Electronic Supplementary Material (ESI) for Reaction Chemistry & Engineering.

Supplementary Information

Understanding the Origin of Structure Sensitivity in Hydrodechlorination of Trichloroethylene on Palladium Catalyst

Chaitra S. Shenoy[a], Tuhin S. Khan[b]*, Kirti Verma[a], Mesfin Tsige[c], Kshitij C. Jha[c,d,e], M. Ali Haider[a]*, Shelaka Gupta[f]*

[a] Renewable Energy and Chemicals Laboratory, Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

[b] Light Stock Processing Division, CSIR - Indian Institute of Petroleum, Mohkampur, Dehradun 248005, India

[c] College of Polymer Science and Polymer Engineering, The University of Akron, Akron, Ohio 44325, United States

[d] Biena Tech LLC, 526 S Main St, Akron, Ohio 44311, United States

[e] Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas, New Delhi 110016, India

[f] Department of Chemical Engineering, Indian Institute of Technology Hyderabad, Kandi, Sangareddy, Telangana 502285, India

* Corresponding Authors: Tuhin S. Khan (tuhins.khan@iip.res.in), M. Ali Haider (haider@iitd.ac.in), Shelaka Gupta (shelaka@che.iith.ac.in)

Table S1: Hydrogenation of chlorinated intermediates on different Pd facets

	Elementary Step	E_a (kJ/mol)	E_{rxn} (kJ/mol)
Pd (111)	$CHCl\text{-}CCl_2$* + H* → $CH_2Cl\text{-}CCl_2$*	110	-22
	$CHCl\text{-}CCl_2$* + H* → $CHCl\text{-}CHCl_2$*	130	-8
	CHCl-CCl* + H* → CH_2Cl-CCl*	87	-1
	CHCl-CCl* + H* → CHCl-CHCl* (cis)	106	-15
	CHCl-CCl* + H* → CHCl-CHCl (trans)	106	-31
	CH-CCl* + H* → CH-CHCl	75	-13
	CH-CCl* + H* → CH_2-CCl*	69	-28
Pd (211)	$CHCl\text{-}CCl_2$* + H* → $CH_2Cl\text{-}CCl_2$*	-	-
	$CHCl\text{-}CCl_2$* + H* → $CHCl\text{-}CHCl_2$*	115	-17
	CHCl-CCl* + H* → CH_2Cl-CCl*	-	-
	CHCl-CCl* + H* → CHCl-CHCl* (cis)	84	-19
	CHCl-CCl* + H* → CHCl-CHCl (trans)	-	-
	CH-CCl* + H* → CH-CHCl	-	-
	CH-CCl* + H* → CH_2-CCl*	68	-27
Pd (100)	$CHCl\text{-}CCl_2$* + H* → $CH_2Cl\text{-}CCl_2$*	88	-23
	$CHCl\text{-}CCl_2$* + H* → $CHCl\text{-}CHCl_2$*	99	-14
	CHCl-CCl* + H* → CH_2Cl-CCl*	-	-
	CHCl-CCl* + H* → CHCl-CHCl* (cis)	94	-29
	CHCl-CCl* + H* → CHCl-CHCl (trans)	77	-39
	CH-CCl* + H* → CH-CHCl	-	-
	CH-CCl* + H* → CH_2-CCl*	-	-
Pd (110)	$CHCl\text{-}CCl_2$* + H* → $CH_2Cl\text{-}CCl_2$*	-	-
	$CHCl\text{-}CCl_2$* + H* → $CHCl\text{-}CHCl_2$*	-	-
	CH-CCl* + H* → CH-CHCl	-	-
	CH-CCl* + H* → CH_2-CCl*	-	-

Table S2. Comparison between ethylene desorption energy and ethylene hydrogenation to ethyl species on different Pd facets

Sr. No	Pd facets	Ethylene desorption energy (kJ/mol)	Ethylene hydrogenation barrier to ethyl species (kJ/mol)
1.	Pd (111)	143	85
2.	Pd (211)	106	77
3.	Pd (100)	110	80
4.	Pd (110)	92	56

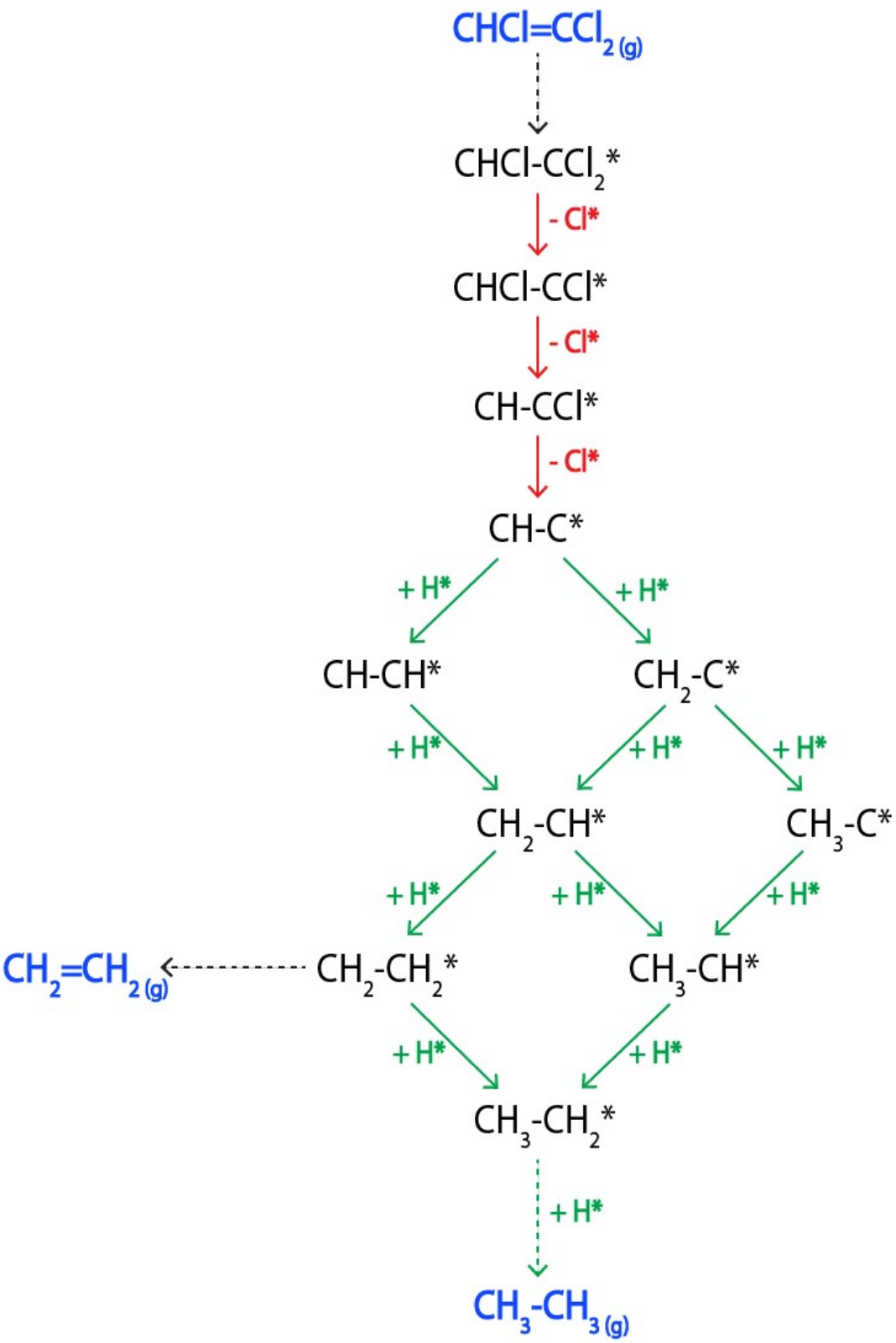

Figure S1. Mechanistic routes for hydrodechlorination of trichloroethylene

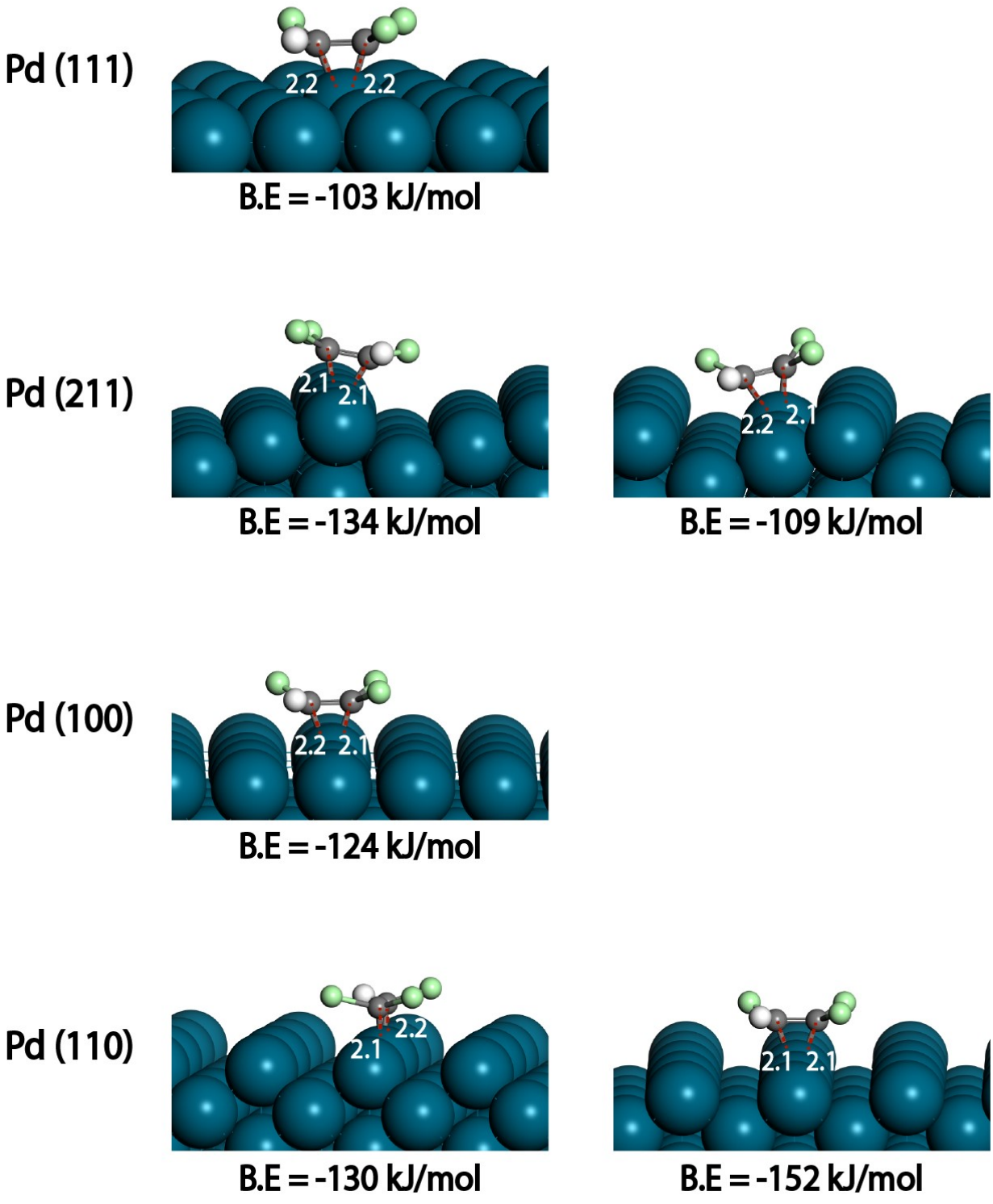

Figure S2. The π-binding modes of trichloroethylene on different Pd facets

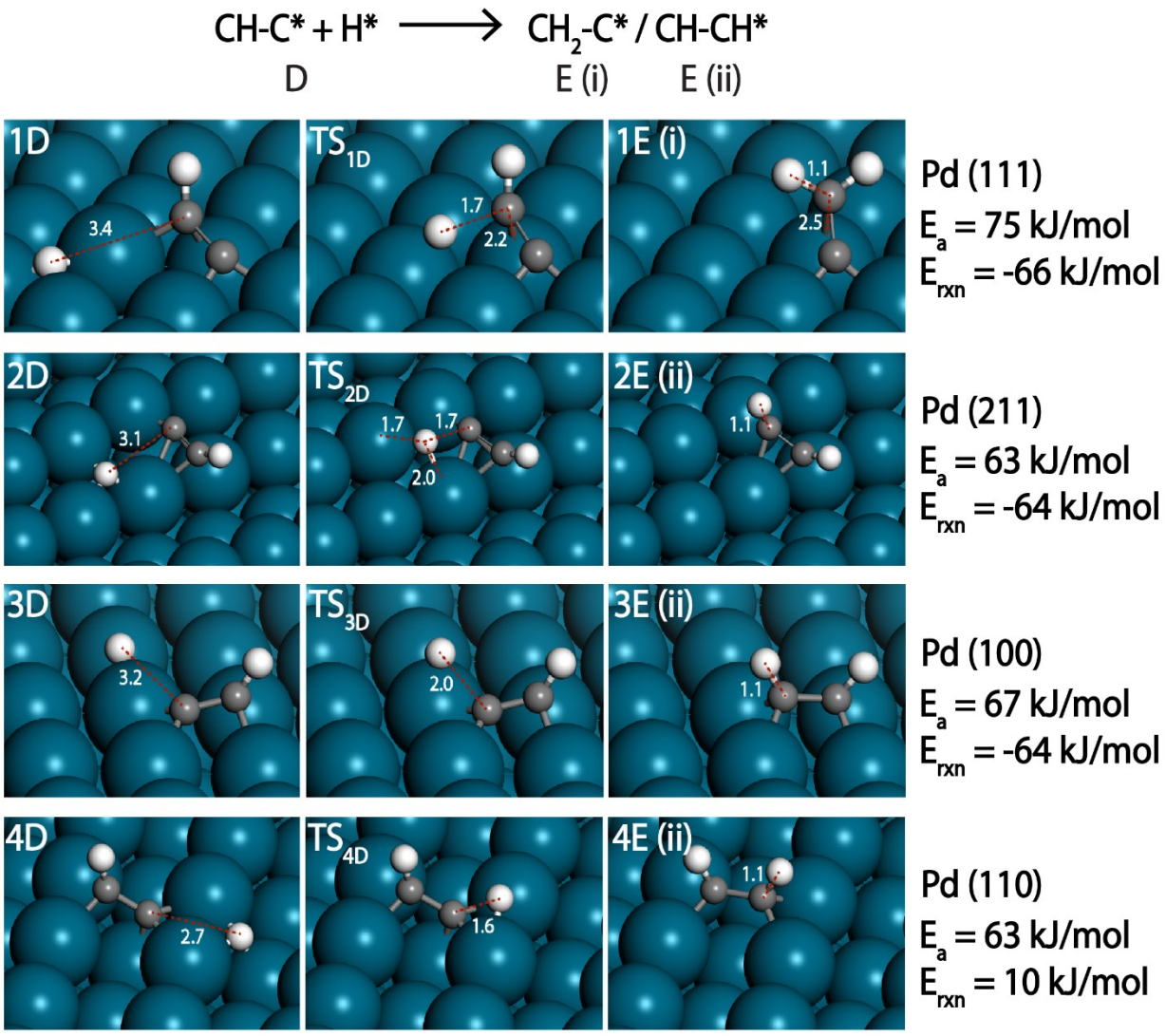

Figure S3. Reactant, transition and product state structures for the first hydrogenation step on the Pd (111), Pd (211), Pd (100) and Pd (110) surfaces. The Pd atoms are displayed in blue, C atoms in grey and H atom in white color (Distances are marked in Å).

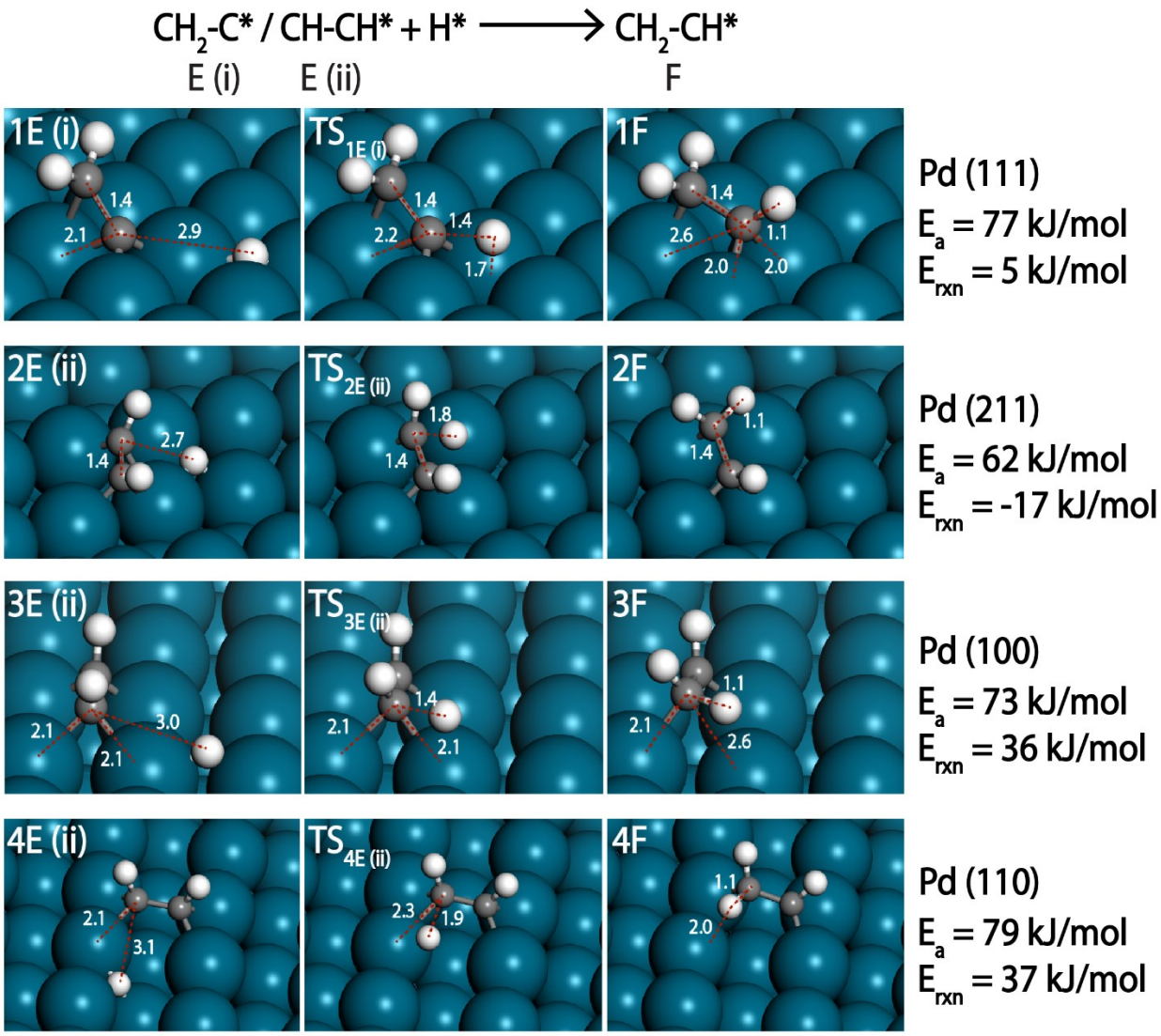

Figure S4. Reactant, transition and product state structures for the second hydrogenation step on the Pd (111), Pd (211), Pd (100) and Pd (110) surfaces. The Pd atoms are displayed in blue, C atoms in grey and H atom in white color (Distances are marked in Å).

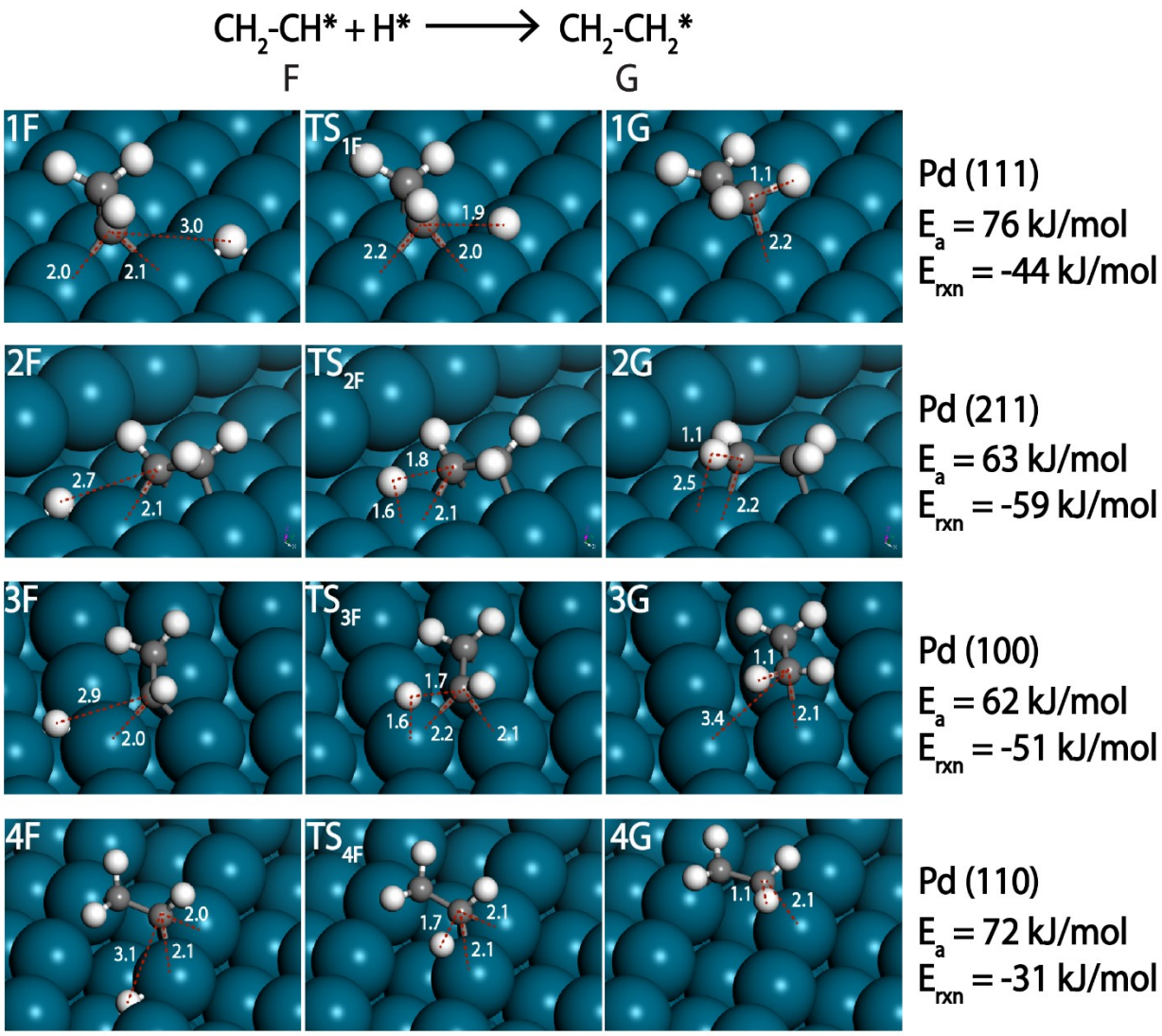

Figure S5. Reactant, transition and product state structures for the third hydrogenation step (ethylene formation) on Pd (111), Pd (211), Pd (100) and Pd (110) surfaces. The Pd atoms are displayed in blue, C atoms in grey and H atom in white color (Distances are marked in Å).

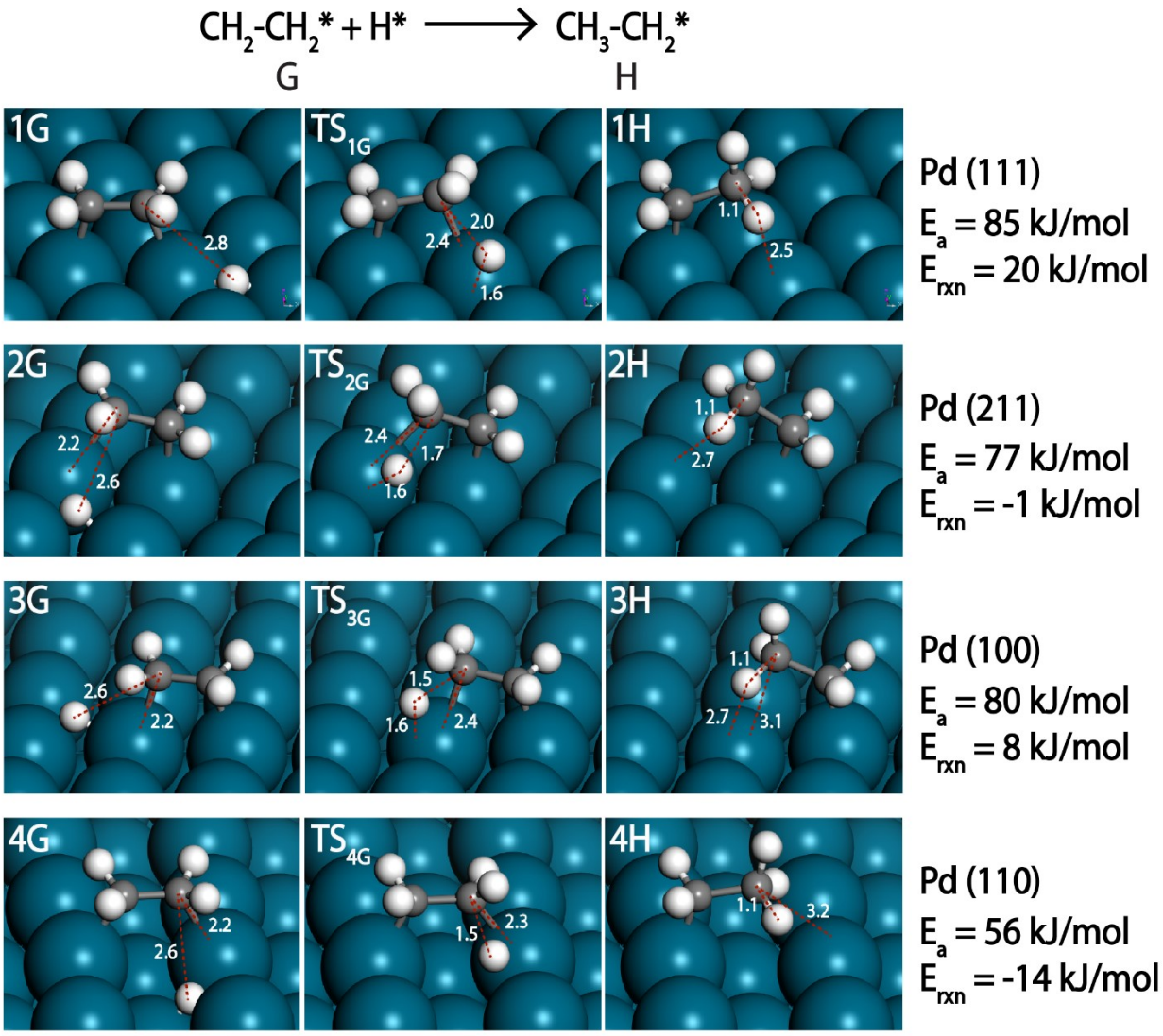

Figure S6. Reactant, transition and product state structures for the hydrogenation of ethylene on the Pd (111), Pd (211), Pd (100) and Pd (110) surfaces. The Pd atoms are displayed in blue, C atoms in grey and H atom in white color (Distances are marked in Å).

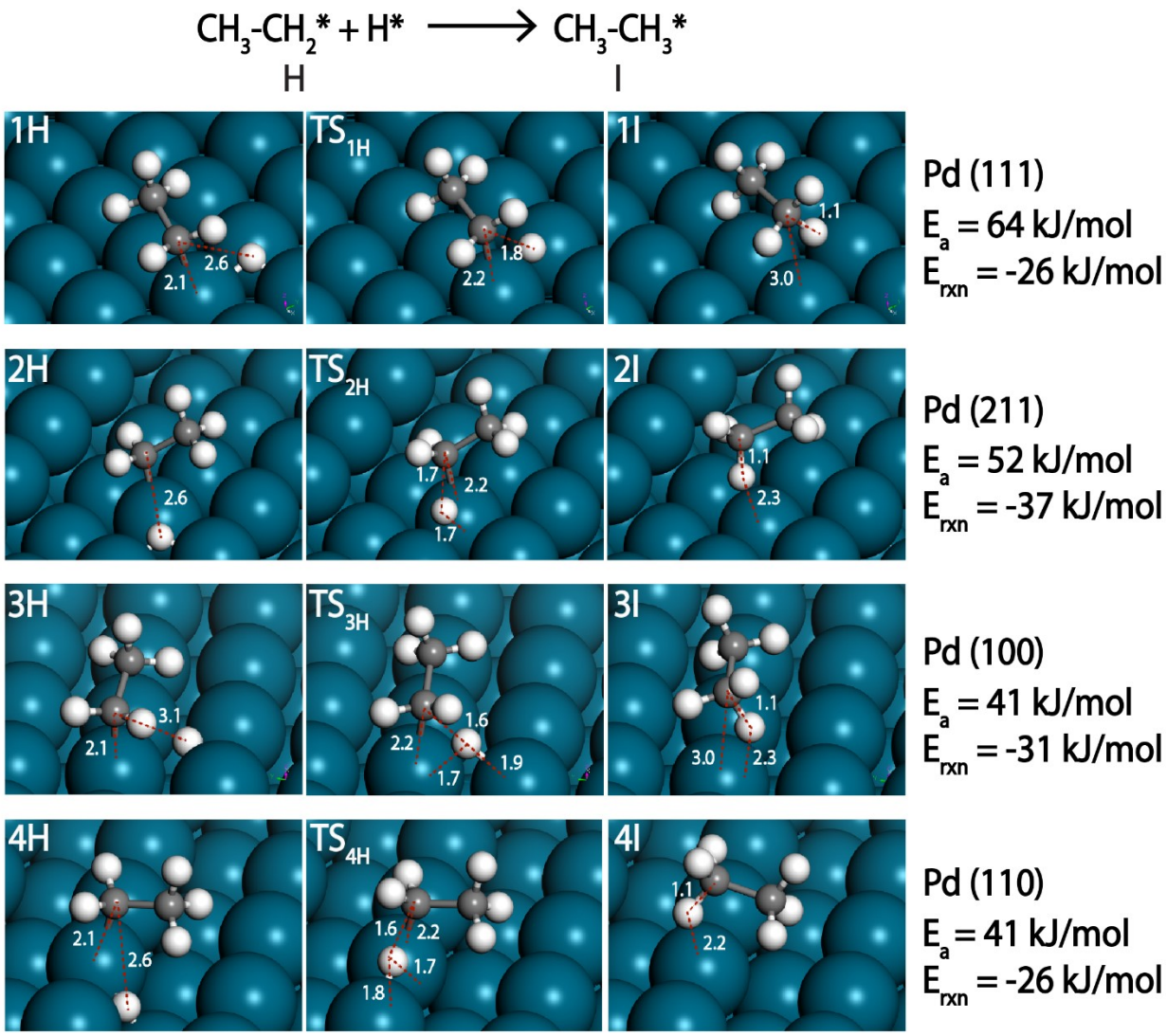

Figure S7. Reactant, transition and product state structures for the hydrogenation of ethyl (ethane formation) on Pd (111), Pd (211), Pd (100) and Pd (110) surfaces. The Pd atoms are displayed in blue, C atoms in grey and H atom in white color (Distances are marked in Å).

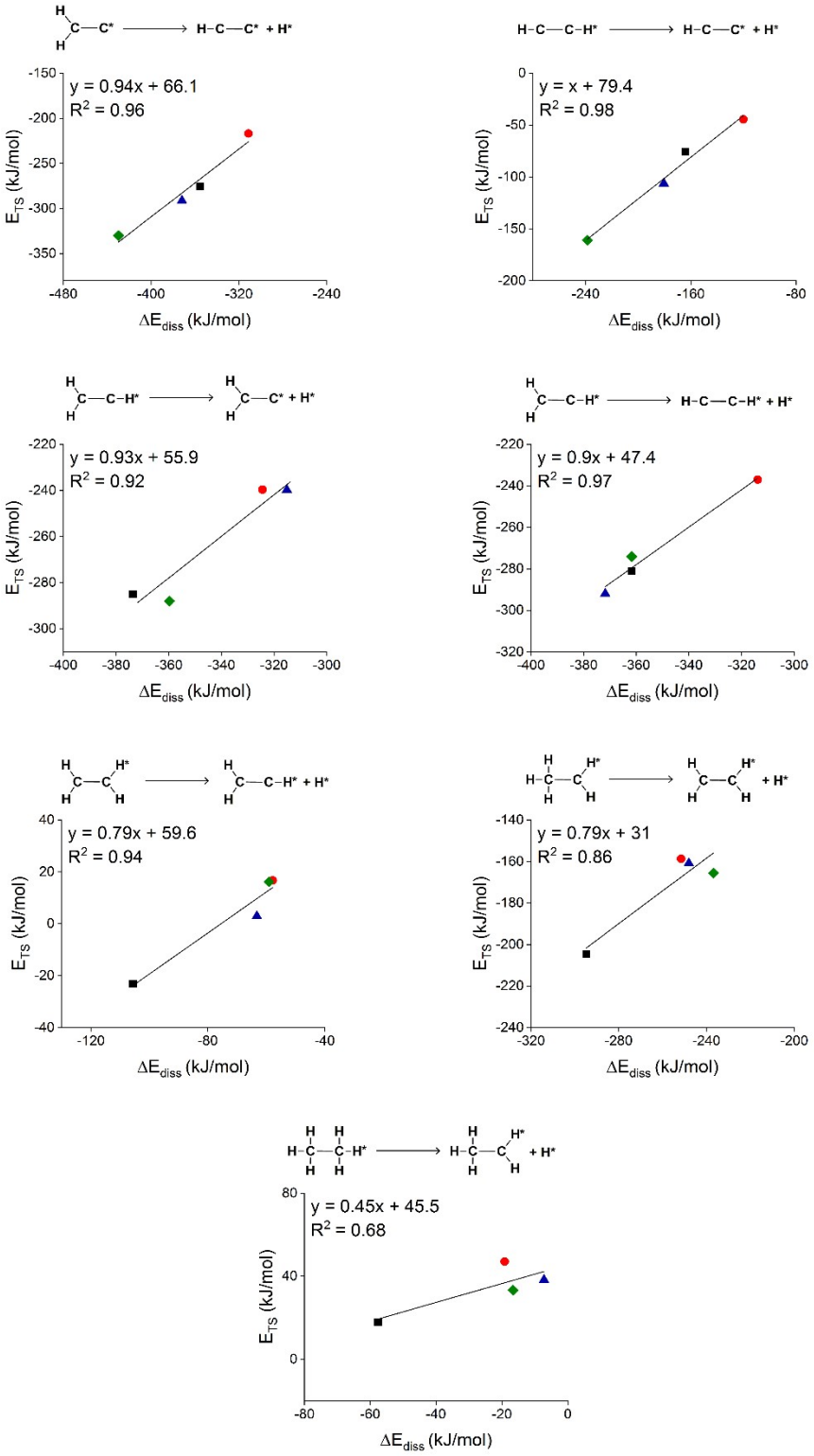

Figure S8. The transition state scaling for the hydrogenation steps on the Pd (111) (■), Pd (211) (●), Pd (100) (▲) and Pd (110) (♦) surfaces.

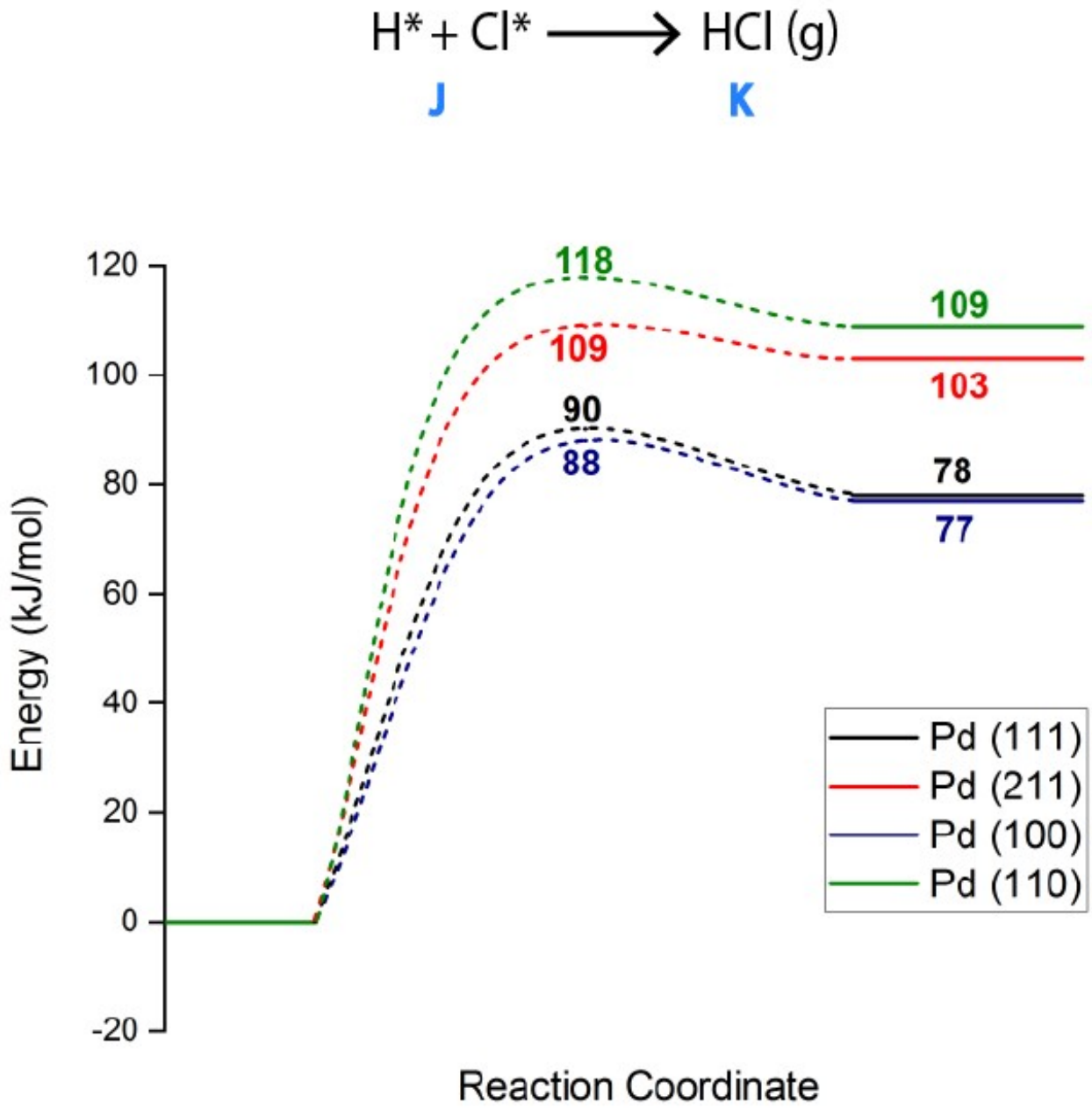

Figure S9. The energy diagram for formation of hydrogen chloride on the Pd (111), Pd (211), Pd (100) and Pd (110) surfaces.