NREL
Transforming ENERGY

Assessing the role of interfacial and metal sites in Pt/TiO_2-catalyzed acetic acid hydrodeoxygenation

Sean A. Tacey and Carrie A. Farberow

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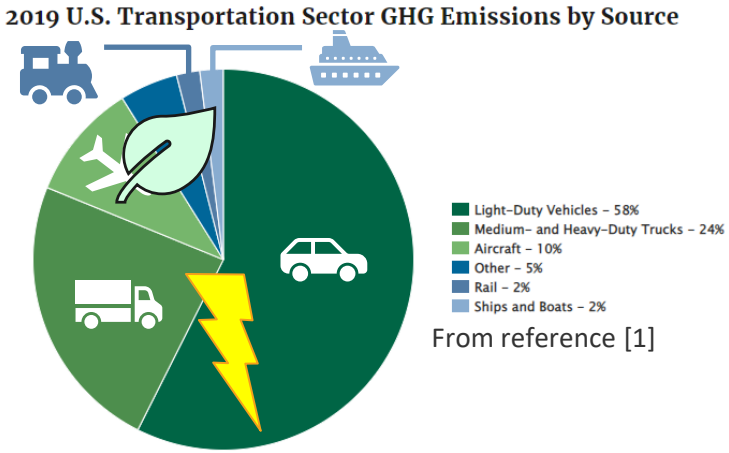
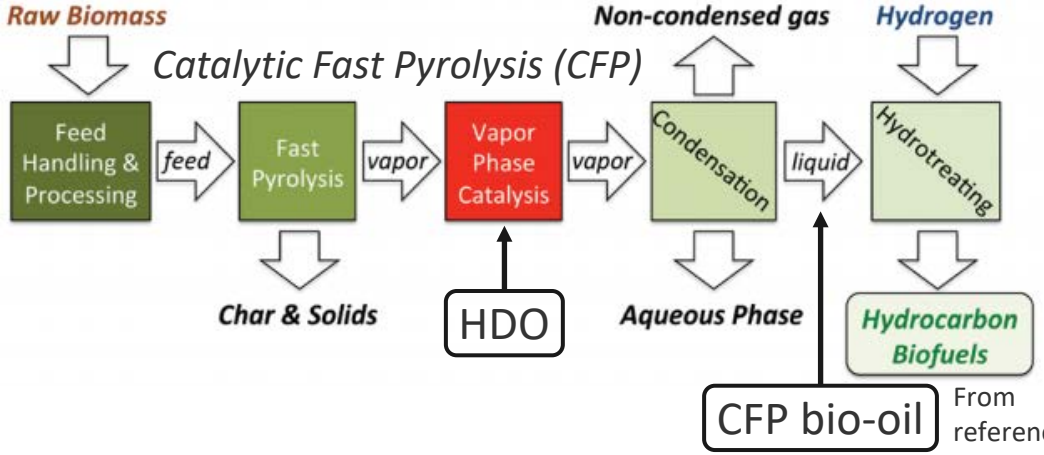
Bioenergy - CFP vapors upgraded through HDO reactions

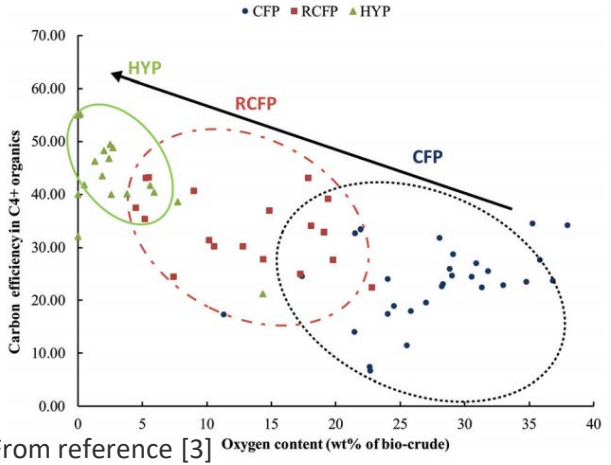


From reference [1]



From reference [2]

- Bifunctional metal-acid catalysts are **key** for hydrodeoxygenation (HDO) reactions.[4]
- Promising materials include:[4]
  - Reducible metal-oxide-supported noble metals
  - Molybdenum carbide



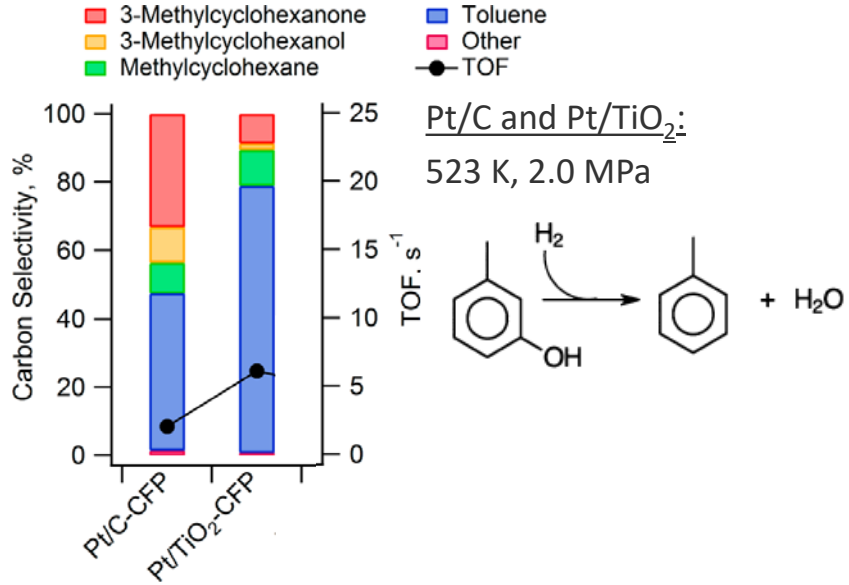
From reference [3]

1. https://www.epa.gov/greenvehicles/fast-facts-transportation-greenhouse-gas-emissions
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** and **interfacial vacancies** influence the deoxygenation mechanism.

m-Cresol HDO

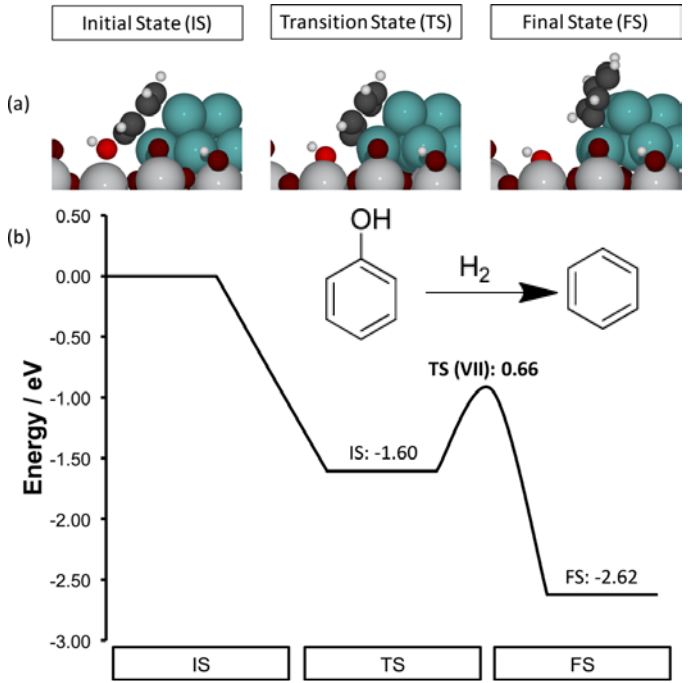


Pt/C and Pt/TiO_2:

523 K, 2.0 MPa

M.B. Griffin, et al. *ACS Catal.*, **6** (2016) 2715.

Phenol HDO



Ru/TiO_2:

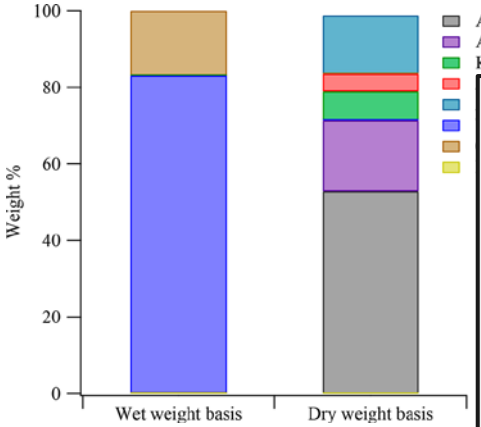
573 K, 46 bar

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.

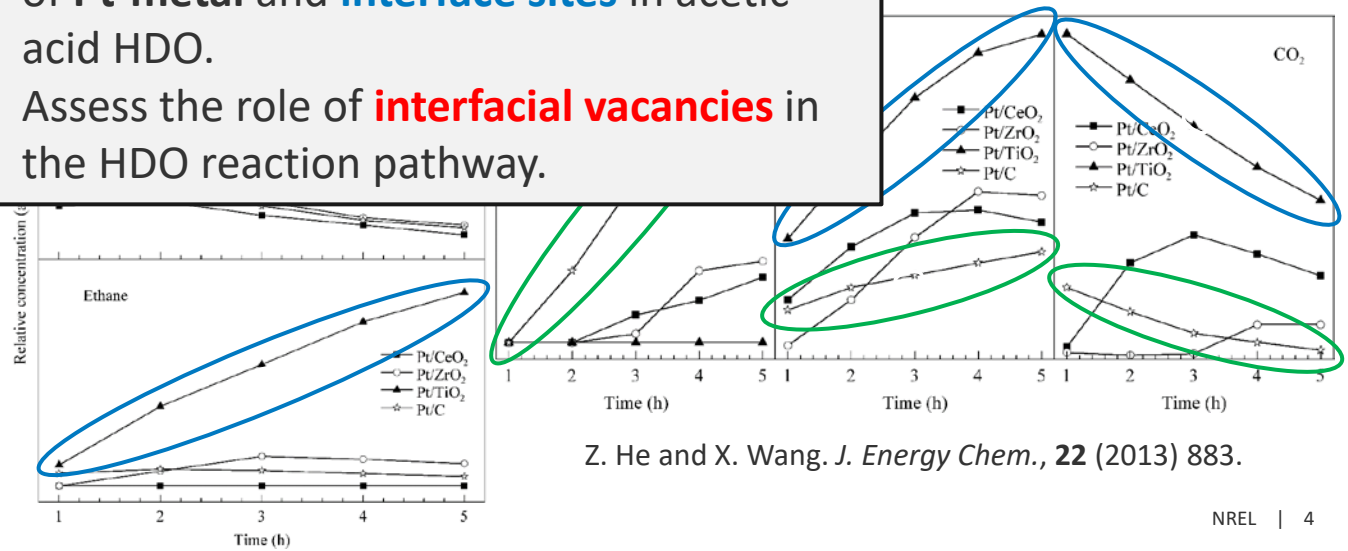


A.K. Starace, et al. *ACS Sustain. Chem. Eng.*, **5** (2017)

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.

Carboxylic acids make raw CFP bio-oil acidic and corrosive.



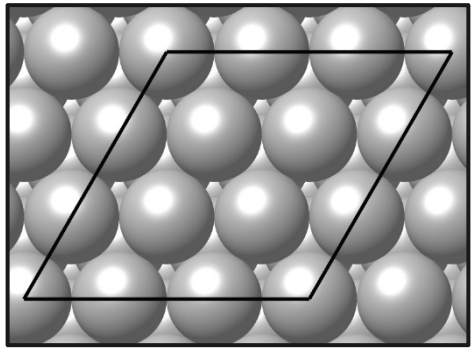
Z. He and X. Wang. *J. Energy Chem.*, **22** (2013) 883.

Computational methods

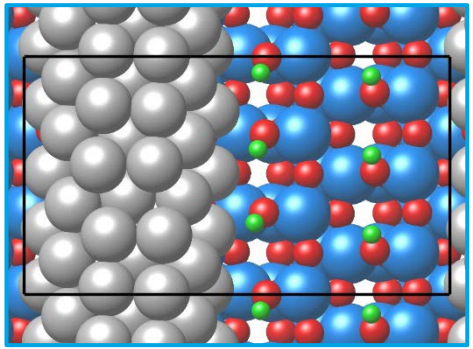
Grey – Pt, Blue – Ti, Red – O, Green – H

- 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]

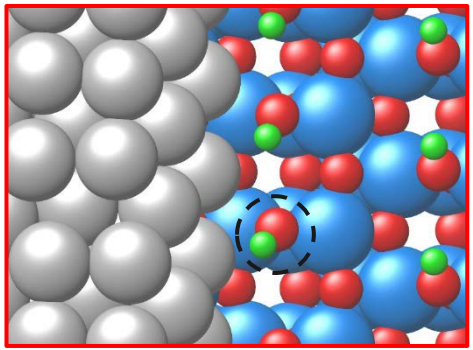
  U_{eff} = 2.5 eV for Ti cations[8]
- CI-NEB calculations for elementary-step activation barriers[9,10]



Pt(111)



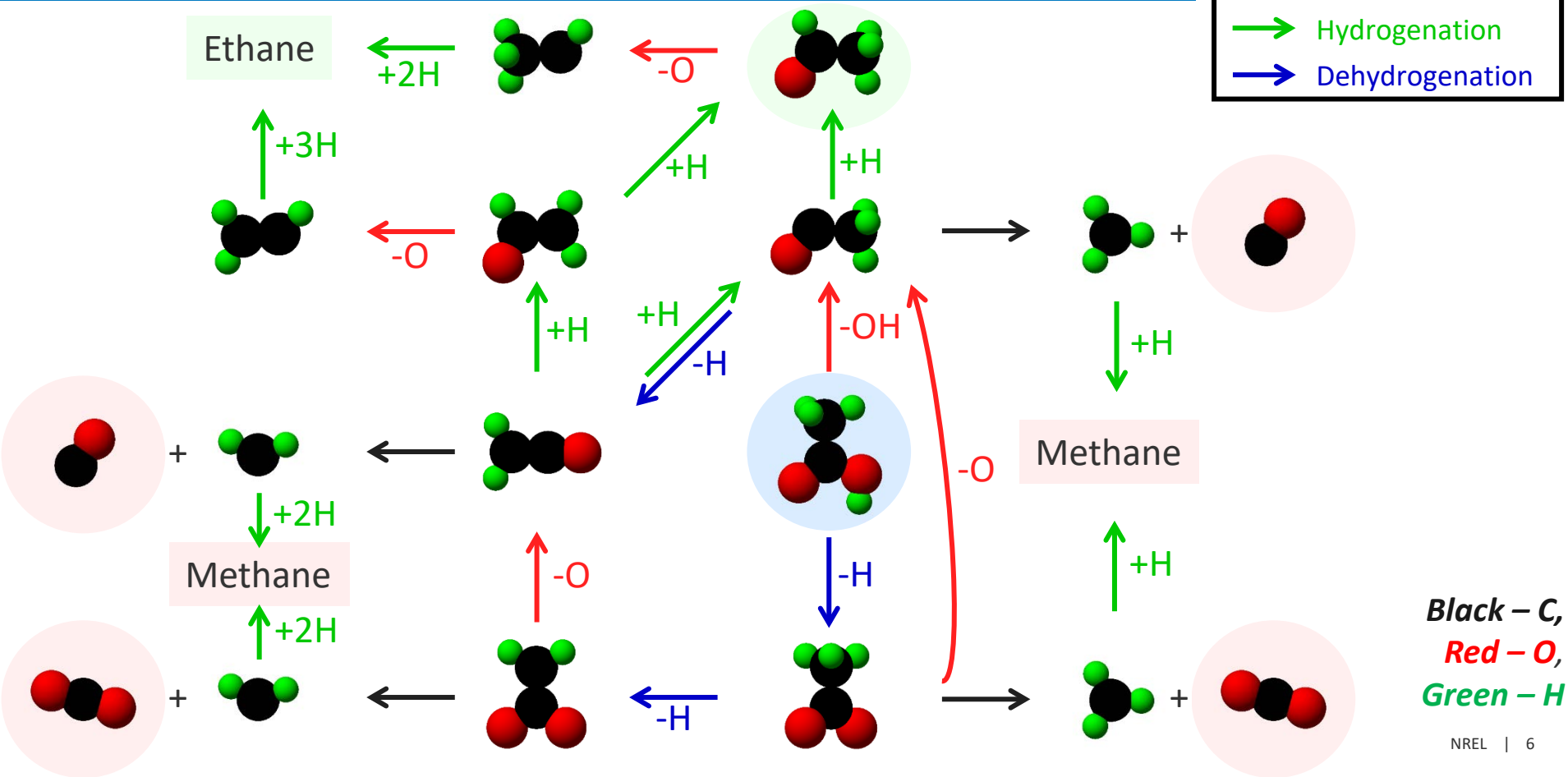
Pt_{NW}/OH-aTiO_2(101)



Pt_{NW}/OH_v-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.

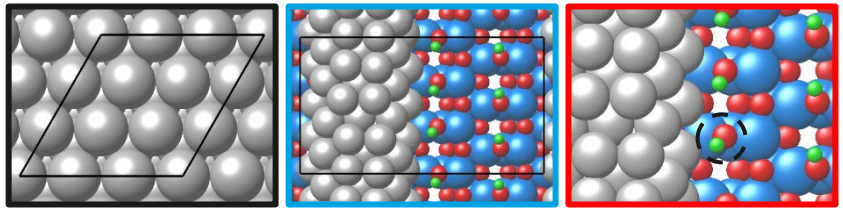
Acetic acid HDO reaction pathway



Adsorption of surface intermediates

1 eV = 96.5 kJ/mol

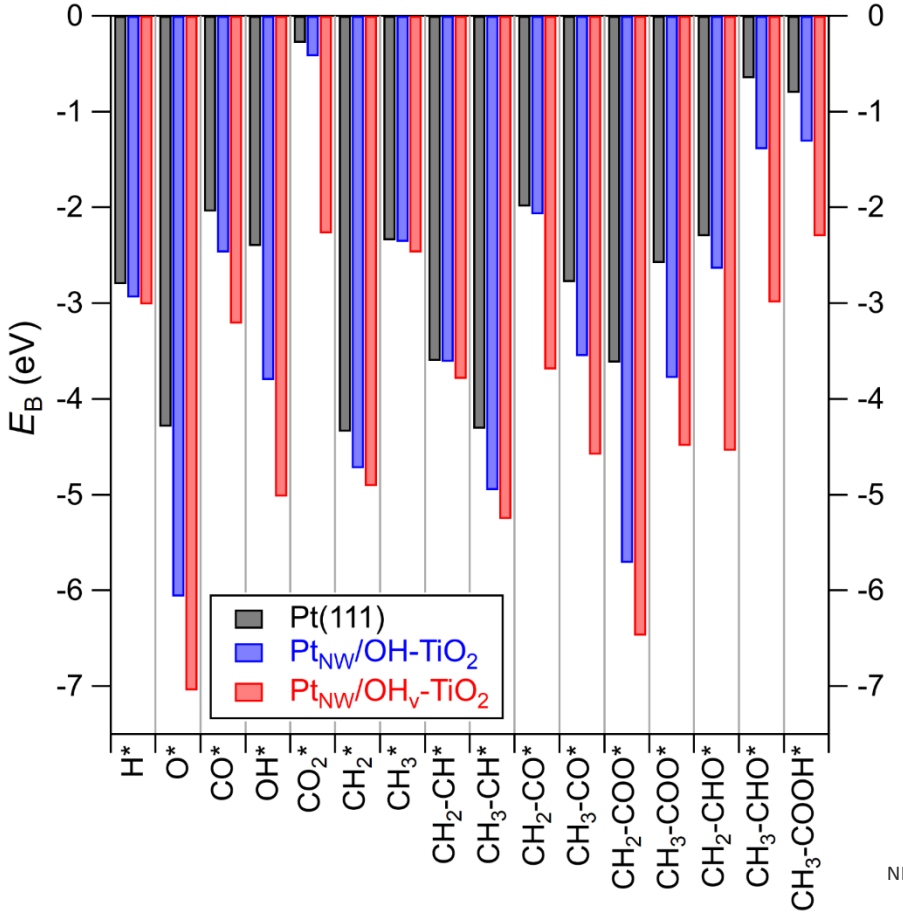
$E_B = E_{tot} - E_{slab} - E_{gas}$



Relative to **Pt(111)**, interface stabilizes adsorption on average by:

$Pt_{NW}/OH\text{-}TiO_2$: –0.56 eV

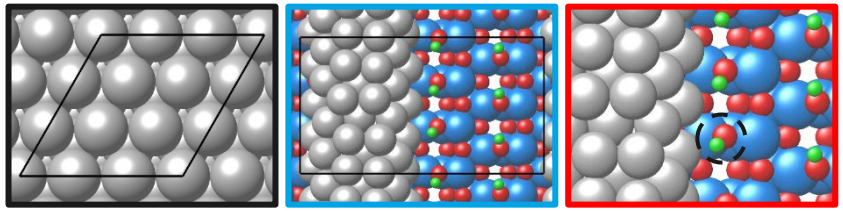
$Pt_{NW}/OH_v\text{-}TiO_2$: –1.56 eV



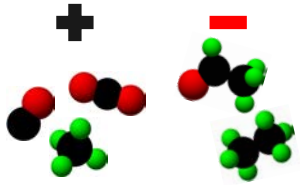
Grey – Pt, Blue – Ti, Red – O, Green – H

Reaction energies for elementary steps

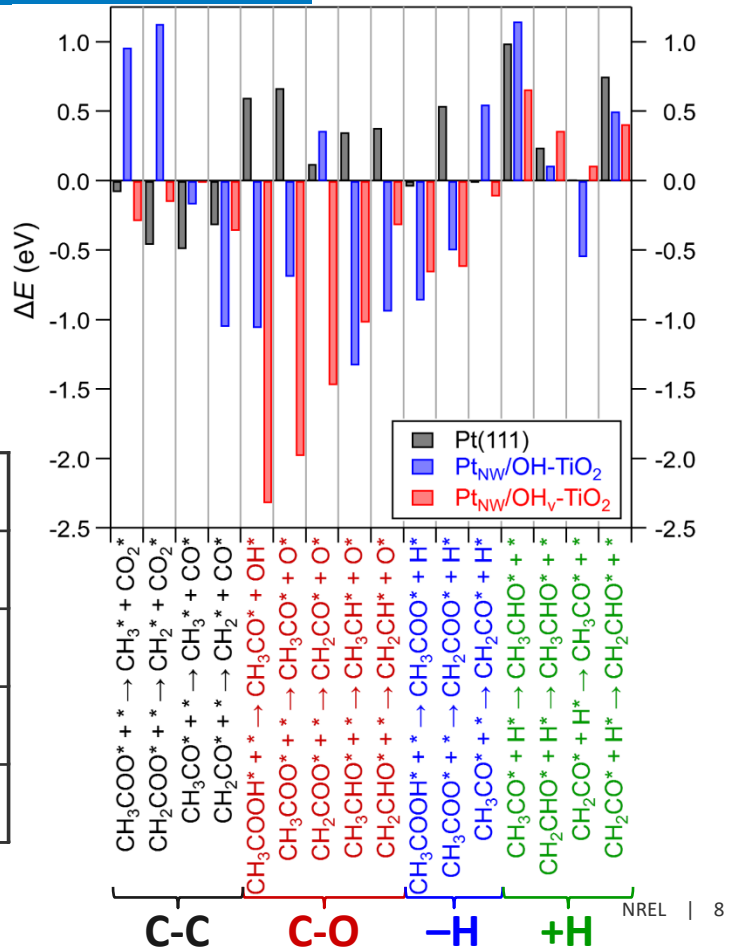
1 eV = 96.5 kJ/mol



Desired

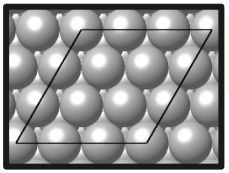


	<ΔE> (eV)			
Surface	**C-C**	**C-O**	**–H**	**+H**
Pt(111)	**–0.34**	**+0.43**	**+0.16**	**+0.50**
$Pt_{NW}/OH\text{-}TiO_2(101)$	**+0.22**	**–0.73**	**–0.27**	**+0.30**
$Pt_{NW}/OH_v\text{-}TiO_2(101)$	**–0.20**	**–1.42**	**–0.46**	**+0.38**



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

Reaction pathway: Pt(111)



C-C bond breaking

C-O bond breaking

Hydrogenation

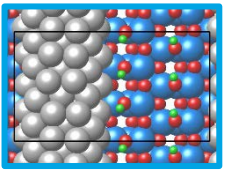
Dehydrogenation

Undesired decarboxylation products **energetically preferred** on Pt(111).

Agrees with experimental results that indicate Pt/C will preferentially form C1 products.[1]

1. Z. He and X. Wang. *J. Energy Chem.*, **22** (2013) 883.

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



Ethane

+2H

1.34

-O

1.39

+3H

+H

1.15

+H

-O

0.61

+H

-H

0.73

+H

0.98

-OH

0.86

+

+2H

Methane

1.41

-O

0.24

-H

+2H

1.99

0.78

-H

3.16

+

+H

Desorption

C-C bond breaking

C-O bond breaking

Hydrogenation

Dehydrogenation

$Pt_{NW}/OH\text{-}aTiO_2(101)$ interface follows **desired deoxygenation pathway**, consistent with experimental selectivity trends.[1]

Spectroscopic evidence shows the presence of **acetate and acyl (CH_x-CO) species** during AA-HDO.[2]

1. Z. He and X. Wang. *J. Energy Chem.*, **22** (2013) 883.

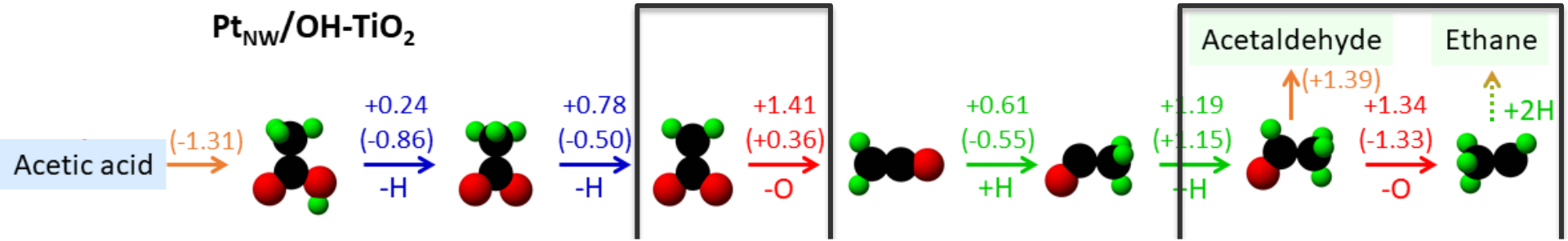
2. W. Rachmady and M. A. Vannice, *J. Catal.*, **207** (2002) 317.

Reaction pathway: Pt_{NW}/OH_v-aTiO_2(101)

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

- **Vacancy** may play a key role in facilitating first **C-O bond-dissociation step**.
- **Vacancy concentration** could dictate **ethane vs. acetaldehyde** product selectivity, though vacancy formation may be rate-limiting.

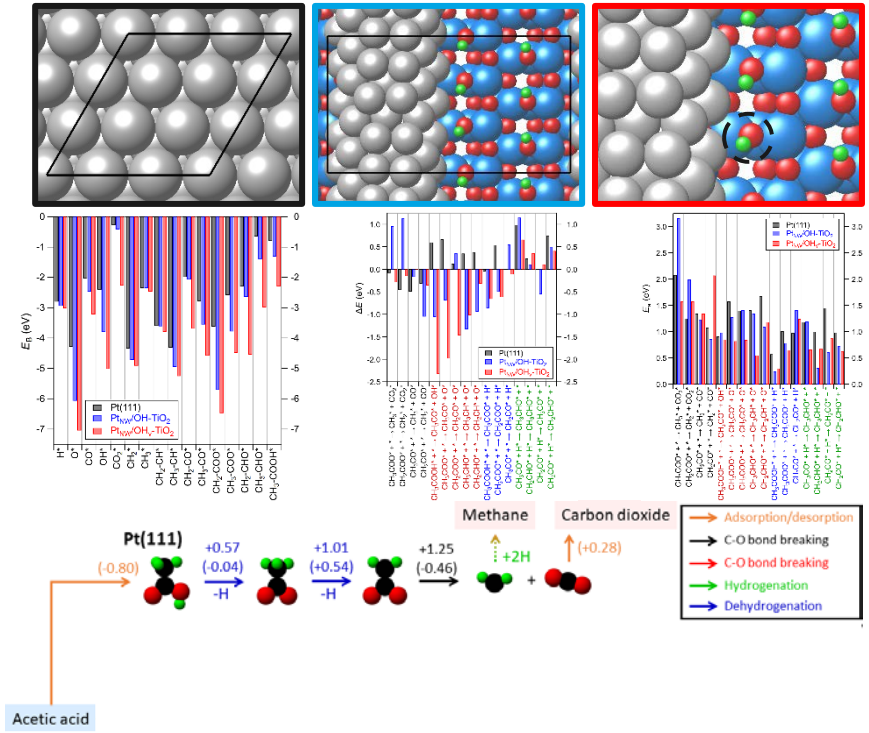
Adsorption/desorption
C-C bond breaking
C-O bond breaking
Hydrogenation
Dehydrogenation



Black – C, Red – O, Green – H

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 energetics** for **C-O bond-breaking steps** relative to **C-C bond-breaking steps**.
- **Pt-metal** sites favor undesired decarboxylation products.
- **Pt-TiO_2-interface sites** shift selectivity toward ethane and acetaldehyde.
- **Interfacial vacancy** may play a key role in lowering barrier for **C-O bond-breaking step**.
- 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

Acknowledgements

Catalytic Carbon Transformation & Scale-Up Center

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Contact info

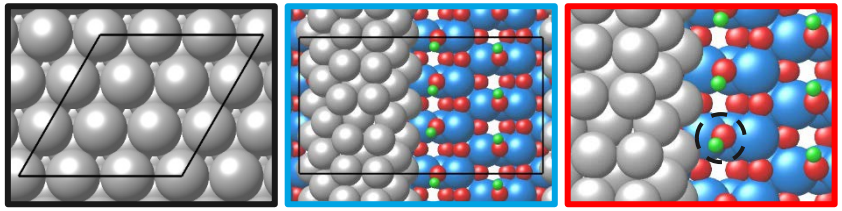
Email – Sean.Tacey@nrel.gov

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

Activation barriers for elementary steps

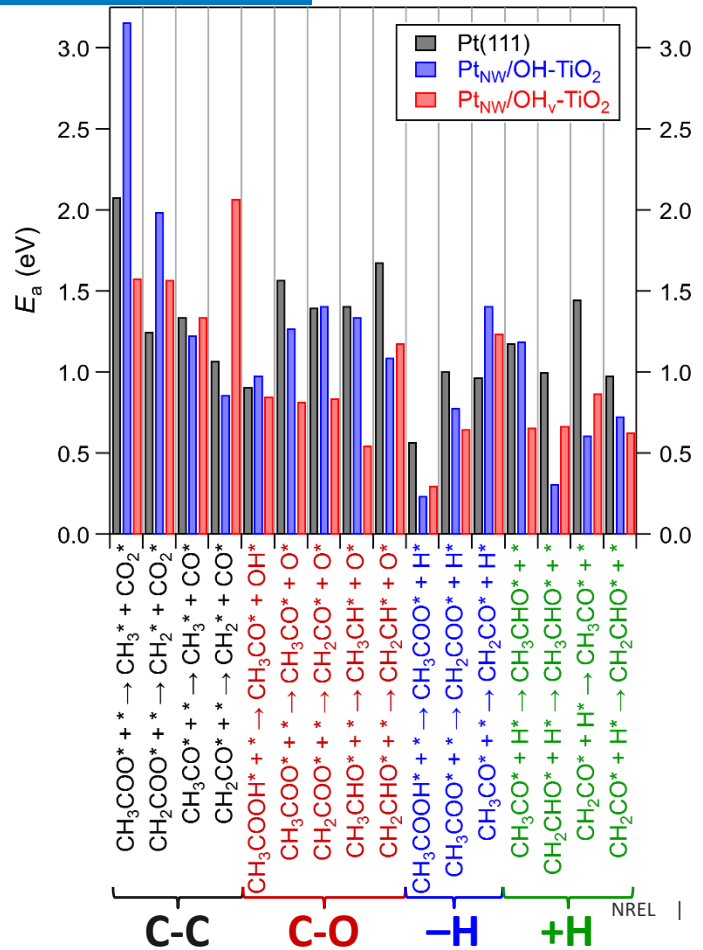
1 eV = 96.5 kJ/mol

$E_a = E_{TS} - E_{BIS}$



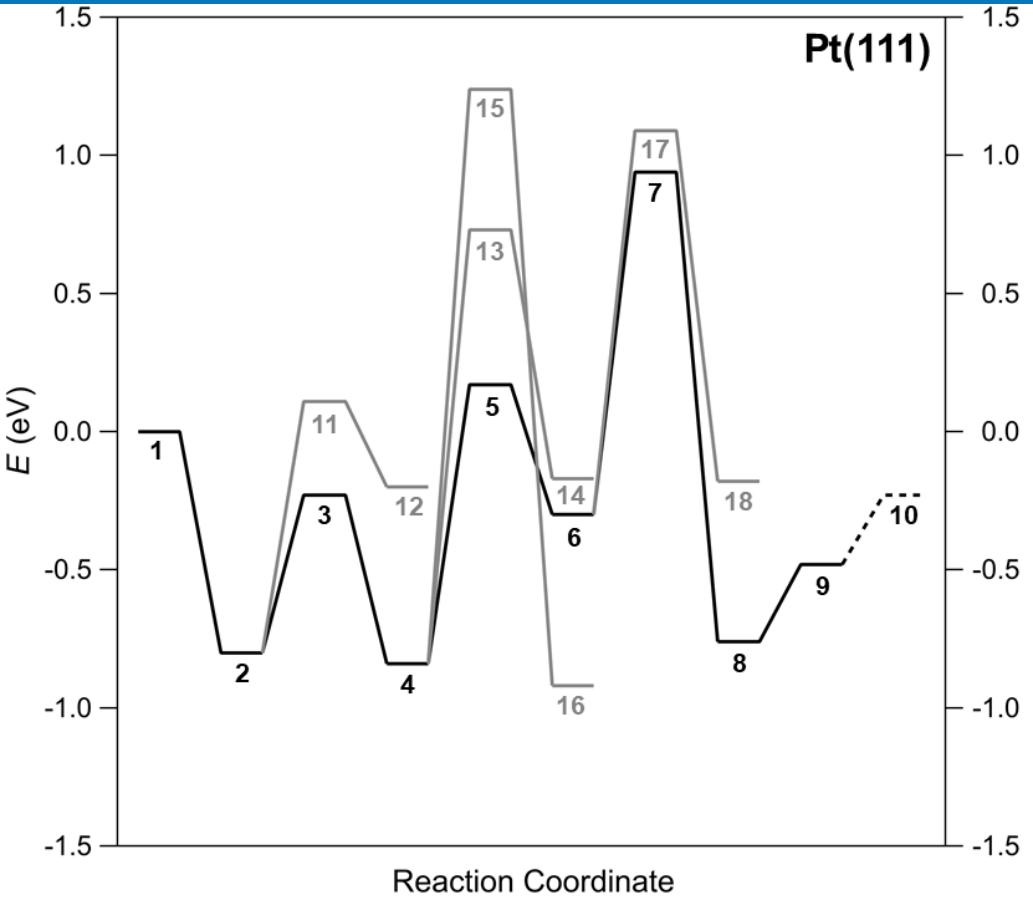
Desired ↑ ↓

	<ΔE> (eV)			
Surface	**C-C**	**C-O**	**–H**	**+H**
Pt(111)	**+1.44**	**+1.39**	**+0.85**	**+1.15**
$Pt_{NW}/OH\text{-}TiO_2(101)$	**+1.81**	**+1.22**	**+0.81**	**+0.70**
$Pt_{NW}/OH_v\text{-}TiO_2(101)$	**+1.64**	**+0.85**	**+0.73**	**+0.71**



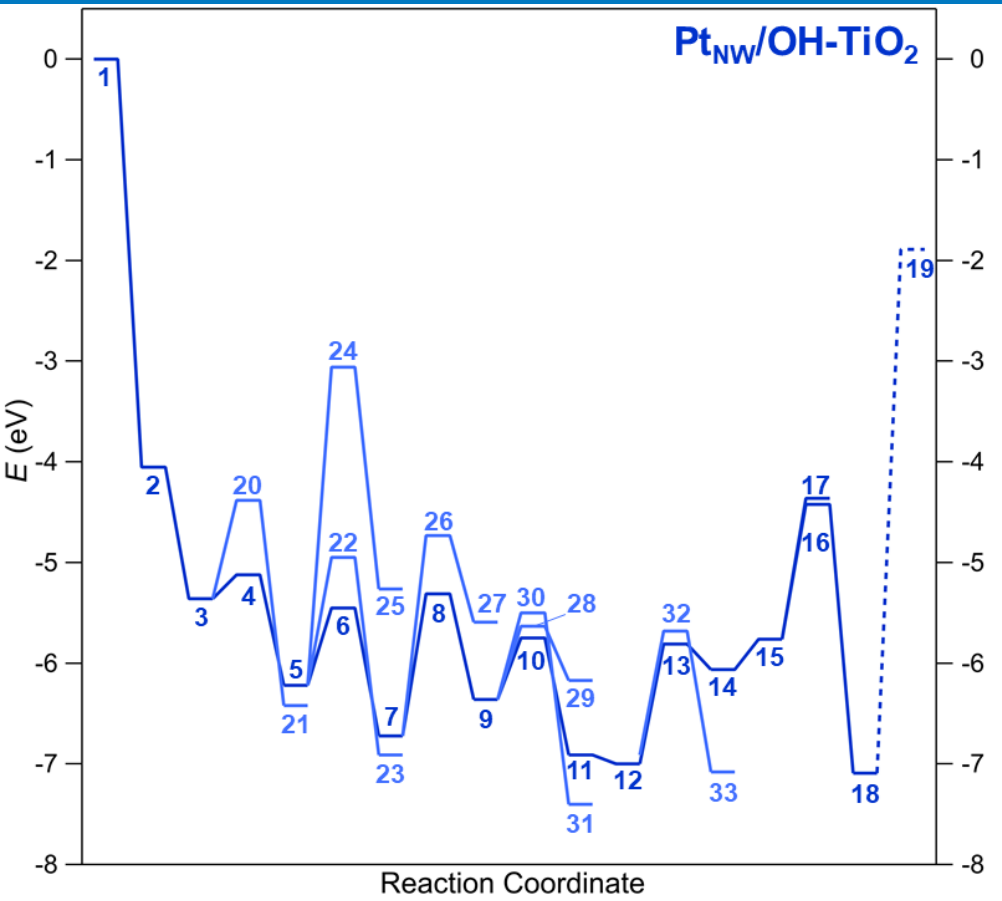
Grey – Pt, Blue – Ti, Red – O, Green – H

Pt(111): Reaction Energy Diagram



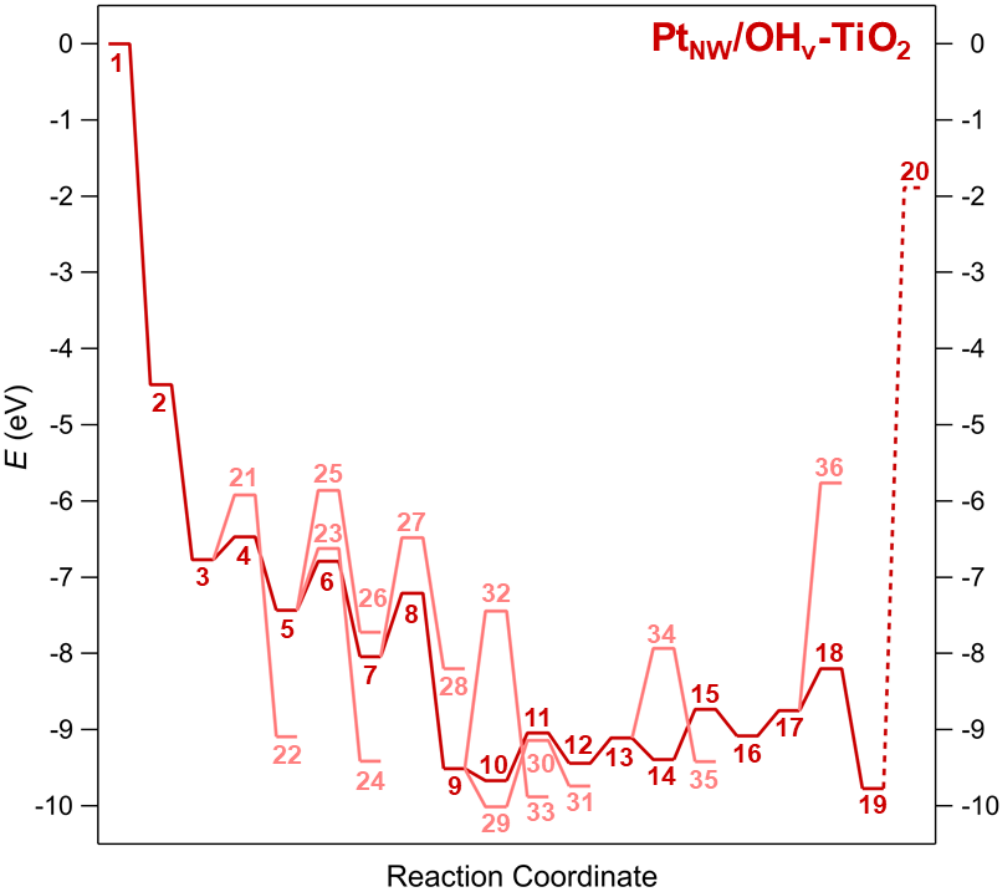
1. $CH_3COOH(g)$
2. CH_3COOH^*
3. $CH_3COO–H^‡$
4. $CH_3COO^*|H^*$
5. $(CH_2–H)COO^‡|H^*$
6. $CH_2COO^*|2H^*$
7. $CH_2–COO^‡|2H^*$
8. $CH_2^*|CO_2^*|2H^*$
9. $CH_2^*|2H^*|CO_2(g)$
10. $CH_4(g)|CO_2(g)$
11. $CH_3CO–OH^‡$
12. $CH_3CO^*|OH^*$
13. $CH_3CO–O^‡|H^*$
14. $CH_3CO^*|O^*|H^*$
15. $CH_3–COO^‡|H^*$
16. $CH_3^*|CO_2^*|H^*$
17. $CH_2CO–O^‡|2H^*$
18. $CH_2CO^*|O^*|2H^*$

$Pt_{NW}/OH\text{-}TiO_2$: Reaction Energy Diagram



1. $CH_3COOH(g)|3H_2(g)$
2. $CH_3COOH(g)|6H^*$
3. $CH_3COOH^*|6H^*$
4. $CH_3COO–H^‡|6H^*$
5. $CH_3COO^*|7H^*$
6. $(CH_2–H)COO^‡|7H^*$
7. $CH_2COO^*|8H^*$
8. $CH_2CO–O^‡|8H^*$
9. $CH_2CO^*|O^*|8H^*$
10. $(CH_2–H)CO^‡|O^*|8H^*$
11. $CH_3CO^*|O^*|7H^*$
12. $CH_3CO^*+H^*+H_v|O^*|7H^*$
13. $CH_3(C–H)O^‡+H_v|O^*|7H^*$
14. $CH_3CHO^*|H_v|O^*|7H^*$
15. $CH_3CHO^*|O^*|6H^*$
16. $CH_3CH–O^‡|O^*|6H^*$
17. $CH_3CHO(g)|O^*|6H^*$
18. $CH_3CH^*|2O^*|6H^*$
19. $CH_3CH_3(g)|2H_2O(g)$
20. $CH_3CO–OH^‡|6H^*$
21. $CH_3CO^*|OH^*|6H^*$
22. $CH_3CO–O^‡|7H^*$
23. $CH_3CO^*|O^*|7H^*$
24. $CH_3–COO^‡|7H^*$
25. $CH_3^*|CO_2^*|7H^*$
26. $CH_2–COO^‡|8H^*$
27. $CH_2^*|CO_2^*|8H^*$
28. $CH_2(C–H)O^‡+H_v|O^*|8H^*$
29. $CH_2CHO^*|H_v|O^*|8H^*$
30. $CH_2–CO^‡|O^*|8H^*$
31. $CH_2^*|CO^*|O^*|8H^*$
32. $CH_3–CO^‡|O^*|7H^*$
33. $CH_3^*|CO^*|O^*|7H^*$

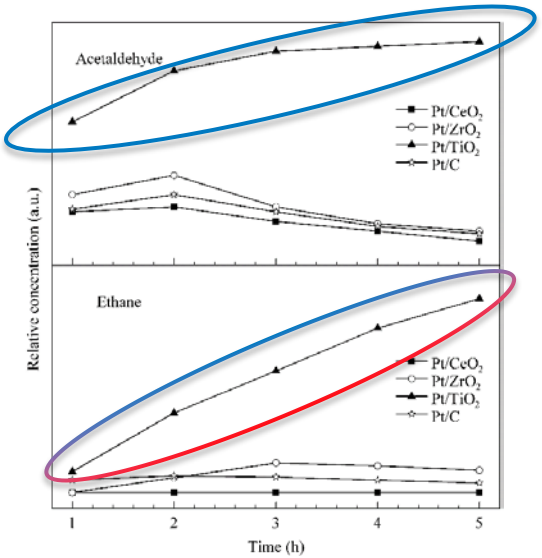
Pt_{NW}/OH_v-TiO_2: Reaction Energy Diagram

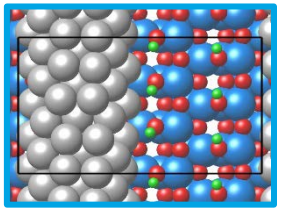


1. $CH_3COOH(g)|3H_2(g)$
2. $CH_3COOH(g)|6H^*$
3. $CH_3COOH^*|6H^*$
4. $CH_3COO–H^‡|6H^*$
5. $CH_3COO^*|7H^*$
6. $(CH_2–H)COO^‡|7H^*$
7. $CH_2COO^*|8H^*$
8. $CH_2CO–O^‡|8H^*$
9. $CH_2CO^*|O^*|8H^*$
10. $CH_2CO^*+H^*+H_v|O^*|8H^*$
11. $CH_2(C–H)O^‡+H_v|O^*|8H^*$
12. $CH_2CHO^*|H_v|O^*|8H^*$
13. $CH_2CHO^*|O^*|7H^*$
14. $CH_2CHO^*+H^*+H_v|O^*|7H^*$
15. $(CH_2–H)CHO^‡+H_v|O^*|7H^*$
16. $CH_3CHO^*|H_v|O^*|7H^*$
17. $CH_3CHO^*|O^*|6H^*$
18. $CH_3CH–O^‡|O^*|6H^*$
19. $CH_3CH^*|2O^*|6H^*$
20. $CH_3CH_3(g)|2H_2O(g)$
21. $CH_3CO–OH^‡|6H^*$
22. $CH_3CO^*|OH^*|6H^*$
23. $CH_3CO–O^‡|7H^*$
24. $CH_3CO^*|O^*|7H^*$
25. $CH_3–COO^‡|7H^*$
26. $CH_3^*|CO_2^*|7H^*$
27. $CH_2–COO^‡|8H^*$
28. $CH_2^*|CO_2^*|8H^*$
29. $CH_2CO^*+H^*+H_v|O^*|8H^*$
30. $(CH_2–H)CO^‡+H_v|O^*|8H^*$
31. $CH_3CO^*|H_v|O^*|8H^*$
32. $CH_2–CO^‡|O^*|8H^*$
33. $CH_2^*|CO^*|O^*|8H^*$
34. $CH_2CH–O^‡|O^*|7H^*$
35. $CH_2CH^*|2O^*|7H^*$
36. $CH_3CHO(g)|O^*|6H^*$

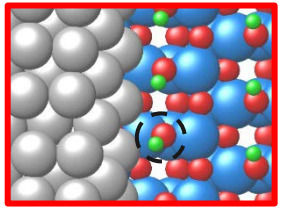
Model results agree with experimental Pt/TiO_2 data

Black – C, Red – O, Green – H

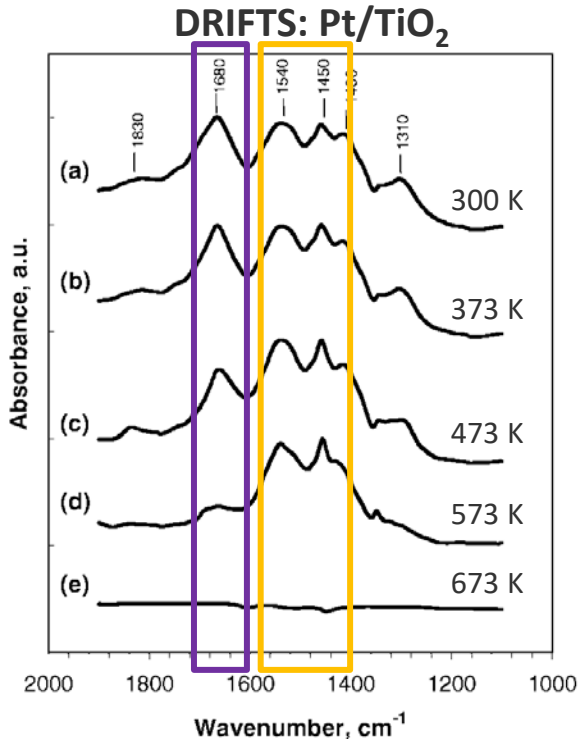


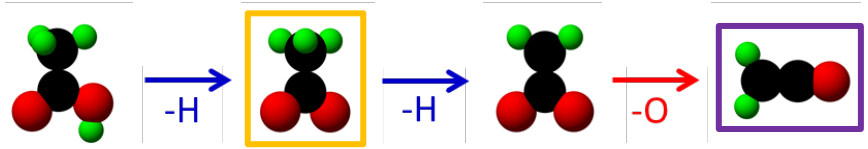


$Pt_{NW}/OH\text{-}aTiO_2$



$Pt_{NW}/OH_v\text{-}aTiO_2$





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