

1                   Supporting Information for

2                   **Theoretical Investigation of Solvent Effects on the**  
3                   **Hydrodeoxygenation of Propionic Acid over a Ni (111)**  
4                   **Catalyst Model**

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6       Mehdi Zare, Rajadurai Vijay Solomon, Wenqiang Yang, Adam Yonge, and Andreas Heyden\*

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8       *Department of Chemical Engineering, University of South Carolina, 301 Main Street, Columbia,*  
9                   *South Carolina 29208, USA*

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23      \*Corresponding author: email: [heyden@cec.sc.edu](mailto:heyden@cec.sc.edu)

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**Table S1.** Solvent effect on the stability of various adsorbed species in the propionic acid conversion to ethane and ethylene over a Ni (111) catalyst surface model at two different temperatures of 298 K and 473 K based on two implicit solvation schemes: iSMS and VASPsol.  $\Delta\Delta G_{rxn}$  indicates the difference in the adsorption free energy of the corresponding intermediates in the presence and absence of water. Asterisk (\*) represents a surface adsorption site and multiple asterisks are indicative of the number of occupied active sites.

Adsorbed species	$\Delta\Delta G_{rxn}$ , eV			
	T=298 K		T=473 K	
	iSMS	VASPsol	iSMS	VASPsol
CH <sub>2</sub> C***	-0.04	0.02	-0.08	0.05
CH <sub>2</sub> CH***	0.02	-0.08	-0.01	-0.07
CH <sub>2</sub> CH <sub>2</sub> **	0.06	-0.08	0.10	-0.08
CH <sub>2</sub> CHCO****	-0.05	-0.07	-0.09	-0.05
CH <sub>2</sub> CHCOOH****	-0.10	-0.34	-0.11	-0.29
CH <sub>3</sub> C***	0.02	-0.04	-0.01	-0.03
CH <sub>3</sub> CCO****	-0.09	-0.07	-0.12	-0.06
CH <sub>3</sub> CCOO***	-0.63	-0.29	-0.55	-0.26
CH <sub>3</sub> CCOOH***	-0.12	-0.28	-0.12	-0.26
CH <sub>3</sub> CH***	0.03	-0.05	0.00	-0.03
CH <sub>3</sub> CH <sub>2</sub> **	0.03	-0.06	0.01	-0.05
CH <sub>3</sub> CH <sub>2</sub> CO***	-0.02	-0.11	-0.05	-0.12
CH <sub>3</sub> CH <sub>2</sub> COO**	-0.05	-0.11	-0.06	-0.10
CH <sub>3</sub> CH <sub>2</sub> COOH*	-0.07	-0.44	-0.03	-0.40
CH <sub>3</sub> CH <sub>3</sub> *	0.05	-0.04	0.02	-0.06
CH <sub>3</sub> CHCO**	-0.06	-0.11	-0.09	-0.11
CH <sub>3</sub> CHCOO***	-0.34	-0.12	-0.31	-0.10
CH <sub>3</sub> CHCOOH**	-0.10	-0.30	-0.10	-0.28
CHCH****	0.02	-0.06	0.05	-0.05
CHCHCO***	-0.11	-0.12	-0.15	-0.10
CHCHCOOH****	-0.13	-0.31	-0.13	-0.26
CO***	-0.15	-0.08	-0.25	-0.08
CO <sub>2</sub> *	0.05	-0.10	-0.04	-0.07
COOH**	-0.18	-0.25	-0.16	-0.21
H*	-0.02	0.00	-0.01	0.00
H <sub>2</sub> O*	-0.04	-0.31	0.02	-0.25
OH*	-0.02	-0.21	0.00	-0.18

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**Table S2.** Solvent effect on the stability of transition states in the propionic acid conversion to ethane and ethylene over a Ni (111) catalyst surface model at two different temperatures of 298 K and 473 K based on two implicit solvation schemes: iSMS and VASPsol. Solvent effect on TS indicates the difference in the adsorption free energy of the corresponding transition state in the presence and absence of water.

#	Reaction	Solvent effect on TS, eV			
		T=298 K		T=473 K	
		iSMS	VASPsol	iSMS	VASPsol
1	$\text{CH}_3\text{CH}_2\text{COOH}^* + 3^* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{***} + \text{OH}^*$	-0.03	-0.16	-0.05	-0.11
2	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CHCOOH}^{**} + \text{H}^*$	-0.10	-0.39	-0.09	-0.37
3	$\text{CH}_3\text{CH}_2\text{CO}^{***} + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}^{***}$	-0.04	-0.10	-0.07	-0.10
4	$\text{CH}_3\text{CH}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{H}^*$	-0.05	-0.10	-0.08	-0.07
5	$\text{CH}_3\text{CHCOOH}^{**} + * \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{OH}^*$	-0.12	-0.17	-0.14	-0.15
6	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCOOH}^{****} + \text{H}^*$	-0.11	-0.36	-0.10	-0.32
7	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CCOOH}^{***} + \text{H}^*$	-0.10	-0.30	-0.10	-0.25
8	$\text{CH}_3\text{CHCO}^{**} + 4^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}^{***}$	-0.06	-0.11	-0.10	-0.11
9	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$	-0.13	-0.07	-0.15	-0.04
10	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{H}^*$	-0.05	-0.13	-0.09	-0.10
11	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{OH}^*$	-0.08	-0.19	-0.11	-0.16
12	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CHCHCOOH}^{****} + \text{H}^*$	-0.10	-0.34	-0.10	-0.30
13	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{OH}^*$	-0.18	-0.19	-0.20	-0.17
14	$\text{CH}_3\text{CCO}^{****} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}^{***}$	-0.17	-0.09	-0.20	-0.07
15	$\text{CH}_2\text{CHCO}^{****} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{CO}^{***}$	-0.05	-0.12	-0.09	-0.10
16	$\text{CH}_2\text{CHCO}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{H}^*$	-0.05	-0.11	-0.09	-0.10
17	$\text{CHCHCOOH}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{OH}^*$	-0.24	-0.17	-0.26	-0.14
18	$\text{CHCHCO}^{****} + 3^* \rightarrow \text{CHCH}^{****} + \text{CO}^{***}$	-0.13	-0.12	-0.17	-0.11
19	$\text{CH}_2\text{CH}^{***} + 2^* \rightarrow \text{CHCH}^{****} + \text{H}^*$	0.05	-0.08	0.01	-0.07
20	$\text{CH}_2\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	0.07	-0.09	0.04	-0.09
21	$\text{CH}_2\text{CH}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	0.01	-0.05	-0.03	-0.05
22	$\text{CH}_3\text{C}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	0.01	-0.08	-0.02	-0.07
23	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	0.00	-0.10	-0.03	-0.09
24	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{H}^*$	0.04	-0.05	0.01	-0.04
25	$\text{CH}_3\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{H}^*$	0.05	-0.05	0.02	-0.02
26	$\text{CH}_3\text{CH}_3^* + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{H}^*$	0.04	-0.08	0.02	-0.08
27	$\text{CH}_3\text{CH}_2^{**} + * \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$	0.03	-0.13	0.00	-0.11
28	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{COO}^{**} + \text{H}^*$	-0.11	-0.15	-0.12	-0.16
29	$\text{CH}_3\text{CH}_2\text{COO}^{**} + * \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}_2^*$	-0.06	-0.12	-0.10	-0.09
30	$\text{CH}_3\text{CH}_2\text{COO}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.24	-0.12	-0.23	-0.11
31	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.24	-0.10	-0.25	-0.09
32	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{COOH}^{**}$	-0.12	-0.29	-0.12	-0.23
33	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}_2^*$	-0.18	-0.12	-0.19	-0.10
34	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	-0.20	-0.09	-0.20	-0.08
35	$\text{CH}_3\text{CCOOH}^{***} + * \rightarrow \text{CH}_3\text{CCO}^{***} + \text{H}^*$	-0.32	-0.16	-0.30	-0.15
36	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{COOH}^{**}$	-0.16	-0.30	-0.17	-0.25
37	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{COOH}^{**}$	-0.11	-0.32	-0.11	-0.26
38	$\text{CH}_3\text{CCOO}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}_2^*$	-0.34	-0.16	-0.35	-0.15
39	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$	-0.34	-0.17	-0.34	-0.15
40	$\text{COOH}^{**} + 2^* \rightarrow \text{CO}^{***} + \text{OH}^*$	-0.12	-0.25	-0.12	-0.23
41	$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	-0.04	-0.53	-0.03	-0.58

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1   **Table S3.** Solvent effect on the reaction free energies of all elementary surface reactions of the propionic acid  
 2 conversion to ethane and ethylene over a Ni (111) catalyst surface model at two different temperature of 298 K and  
 3 473 K based on two different implicit solvation schemes: iSMS and VASPsol.  $\Delta\Delta G_{rxn}$  indicates the reaction free  
 4 energy difference between corresponding reaction in liquid water and in a gas phase.

#	Reaction	$\Delta\Delta G_{rxn}$			
		T=298 K		T=473 K	
		iSMS	VASPsol	iSMS	VASPsol
1	$\text{CH}_3\text{CH}_2\text{COOH}^* + 3^* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{***} + \text{OH}^*$	0.03	0.13	0.00	0.10
2	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CHCOOH}^{**} + \text{H}^*$	-0.04	0.14	-0.07	0.12
3	$\text{CH}_3\text{CH}_2\text{CO}^{***} + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}^{***}$	-0.10	-0.04	-0.14	-0.01
4	$\text{CH}_3\text{CH}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{H}^*$	-0.05	0.00	-0.06	0.01
5	$\text{CH}_3\text{CHCOOH}^{**} + * \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{OH}^*$	0.02	-0.01	0.01	-0.01
6	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCOOH}^{****} + \text{H}^*$	-0.02	-0.03	-0.02	-0.01
7	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CCOOH}^{***} + \text{H}^*$	-0.03	0.02	-0.03	0.02
8	$\text{CH}_3\text{CHCO}^{**} + 4^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}^{***}$	-0.07	-0.03	-0.10	0.00
9	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$	-0.05	0.04	-0.05	0.06
10	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{H}^*$	-0.01	0.04	-0.01	0.06
11	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{OH}^*$	0.03	0.06	0.02	0.06
12	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CHCHCOOH}^{****} + \text{H}^*$	-0.05	0.04	-0.05	0.03
13	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{OH}^*$	0.01	0.01	-0.01	0.02
14	$\text{CH}_3\text{CCO}^{****} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}^{***}$	-0.04	-0.06	-0.08	-0.05
15	$\text{CH}_2\text{CHCO}^{****} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{CO}^{***}$	-0.07	-0.09	-0.11	-0.10
16	$\text{CH}_2\text{CHCO}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{H}^*$	-0.08	-0.04	-0.08	-0.05
17	$\text{CHCHCOOH}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{OH}^*$	0.00	-0.02	-0.01	-0.03
18	$\text{CHCHCO}^{****} + 3^* \rightarrow \text{CHCH}^{****} + \text{CO}^{***}$	-0.02	-0.02	-0.06	-0.03
19	$\text{CH}_2\text{CH}^{**} + 2^* \rightarrow \text{CHCH}^{****} + \text{H}^*$	-0.02	0.02	-0.03	0.02
20	$\text{CH}_2\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_2\text{CH}^{**} + \text{H}^*$	-0.05	0.00	-0.06	0.01
21	$\text{CH}_2\text{CH}^{**} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.08	0.10	-0.09	0.13
22	$\text{CH}_3\text{C}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.07	0.06	-0.08	0.08
23	$\text{CH}_3\text{CH}^{**} + * \rightarrow \text{CH}_2\text{CH}^{**} + \text{H}^*$	-0.02	-0.02	-0.03	-0.04
24	$\text{CH}_3\text{CH}^{**} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{H}^*$	-0.02	0.01	-0.03	0.01
25	$\text{CH}_3\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_3\text{CH}^{**} + \text{H}^*$	-0.02	0.02	-0.03	0.02
26	$\text{CH}_3\text{CH}_3^* + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{H}^*$	-0.04	-0.02	-0.05	0.02
27	$\text{CH}_3\text{CH}_2^{**} + * \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$	0.01	-0.01	0.01	-0.02
28	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{COO}^{**} + \text{H}^*$	0.01	0.33	-0.03	0.30
29	$\text{CH}_3\text{CH}_2\text{COO}^{**} + * \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}_2^*$	0.13	-0.05	0.06	-0.02
30	$\text{CH}_3\text{CH}_2\text{COO}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.31	-0.01	-0.27	0.00
31	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.26	0.19	-0.23	0.18
32	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_3\text{CH}^{**} + \text{COOH}^{**}$	-0.05	0.01	-0.06	0.04
33	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CH}^{**} + \text{CO}_2^*$	0.42	-0.03	0.31	0.00
34	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	-0.30	-0.18	-0.26	-0.14
35	$\text{CH}_3\text{CCOOH}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	-0.52	0.00	-0.45	0.00
36	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{COOH}^{**}$	-0.04	-0.01	-0.06	0.02
37	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CH}^{**} + \text{COOH}^{**}$	-0.05	0.02	-0.07	0.01
38	$\text{CH}_3\text{CCOO}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}_2^*$	0.70	0.15	0.54	0.16
39	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$	0.22	0.15	0.15	0.14
40	$\text{COOH}^{**} + 2^* \rightarrow \text{CO}^{***} + \text{OH}^*$	0.01	-0.04	-0.03	-0.06
41	$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	0.00	0.11	0.00	0.07

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1 **Table S4.** Solvent effect on the activation free energies of all elementary surface reactions of the propionic acid  
 2 conversion to ethane and ethylene over a Ni (111) catalyst surface model at two different temperature of 298 K and  
 3 473 K based on two different implicit solvation schemes: iSMS and VASPsol.  $\Delta\Delta G^{\text{act}}$  indicates the activation free  
 4 energy differences between corresponding reaction in liquid water and in the gas phase.

#	Reaction	$\Delta\Delta G^{\text{act}}$			
		T=298 K		T=473 K	
		iSMS	VASPsol	iSMS	VASPsol
1	$\text{CH}_3\text{CH}_2\text{COOH}^* + 3^* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{***} + \text{OH}^*$	0.04	0.29	0.00	0.29
2	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CHCOOH}^{**} + \text{H}^*$	-0.03	0.05	-0.03	0.03
3	$\text{CH}_3\text{CH}_2\text{CO}^{***} + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}^{***}$	-0.02	0.01	-0.03	0.02
4	$\text{CH}_3\text{CH}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{H}^*$	-0.03	0.01	-0.03	0.05
5	$\text{CH}_3\text{CHCOOH}^{**} + * \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{OH}^*$	-0.02	0.13	-0.03	0.13
6	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCOOH}^{****} + \text{H}^*$	-0.01	-0.06	0.00	-0.04
7	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CCOOH}^{***} + \text{H}^*$	0.00	0.00	0.00	0.02
8	$\text{CH}_3\text{CHCO}^{**} + 4^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}^{***}$	-0.01	0.00	-0.01	0.00
9	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$	-0.08	0.04	-0.06	0.07
10	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{H}^*$	0.01	-0.02	0.00	0.01
11	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{OH}^*$	0.03	0.15	0.00	0.13
12	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CHCHCOOH}^{****} + \text{H}^*$	0.01	0.00	0.01	-0.01
13	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{OH}^*$	-0.06	0.10	-0.08	0.09
14	$\text{CH}_3\text{CCO}^{****} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}^{***}$	-0.08	0.21	-0.08	0.18
15	$\text{CH}_2\text{CHCO}^{****} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{CO}^{***}$	0.00	-0.04	-0.01	-0.05
16	$\text{CH}_2\text{CHCO}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{H}^*$	0.00	-0.04	0.00	-0.05
17	$\text{CHCHCOOH}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{OH}^*$	-0.11	0.14	-0.12	0.12
18	$\text{CHCHCO}^{****} + 3^* \rightarrow \text{CHCH}^{****} + \text{CO}^{***}$	-0.02	0.00	-0.03	0.00
19	$\text{CH}_2\text{CH}^{***} + 2^* \rightarrow \text{CHCH}^{****} + \text{H}^*$	0.02	-0.01	0.02	0.00
20	$\text{CH}_2\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	0.01	-0.02	0.01	-0.01
21	$\text{CH}_2\text{CH}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.02	0.03	-0.02	0.02
22	$\text{CH}_3\text{C}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.01	-0.04	-0.01	-0.04
23	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	-0.02	-0.05	-0.03	-0.06
24	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{H}^*$	0.02	0.00	0.02	-0.01
25	$\text{CH}_3\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{H}^*$	0.02	0.02	0.01	0.03
26	$\text{CH}_3\text{CH}_3^* + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{H}^*$	-0.01	-0.04	-0.02	-0.01
27	$\text{CH}_3\text{CH}_2^{**} + * \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$	0.00	-0.07	-0.01	-0.06
28	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{COO}^{**} + \text{H}^*$	-0.04	0.29	-0.07	0.24
29	$\text{CH}_3\text{CH}_2\text{COO}^{**} + * \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}_2^*$	-0.01	-0.01	-0.04	0.01
30	$\text{CH}_3\text{CH}_2\text{COO}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.19	-0.01	-0.17	-0.01
31	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.14	0.21	-0.14	0.19
32	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{COOH}^{**}$	-0.02	0.01	-0.02	0.05
33	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}_2^*$	0.16	0.01	0.12	0.00
34	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	0.14	0.03	0.12	0.03
35	$\text{CH}_3\text{CCOO}^{***} + * \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$	-0.20	0.12	-0.18	0.11
36	$\text{CH}_3\text{CCOO}^{***} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{COOH}^{**}$	-0.04	-0.01	-0.05	0.01
37	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{COOH}^{**}$	0.00	0.02	-0.01	0.03
38	$\text{CH}_3\text{CCOO}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}_2^*$	0.28	0.13	0.21	0.11
39	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$	-0.15	0.08	-0.18	0.06
40	$\text{COOH}^{**} + 2^* \rightarrow \text{CO}^{***} + \text{OH}^*$	0.06	-0.01	0.04	-0.02
41	$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	0.00	-0.22	-0.01	-0.33

5

6

1   **Table S5.** Overall turnover frequency of hydrodeoxygénéation of propionic acid over a Ni (111) catalyst surface model  
 2   at a temperature of 473 K in vapor phase, and at different partial pressures of hydrogen and carbon monoxide.

$P_{CO} \setminus P_{H_2}$ (bar)	0.01	0.1	1	10	30
<b>0.0001</b>	$3.99 \times 10^{-6}$	$1.98 \times 10^{-8}$	$8.72 \times 10^{-11}$	$7.23 \times 10^{-13}$	$7.72 \times 10^{-14}$
<b>0.001</b>	$2.66 \times 10^{-6}$	$3.46 \times 10^{-8}$	$1.30 \times 10^{-10}$	$7.41 \times 10^{-13}$	$7.76 \times 10^{-14}$
<b>0.01</b>	$6.92 \times 10^{-7}$	$1.63 \times 10^{-8}$	$1.86 \times 10^{-10}$	$8.76 \times 10^{-13}$	$8.10 \times 10^{-14}$
<b>0.1</b>	$8.98 \times 10^{-8}$	$5.09 \times 10^{-9}$	$9.26 \times 10^{-11}$	$1.20 \times 10^{-12}$	$1.02 \times 10^{-13}$
<b>1</b>	$5.72 \times 10^{-9}$	$9.47 \times 10^{-10}$	$3.30 \times 10^{-11}$	$8.55 \times 10^{-13}$	$1.24 \times 10^{-13}$

3  
 4   **Table S6.** Overall turnover frequency of hydrodeoxygénéation of propionic acid over a Ni (111) catalyst surface model  
 5   at a temperature of 473 K in vapor phase, and at different partial pressures of hydrogen and carbon monoxide based  
 6   on considering only 1 site for adsorbed CO and analogues change in counting sites for other adsorbates attached to  
 7   the surface through their carbon atom. The number of sites assigned to each adsorbate in this calculation is included  
 8   in Table S7.

$P_{CO} \setminus P_{H_2}$ (bar)	0.01	0.1	1	10	30
<b>0.0001</b>	$1.14 \times 10^{-8}$	$1.02 \times 10^{-8}$	$6.12 \times 10^{-9}$	$1.77 \times 10^{-9}$	$6.63 \times 10^{-10}$
<b>0.001</b>	$9.91 \times 10^{-12}$	$9.61 \times 10^{-12}$	$8.87 \times 10^{-12}$	$6.99 \times 10^{-12}$	$5.54 \times 10^{-12}$
<b>0.01</b>	$8.50 \times 10^{-15}$	$7.46 \times 10^{-15}$	$7.07 \times 10^{-15}$	$6.74 \times 10^{-15}$	$6.50 \times 10^{-15}$
<b>0.1</b>	$2.99 \times 10^{-17}$	$1.27 \times 10^{-17}$	$7.33 \times 10^{-18}$	$5.59 \times 10^{-18}$	$5.24 \times 10^{-18}$
<b>1</b>	$4.20 \times 10^{-19}$	$1.35 \times 10^{-19}$	$4.49 \times 10^{-20}$	$1.64 \times 10^{-20}$	$1.09 \times 10^{-20}$

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 10

1   **Table S7.** Number of occupied sites used for microkinetic modeling result displayed in Table S6.

Adsorbed Species	# of occupied site
CH <sub>2</sub> C	2
CH <sub>2</sub> CH	3
CH <sub>2</sub> CH	2
CH <sub>2</sub> CHCO	3
CH <sub>2</sub> CHCOOH	3
CH <sub>3</sub> C	1
CH <sub>3</sub> CCO	3
CH <sub>3</sub> CCOO	3
CH <sub>3</sub> CCOOH	3
CH <sub>3</sub> CH	2
CH <sub>3</sub> CH <sub>2</sub>	1
CH <sub>3</sub> CH <sub>2</sub> CO	3
CH <sub>3</sub> CH <sub>2</sub> COO	2
CH <sub>3</sub> CH <sub>2</sub> COOH	1
CH <sub>3</sub> CH <sub>3</sub>	1
CH <sub>3</sub> CHCO	2
CH <sub>3</sub> CHCOO	3
CH <sub>3</sub> CHCOOH	2
CHCH	3
CHCHCO	4
CHCHCOOH	3
CO	1
CO <sub>2</sub>	1
COOH	2
H	1
H <sub>2</sub> O	1
OH	1

2

3

1      **Table S8.** Solvent effect on the stability of various adsorbed species in the propionic acid conversion to ethane and  
 2      ethylene over a Ni (111) catalyst surface model at 473 K in the presence of two different solvents, water and 1,4-  
 3      dioxane, using iSMS methodology.  $\Delta\Delta G_{rxn}$  indicates the difference in the adsorption free energy of the corresponding  
 4      intermediates in the presence and absence of solvent. Asterisk (\*) represents a surface adsorption site and multiple  
 5      asterisks are indicative of the number of occupied active sites. Note that calculations for solvents were performed with  
 6      the help of the COSMO-RS package with three different Ni cavity radii: with default value, with a 10% increased  
 7      value and a 10% decreased value relative to the default.

Adsorbed species	$\Delta\Delta G_{rxn}$ , eV @ 473 K					
	Water			1,4-dioxane		
	Default	+10%	-10%	Default	+10%	-10%
CH <sub>2</sub> C***	-0.08	-0.09	-0.06	-0.05	-0.04	-0.03
CH <sub>2</sub> CH***	-0.01	-0.03	0.05	0.00	0.00	0.05
CH <sub>2</sub> CH <sub>2</sub> **	0.10	0.02	0.20	0.12	0.06	0.18
CH <sub>2</sub> CHCO****	-0.09	-0.13	-0.04	-0.03	-0.04	0.01
CH <sub>2</sub> CHCOOH****	-0.11	-0.16	-0.03	-0.04	-0.07	0.01
CH <sub>3</sub> ***	-0.01	-0.03	0.03	-0.01	0.00	0.02
CH <sub>3</sub> CCO****	-0.12	-0.15	-0.09	-0.06	-0.06	-0.04
CH <sub>3</sub> CCOO***	-0.55	-0.51	-0.58	-0.33	-0.27	-0.36
CH <sub>3</sub> CCOOH**	-0.12	-0.17	-0.08	-0.07	-0.09	-0.04
CH <sub>3</sub> CH***	0.00	-0.02	0.07	-0.01	0.01	0.05
CH <sub>3</sub> CH <sub>2</sub> **	0.01	-0.02	0.07	-0.01	0.00	0.03
CH <sub>3</sub> CH <sub>2</sub> CO***	-0.05	-0.08	0.01	-0.04	-0.04	0.00
CH <sub>3</sub> CH <sub>2</sub> COO**	-0.06	-0.09	-0.03	-0.04	-0.04	-0.04
CH <sub>3</sub> CH <sub>2</sub> COOH*	-0.03	-0.11	0.06	0.02	-0.04	0.08
CH <sub>3</sub> CH <sub>3</sub> *	0.02	-0.02	0.07	0.02	-0.01	0.04
CH <sub>3</sub> CHCO**	-0.09	-0.13	-0.05	-0.05	-0.06	-0.02
CH <sub>3</sub> CHCOO***	-0.31	-0.30	-0.33	-0.17	-0.13	-0.18
CH <sub>3</sub> CHCOOH**	-0.10	-0.15	-0.04	-0.06	-0.07	-0.03
CHCH****	0.05	-0.01	0.13	0.08	0.05	0.13
CHCHCO****	-0.15	-0.19	-0.14	-0.05	-0.08	-0.05
CHCHCOOH****	-0.13	-0.19	-0.09	-0.06	-0.09	-0.03
CO***	-0.25	-0.25	-0.25	-0.18	-0.16	-0.20
CO <sub>2</sub> *	-0.04	-0.08	0.04	0.01	-0.02	0.04
COOH**	-0.16	-0.17	-0.13	-0.08	-0.07	-0.05
H*	-0.01	0.02	0.03	0.00	0.03	0.03
H <sub>2</sub> O*	0.02	-0.03	0.09	0.07	0.03	0.13
OH*	0.00	-0.03	0.06	0.02	0.01	0.08

8

9

1 **Table S9.** Solvent effect on the reaction free energies of all elementary surface reactions of the propionic acid  
 2 conversion to ethane and ethylene over a Ni (111) catalyst surface model at 473 K based on iSMS methodology in the  
 3 presence of water and 1,4-dioxane.  $\Delta\Delta G_{rxn}$  indicates the reaction free energy difference between corresponding  
 4 reaction in solvent and in a gas phase. Note that calculations for solvents were performed with the help of the COSMO-  
 5 RS package with three different Ni cavity radii: with default value, with a 10% increased value and a 10% decreased  
 6 value relative to the default.

#	Reaction	$\Delta\Delta G_{rxn}$ , eV @ 473 K					
		Water			1,4-dioxane		
		Default	+10%	-10%	Default	+10%	-10%
1	$\text{CH}_3\text{CH}_2\text{COOH}^* + 3^* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{***} + \text{OH}^*$	0.00	0.01	0.05	0.03	0.04	0.08
2	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CHCOOH}^{**} + \text{H}^*$	-0.07	-0.04	-0.07	-0.03	0.00	-0.03
3	$\text{CH}_3\text{CH}_2\text{CO}^{***} + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}^{***}$	-0.14	-0.12	-0.18	-0.10	-0.07	-0.15
4	$\text{CH}_3\text{CH}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{H}^*$	-0.06	-0.07	-0.07	-0.02	-0.02	-0.03
5	$\text{CH}_3\text{CHCOOH}^{**} + * \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{OH}^*$	0.01	-0.02	0.05	0.04	0.02	0.09
6	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCOOH}^{****} + \text{H}^*$	-0.02	-0.02	0.00	0.01	0.01	0.02
7	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CCOOH}^{***} + \text{H}^*$	-0.03	-0.03	-0.06	-0.01	-0.02	-0.03
8	$\text{CH}_3\text{CHCO}^{**} + 4^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}^{***}$	-0.10	-0.07	-0.14	-0.09	-0.04	-0.12
9	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$	-0.05	-0.03	-0.06	-0.02	0.00	-0.03
10	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{H}^*$	-0.01	0.00	-0.01	0.01	0.02	0.01
11	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{OH}^*$	0.02	0.00	0.04	0.04	0.04	0.08
12	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CHCHCOOH}^{****} + \text{H}^*$	-0.05	-0.04	-0.07	-0.03	-0.03	-0.04
13	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{OH}^*$	-0.01	-0.02	0.04	0.03	0.04	0.09
14	$\text{CH}_3\text{CCO}^{****} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}^{***}$	-0.08	-0.06	-0.13	-0.08	-0.05	-0.12
15	$\text{CH}_2\text{CHCO}^{****} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{CO}^{***}$	-0.11	-0.09	-0.15	-0.10	-0.07	-0.14
16	$\text{CH}_2\text{CHCO}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{H}^*$	-0.08	-0.08	-0.11	-0.03	-0.04	-0.07
17	$\text{CHCHCOOH}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{OH}^*$	-0.01	-0.04	0.00	0.03	0.02	0.06
18	$\text{CHCHCO}^{****} + 3^* \rightarrow \text{CHCH}^{****} + \text{CO}^{***}$	-0.06	-0.04	-0.08	-0.08	-0.03	-0.09
19	$\text{CH}_2\text{CH}^{***} + 2^* \rightarrow \text{CHCH}^{****} + \text{H}^*$	-0.03	-0.03	-0.03	-0.01	0.00	-0.02
20	$\text{CH}_2\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	-0.06	-0.05	-0.09	-0.03	-0.02	-0.06
21	$\text{CH}_2\text{CH}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.09	-0.08	-0.13	-0.06	-0.05	-0.09
22	$\text{CH}_3\text{C}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.08	-0.07	-0.11	-0.05	-0.04	-0.06
23	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	-0.03	-0.02	-0.03	-0.01	0.00	-0.01
24	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{H}^*$	-0.03	-0.02	-0.05	-0.01	-0.01	-0.04
25	$\text{CH}_3\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{H}^*$	-0.03	-0.02	-0.02	-0.01	0.01	0.01
26	$\text{CH}_3\text{CH}_3^* + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{H}^*$	-0.05	-0.03	-0.05	-0.03	0.00	-0.02
27	$\text{CH}_3\text{CH}_2^{**} + * \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$	0.01	0.01	0.04	0.02	0.02	0.05
28	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{COO}^{**} + \text{H}^*$	-0.03	0.02	-0.06	0.00	0.04	-0.05
29	$\text{CH}_3\text{CH}_2\text{COO}^{**} + * \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}_2^*$	0.06	0.03	0.17	0.04	0.03	0.13
30	$\text{CH}_3\text{CH}_2\text{COO}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.27	-0.22	-0.32	-0.14	-0.10	-0.15
31	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.23	-0.17	-0.30	-0.11	-0.06	-0.17
32	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{COOH}^{**}$	-0.06	-0.05	-0.02	-0.02	0.00	0.03
33	$\text{CH}_3\text{CHCOO}^{**} + * \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}_2^*$	0.31	0.24	0.47	0.17	0.13	0.29
34	$\text{CH}_3\text{CHCOO}^{**} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	-0.26	-0.23	-0.27	-0.17	-0.14	-0.19
35	$\text{CH}_3\text{CCOOH}^{**} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	-0.45	-0.36	-0.51	-0.27	-0.19	-0.32
36	$\text{CH}_3\text{CCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{COOH}^{**}$	-0.06	-0.04	-0.02	-0.02	0.01	0.02
37	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{COOH}^{**}$	-0.07	-0.05	-0.05	-0.04	-0.01	-0.01
38	$\text{CH}_3\text{CCOO}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}_2^*$	0.54	0.44	0.68	0.33	0.26	0.44
39	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$	0.15	0.12	0.19	0.08	0.07	0.09
40	$\text{COOH}^{**} + 2^* \rightarrow \text{CO}^{***} + \text{OH}^*$	-0.03	-0.04	-0.06	-0.03	-0.03	-0.05
41	$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	0.00	0.01	0.00	0.00	0.02	0.01

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8

1 **Table S10.** Solvent effect on the activation free energies of all elementary surface reactions of the propionic acid  
 2 conversion to ethane and ethylene over a Ni (111) catalyst surface model at 473 K based on iSMS methodology in the  
 3 presence of water and 1,4-dioxane.  $\Delta\Delta G^{\text{act}}$  indicates the activation free energy difference between corresponding  
 4 reaction in solvent and in a gas phase. Note that calculations for solvents were performed with the help of the COSMO-  
 5 RS package with three different Ni cavity radii: with default value, with a 10% increased value and a 10% decreased  
 6 value relative to the default.

#	Reaction	$\Delta\Delta G^{\text{act}}$ , eV @ 473 K					
		Water			1,4-dioxane		
		Default	+10%	-10%	Default	+10%	-10%
1	$\text{CH}_3\text{CH}_2\text{COOH}^* + 3^* \rightarrow \text{CH}_3\text{CH}_2\text{CO}^{***} + \text{OH}^*$	0.00	0.03	0.02	0.00	0.01	0.02
2	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CHCOOH}^{**} + \text{H}^*$	-0.03	-0.01	-0.02	-0.01	0.01	0.00
3	$\text{CH}_3\text{CH}_2\text{CO}^{***} + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}^{***}$	-0.03	-0.02	-0.01	0.01	0.00	0.01
4	$\text{CH}_3\text{CH}_2\text{CO}^{***} \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{H}^*$	-0.03	-0.03	-0.02	0.00	0.00	0.01
5	$\text{CH}_3\text{CHCOOH}^{**} + * \rightarrow \text{CH}_3\text{CHCO}^{**} + \text{OH}^*$	-0.03	-0.03	-0.05	0.00	-0.01	-0.01
6	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_3\text{CHCOOH}^{****} + \text{H}^*$	0.00	-0.01	0.02	0.04	0.02	0.05
7	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CCOOH}^{***} + \text{H}^*$	0.00	0.00	0.01	0.01	0.00	0.02
8	$\text{CH}_3\text{CHCO}^{**} + 4^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}^{***}$	-0.01	0.00	-0.04	0.01	0.01	-0.02
9	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{H}^*$	-0.06	-0.05	-0.08	-0.03	-0.02	-0.05
10	$\text{CH}_3\text{CHCO}^{**} + 3^* \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{H}^*$	0.00	0.00	-0.02	0.01	0.01	0.00
11	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CHCO}^{****} + \text{OH}^*$	0.00	0.01	-0.03	0.01	0.02	-0.01
12	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CHCHCOOH}^{****} + \text{H}^*$	0.01	0.00	0.01	0.00	-0.01	0.01
13	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{CCO}^{****} + \text{OH}^*$	-0.08	-0.05	-0.08	-0.03	-0.01	-0.02
14	$\text{CH}_3\text{CCO}^{****} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}^{***}$	-0.08	-0.06	-0.11	-0.07	-0.05	-0.09
15	$\text{CH}_2\text{CHCO}^{****} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{CO}^{***}$	-0.01	-0.01	-0.01	0.00	0.00	-0.01
16	$\text{CH}_2\text{CHCO}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{H}^*$	0.00	0.00	0.00	0.01	0.00	0.00
17	$\text{CHCHCOOH}^{****} + * \rightarrow \text{CHCHCO}^{****} + \text{OH}^*$	-0.12	-0.07	-0.17	-0.06	-0.01	-0.11
18	$\text{CHCHCO}^{****} + 3^* \rightarrow \text{CHCH}^{****} + \text{CO}^{***}$	-0.03	-0.01	-0.04	-0.02	0.00	-0.03
19	$\text{CH}_2\text{CH}^{***} + 2^* \rightarrow \text{CHCH}^{****} + \text{H}^*$	0.02	0.01	0.04	0.02	0.02	0.04
20	$\text{CH}_2\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	0.01	-0.01	0.01	0.01	0.01	0.01
21	$\text{CH}_2\text{CH}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.02	-0.02	-0.02	-0.01	-0.01	-0.01
22	$\text{CH}_3\text{C}^{***} + * \rightarrow \text{CH}_2\text{C}^{***} + \text{H}^*$	-0.01	-0.03	-0.01	0.01	-0.01	0.02
23	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{H}^*$	-0.03	-0.03	-0.06	0.00	-0.02	-0.03
24	$\text{CH}_3\text{CH}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{H}^*$	0.02	0.01	0.02	0.01	0.01	0.02
25	$\text{CH}_3\text{CH}_2^{**} + 2^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{H}^*$	0.01	0.01	0.03	0.02	0.02	0.05
26	$\text{CH}_3\text{CH}_3^* + 2^* \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{H}^*$	-0.02	-0.02	0.00	-0.01	0.00	0.01
27	$\text{CH}_3\text{CH}_2^{**} + * \rightarrow \text{CH}_2\text{CH}_2^{**} + \text{H}^*$	-0.01	-0.02	0.01	0.02	0.01	0.04
28	$\text{CH}_3\text{CH}_2\text{COOH}^* + 2^* \rightarrow \text{CH}_3\text{CH}_2\text{COO}^{**} + \text{H}^*$	-0.07	-0.03	-0.09	-0.03	-0.01	-0.06
29	$\text{CH}_3\text{CH}_2\text{COO}^{**} + * \rightarrow \text{CH}_3\text{CH}_2^{**} + \text{CO}_2^*$	-0.04	-0.06	-0.02	-0.03	-0.06	0.01
30	$\text{CH}_3\text{CH}_2\text{COO}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.17	-0.16	-0.19	-0.09	-0.07	-0.06
31	$\text{CH}_3\text{CHCOOH}^{**} + 2^* \rightarrow \text{CH}_3\text{CHCOO}^{***} + \text{H}^*$	-0.14	-0.10	-0.18	-0.07	-0.04	-0.09
32	$\text{CH}_3\text{CHCOOH}^{**} + 3^* \rightarrow \text{CH}_3\text{CH}^{***} + \text{COOH}^{**}$	-0.02	-0.03	-0.02	0.02	0.00	0.03
33	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CH}^{***} + \text{CO}_2^*$	0.12	0.08	0.17	0.10	0.06	0.13
34	$\text{CH}_3\text{CHCOO}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	0.12	0.07	0.15	0.09	0.06	0.11
35	$\text{CH}_3\text{CCOOH}^{***} + * \rightarrow \text{CH}_3\text{CCOO}^{***} + \text{H}^*$	-0.18	-0.14	-0.26	-0.07	-0.04	-0.13
36	$\text{CH}_3\text{CCOOH}^{***} + 2^* \rightarrow \text{CH}_3\text{C}^{***} + \text{COOH}^{**}$	-0.05	-0.04	-0.05	-0.02	-0.01	-0.02
37	$\text{CH}_2\text{CHCOOH}^{****} + * \rightarrow \text{CH}_2\text{CH}^{***} + \text{COOH}^{**}$	-0.01	-0.01	-0.04	0.00	0.00	-0.02
38	$\text{CH}_3\text{CCOO}^{***} + * \rightarrow \text{CH}_3\text{C}^{***} + \text{CO}_2^*$	0.21	0.18	0.24	0.14	0.12	0.17
39	$\text{COOH}^{**} \rightarrow \text{CO}_2^* + \text{H}^*$	-0.18	-0.13	-0.25	-0.14	-0.09	-0.20
40	$\text{COOH}^{**} + 2^* \rightarrow \text{CO}^{***} + \text{OH}^*$	0.04	0.01	0.05	0.03	0.02	0.04
41	$\text{H}_2\text{O}^* + * \rightarrow \text{OH}^* + \text{H}^*$	-0.01	0.02	-0.05	-0.01	0.01	-0.03

7

8

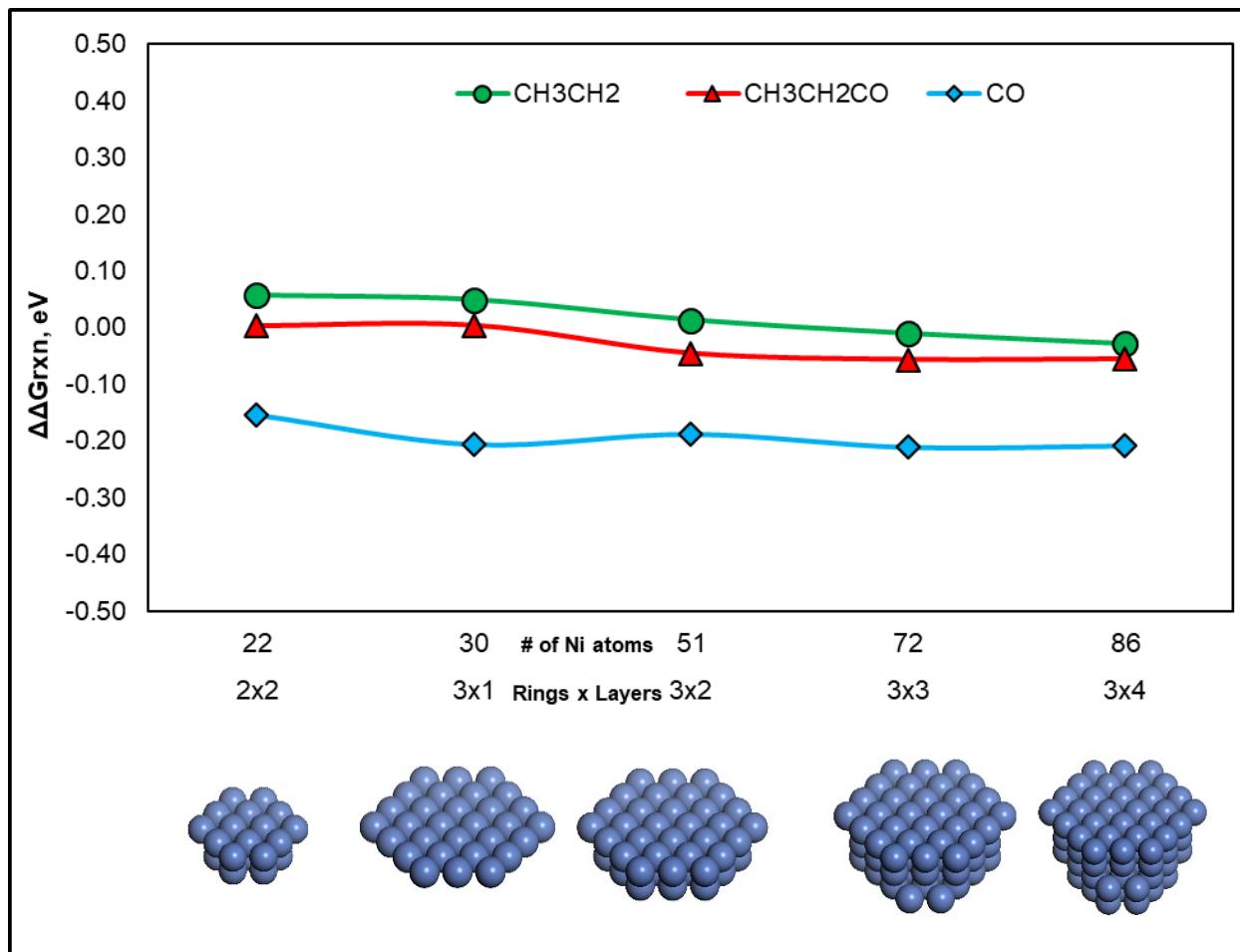
1 **Table S11.** Overall, decarbonylation, and decarboxylation turnover frequencies as well as important steady state  
 2 surface coverages for the HDO of PAC over a Ni(111) catalyst surface model in the gas phase and in liquid water at  
 3 473 K. Calculations in water were performed with the help of the *iSMS* and VASPsol schemes. Also,  $a_i$  denotes the  
 4 reaction order with respect to partial pressure/fugacity of component  $i$  and  $X_{rc}^n$  indicates Campbell's degree of rate  
 5 control for reaction step  $n$ .

Properties	Gas	<i>iSMS</i>	VASPsol
<b>DCN TOF</b>	$3.46 \times 10^{-08}$	$6.70 \times 10^{-09}$	$1.68 \times 10^{-08}$
<b>DCX TOF</b>	$8.72 \times 10^{-13}$	$1.47 \times 10^{-11}$	$1.24 \times 10^{-10}$
<b>Overall TOF (s<sup>-1</sup>)</b>	$3.46 \times 10^{-08}$	$6.71 \times 10^{-09}$	$1.69 \times 10^{-08}$
<b><math>\theta^*</math></b>	0.011	0.003	0.008
<b><math>\theta_{H^*}</math></b>	0.631	0.206	0.418
<b><math>\theta_{CO^{**}}</math></b>	0.357	0.789	0.474
<b><math>\theta_{CH_3C^{***}}</math></b>	0.000	0.000	0.000
<b><math>\theta_{PAC^*}</math></b>	0.000	0.000	0.021
<b><math>\theta_{CH_3CH_2COO^{**}}</math></b>	0.001	0.000	0.010
<b><math>a_{CO}</math></b>	0.0	-0.7	-1.0
<b><math>a_{H_2}</math></b>	-2.2	-1.4	-1.2
<b><math>a_{PAC}</math></b>	1.0	1.0	1.0
<b><math>X_{rc}^1</math></b>	0.65	0.10	0.03
<b><math>X_{rc}^8</math></b>	0.26	0.01	0.68
<b><math>X_{rc}^9</math></b>	0.03	0.88	0.16

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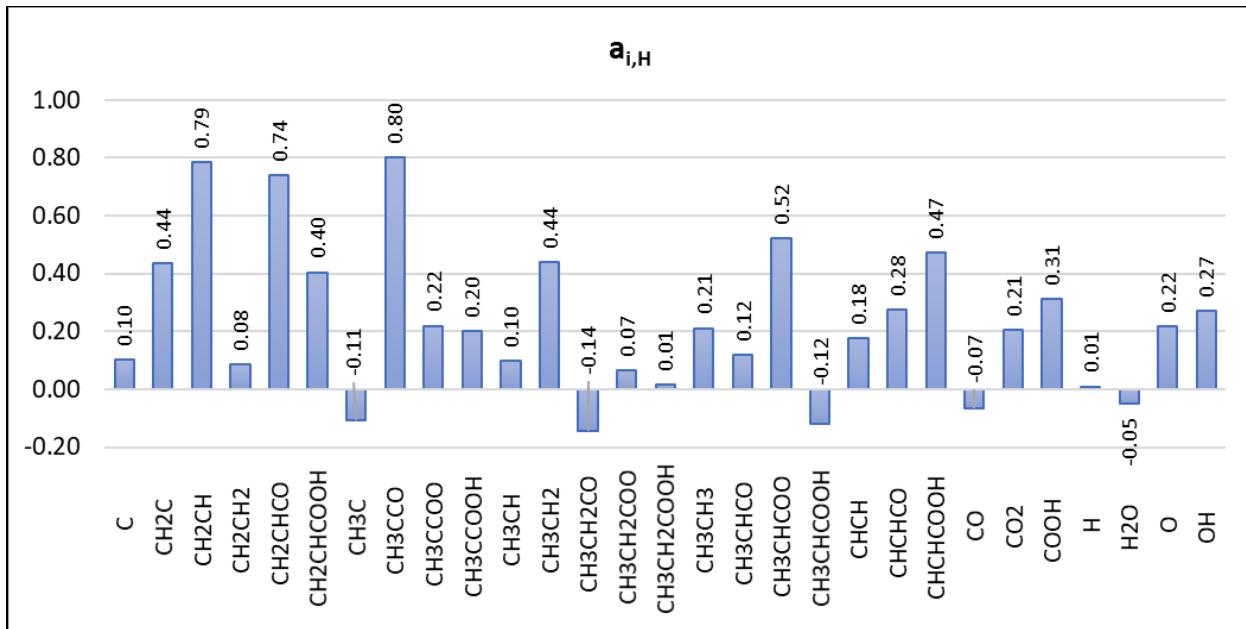
2

3 **Figure S1.** Adsorption of different sized molecules ( $\text{CO}$ ,  $\text{CH}_3\text{CH}_2$ , and  $\text{CH}_3\text{CH}_2\text{C}$ ) on a  $\text{Ni}(111)$  surface model with  
4 various cluster sizes used in iSMS calculations in liquid water at 473 K. We employed a 3x2 cluster model for all  
5 surface reactions since the computational cost for larger models increases dramatically while the solvent effect does  
6 not change significantly. For adsorption/desorption processes of saturated molecules such as  $\text{C}_2\text{H}_4$ ,  $\text{C}_3\text{H}_6$ ,  $\text{C}_2\text{H}_2$ ,  
7  $\text{CH}_3\text{CH}_2\text{COOH}$ ,  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{H}$ ,  $\text{H}_2\text{O}$ , where error cancellation of solvation effects is smaller than for surface reactions,  
8 a 3x4 model with 86 metal atoms was used.

9

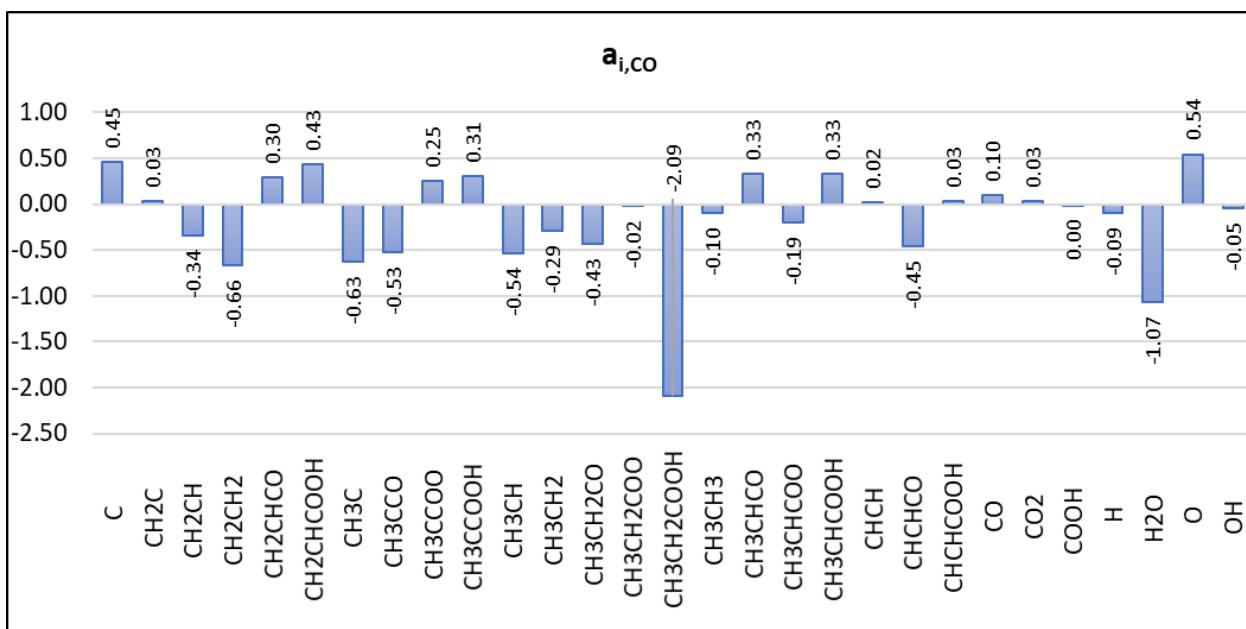
10

1 a)



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3 b)

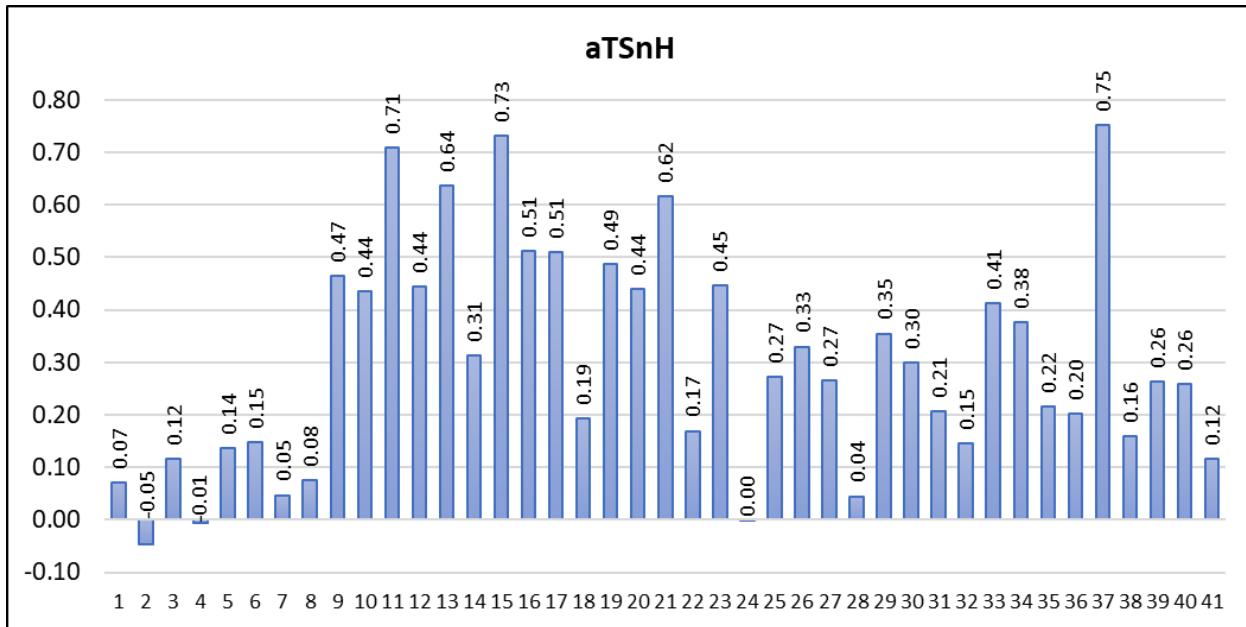


5 **Figure S2.** Lateral interaction correction terms for various intermediates using a 1/4 ML coverage of CO and H.  
6 Shown are the correction terms of the lateral interaction effect of H (a) and CO (b) for each individual adsorbed  
7 species.

8

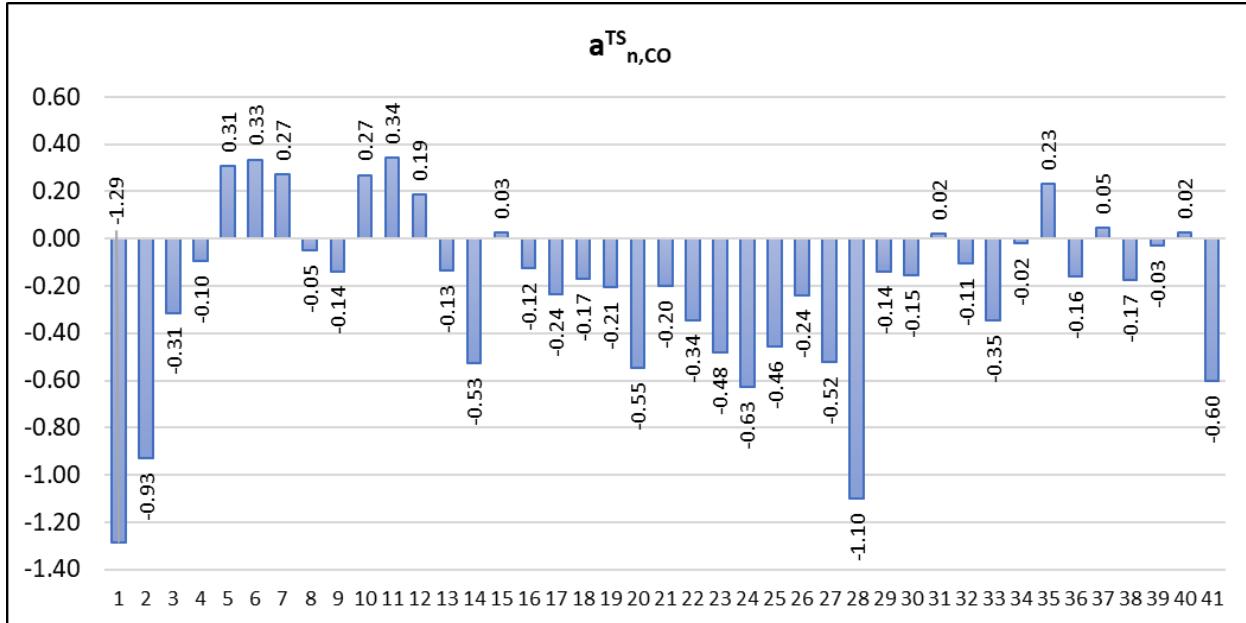
1

2 a)



3

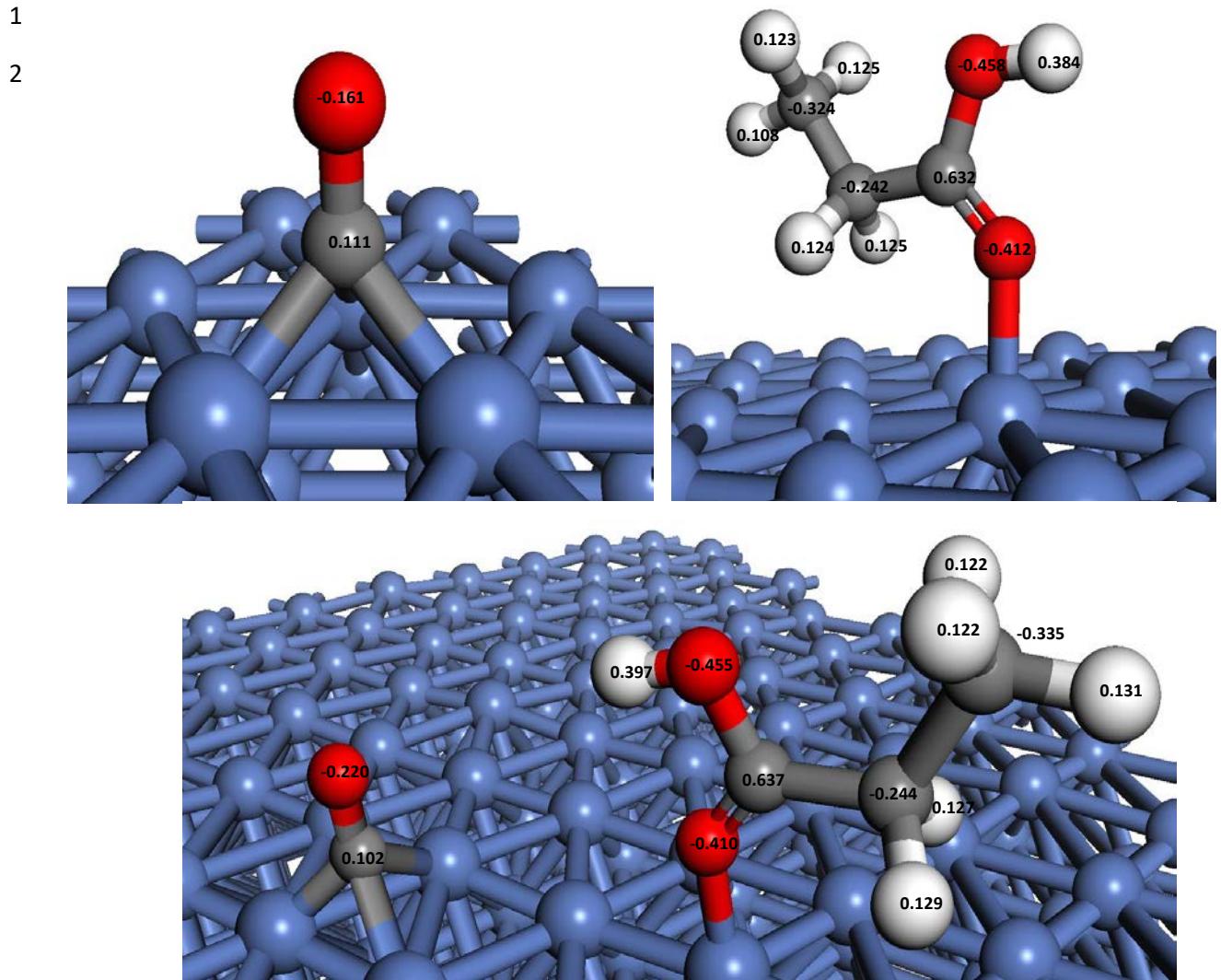
4 b)



5

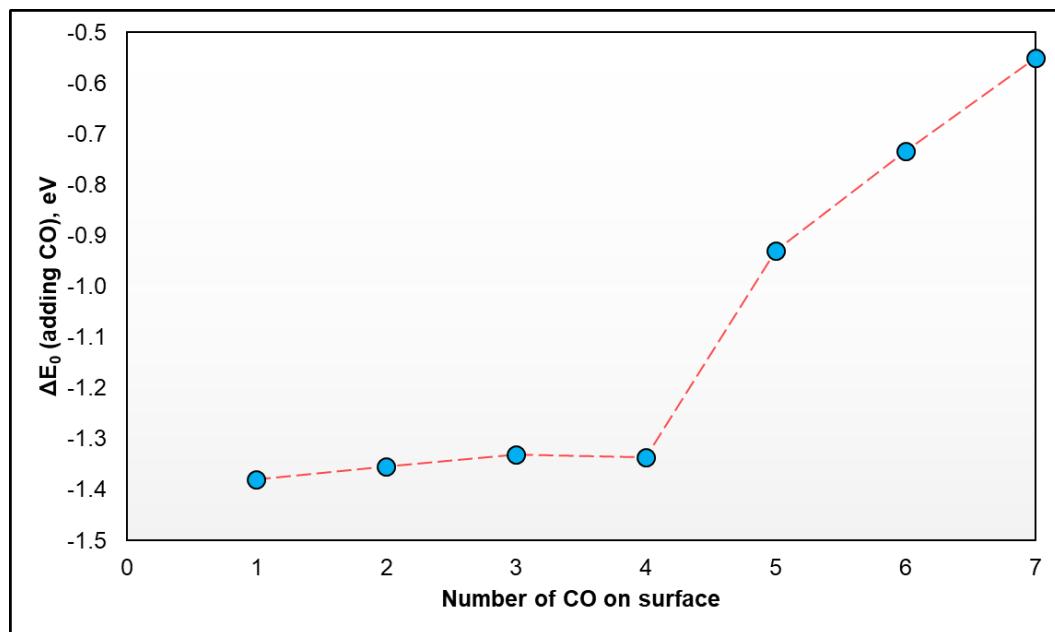
**Figure S3.** Lateral interaction correction terms for the transition state of each elementary step using 1/4 ML coverages of CO and H. Shown are the correction terms of the lateral interaction effect of H (a) and CO (b) on the transition state of each elementary step.

9



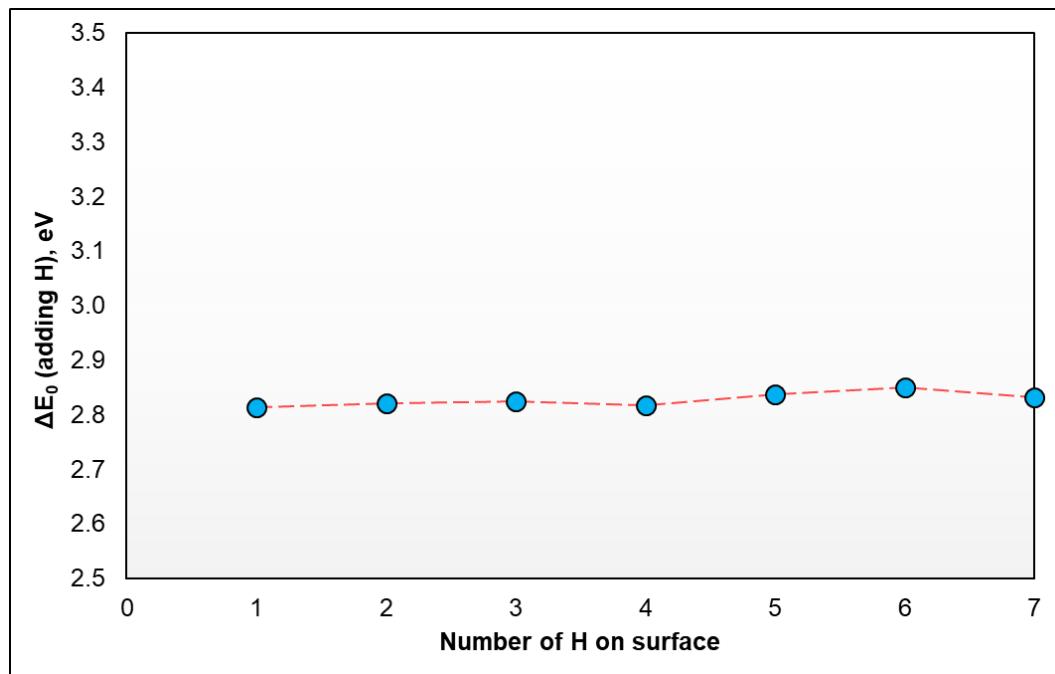
**Figure S4.** Partial charges computed using the DDEC6 charge model<sup>1</sup> on adsorbed CO (top left), adsorbed PAC (top right), and coadsorbed CO and PAC on a Ni (111) catalyst surface model. In the coadsorbed state, CO is a Lewis acid, which accepts electrons, while PAC is a Lewis base, which donates electrons. This coadsorbed Lewis acid and base pair explains the attractive interaction between adsorbed CO and PAC.

1 a)



2

3 b)



4

5 **Figure S5.** Differential zero-point energy corrected (ZPC) energy of adding a) an extra CO as a function of number  
6 of CO already adsorbed on a Ni(111) surface containing 12 surface atoms with  $(3 \times 2\sqrt{3})$  periodicity and b) an extra  
7 H as a function of number of H already adsorbed on the same Ni surface. Adding the fifth CO increases the energy  
8 significantly (by over 0.45 eV) which we attribute to the fact that the surface is essentially fully covered with 4 CO  
9 and adding an extra CO weakens the bond strength of adsorbed CO molecules on the surface due to a strong repulsive  
10 interaction between them. On the other hand, the differential ZPC barely increases when adding an extra hydrogen  
11 atom. Consequently, it can be concluded that a CO molecule occupies 3 Ni sites on the surface while H adsorbs on  
12 only 1 Ni site.

1

2 1. T. A. Manz and N. G. Limas, *RSC Advances*, 2016, **6**, 47771-47801.

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