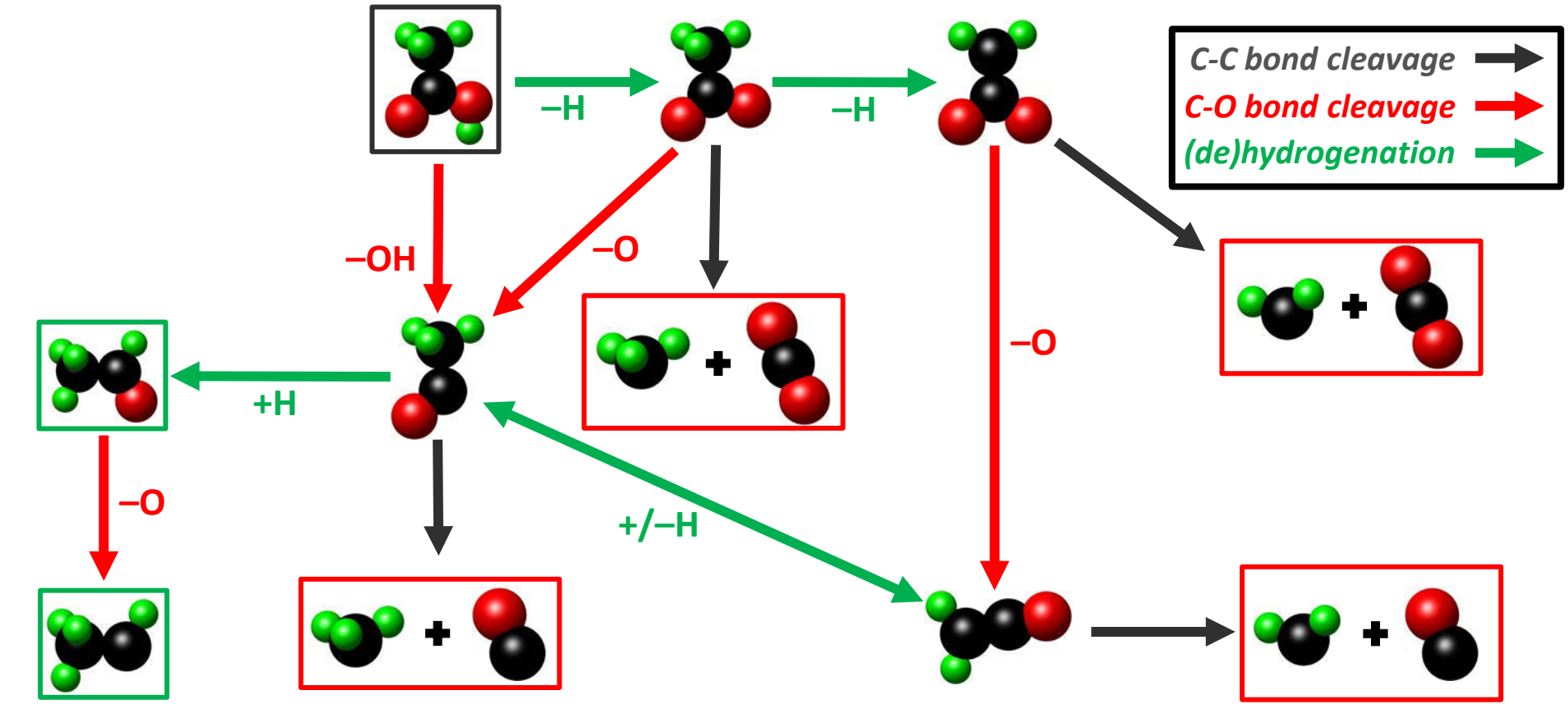
$Pt_{NW}/OH\text{-}aTiO_2(101)$



$Pt_{NW}/OH(vac)\text{-}aTiO_2(101)$

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



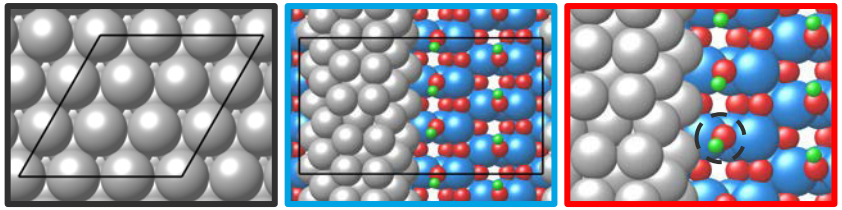
Black – C, Red – O, Green – H

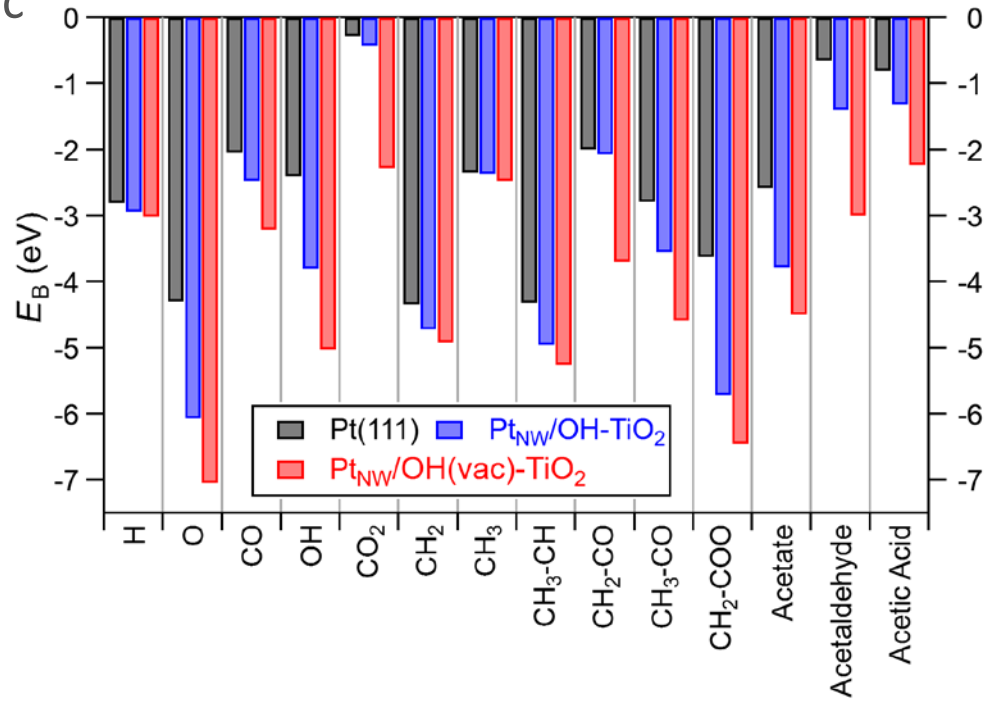
Adsorption of surface intermediates

1 eV = 96.5 kJ/mol

$E_B = E_{tot} - E_{slab} - E_{gas}$

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**

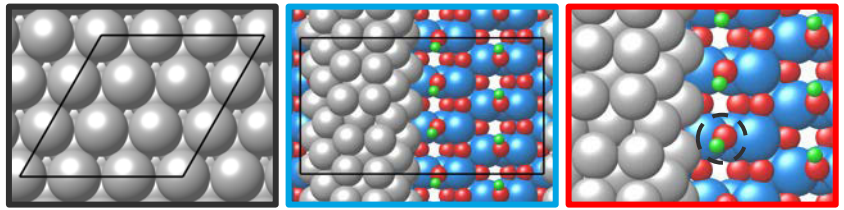
$Pt_{NW}/OH(vac)-TiO_2$: **1.60 eV**

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

Reaction energies for elementary steps

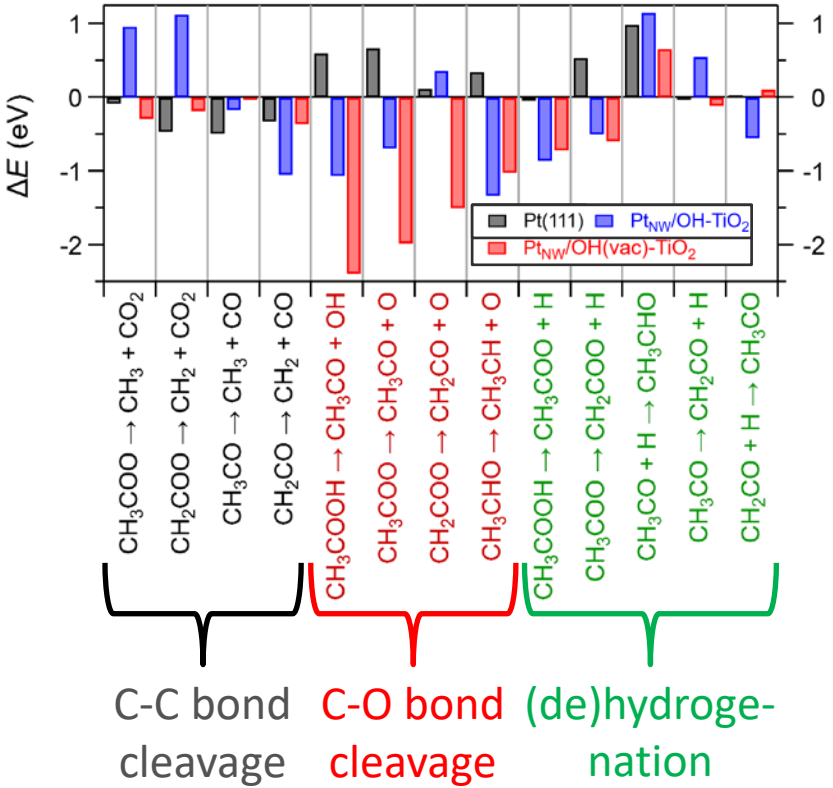
1 eV = 96.5 kJ/mol

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



Desired ✚ ➖

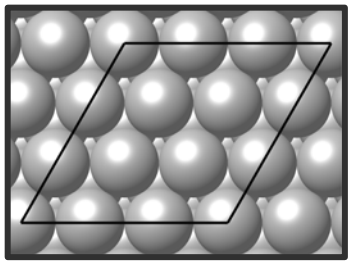
	<ΔE> (eV)		
Surface	**C-C**	**C-O**	**(de)H**
Pt(111)	**–0.34**	**+0.44**	**+0.37**
Pt_{NW}/OH-TiO_2(101)	**+0.22**	**–0.68**	**–0.04**
Pt_{NW}/OH(vac)-TiO_2(101)	**–0.21**	**–1.72**	**–0.13**



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

Reaction pathway: Pt(111)

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

–O

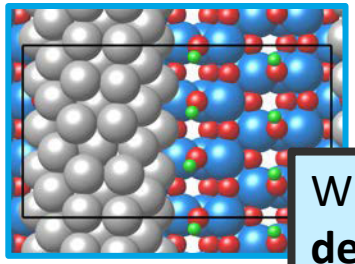
+/–H

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

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

Reaction pathway: $Pt_{NW}/OH\text{-}aTiO_2(101)$

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)
1.41
(+0.36)
–O
–O
1.30
(–0.55)
0.86 (–1.05)

While following a different pathway, **decarbonylation/decarboxylation products** are still **energetically preferred** at the $Pt_{NW}/OH\text{-}aTiO_2(101)$ interface.

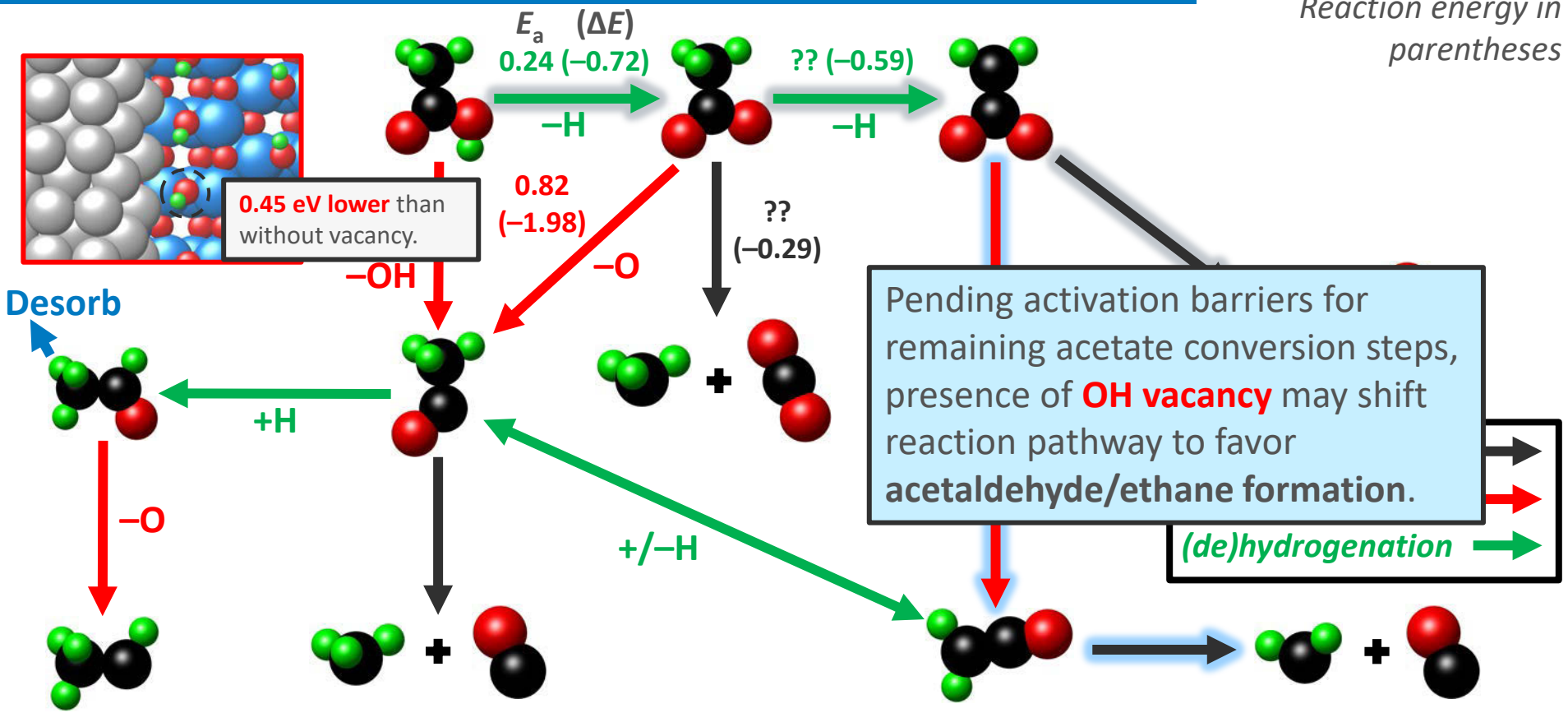
Need to assess the role of **OH vacancies** on the reaction pathway.

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

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

Reaction pathway: $Pt_{NW}/OH(vac)\text{-}aTiO_2(101)$

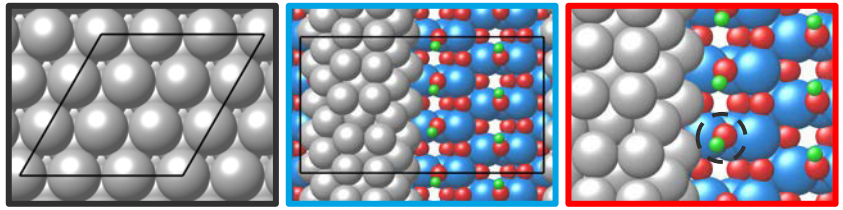
All energies in eV
1 eV = 96.5 kJ/mol
Reaction energy in parentheses

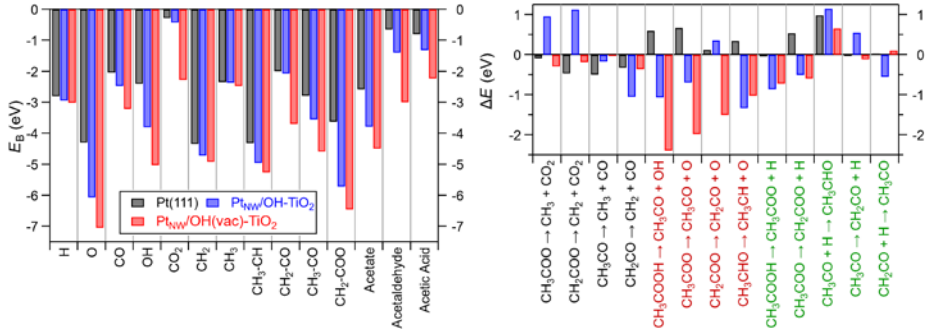


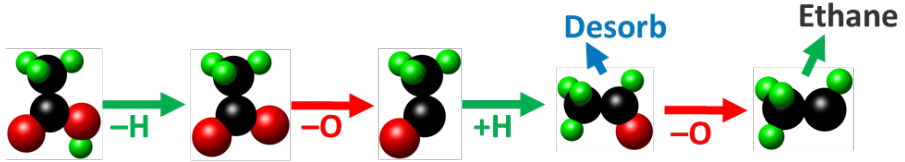
Black – C, Red – O, Green – H, Grey – Pt, Blue – Ti

Conclusions

- Pt(111) and anatase-supported Pt-nanowire models were used to explore the **role of metal and interface sites in acetic acid HDO**.
- Relative to Pt(111), interface sites **stabilize adsorption** energies and **reaction energies** for **C-O bond-breaking steps**.
- **Pt-metal** and **defect-free Pt-anatase-interfacial** sites favor undesired decarbonylation/decarboxylation products.
- Presence of **interfacial vacancy** may shift selectivity toward desired deoxygenation products (ethane, acetaldehyde).
- These fundamental insights will facilitate the **rational design of improved catalysts** for upgrading CFP bio-oil.







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

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Thank you!

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