Supporting Information

Surface Structure Sensitivity of Hydrodeoxygenation of Biomass derived Organic Acids over Palladium Catalysts: A Microkinetic Modeling Approach

Subrata Kumar Kundu,[a] Rajadurai Vijay Solomon,[a] Wenqiang Yang,[a] Eric Walker,[a,b,c] Osman Mamun,[a] Jesse Q. Bond[d] and Andreas Heyden[a,*]

[a]Department of Chemical Engineering, University of South Carolina, 301 South Main Street, Columbia, SC 29208, USA.
[b]Institute for Computational and Data Sciences, University at Buffalo, The State University of New York, Buffalo, New York 14260, USA
[c]Department of Chemical and Biological Engineering, University at Buffalo, The State University of New York, Buffalo, New York 14260, USA
[d]Department of Biomedical and Chemical Engineering, Syracuse University, 329 Link Hall, Syracuse, NY 13244, USA.

*heyden@cec.sc.edu

+1-803-777-5025

Table S1. Effects of solvents, i.e., water and 1,4-dioxane, on reaction free energies and activation energies in eV of all the elementary reaction steps in the HDO of propanoic acid over Pd(100) and Pd(111) at a temperature of 473 K, a propionic acid gas phase partial pressure of 1 bar, a CO gas phase partial pressure of 1×10^{-5} bar, and a hydrogen partial pressure of 0.01 bar using ±10% of the default COSMO palladium cavity radius.

#	Facet	Surface reactions	Water (+10%)		Water (-10%)		1,4-dioxane (+10%)		1,4-dioxane (-10%)	
			$\Delta\Delta G^{water}_{Rxn}$ (eV)	$\Delta\Delta G^{water}_{TS}$ (eV)	$\Delta\Delta G^{water}_{Rxn}$ (eV)	$\Delta\Delta G^{water}_{TS}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)
0	100	$CH_3CH_2COOH(g) + * \rightarrow CH_3CH_2COOH*$	0.33	N/A	-0.28	N/A	-0.19	N/A	-0.19	N/A
	111	$CH_3CH_2COOH(g) + * \rightarrow CH_3CH_2COOH*$	-0.22	N/A	-0.15	N/A	-0.15	N/A	-0.10	N/A
1	100	$CH_3CH_2COOH* + 2* \rightarrow CH_3CH_2CO** + OH*$	-0.09	-0.01	-0.19	-0.10	-0.02	0.01	-0.10	-0.04
	111	$CH_3CH_2COOH* + 3* \rightarrow CH_3CH_2CO*** + OH*$	0.01	-0.03	0.04	-0.06	0.04	0.02	0.08	0.00
2	100	$CH_3CH_2COOH* + 2* \rightarrow CH_3CHCOOH** + H*$	-0.15	-0.05	-0.30	-0.05	-0.06	0.01	-0.17	0.00
	111	$CH_3CH_2COOH* + 2* \rightarrow CH_3CHCOOH** + H*$	-0.03	-0.05	-0.05	-0.07	0.01	0.00	0.02	0.00
3	100	$CH_3CH_2CO** \rightarrow CH_3CH_2* + CO*$	-0.12	-0.01	-0.11	0.01	-0.07	-0.01	-0.08	0.00
	111	$CH_3CH_2CO*** \rightarrow CH_3CH_2* + CO* + *$	-0.17	-0.01	-0.28	0.00	-0.11	0.00	-0.21	0.02
4	100	$CH_3CH_2CO** + * \rightarrow CH_3CHCO** + H*$	-0.17	-0.02	-0.29	-0.05	-0.10	0.00	-0.21	-0.02
	111	$CH_3CH_2CO*** \rightarrow CH_3CHCO** + H*$	-0.08	-0.05	-0.14	-0.08	-0.05	-0.03	-0.08	-0.03
5	100	$CH_3CHCOOH** + * \rightarrow CH_3CHCO** + OH*$	-0.11	-0.01	-0.19	-0.02	-0.05	0.00	-0.14	-0.02
	111	$CH_3CHCOOH** + * \rightarrow CH_3CHCO** + OH*$	-0.04	-0.02	-0.05	-0.09	-0.01	-0.01	-0.02	-0.08
6	100	$CH_3CHCOOH** + 2* \rightarrow CH_2CHCOOH*** + H*$	-0.17	-0.06	-0.33	-0.04	-0.10	-0.03	-0.23	-0.02
	111	$CH_3CHCOOH** + 2* \rightarrow CH_2CHCOOH*** + H*$	-0.06	-0.05	-0.10	-0.04	-0.03	0.00	-0.06	0.00
7	100	$CH_3CHCOOH** + * \rightarrow CH_3CCOOH** + H*$	-0.16	-0.04	-0.32	-0.13	-0.13	-0.04	-0.25	-0.09
	111	$CH_3CHCOOH** + 2* \rightarrow CH_3CCOOH*** + H*$	-0.09	-0.06	-0.17	-0.10	-0.08	-0.03	-0.14	-0.05
8	100	$CH_3CHCO** \rightarrow CH_3CH* + CO*$	-0.09	0.06	-0.10	0.13	-0.05	0.04	-0.07	0.09
	111	$CH_3CHCO** + * \rightarrow CH_3CH** + CO*$	-0.13	0.02	-0.21	0.06	-0.09	0.02	-0.15	0.04

#	Facet	Surface reactions	Water (+10%)		Water (-10%)		1,4-dioxane (+10%)		1,4-dioxane (-10%)	
			$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)
9	100	$CH_3CHCO^{**} + * \rightarrow CH_3CCO^{**} + H^*$	-0.11	0.00	-0.23	0.00	-0.06	0.02	-0.15	0.02
	111	$CH_3CHCO^{**} + 2^* \rightarrow CH_3CCO^{***} + H^*$	-0.04	-0.03	-0.10	-0.06	-0.03	-0.01	-0.06	-0.03
10	100	$CH_3CHCO^{**} + 2^* \rightarrow CH_2CHCO^{***} + H^*$	-0.15	-0.06	-0.32	-0.02	-0.09	-0.02	-0.21	0.03
	111	$CH_3CHCO^{**} + 2^* \rightarrow CH_2CHCO^{***} + H^*$	-0.02	-0.06	-0.03	-0.03	0.00	-0.03	0.00	0.01
11	100	$CH_2CHCOOH^{***} + * \rightarrow CH_2CHCO^{***} + OH^*$	-0.10	0.04	-0.17	-0.04	-0.05	-0.01	-0.12	-0.06
	111	$CH_2CHCOOH^{***} + * \rightarrow CH_2CHCO^{***} + OH^*$	-0.01	-0.04	0.03	-0.07	0.02	-0.01	0.05	-0.03
12	100	$CH_2CHCOOH^{***} + * \rightarrow CHCHCOOH^{***} + H^*$	-0.17	-0.04	-0.31	-0.09	-0.13	-0.03	-0.26	-0.08
	111	$CH_2CHCOOH^{***} + * \rightarrow CHCHCOOH^{***} + H^*$	-0.06	-0.02	-0.10	-0.01	-0.03	-0.01	-0.06	0.00
13	100	$CH_3CCOOH^{**} + * \rightarrow CH_3CCO^{**} + OH^*$	-0.06	0.04	-0.10	0.05	0.01	0.06	-0.04	0.04
	111	$CH_3CCOOH^{***} + * \rightarrow CH_3CCO^{***} + OH^*$	0.01	0.03	0.02	-0.02	0.04	0.04	0.06	0.02
14	100	$CH_3CCO^{**} \rightarrow CH_3C^* + CO^*$	-0.15	-0.03	-0.20	-0.06	-0.10	-0.04	-0.16	-0.05
	111	$CH_3CCO^{***} \rightarrow CH_3C^* + CO^* + *$	-0.14	0.02	-0.18	0.05	-0.09	0.02	-0.12	0.04
15	100	$CH_2CHCO^{***} + * \rightarrow CH_2CH^{***} + CO^*$	-0.19	-0.02	-0.31	-0.04	-0.13	-0.02	-0.26	-0.05
	111	$CH_2CHCO^{***} + * \rightarrow CH_2CH^{***} + CO^*$	-0.18	-0.01	-0.28	-0.02	-0.13	0.00	-0.21	-0.01
16	100	$CH_2CHCO^{***} \rightarrow CHCHCO^{**} + H^*$	-0.18	-0.04	-0.34	-0.07	-0.12	-0.02	-0.27	-0.05
	111	$CH_2CHCO^{***} + 2^* \rightarrow CHCHCO^{****} + H^*$	-0.05	-0.02	-0.11	-0.05	-0.04	-0.01	-0.07	-0.05
17	100	$CHCHCOOH^{***} \rightarrow CHCHCO^{**} + OH^*$	-0.10	0.01	-0.21	-0.05	-0.04	0.01	-0.12	-0.03
	111	$CHCHCOOH^{***} + 2^* \rightarrow CHCHCO^{****} + OH^*$	0.00	0.01	0.02	-0.03	0.02	0.02	0.03	-0.02
18	100	$CHCHCO^{**} + * \rightarrow CHCH^{**} + CO^*$	-0.13	0.03	-0.22	0.02	-0.09	0.01	-0.18	0.00
	111	$CHCHCO^{****} \rightarrow CHCH^{***} + CO^*$	-0.15	0.04	-0.24	0.05	-0.11	0.03	-0.18	0.02
19	100	$CH_2CH^{***} \rightarrow CHCH^{**} + H^*$	-0.12	-0.01	-0.25	-0.04	-0.08	-0.01	-0.19	-0.02
	111	$CH_2CH^{***} + * \rightarrow CHCH^{***} + H^*$	-0.03	-0.02	-0.06	-0.03	-0.02	-0.01	-0.04	-0.02
20	100	$CH_2CH_2^{**} + 2^* \rightarrow CH_2CH^{***} + H^*$	-0.18	-0.01	-0.35	0.04	-0.11	0.00	-0.26	0.04
	111	$CH_2CH_2^{**} + 2^* \rightarrow CH_2CH^{***} + H^*$	-0.05	-0.02	-0.09	-0.02	-0.03	0.00	-0.06	-0.01

#	Facet	Surface reactions	Water (+10%)		Water (-10%)		1,4-dioxane (+10%)		1,4-dioxane (-10%)	
			$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)
21	100	$CH_2CH^{***} \rightarrow CH_2C^* + H^* + *$	-0.08	0.00	-0.15	0.00	-0.06	0.00	-0.11	0.00
	111	$CH_2CH^{***} \rightarrow CH_2C^{**} + H^*$	-0.01	0.00	-0.06	-0.04	-0.01	0.00	-0.04	-0.02
22	100	$CH_3C^* + * \rightarrow CH_2C^* + H^*$	-0.16	-0.08	-0.36	-0.14	-0.11	-0.05	-0.27	-0.12
	111	$CH_3C^* + 2^* \rightarrow CH_2C^{**} + H^*$	-0.03	-0.04	-0.10	-0.05	-0.03	-0.03	-0.08	-0.04
23	100	$CH_3CH^* + 3^* \rightarrow CH_2CH^{***} + H^*$	-0.25	-0.13	-0.53	-0.23	-0.16	-0.08	-0.41	-0.17
	111	$CH_3CH^{**} + 2^* \rightarrow CH_2CH^{***} + H^*$	-0.06	-0.07	-0.10	-0.06	-0.05	-0.04	-0.06	-0.03
24	100	$CH_3CH^* + * \rightarrow CH_3C^* + H^*$	-0.17	-0.07	-0.33	-0.17	-0.11	-0.05	-0.24	-0.13
	111	$CH_3CH^{**} \rightarrow CH_3C^* + H^*$	-0.05	-0.02	-0.07	-0.01	-0.03	-0.01	-0.02	0.00
25	100	$CH_3CH_2^* + * \rightarrow CH_3CH^* + H^*$	-0.14	-0.04	-0.28	-0.08	-0.08	-0.02	-0.19	-0.05
	111	$CH_3CH_2^* + 2^* \rightarrow CH_3CH^{**} + H^*$	-0.05	-0.04	-0.07	-0.03	-0.02	-0.01	-0.02	0.01
26	100	$CH_3CH_3^* + * \rightarrow CH_3CH_2^* + H^*$	-0.15	-0.07	-0.29	-0.17	-0.09	-0.03	-0.20	-0.12
	111	$CH_3CH_3^* + * \rightarrow CH_3CH_2^* + H^*$	-0.03	-0.04	-0.05	-0.04	-0.01	-0.02	-0.01	0.02
27	100	$CH_3CH_2^* + 2^* \rightarrow CH_2CH_2^{**} + H^*$	-0.21	-0.09	-0.47	-0.16	-0.13	-0.04	-0.34	-0.10
	111	$CH_3CH_2^* + 2^* \rightarrow CH_2CH_2^{**} + H^*$	-0.06	-0.05	-0.09	-0.02	-0.03	-0.02	-0.02	0.03
28	100	$CH_3CH_2COOH^* + 2^* \rightarrow CH_3CH_2COO^{**} + H^*$	-0.11	0.02	-0.33	-0.05	-0.07	0.00	-0.25	-0.05
	111	$CH_3CH_2COOH^* + 2^* \rightarrow CH_3CH_2COO^{**} + H^*$	0.04	-0.01	-0.06	-0.08	0.03	0.02	-0.06	-0.03
29	100	$CH_3CH_2COO^{**} \rightarrow CH_3CH_2^* + CO_2^*$	0.01	-0.04	0.22	-0.05	0.05	-0.03	0.21	-0.03
	111	$CH_3CH_2COO^{**} \rightarrow CH_3CH_2^* + CO_2^*$	0.01	-0.07	0.10	-0.07	0.02	-0.04	0.08	-0.02
30	100	$CH_3CH_2COO^{**} + 2^* \rightarrow CH_3CHCOO^{***} + H^*$	-0.20	-0.06	-0.35	-0.04	-0.11	0.00	-0.22	0.03
	111	$CH_3CH_2COO^{**} + 2^* \rightarrow CH_3CHCOO^{***} + H^*$	-0.19	-0.15	-0.27	-0.21	-0.08	-0.06	-0.11	-0.07
31	100	$CH_3CHCOOH^{**} + 2^* \rightarrow CH_3CHCOO^{***} + H^*$	-0.16	0.01	-0.38	0.01	-0.11	0.02	-0.30	0.00
	111	$CH_3CHCOOH^{**} + 2^* \rightarrow CH_3CHCOO^{***} + H^*$	-0.12	-0.04	-0.27	-0.12	-0.06	-0.01	-0.18	-0.09
32	100	$CH_3CHCOOH^{**} + * \rightarrow CH_3CH^* + COOH^{**}$	-0.12	-0.04	-0.09	-0.05	-0.05	-0.03	-0.03	-0.04
	111	$CH_3CHCOOH^{**} + 2^* \rightarrow CH_3CH^{**} + COOH^*$	-0.12	-0.04	-0.17	-0.06	-0.06	-0.02	-0.11	-0.05

#	Facet	Surface reactions	Water	Water	1,4-dioxane	1,4-dioxane

			(+10%)		(-10%)		(+10%)		(-10%)	
			$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)
33	100	$CH_3CHCOO^{***} \rightarrow CH_3CH^* + CO_2^* + *$	0.07	0.04	0.29	0.11	0.07	0.02	0.23	0.10
	111	$CH_3CHCOO^{***} \rightarrow CH_3CH^{**} + CO_2^*$	0.15	0.00	0.30	0.02	0.09	-0.02	0.17	0.00
34	100	$CH_3CHCOO^{***} \rightarrow CH_3CCOO^{**} + H^*$	-0.27	-0.11	-0.45	-0.15	-0.18	-0.05	-0.33	-0.08
	111	$CH_3CHCOO^{***} + * \rightarrow CH_3CCOO^{***} + H^*$	-0.14	-0.10	-0.20	-0.14	-0.09	-0.06	-0.14	-0.10
35	100	$CH_3CCOOH^{**} + * \rightarrow CH_3CCOO^{**} + H^*$	-0.27	-0.05	-0.52	-0.11	-0.16	0.01	-0.38	-0.03
	111	$CH_3CCOOH^{***} + * \rightarrow CH_3CCOO^{***} + H^*$	-0.17	-0.06	-0.31	-0.12	-0.08	0.00	-0.18	-0.03
36	100	$CH_3CCOOH^{**} + * \rightarrow CH_3C^* + COOH^{**}$	-0.13	-0.04	-0.11	0.00	-0.04	0.02	-0.03	0.01
	111	$CH_3CCOOH^{***} \rightarrow CH_3C^* + COOH^{**}$	-0.07	-0.01	-0.06	-0.01	-0.01	0.02	0.00	0.02
37	100	$CH_2CHCOOH^{***} + 2^* \rightarrow CH_2CH^{***} + COOH^{**}$	-0.21	-0.02	-0.29	-0.03	-0.12	-0.03	-0.21	-0.04
	111	$CH_2CHCOOH^{***} + 2^* \rightarrow CH_2CH^{***} + COOH^{**}$	-0.12	-0.04	-0.16	-0.09	-0.07	-0.02	-0.10	-0.06
38	100	$CH_3CCOO^{**} \rightarrow CH_3C^* + CO_2^*$	0.17	0.16	0.41	0.28	0.14	0.11	0.31	0.20
	111	$CH_3CCOO^{***} \rightarrow CH_3C^* + CO_2^* + *$	0.24	0.22	0.43	0.33	0.15	0.13	0.28	0.20
39	100	$COOH^{**} \rightarrow CO_2^* + H^*$	0.04	0.02	0.00	0.03	0.02	0.01	-0.03	-0.01
	111	$COOH^{**} \rightarrow CO_2^* + H^*$	0.14	0.01	0.19	-0.01	0.08	-0.01	0.10	-0.02
40	100	$COOH^{**} \rightarrow CO^* + OH^*$	-0.08	-0.04	-0.19	-0.07	-0.05	-0.01	-0.17	-0.04
	111	$COOH^{**} \rightarrow CO^* + OH^*$	-0.06	-0.02	-0.09	-0.04	-0.04	0.00	-0.06	-0.02
41	100	$H_2O^* + * \rightarrow OH^* + H^*$	-0.08	-0.10	-0.32	-0.27	-0.07	-0.05	-0.25	-0.18
	111	$H_2O^* + * \rightarrow OH^* + H^*$	0.04	-0.03	0.00	-0.14	0.03	-0.01	0.00	-0.10
42	100	$CH_3CH_3(g) + * \rightarrow CH_3CH_3^*$	-0.12	N/A	-0.02	N/A	-0.05	N/A	-0.01	N/A
	111	$CH_3CH_3(g) + * \rightarrow CH_3CH_3^*$	-0.05	N/A	-0.01	N/A	-0.03	N/A	-0.02	N/A
43	100	$CH_2CH_2(g) + 2^* \rightarrow CH_2CH_2^{**}$	-0.20	N/A	-0.22	N/A	-0.09	N/A	-0.13	N/A
	111	$CH_2CH_2(g) + 2^* \rightarrow CH_2CH_2^{**}$	-0.10	N/A	-0.06	N/A	-0.05	N/A	0.00	N/A
44	100	$H_2O(g) + * \rightarrow H_2O^*$	-0.21	N/A	-0.17	N/A	-0.10	N/A	-0.09	N/A
	111	$H_2O(g) + * \rightarrow H_2O^*$ (water: solvent in liquid env)	-0.14	N/A	-0.08	N/A	-0.08	N/A	-0.01	N/A

#	Facet	Surface reactions	Water		Water		1,4-dioxane		1,4-dioxane	

			(+10%)		(-10%)		(+10%)		(-10%)	
			$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}^{water}$ (eV)	$\Delta\Delta G_{TS}^{water}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)	$\Delta\Delta G_{Rxn}$ (eV)	$\Delta\Delta G_{TS}$ (eV)
45	100	CO_2(g) + * → CO_2*	-0.16	N/A	-0.07	N/A	-0.07	N/A	-0.03	N/A
	111	CO_2(g) + * → CO_2*	-0.09	N/A	-0.05	N/A	-0.06	N/A	-0.04	N/A
46	100	CHCH(g) + 2* → CHCH**	-0.23	N/A	-0.26	N/A	-0.10	N/A	-0.15	N/A
	111	CHCH(g) + 3* → CHCH***	-0.14	N/A	-0.12	N/A	-0.07	N/A	-0.05	N/A
47	100	CO (g) + * → CO*	-0.25	N/A	-0.33	N/A	-0.15	N/A	-0.24	N/A
	111	CO (g) + * → CO*	-0.23	N/A	-0.33	N/A	-0.16	N/A	-0.23	N/A
48	100	H_2 (g) + 2* → H* + H*	-0.27	N/A	-0.56	N/A	-0.18	N/A	-0.42	N/A
	111	H_2 (g) + 2* → H* + H*	-0.04	N/A	-0.09	N/A	-0.03	N/A	-0.05	N/A
49	100	$C_4H_8O_2$ (g) + * → $C_4H_8O_2$*	-0.37	N/A	-0.27	N/A	-0.18	N/A	-0.15	N/A
	111	$C_4H_8O_2$ (g) + * → $C_4H_8O_2$* (1,4-dioxane: solvent in liquid env)	-0.27	N/A	-0.16	N/A	-0.17	N/A	-0.10	N/A

Table S2. CO and H lateral interaction coefficients, a_{CO} and a_H, of surface intermediates on Pd(100) and Pd(111) at a temperature of 473 K.

Pd(100)		
Species	a_{CO}	a_H
CH_2C^*	1.084	0.301
CH_2CH^{***}	1.469	-0.071
$CH_2CH_2^{**}$	0.517	-0.135
CH_2CHCO^{***}	1.502	-0.232
$CH_2CHCOOH^{***}$	0.133	-1.131
CH_3C^*	1.114	0.324
CH_3CCO^{**}	2.225	0.102
CH_3CCOO^{**}	2.059	0.247
CH_3CCOOH^{**}	0.853	0.700
CH_3CH^*	0.913	-0.389
$CH_3CH_2^*$	0.300	0.311
$CH_3CH_2CO^{**}$	-0.381	0.583
$CH_3CH_2COO^{**}$	-0.160	0.018
$CH_3CH_2COOH^*$	0.648	0.359
$CH_3CH_3^*$	-0.169	0.094
CH_3CHCO^{**}	0.138	-0.749
CH_3CHCOO^{***}	1.248	-0.707
$CH_3CHCOOH^{**}$	0.939	-0.983
$CHCH^{**}$	1.684	-0.525
$CHCHCO^{**}$	0.607	0.105
$CHCHCOOH^{***}$	0.505	-0.266
CO^*	1.545	-0.169
CO_2^*	-0.016	0.076
$COOH^{**}$	0.973	0.418
H^*	0.484	0.339
H_2O^*	-0.723	-0.077
OH^*	0.729	0.344
$C_4H_8O_2^*$ (1,4-dioxane)	0.077	-0.474

Pd(111)		
Species	a_{CO}	a_H
CH_2C^{**}	0.374	0.318
CH_2CH^{***}	0.231	0.330
$CH_2CH_2^{**}$	-0.061	0.257
CH_2CHCO^{***}	0.512	0.390
$CH_2CHCOOH^{***}$	-0.176	0.317
CH_3C^*	-0.023	0.057
CH_3CCO^{***}	1.577	0.628
CH_3CCOO^{***}	2.282	0.813
CH_3CCOOH^{***}	0.910	0.613
CH_3CH^{**}	0.136	0.228
$CH_3CH_2^*$	-0.050	0.225
$CH_3CH_2CO^{***}$	0.321	0.358
$CH_3CH_2COO^{**}$	0.088	0.235
$CH_3CH_2COOH^*$	-0.753	0.188
$CH_3CH_3^*$	-0.121	0.043
CH_3CHCO^{**}	0.254	0.276
CH_3CHCOO^{***}	1.160	0.477
$CH_3CHCOOH^{**}$	0.882	0.877
$CHCH^{***}$	0.857	0.536
$CHCHCO^{****}$	1.276	0.742
$CHCHCOOH^{***}$	0.452	0.640
CO^*	0.583	0.387
CO_2^*	-0.043	0.003
$COOH^{**}$	0.004	0.317
H^*	0.260	0.113
H_2O^*	-0.507	0.026
OH^*	0.140	0.318
$C_4H_8O_2^*$ (1,4-dioxane)	0.374	0.467

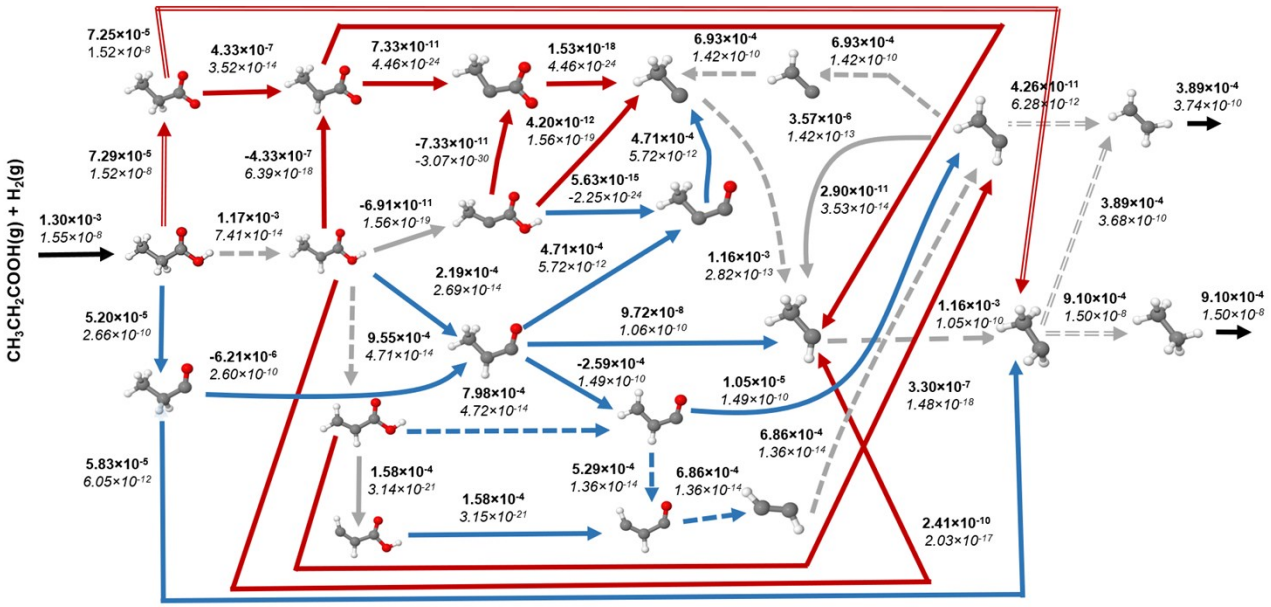

Figure S1. TOFs (s^{-1}) of various elementary steps in water with +10% increased palladium COSMO cavity radius at a temperature of 473 K, a propionic acid gas phase partial pressure of 1 bar, a CO gas phase partial pressure of 1×10^{-5} bar, and a hydrogen partial pressure of 0.01 bar. Black arrows are the adsorption/desorption steps, blue arrows are DCN steps, red arrows are DCX steps, and gray arrows are the steps involved in both DCN and DCX steps. Bold letters indicate rates of elementary steps on Pd(100) and italic letters for the rate of elementary steps on Pd(111). Dominate pathways over Pd(100) and Pd(111) are shown in dashed arrows and double line arrows, respectively. Gray double and dashed line arrows demonstrate an overlapped dominant pathway for Pd(100) and Pd(111).

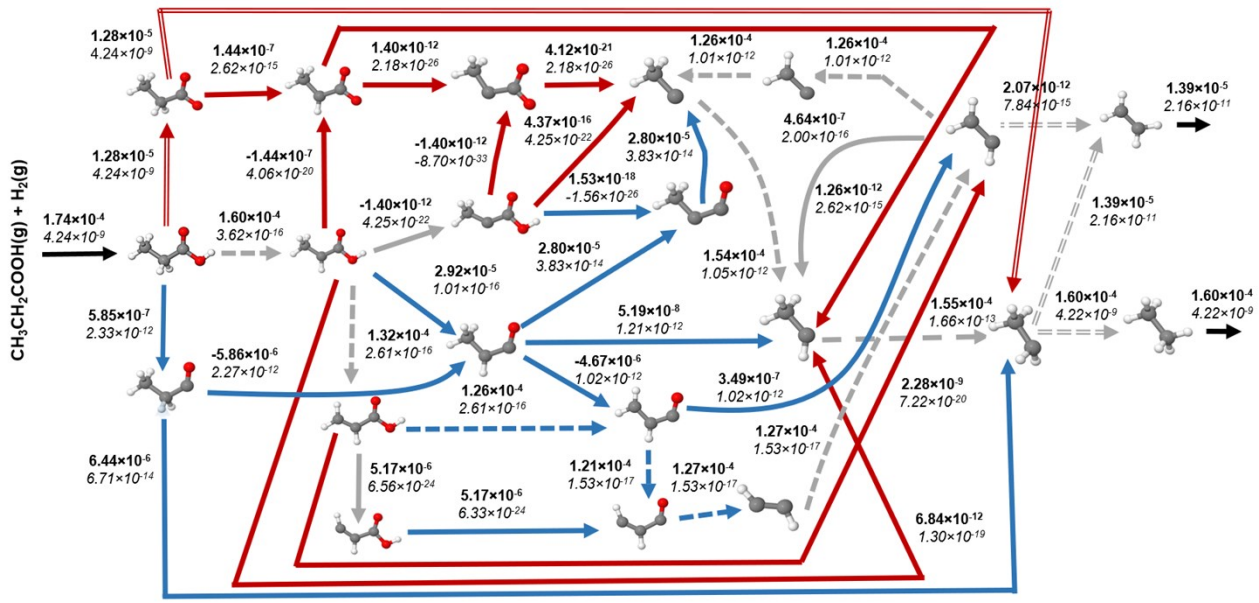

Figure S2. TOFs (s^{-1}) of various elementary steps in water with –10% decreased palladium COSMO cavity radius at a temperature of 473 K, a propionic acid gas phase partial pressure of 1 bar, a CO gas phase partial pressure of 1×10^{-5} bar, and a hydrogen partial pressure of 0.01 bar. Black arrows are the adsorption/desorption steps, blue arrows are DCN steps, red arrows are DCX steps, and gray arrows are the steps involved in both DCN and DCX steps. Bold letters indicate rates of elementary steps on Pd(100) and italic letters for the rate of elementary steps on Pd(111). Dominate pathways over Pd(100) and Pd(111) are shown in dashed arrows and double line arrows, respectively. Gray double and dashed line arrows demonstrate an overlapped dominant pathway for Pd(100) and Pd(111).

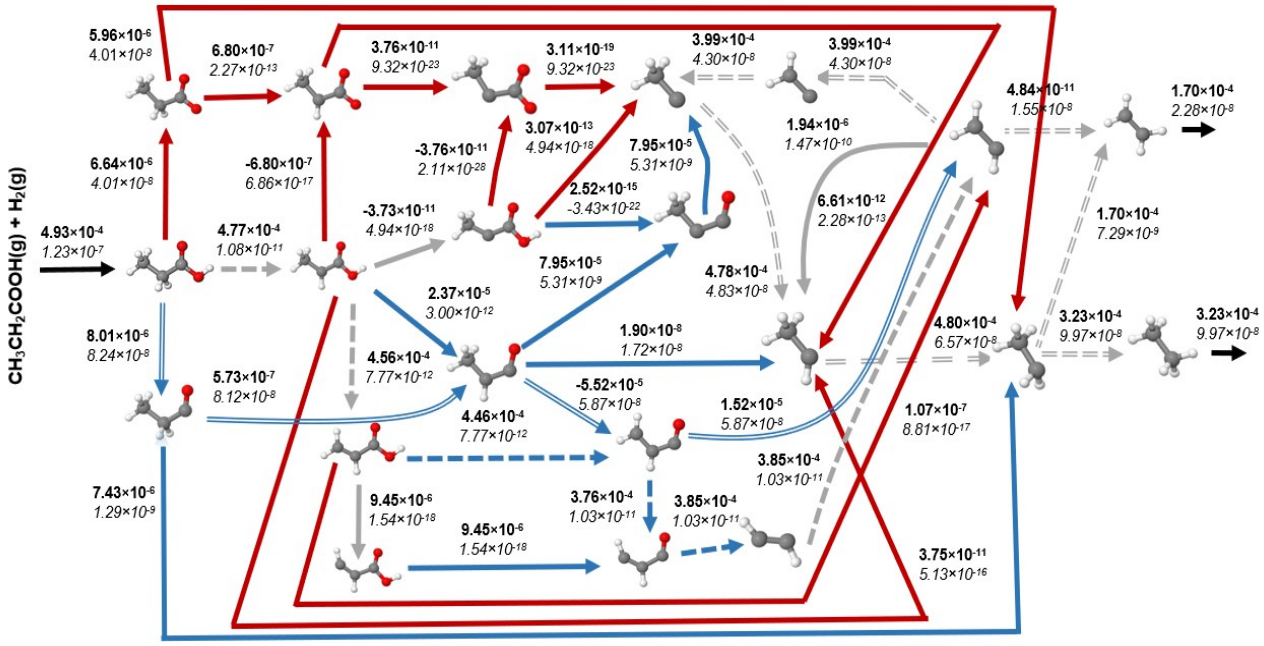

Figure S3. TOFs (s^{-1}) of various elementary steps in 1,4-dioxane with +10% increased palladium COSMO cavity radius at a temperature of 473 K, a propionic acid gas phase partial pressure of 1 bar, a CO gas phase partial pressure of 1×10^{-5} bar and a hydrogen partial pressure of 0.01 bar. Black arrows are the adsorption/desorption steps, blue arrows are DCN steps, red arrows are DCX steps, and gray arrows are the steps involved in both DCN and DCX steps. Bold letters indicate rates of elementary steps on Pd(100) and italic letters for the rate of elementary steps on Pd(111). Dominate pathways over Pd(100) and Pd(111) are shown in dashed arrows and double line arrows, respectively. Gray double and dashed line arrows demonstrate an overlapped dominant pathway for Pd(100) and Pd(111).

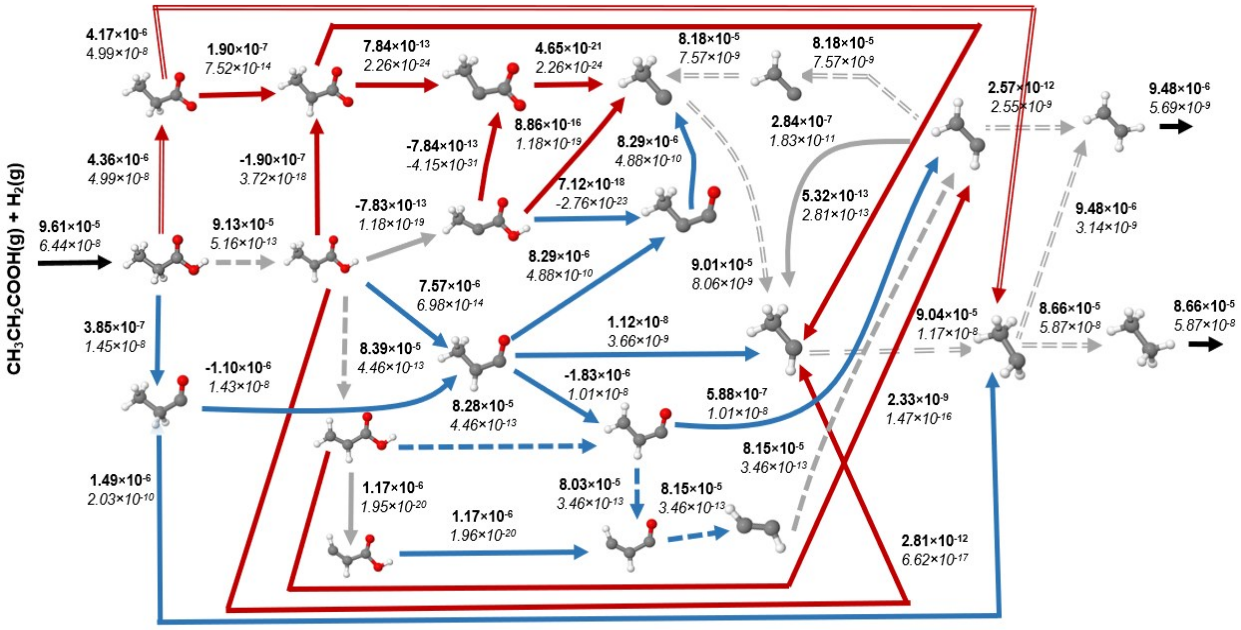

Figure S4. TOFs (s^{-1}) of various elementary steps in 1,4-dioxane with –10% decreased palladium COSMO cavity radius at a temperature of 473 K, a propionic acid gas phase partial pressure of 1 bar, a CO gas phase partial pressure of 1×10^{-5} bar, and a hydrogen partial pressure of 0.01 bar. Black arrows are the adsorption/desorption steps, blue arrows are DCN steps, red arrows are DCX steps, and gray arrows are the steps involved in both DCN and DCX steps. Bold letters indicate the rate of elementary steps on Pd(100) and italic letters for the rate of elementary steps on Pd(111). Dominate pathways over Pd(100) and Pd(111) are shown in dashed arrows and double line arrows, respectively. Gray double and dashed line arrows demonstrate an overlapped dominant pathway for Pd(100) and Pd(111).

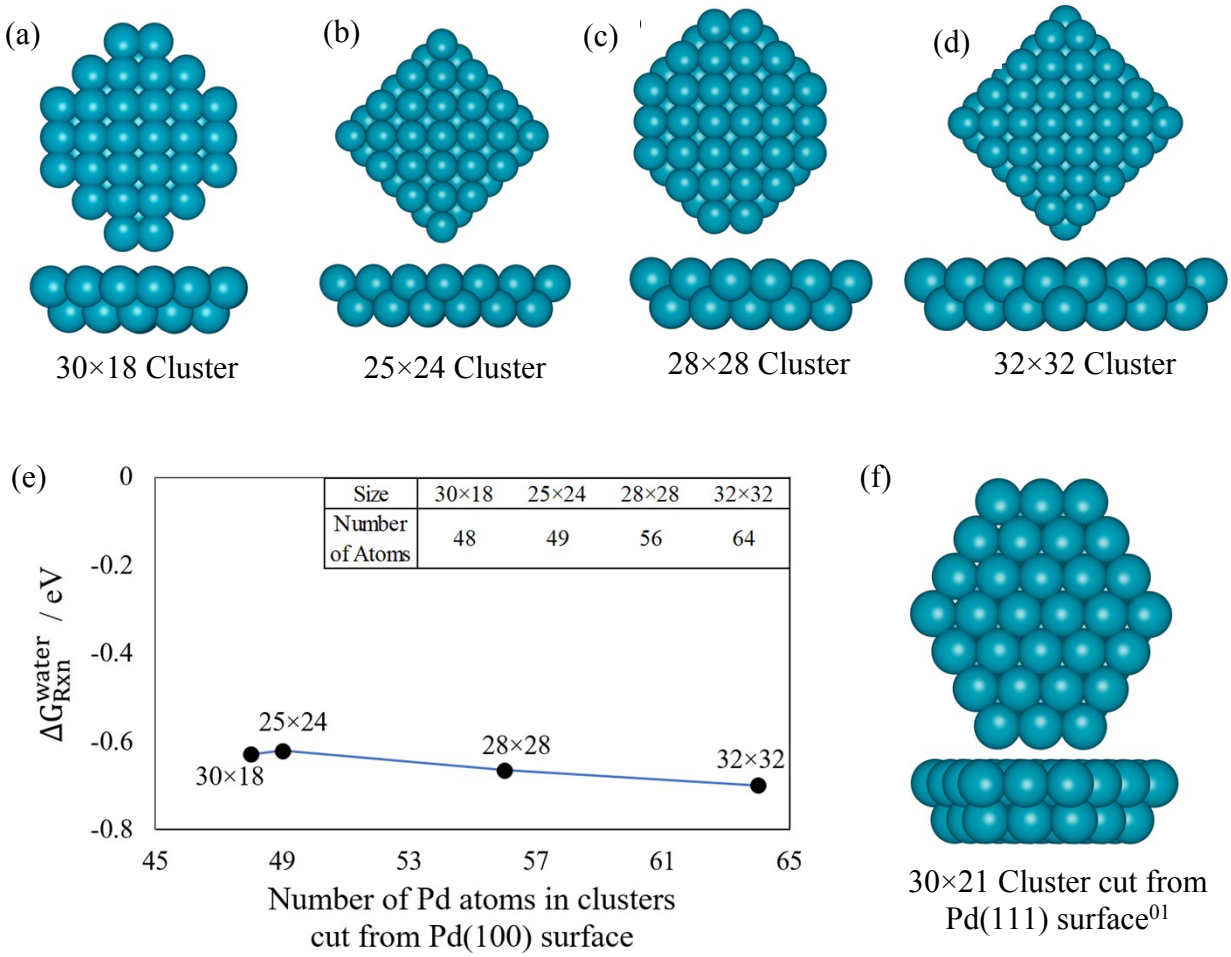

Figure S5: (a-d) Different shapes of cluster sizes cut from Pd(100) surface, which are used in solvation calculations for HDO of propanoic acid on Pd(100). A M×N cluster size notation indicates that the top layer contains M Pd atoms and the bottom layer contains N Pd atoms. (e) Plot of CO adsorption energy on Pd(100) surface in liquid water vs. number of metal atoms in the respective cluster. A 32×32 cluster model represents a converged reaction energy in water with cluster size. (f) 30×21 cluster model (consists of 51 Pd atoms) cut from Pd(111) surface used in solvation calculations for HDO of propanoic acid on Pd(111).[01]

References:

1. S. Behtash, J. Lu, E. Walker, O. Mamun and A. Heyden, *Journal of Catalysis*, 2016, **333**, 171–183.

Sample MATLAB code for microkinetic modeling for Pd(100)

```
format long
close all
%change according to the number of species
M=zeros(29,29);
M(29,29) = 1;
optode = odeset('NonNegative',1:29,'Abstol',1E-25,'RelTol',1E-25); % ,'Mass',M
%optlsq = optimset('TolFun',1E-50,'TolX',1E-50);
%y01 = drchrnd([1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1],1);
%atom_sites=[1 3 2 3 3 1 2 2 2 1 1 2 2 1 1 2 3 2 2 2 3 1 1 2 1 1 1 1 1];
%y02=y01./atom_sites;
%y0 = y02';
y0=zeros(29,1);
y0(28)=1;
[t,y] = ode15s(@PAC_function,[0,50000000],y0,optode);
%y = lsqnonlin(@LAtoGVLODElsq,y0,zeros(1,29),ones(1,29)) %number 28 equals to the species
number
loglog(t,y(:,1),'b',t,y(:,2),'b',t,y(:,3),'b',t,y(:,4),'b',t,y(:,5),'b',t,y(:,6),'r',t,y(:,7),'b',t,y(:,8),'b',t,y(:,9),'b'
,t,y(:,10),'b',t,y(:,11),'b',t,y(:,12),'b',t,y(:,13),'b',t,y(:,14),'b',t,y(:,15),'b',t,y(:,16),'b',t,y(:,17),'b',t,y(:,1
8),'b',t,y(:,19),'b',t,y(:,20),'b',t,y(:,21),'b',t,y(:,22),'r',t,y(:,23),'b',t,y(:,24),'b',t,y(:,25),'g',t,y(:,26),'b',t,
y(:,27),'b',t,y(:,28), 'b',t,y(:,29),'k');
title('Solution of balance Equation');
xlabel('time t'); ylabel('solution y');
l = legend('y 1','y 2','y 3','y 4','y 5','y 6','y 7','y 8','y 9','y 10','y 11','y 12','y 13','y 14','y 15','y 16','y
17','y 18','y 19','y 20','y 21','y 22','y 23','y 24','y 25','y 26','y 27','y 28', 'y 29');
set(l,'Edgecolor',[1 1 1]);
y=y(end,:);
y_site_balance = y.* [1 3 2 3 3 1 2 2 2 1 1 2 2 1 1 2 3 2 2 2 3 1 1 2 1 1 1 1 1]; %update after first
code run
sum(y_site_balance)
KB = 8.6173303e-5;
H = 4.135667662e-15;
Pch3ch2cooh= 1;
Pco2= 1;
Ph2o= 1;
Pch2ch2= 0;
Pch3ch3= 0;
Pchch= 0;
Pco =   1e-05;
Ph2 =   0.01;
Pc4h8o2= 0;
T = 473;
```

```
k0f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_0*KB*T)));
K0 = exp(-(Gr0)/(KB*T));
k0b = k0f/K0;
k1f = (KB*T/H)*exp(-(Ga1)/(KB*T));
K1 = exp(-(Gr1)/(KB*T));
k1b = k1f/K1;
k2f = (KB*T/H)*exp(-(Ga2)/(KB*T));
K2 = exp(-(Gr2)/(KB*T));
k2b = k2f/K2;
k3f = (KB*T/H)*exp(-(Ga3)/(KB*T));
K3 = exp(-(Gr3)/(KB*T));
k3b = k3f/K3;
k4f = (KB*T/H)*exp(-(Ga4)/(KB*T));
K4 = exp(-(Gr4)/(KB*T));
k4b = k4f/K4;
k5f = (KB*T/H)*exp(-(Ga5)/(KB*T));
K5 = exp(-(Gr5)/(KB*T));
k5b = k5f/K5;
k6f = (KB*T/H)*exp(-(Ga6)/(KB*T));
K6 = exp(-(Gr6)/(KB*T));
k6b = k6f/K6;
k7f = (KB*T/H)*exp(-(Ga7)/(KB*T));
K7 = exp(-(Gr7)/(KB*T));
k7b = k7f/K7;
k8f = (KB*T/H)*exp(-(Ga8)/(KB*T));
K8 = exp(-(Gr8)/(KB*T));
k8b = k8f/K8;
k9f = (KB*T/H)*exp(-(Ga9)/(KB*T));
K9 = exp(-(Gr9)/(KB*T));
k9b = k9f/K9;
k10f = (KB*T/H)*exp(-(Ga10)/(KB*T));
K10 = exp(-(Gr10)/(KB*T));
k10b = k10f/K10;
k11f = (KB*T/H)*exp(-(Ga11)/(KB*T));
K11 = exp(-(Gr11)/(KB*T));
k11b = k11f/K11;
k12f = (KB*T/H)*exp(-(Ga12)/(KB*T));
K12 = exp(-(Gr12)/(KB*T));
k12b = k12f/K12;
k13f = (KB*T/H)*exp(-(Ga13)/(KB*T));
```

```
K13 = exp(-(Gr13)/(KB*T));
k13b = k13f/K13;
k14f = (KB*T/H)*exp(-(Ga14)/(KB*T));
K14 = exp(-(Gr14)/(KB*T));
k14b = k14f/K14;
k15f = (KB*T/H)*exp(-(Ga15)/(KB*T));
K15 = exp(-(Gr15)/(KB*T));
k15b = k15f/K15;
k16f = (KB*T/H)*exp(-(Ga16)/(KB*T));
K16 = exp(-(Gr16)/(KB*T));
k16b = k16f/K16;
k17f = (KB*T/H)*exp(-(Ga17)/(KB*T));
K17 = exp(-(Gr17)/(KB*T));
k17b = k17f/K17;
k18f = (KB*T/H)*exp(-(Ga18)/(KB*T));
K18 = exp(-(Gr18)/(KB*T));
k18b = k18f/K18;
k19f = (KB*T/H)*exp(-(Ga19)/(KB*T));
K19 = exp(-(Gr19)/(KB*T));
k19b = k19f/K19;
k20f = (KB*T/H)*exp(-(Ga20)/(KB*T));
K20 = exp(-(Gr20)/(KB*T));
k20b = k20f/K20;
k21f = (KB*T/H)*exp(-(Ga21)/(KB*T));
K21 = exp(-(Gr21)/(KB*T));
k21b = k21f/K21;
k22f = (KB*T/H)*exp(-(Ga22)/(KB*T));
K22 = exp(-(Gr22)/(KB*T));
k22b = k22f/K22;
k23f = (KB*T/H)*exp(-(Ga23)/(KB*T));
K23 = exp(-(Gr23)/(KB*T));
k23b = k23f/K23;
k24f = (KB*T/H)*exp(-(Ga24)/(KB*T));
K24 = exp(-(Gr24)/(KB*T));
k24b = k24f/K24;
k25f = (KB*T/H)*exp(-(Ga25)/(KB*T));
K25 = exp(-(Gr25)/(KB*T));
k25b = k25f/K25;
k26f = (KB*T/H)*exp(-(Ga26)/(KB*T));
K26 = exp(-(Gr26)/(KB*T));
k26b = k26f/K26;
```

```
k27f = (KB*T/H)*exp(-(Ga27)/(KB*T));
K27 = exp(-(Gr27)/(KB*T));
k27b = k27f/K27;
k28f = (KB*T/H)*exp(-(Ga28)/(KB*T));
K28 = exp(-(Gr28)/(KB*T));
k28b = k28f/K28;
k29f = (KB*T/H)*exp(-(Ga29)/(KB*T));
K29 = exp(-(Gr29)/(KB*T));
k29b = k29f/K29;
k30f = (KB*T/H)*exp(-(Ga30)/(KB*T));
K30 = exp(-(Gr30)/(KB*T));
k30b = k30f/K30;
k31f = (KB*T/H)*exp(-(Ga31)/(KB*T));
K31 = exp(-(Gr31)/(KB*T));
k31b = k31f/K31;
k32f = (KB*T/H)*exp(-(Ga32)/(KB*T));
K32 = exp(-(Gr32)/(KB*T));
k32b = k32f/K32;
k33f = (KB*T/H)*exp(-(Ga33)/(KB*T));
K33 = exp(-(Gr33)/(KB*T));
k33b = k33f/K33;
k34f = (KB*T/H)*exp(-(Ga34)/(KB*T));
K34 = exp(-(Gr34)/(KB*T));
k34b = k34f/K34;
k35f = (KB*T/H)*exp(-(Ga35)/(KB*T));
K35 = exp(-(Gr35)/(KB*T));
k35b = k35f/K35;
k36f = (KB*T/H)*exp(-(Ga36)/(KB*T));
K36 = exp(-(Gr36)/(KB*T));
k36b = k36f/K36;
k37f = (KB*T/H)*exp(-(Ga37)/(KB*T));
K37 = exp(-(Gr37)/(KB*T));
k37b = k37f/K37;
k38f = (KB*T/H)*exp(-(Ga38)/(KB*T));
K38 = exp(-(Gr38)/(KB*T));
k38b = k38f/K38;
k39f = (KB*T/H)*exp(-(Ga39)/(KB*T));
K39 = exp(-(Gr39)/(KB*T));
k39b = k39f/K39;
k40f = (KB*T/H)*exp(-(Ga40)/(KB*T));
K40 = exp(-(Gr40)/(KB*T));
```

```
k40b = k40f/K40;
k41f = (KB*T/H)*exp(-(Ga41)/(KB*T));
K41 = exp(-(Gr41)/(KB*T));
k41b = k41f/K41;
k42f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_42*KB*T)));
K42 = exp(-(Gr42)/(KB*T));
k42b = k42f/K42;
k43f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_43*KB*T)));
K43 = exp(-(Gr43)/(KB*T));
k43b = k43f/K43;
k44f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_44*KB*T)));
K44 = exp(-(Gr44)/(KB*T));
k44b = k44f/K44;
k45f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_45*KB*T)));
K45 = exp(-(Gr45)/(KB*T));
k45b = k45f/K45;
k46f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_46*KB*T)));
K46 = exp(-(Gr46)/(KB*T));
k46b = k46f/K46;
k47f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_47*KB*T)));
K47 = exp(-(Gr47)/(KB*T));
k47b = k47f/K47;
k48f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_48*KB*T)));
K48 = exp(-(Gr48)/(KB*T));
k48b = k48f/K48;
k49f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_49*KB*T)));
K49 = exp(-(Gr49)/(KB*T));
k49b = k49f/K49;
r0=k0f*Pch3ch2cooh*y(28)-k0b*y(14);
r1=k1f*y(14)*y(28)^2-k1b*y(12)*y(27);
r2=k2f*y(14)*y(28)^2-k2b*y(18)*y(25);
r3=k3f*y(12)-k3b*y(11)*y(22);
r4=k4f*y(12)*y(28)-k4b*y(16)*y(25);
r5=k5f*y(18)*y(28)-k5b*y(16)*y(27);
r6=k6f*y(18)*y(28)^2-k6b*y(5)*y(25);
r7=k7f*y(18)*y(28)-k7b*y(9)*y(25);
r8=k8f*y(16)-k8b*y(10)*y(22);
r9=k9f*y(16)*y(28)-k9b*y(7)*y(25);
r10=k10f*y(16)*y(28)^2-k10b*y(4)*y(25);
r11=k11f*y(5)*y(28)-k11b*y(4)*y(27);
r12=k12f*y(5)*y(28)-k12b*y(21)*y(25);
```

```
r13=k13f*y(9)*y(28)-k13b*y(7)*y(27);
r14=k14f*y(7)-k14b*y(6)*y(22);
r15=k15f*y(4)*y(28)-k15b*y(2)*y(22);
r16=k16f*y(4)-k16b*y(20)*y(25);
r17=k17f*y(21)-k17b*y(20)*y(27);
r18=k18f*y(20)*y(28)-k18b*y(19)*y(22);
r19=k19f*y(2)-k19b*y(19)*y(25);
r20=k20f*y(3)*y(28)^2-k20b*y(2)*y(25);
r21=k21f*y(2)-k21b*y(1)*y(25)*y(28);
r22=k22f*y(6)*y(28)-k22b*y(1)*y(25);
r23=k23f*y(10)*y(28)^3-k23b*y(2)*y(25);
r24=k24f*y(10)*y(28)-k24b*y(6)*y(25);
r25=k25f*y(11)*y(28)-k25b*y(10)*y(25);
r26=k26f*y(15)*y(28)-k26b*y(11)*y(25);
r27=k27f*y(11)*y(28)^2-k27b*y(3)*y(25);
r28=k28f*y(14)*y(28)^2-k28b*y(13)*y(25);
r29=k29f*y(13)-k29b*y(11)*y(23);
r30=k30f*y(13)*y(28)^2-k30b*y(17)*y(25);
r31=k31f*y(18)*y(28)^2-k31b*y(17)*y(25);
r32=k32f*y(18)*y(28)-k32b*y(10)*y(24);
r33=k33f*y(17)-k33b*y(10)*y(23)*y(28);
r34=k34f*y(17)-k34b*y(8)*y(25);
r35=k35f*y(9)*y(28)-k35b*y(8)*y(25);
r36=k36f*y(9)*y(28)-k36b*y(6)*y(24);
r37=k37f*y(5)*y(28)^2-k37b*y(2)*y(24);
r38=k38f*y(8)-k38b*y(6)*y(23);
r39=k39f*y(24)-k39b*y(23)*y(25);
r40=k40f*y(24)-k40b*y(22)*y(27);
r41=k41f*y(26)*y(28)-k41b*y(27)*y(25);
r42=k42f*Pch3ch3*y(28)-k42b*y(15);
r43=k43f*Pch2ch2*y(28)^2-k43b*y(3);
r44=k44f*Ph2o*y(28)-k44b*y(26);
r45=k45f*Pco2*y(28)-k45b*y(23);
r46=k46f*Pchch*y(28)^2-k46b*y(19);
r47=k47f*Pco*y(28)-k47b*y(22);
r48=k48f*Ph2*y(28)^2-k48b*y(25)*y(25);
r49=k49f*Pc4h8o2*y(29)-k49b*y(1);
f0 = k0f*Pch3ch2cooh*y(28);
b0 = k0b*y(14);
f1 = k1f*y(14)*y(28)^2;
b1 = k1b*y(12)*y(27);
```

```
f2 = k2f*y(14)*y(28)^2;
b2 = k2b*y(18)*y(25);
f3 = k3f*y(12);
b3 = k3b*y(11)*y(22);
f4 = k4f*y(12)*y(28);
b4 = k4b*y(16)*y(25);
f5 = k5f*y(18)*y(28);
b5 = k5b*y(16)*y(27);
f6 = k6f*y(18)*y(28)^2;
b6 = k6b*y(5)*y(25);
f7 = k7f*y(18)*y(28);
b7 = k7b*y(9)*y(25);
f8 = k8f*y(16);
b8 = k8b*y(10)*y(22);
f9 = k9f*y(16)*y(28);
b9 = k9b*y(7)*y(25);
f10 = k10f*y(16)*y(28)^2;
b10 = k10b*y(4)*y(25);
f11 = k11f*y(5)*y(28);
b11 = k11b*y(4)*y(27);
f12 = k12f*y(5)*y(28);
b12 = k12b*y(21)*y(25);
f13 = k13f*y(9)*y(28);
b13 = k13b*y(7)*y(27);
f14 = k14f*y(7);
b14 = k14b*y(6)*y(22);
f15 = k15f*y(4)*y(28);
b15 = k15b*y(2)*y(22);
f16 = k16f*y(4);
b16 = k16b*y(20)*y(25);
f17 = k17f*y(21);
b17 = k17b*y(20)*y(27);
f18 = k18f*y(20)*y(28);
b18 = k18b*y(19)*y(22);
f19 = k19f*y(2);
b19 = k19b*y(19)*y(25);
f20 = k20f*y(3)*y(28)^2;
b20 = k20b*y(2)*y(25);
f21 = k21f*y(2);
b21 = k21b*y(1)*y(25)*y(28);
f22 = k22f*y(6)*y(28);
```

```
b22 = k22b*y(1)*y(25);
f23 = k23f*y(10)*y(28)^3;
b23 = k23b*y(2)*y(25);
f24 = k24f*y(10)*y(28);
b24 = k24b*y(6)*y(25);
f25 = k25f*y(11)*y(28);
b25 = k25b*y(10)*y(25);
f26 = k26f*y(15)*y(28);
b26 = k26b*y(11)*y(25);
f27 = k27f*y(11)*y(28)^2;
b27 = k27b*y(3)*y(25);
f28 = k28f*y(14)*y(28)^2;
b28 = k28b*y(13)*y(25);
f29 = k29f*y(13);
b29 = k29b*y(11)*y(23);
f30 = k30f*y(13)*y(28)^2;
b30 = k30b*y(17)*y(25);
f31 = k31f*y(18)*y(28)^2;
b31 = k31b*y(17)*y(25);
f32 = k32f*y(18)*y(28);
b32 = k32b*y(10)*y(24);
f33 = k33f*y(17);
b33 = k33b*y(10)*y(23)*y(28);
f34 = k34f*y(17);
b34 = k34b*y(8)*y(25);
f35 = k35f*y(9)*y(28);
b35 = k35b*y(8)*y(25);
f36 = k36f*y(9)*y(28);
b36 = k36b*y(6)*y(24);
f37 = k37f*y(5)*y(28)^2;
b37 = k37b*y(2)*y(24);
f38 = k38f*y(8);
b38 = k38b*y(6)*y(23);
f39 = k39f*y(24);
b39 = k39b*y(23)*y(25);
f40 = k40f*y(24);
b40 = k40b*y(22)*y(27);
f41 = k41f*y(26)*y(28);
b41 = k41b*y(27)*y(25);
f42 = k42f*Pch3ch3*y(28);
b42 = k42b*y(15);
```

```
f43 = k43f*Pch2ch2*y(28)^2;
b43 = k43b*y(3);
f44 = k44f*Ph2o*y(28);
b44 = k44b*y(26);
f45 = k45f*Pco2*y(28);
b45 = k45b*y(23);
f46 = k46f*Pchch*y(28)^2;
b46 = k46b*y(19);
f47 = k47f*Pco*y(28);
b47 = k47b*y(22);
f48 = k48f*Ph2*y(28)^2;
b48 = k48b*y(25)*y(25);
f49 = k49f*Pc4h8o2*y(29);
b49 = k49b*y(1);
r=[r0 r1 r2 r3 r4 r5 r6 r7 r8 r9 r10 r11 r12 r13 r14 r15 r16 r17 r18 r19 r20 r21 r22 r23 r24 r25 r26
r27 r28 r29 r30 r31 r32 r33 r34 r35 r36 r37 r38 r39 r40 r41 r42 r43 r44 r45 r46 r47 r48 r49];
f=[f0 f1 f2 f3 f4 f5 f6 f7 f8 f9 f10 f11 f12 f13 f14 f15 f16 f17 f18 f19 f20 f21 f22 f23 f24 f25 f26
f27 f28 f29 f30 f31 f32 f33 f34 f35 f36 f37 f38 f39 f40 f41 f42 f43 f44 f45 f46 f47 f48 f49];
b=[b0 b1 b2 b3 b4 b5 b6 b7 b8 b9 b10 b11 b12 b13 b14 b15 b16 b17 b18 b19 b20 b21 b22 b23 b24
b25 b26 b27 b28 b29 b30 b31 b32 b33 b34 b35 b36 b37 b38 b39 b40 b41 b42 b43 b44 b45 b46
b47 b48 b49];
r=r';
f=f';
b=b';
y=y';
%coverage
fileID = fopen('coverage','a');
fmt = '%5d\r\n';
fprintf(fileID,fmt,y);
fclose(fileID);
%Rate for each iteration
rate = fopen('rate','a');
frate=fopen('frate','a');
brate=fopen('brate','a');
fmt = '%5d\r\n';
fprintf(rate,fmt,r);
fprintf(frate,fmt,f);
fprintf(brate,fmt,b);
fclose(rate);
fclose(frate);
fclose(brate);
```

```
%TOF for each iteration
PAC_rate=fopen('TOF','a');
PAC_TOF=r1+r2+r28;
fmt = '%5d\r\n';
fprintf(PAC_rate,fmt,PAC_TOF);
fclose(PAC_rate);
```

Sample MATLAB code for microkinetic modeling for Pd(111)

```
format long
close all
%change according to the number of species
M=zeros(29,29);
M(29,29) = 1;
optode = odeset('NonNegative',1:29,'Abstol',1E-25,'RelTol',1E-25); % ,'Mass',M
%optlsq = optimset('TolFun',1E-50,'TolX',1E-50);
%y01 = drchrnd([1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1],1);
%atom_sites=[1 3 2 3 3 1 2 2 2 1 1 2 2 1 1 2 3 2 2 2 3 1 1 2 1 1 1 1 1];
%y02=y01./atom_sites;
%y0 = y02';
y0=zeros(29,1);
y0(29)=1;
[t,y] = ode15s(@PAC_function,[0,50000000],y0,optode);
%y = lsqnonlin(@LAtoGVLODElsq,y0,zeros(1,29),ones(1,29)) %number 29 equals to the species
number
loglog(t,
y(:,1),'b',t,y(:,2),'b',t,y(:,3),'b',t,y(:,4),'b',t,y(:,5),'b',t,y(:,6),'r',t,y(:,7),'b',t,y(:,8),'b',t,y(:,9),'b',t,y(:,10)
,'b',t,y(:,11),'b',t,y(:,12),'b',t,y(:,13),'b',t,y(:,14),'b',t,y(:,15),'b',t,y(:,16),'b',t,y(:,17),'b',t,y(:,18),'b',t,y
(:,19),'b',t,y(:,20),'b',t,y(:,21),'b',t,y(:,22),'r',t,y(:,23),'b',t,y(:,24),'b',t,y(:,25),'g',t,y(:,26),'b',t,y(:,27),'
b',t,y(:,28),'b',t,y(:,29),'k');
title('Solution of balance Equation');
xlabel('time t'); ylabel('solution y');
l = legend('y 1','y 2','y 3','y 4','y 5','y 6','y 7','y 8','y 9','y 10','y 11','y 12','y 13','y 14','y 15','y 16','y
17','y 18','y 19','y 20','y 21','y 22','y 23','y 24','y 25','y 26','y 27','y 28','y 29');
set(l,'Edgecolor',[1 1 1]);
y=y(end,:);
y_site_balance = y.* [1 3 2 3 3 1 2 2 2 1 1 2 2 1 1 2 3 2 2 2 3 1 1 2 1 1 1 1 1]; %update after first
code run
sum(y_site_balance)
KB = 8.6173303e-5;
H = 4.135667662e-15;
Pch3ch2cooh= 1;
Pco2= 1;
Ph2o= 1;
Pch2ch2= 0;
Pch3ch3= 0;
Pchch= 0;
Pc4h8o2= 0;
Pco =  1e-05;
Ph2 =  0.01;
```

```
T = 473;
k0f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_0*KB*T)));
K0 = exp(-(Gr0)/(KB*T));
k0b = k0f/K0;
k1f = (KB*T/H)*exp(-(Ga1)/(KB*T));
K1 = exp(-(Gr1)/(KB*T));
k1b = k1f/K1;
k2f = (KB*T/H)*exp(-(Ga2)/(KB*T));
K2 = exp(-(Gr2)/(KB*T));
k2b = k2f/K2;
k3f = (KB*T/H)*exp(-(Ga3)/(KB*T));
K3 = exp(-(Gr3)/(KB*T));
k3b = k3f/K3;
k4f = (KB*T/H)*exp(-(Ga4)/(KB*T));
K4 = exp(-(Gr4)/(KB*T));
k4b = k4f/K4;
k5f = (KB*T/H)*exp(-(Ga5)/(KB*T));
K5 = exp(-(Gr5)/(KB*T));
k5b = k5f/K5;
k6f = (KB*T/H)*exp(-(Ga6)/(KB*T));
K6 = exp(-(Gr6)/(KB*T));
k6b = k6f/K6;
k7f = (KB*T/H)*exp(-(Ga7)/(KB*T));
K7 = exp(-(Gr7)/(KB*T));
k7b = k7f/K7;
k8f = (KB*T/H)*exp(-(Ga8)/(KB*T));
K8 = exp(-(Gr8)/(KB*T));
k8b = k8f/K8;
k9f = (KB*T/H)*exp(-(Ga9)/(KB*T));
K9 = exp(-(Gr9)/(KB*T));
k9b = k9f/K9;
k10f = (KB*T/H)*exp(-(Ga10)/(KB*T));
K10 = exp(-(Gr10)/(KB*T));
k10b = k10f/K10;
k11f = (KB*T/H)*exp(-(Ga11)/(KB*T));
K11 = exp(-(Gr11)/(KB*T));
k11b = k11f/K11;
k12f = (KB*T/H)*exp(-(Ga12)/(KB*T));
K12 = exp(-(Gr12)/(KB*T));
k12b = k12f/K12;
k13f = (KB*T/H)*exp(-(Ga13)/(KB*T));
```

```
K13 = exp(-(Gr13)/(KB*T));
k13b = k13f/K13;
k14f = (KB*T/H)*exp(-(Ga14)/(KB*T));
K14 = exp(-(Gr14)/(KB*T));
k14b = k14f/K14;
k15f = (KB*T/H)*exp(-(Ga15)/(KB*T));
K15 = exp(-(Gr15)/(KB*T));
k15b = k15f/K15;
k16f = (KB*T/H)*exp(-(Ga16)/(KB*T));
K16 = exp(-(Gr16)/(KB*T));
k16b = k16f/K16;
k17f = (KB*T/H)*exp(-(Ga17)/(KB*T));
K17 = exp(-(Gr17)/(KB*T));
k17b = k17f/K17;
k18f = (KB*T/H)*exp(-(Ga18)/(KB*T));
K18 = exp(-(Gr18)/(KB*T));
k18b = k18f/K18;
k19f = (KB*T/H)*exp(-(Ga19)/(KB*T));
K19 = exp(-(Gr19)/(KB*T));
k19b = k19f/K19;
k20f = (KB*T/H)*exp(-(Ga20)/(KB*T));
K20 = exp(-(Gr20)/(KB*T));
k20b = k20f/K20;
k21f = (KB*T/H)*exp(-(Ga21)/(KB*T));
K21 = exp(-(Gr21)/(KB*T));
k21b = k21f/K21;
k22f = (KB*T/H)*exp(-(Ga22)/(KB*T));
K22 = exp(-(Gr22)/(KB*T));
k22b = k22f/K22;
k23f = (KB*T/H)*exp(-(Ga23)/(KB*T));
K23 = exp(-(Gr23)/(KB*T));
k23b = k23f/K23;
k24f = (KB*T/H)*exp(-(Ga24)/(KB*T));
K24 = exp(-(Gr24)/(KB*T));
k24b = k24f/K24;
k25f = (KB*T/H)*exp(-(Ga25)/(KB*T));
K25 = exp(-(Gr25)/(KB*T));
k25b = k25f/K25;
k26f = (KB*T/H)*exp(-(Ga26)/(KB*T));
K26 = exp(-(Gr26)/(KB*T));
k26b = k26f/K26;
```

```
k27f = (KB*T/H)*exp(-(Ga27)/(KB*T));
K27 = exp(-(Gr27)/(KB*T));
k27b = k27f/K27;
k28f = (KB*T/H)*exp(-(Ga28)/(KB*T));
K28 = exp(-(Gr28)/(KB*T));
k28b = k28f/K28;
k29f = (KB*T/H)*exp(-(Ga29)/(KB*T));
K29 = exp(-(Gr29)/(KB*T));
k29b = k29f/K29;
k30f = (KB*T/H)*exp(-(Ga30)/(KB*T));
K30 = exp(-(Gr30)/(KB*T));
k30b = k30f/K30;
k31f = (KB*T/H)*exp(-(Ga31)/(KB*T));
K31 = exp(-(Gr31)/(KB*T));
k31b = k31f/K31;
k32f = (KB*T/H)*exp(-(Ga32)/(KB*T));
K32 = exp(-(Gr32)/(KB*T));
k32b = k32f/K32;
k33f = (KB*T/H)*exp(-(Ga33)/(KB*T));
K33 = exp(-(Gr33)/(KB*T));
k33b = k33f/K33;
k34f = (KB*T/H)*exp(-(Ga34)/(KB*T));
K34 = exp(-(Gr34)/(KB*T));
k34b = k34f/K34;
k35f = (KB*T/H)*exp(-(Ga35)/(KB*T));
K35 = exp(-(Gr35)/(KB*T));
k35b = k35f/K35;
k36f = (KB*T/H)*exp(-(Ga36)/(KB*T));
K36 = exp(-(Gr36)/(KB*T));
k36b = k36f/K36;
k37f = (KB*T/H)*exp(-(Ga37)/(KB*T));
K37 = exp(-(Gr37)/(KB*T));
k37b = k37f/K37;
k38f = (KB*T/H)*exp(-(Ga38)/(KB*T));
K38 = exp(-(Gr38)/(KB*T));
k38b = k38f/K38;
k39f = (KB*T/H)*exp(-(Ga39)/(KB*T));
K39 = exp(-(Gr39)/(KB*T));
k39b = k39f/K39;
k40f = (KB*T/H)*exp(-(Ga40)/(KB*T));
K40 = exp(-(Gr40)/(KB*T));
```

```
k40b = k40f/K40;
k41f = (KB*T/H)*exp(-(Ga41)/(KB*T));
K41 = exp(-(Gr41)/(KB*T));
k41b = k41f/K41;
k42f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_42*KB*T)));
K42 = exp(-(Gr42)/(KB*T));
k42b = k42f/K42;
k43f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_43*KB*T)));
K43 = exp(-(Gr43)/(KB*T));
k43b = k43f/K43;
k44f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_44*KB*T)));
K44 = exp(-(Gr44)/(KB*T));
k44b = k44f/K44;
k45f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_45*KB*T)));
K45 = exp(-(Gr45)/(KB*T));
k45b = k45f/K45;
k46f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_46*KB*T)));
K46 = exp(-(Gr46)/(KB*T));
k46b = k46f/K46;
k47f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_47*KB*T)));
K47 = exp(-(Gr47)/(KB*T));
k47b = k47f/K47;
k48f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_48*KB*T)));
K48 = exp(-(Gr48)/(KB*T));
k48b = k48f/K48;
k49f = ((CONV3*sqrt(NA))/(N0*sqrt(2*pi*MASS_gas_49*KB*T)));
K49 = exp(-(Gr49)/(KB*T));
k49b = k49f/K49;
r0=k0f*Pch3ch2cooh*y(29)-k0b*y(15);
r1=k1f*y(15)*y(29)^3-k1b*y(13)*y(28);
r2=k2f*y(15)*y(29)^2-k2b*y(19)*y(26);
r3=k3f*y(13)-k3b*y(12)*y(23)*y(29);
r4=k4f*y(13)-k4b*y(17)*y(26);
r5=k5f*y(19)*y(29)-k5b*y(17)*y(28);
r6=k6f*y(19)*y(29)^2-k6b*y(6)*y(26);
r7=k7f*y(19)*y(29)^2-k7b*y(10)*y(26);
r8=k8f*y(17)*y(29)-k8b*y(11)*y(23);
r9=k9f*y(17)*y(29)^2-k9b*y(8)*y(26);
r10=k10f*y(17)*y(29)^2-k10b*y(5)*y(26);
r11=k11f*y(6)*y(29)-k11b*y(5)*y(28);
r12=k12f*y(6)*y(29)-k12b*y(22)*y(26);
```

```
r13=k13f*y(10)*y(29)-k13b*y(8)*y(28);
r14=k14f*y(8)-k14b*y(7)*y(23)*y(29);
r15=k15f*y(5)*y(29)-k15b*y(3)*y(23);
r16=k16f*y(5)*y(29)^2-k16b*y(21)*y(26);
r17=k17f*y(22)*y(29)^2-k17b*y(21)*y(28);
r18=k18f*y(21)-k18b*y(20)*y(23);
r19=k19f*y(3)*y(29)-k19b*y(20)*y(26);
r20=k20f*y(4)*y(29)^2-k20b*y(3)*y(26);
r21=k21f*y(3)-k21b*y(2)*y(26);
r22=k22f*y(7)*y(29)^2-k22b*y(2)*y(26);
r23=k23f*y(11)*y(29)^2-k23b*y(3)*y(26);
r24=k24f*y(11)-k24b*y(7)*y(26);
r25=k25f*y(12)*y(29)^2-k25b*y(11)*y(26);
r26=k26f*y(16)*y(29)-k26b*y(12)*y(26);
r27=k27f*y(12)*y(29)^2-k27b*y(4)*y(26);
r28=k28f*y(15)*y(29)^2-k28b*y(14)*y(26);
r29=k29f*y(14)-k29b*y(12)*y(24);
r30=k30f*y(14)*y(29)^2-k30b*y(18)*y(26);
r31=k31f*y(19)*y(29)^2-k31b*y(18)*y(26);
r32=k32f*y(19)*y(29)^2-k32b*y(11)*y(25);
r33=k33f*y(18)-k33b*y(11)*y(24);
r34=k34f*y(18)*y(29)-k34b*y(9)*y(26);
r35=k35f*y(10)*y(29)-k35b*y(9)*y(26);
r36=k36f*y(10)-k36b*y(7)*y(25);
r37=k37f*y(6)*y(29)^2-k37b*y(3)*y(25);
r38=k38f*y(9)-k38b*y(7)*y(24)*y(29);
r39=k39f*y(25)-k39b*y(24)*y(26);
r40=k40f*y(25)-k40b*y(23)*y(28);
r41=k41f*y(27)*y(29)-k41b*y(28)*y(26);
r42=k42f*Pch3ch3*y(29)-k42b*y(16);
r43=k43f*Pch2ch2*y(29)^2-k43b*y(4);
r44=k44f*Ph2o*y(29)-k44b*y(27);
r45=k45f*Pco2*y(29)-k45b*y(24);
r46=k46f*Pchch*y(29)^3-k46b*y(20);
r47=k47f*Pco*y(29)-k47b*y(23);
r48=k48f*Ph2*y(29)^2-k48b*y(26)*y(26);
r49=k49f*Pc4h8o2*y(29)-k49b*y(1);
f0 = k0f*Pch3ch2cooh*y(29);
b0 = k0b*y(15);
f1 = k1f*y(15)*y(29)^3;
b1 = k1b*y(13)*y(28);
```

```
f2 = k2f*y(15)*y(29)^2;
b2 = k2b*y(19)*y(26);
f3 = k3f*y(13);
b3 = k3b*y(12)*y(23)*y(29);
f4 = k4f*y(13);
b4 = k4b*y(17)*y(26);
f5 = k5f*y(19)*y(29);
b5 = k5b*y(17)*y(28);
f6 = k6f*y(19)*y(29)^2;
b6 = k6b*y(6)*y(26);
f7 = k7f*y(19)*y(29)^2;
b7 = k7b*y(10)*y(26);
f8 = k8f*y(17)*y(29);
b8 = k8b*y(11)*y(23);
f9 = k9f*y(17)*y(29)^2;
b9 = k9b*y(8)*y(26);
f10 = k10f*y(17)*y(29)^2;
b10 = k10b*y(5)*y(26);
f11 = k11f*y(6)*y(29);
b11 = k11b*y(5)*y(28);
f12 = k12f*y(6)*y(29);
b12 = k12b*y(22)*y(26);
f13 = k13f*y(10)*y(29);
b13 = k13b*y(8)*y(28);
f14 = k14f*y(8);
b14 = k14b*y(7)*y(23)*y(29);
f15 = k15f*y(5)*y(29);
b15 = k15b*y(3)*y(23);
f16 = k16f*y(5)*y(29)^2;
b16 = k16b*y(21)*y(26);
f17 = k17f*y(22)*y(29)^2;
b17 = k17b*y(21)*y(28);
f18 = k18f*y(21);
b18 = k18b*y(20)*y(23);
f19 = k19f*y(3)*y(29);
b19 = k19b*y(20)*y(26);
f20 = k20f*y(4)*y(29)^2;
b20 = k20b*y(3)*y(26);
f21 = k21f*y(3);
b21 = k21b*y(2)*y(26);
f22 = k22f*y(7)*y(29)^2;
```

```
b22 = k22b*y(2)*y(26);
f23 = k23f*y(11)*y(29)^2;
b23 = k23b*y(3)*y(26);
f24 = k24f*y(11);
b24 = k24b*y(7)*y(26);
f25 = k25f*y(12)*y(29)^2;
b25 = k25b*y(11)*y(26);
f26 = k26f*y(16)*y(29);
b26 = k26b*y(12)*y(26);
f27 = k27f*y(12)*y(29)^2;
b27 = k27b*y(4)*y(26);
f28 = k28f*y(15)*y(29)^2;
b28 = k28b*y(14)*y(26);
f29 = k29f*y(14);
b29 = k29b*y(12)*y(24);
f30 = k30f*y(14)*y(29)^2;
b30 = k30b*y(18)*y(26);
f31 = k31f*y(19)*y(29)^2;
b31 = k31b*y(18)*y(26);
f32 = k32f*y(19)*y(29)^2;
b32 = k32b*y(11)*y(25);
f33 = k33f*y(18);
b33 = k33b*y(11)*y(24);
f34 = k34f*y(18)*y(29);
b34 = k34b*y(9)*y(26);
f35 = k35f*y(10)*y(29);
b35 = k35b*y(9)*y(26);
f36 = k36f*y(10);
b36 = k36b*y(7)*y(25);
f37 = k37f*y(6)*y(29)^2;
b37 = k37b*y(3)*y(25);
f38 = k38f*y(9);
b38 = k38b*y(7)*y(24)*y(29);
f39 = k39f*y(25);
b39 = k39b*y(24)*y(26);
f40 = k40f*y(25);
b40 = k40b*y(23)*y(28);
f41 = k41f*y(27)*y(29);
b41 = k41b*y(28)*y(26);
f42 = k42f*Pch3ch3*y(29);
b42 = k42b*y(16);
```

```
f43 = k43f*Pch2ch2*y(29)^2;
b43 = k43b*y(4);
f44 = k44f*Ph2o*y(29);
b44 = k44b*y(27);
f45 = k45f*Pco2*y(29);
b45 = k45b*y(24);
f46 = k46f*Pchch*y(29)^3;
b46 = k46b*y(20);
f47 = k47f*Pco*y(29);
b47 = k47b*y(23);
f48 = k48f*Ph2*y(29)^2;
b48 = k48b*y(26)*y(26);
f49 = k49f*Pc4h8o2*y(29);
b49 = k49b*y(1);
r=[r0 r1 r2 r3 r4 r5 r6 r7 r8 r9 r10 r11 r12 r13 r14 r15 r16 r17 r18 r19 r20 r21 r22 r23 r24 r25 r26
r27 r28 r29 r30 r31 r32 r33 r34 r35 r36 r37 r38 r39 r40 r41 r42 r43 r44 r45 r46 r47 r48 r49];
f=[f0 f1 f2 f3 f4 f5 f6 f7 f8 f9 f10 f11 f12 f13 f14 f15 f16 f17 f18 f19 f20 f21 f22 f23 f24 f25 f26
f27 f28 f29 f30 f31 f32 f33 f34 f35 f36 f37 f38 f39 f40 f41 f42 f43 f44 f45 f46 f47 f48 f49];
b=[b0 b1 b2 b3 b4 b5 b6 b7 b8 b9 b10 b11 b12 b13 b14 b15 b16 b17 b18 b19 b20 b21 b22 b23 b24
b25 b26 b27 b28 b29 b30 b31 b32 b33 b34 b35 b36 b37 b38 b39 b40 b41 b42 b43 b44 b45 b46
b47 b48 b49];
r=r';
f=f';
b=b';
y=y';
%coverage
fileID = fopen('coverage','a');
fmt = '%5d\r\n';
fprintf(fileID,fmt,y);
fclose(fileID);
%Rate for each iteration
rate = fopen('rate','a');
frate=fopen('frate','a');
brate=fopen('brate','a');
fmt = '%5d\r\n';
fprintf(rate,fmt,r);
fprintf(frate,fmt,f);
fprintf(brate,fmt,b);
fclose(rate);
fclose(frate);
fclose(brate);
```

```
%TOF for each iteration
PAC_rate=fopen('TOF','a');
PAC_TOF=r1+r2+r28;
fmt = '%5d\r\n';
fprintf(PAC_rate,fmt,PAC_TOF);
fclose(PAC_rate);
```