Supporting Information

Theoretical Insights into Non-Oxidative Propane Dehydrogenation over Fe_3C

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Data availability: All final structures and scripts used to generate the plots are supplied in an online repository at *https://github.com/tsenftle/PDH-Fe3C*.

1 Computational details

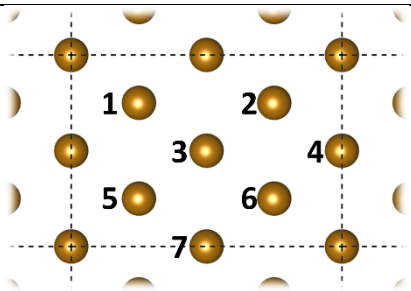
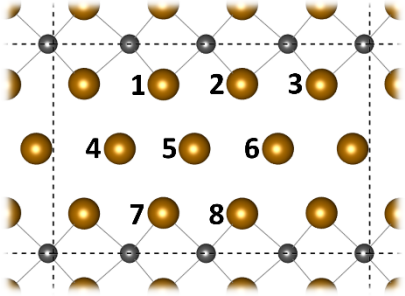
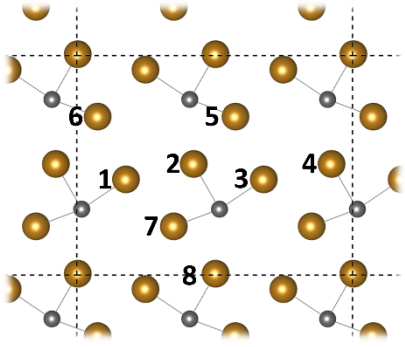
The k-points mesh and number of frozen atoms and total atoms in different models are summarized in Table S1.

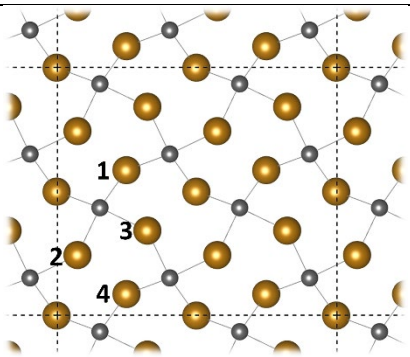
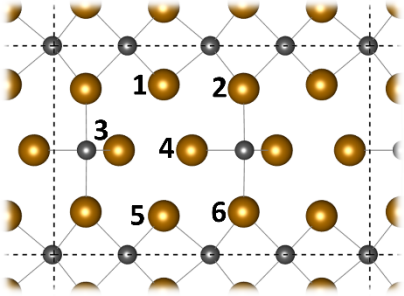
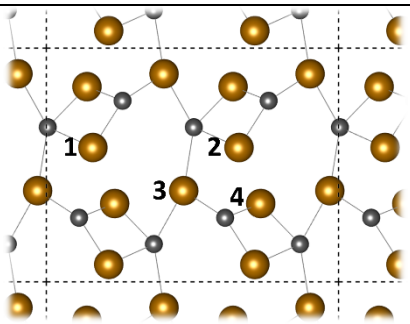
Table S1. K-points and frozen atoms in different structures

Structure	k-points mesh	frozen/total (Fe or Pt)	Frozen/total (C)
Fe, bulk	8×8×8	-	-
Fe_3C, bulk	4×4×4	-	-
Pt, bulk	9×9×9	-	-
Fe_3C(001)	3×3×1	-	-
Fe_3C(010)	3×3×1	-	-
Fe_3C(011)	3×3×1	-	-
Fe(110)-(2×2)	4×3×1	16/40	-
Fe(110)-(4×3)	2×2×1	24/72	
Pt(111)-(2×2)	3×4×1	16/48	-
Fe_3C(010)-CR-(2×2)	1×1×1	16/56	8/24
Fe_3C(001)-ST-1-(2×1)	2×2×1	12/48	4/16
Fe_3C(001)-CR-(2×1)	2×2×1	12/48	4/16
Fe_3C(011)-ST-1-(2×1)	2×3×1	12/48	4/16
Fe_3C(011)-CR-3-(2×1)	2×3×1	16/44	4/16

The adsorption of C_3H_x (x = 4, 5, 6, 7, 8) on Fe_3C surfaces was systematically evaluated on multiple adsorption sites for each surface. These sites are summarized in Table S2, which specifies the surface Fe atoms bonded to the hydrocarbon. The number in parenthesis is the formation energy of the intermediate referenced to C_3H_8 and H_2.

Table S2. Tested adsorption sites of each surface

Surface	Geometry	Tested adsorption site (number of Fe atoms adsorbed with intermediates in relaxed structures)			
		C_3H_4*	C_3H_5*	C_3H_6*	C_3H_7*
Fe(110)		**2-3-4-6 [0.208]**	**2-3-4-6 [0.435]**	2-3-6 [0.129], **3-6-4 [0.099]**	3-6-7 [-0.076], **2-3-6 [-0.211]**, 2-4-6 [-0.123]
Fe_3C(001)-ST-1		1-2-4-5-6 [0.927], **1-4-5-7 [0.602]**	4-5-7-6 [0.772], **1-4-7 [0.550]**, 4-5-7 [0.630]	4-5-7-6 [0.414], **1-4-7 [-0.269]**, 1-4 [-0.080]	**1-4 [-0.364]**, 4-7 [-0.25]
Fe_3C(011)-ST-1		1-2 [1.855], **5-2-3-4 [1.781]**	1-2 [1.490], **5-2-3-4 [0.997]**	1-2 [0.136], **5-2-3-4 [0.072]**, 2-3-4 [0.265], 1-2-7-8 [0.604], 1-2-7 [0.488], 6-1-2 [0.614]	2 [0.296], **1-2** [-0.155]

Fe_3C(010)-CR		**2-3 [2.379]**	**2-3 [1.287]**	**2-3 [0.400]**	**2 [0.309]**
Fe_3C(001)-CR		**3-4-5-6 [1.580]**, 1-3-4-5 [1.595]	4 [1.981], 3-4-5 [1.523], **4-5-6 [1.261]**	**4 [0.521]**, 5 [1.213]	**4 [0.240]**
Fe_3C(011)-CR-3		**1-3-2 [1.380]**, 3-2 [1.950]	3-2 [1.027], **1-3-2 [0.892]**, 1-3 [1.241]	**1-3-2 [0.466]**, 3-2 [0.602]	3 [0.159], **1 [0.090]**

* The most stable site is bold

** The formation energy referring to $C3H_8$ and H_2 are shown in square brackets in eV

The charges of either C atom or PO_4 group from Bader charge analysis are summarized in Table S3 and Table S4, where *e* is the positive elementary charge.

Table S3. Bader charge of C atom on Fe(110) surface

Charge of carbon (*e*)	Pristine	With Phosphate
1 carbon	-1.30	-1.21
2 carbon	-1.32 / -1.32	-1.17 / -0.96

Table S4. Bader charge of PO_4 group on Fe(110) surface

Charge of PO_4 group (*e*)	Phosphate
No carbon	-2.00
1 carbon	-1.97
2 carbon	-1.93

The comparison of the formation energy of 1-propyl and 2-propl referenced to C_3H_8 and H_2 on each surface is reported in Table S5.

Table S5. Comparison of formation energy of 1-propyl and 2-propyl from C_3H_8 and H_2

Surface	1-propyl /eV	2-propyl /eV	difference /eV
001-CR	0.24	0.34	-0.10
001-ST-1	-0.36	-0.15	-0.22
010-CR	0.31	0.30	0.00
011-CR-3	0.16	0.09	0.07
011-ST-1	-0.16	0.07	-0.22
Fe(110)	-0.19	0.14	-0.33

2 Additional figures

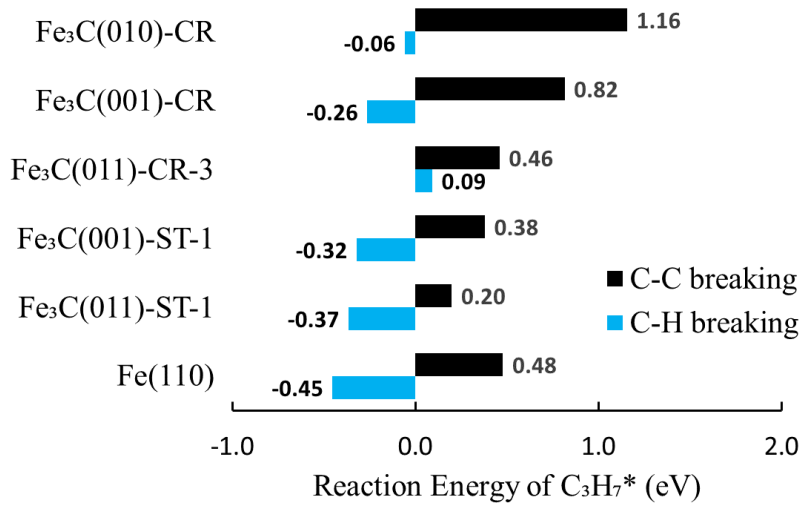


Figure S1. Comparison of the reaction energy for breaking the C-H bond versus the C-C bond of C_3H_7 on each surface.

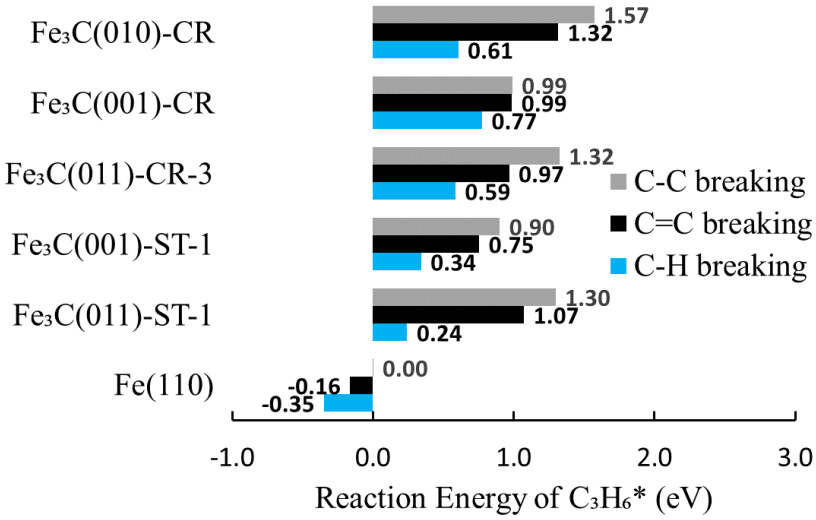


Figure S2. Comparison of the reaction energy for breaking the C-H bond, the C=C bond, and the C-C bond of C_3H_6 on each surface.

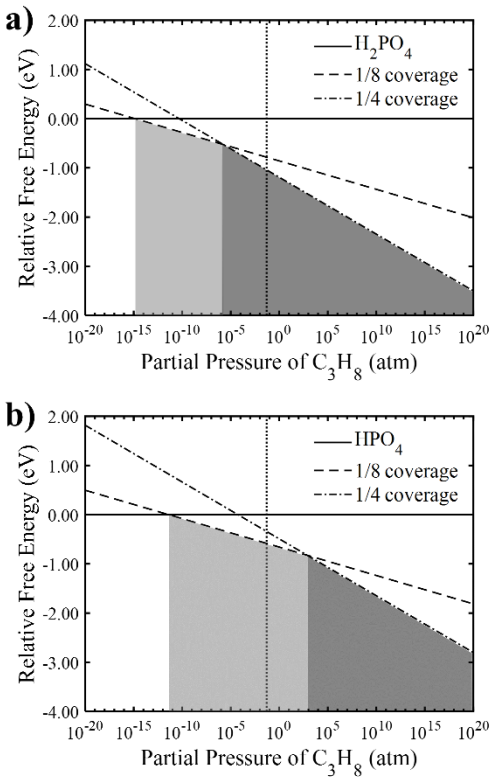


Figure S3. Phase diagrams of carbon coverage on a) Fe(110) with H_2PO_4 adsorbed and b) Fe(110) with HPO_4 adsorbed. The solid line is the surface without carbon and is taken as the reference. The dashed line is the surface with one carbon atom per (2×2) cell. The dash-dotted line is the surface with two carbon atoms per (2×2) cell. The dotted vertical line is the reaction condition, which is at 873.15 K, 0.01 atm H_2, and 0.05 atm C_3H_8. The light gray area represents the stable region of 1/8 coverage of carbon and the dark gray area is for 1/4 coverage of carbon.

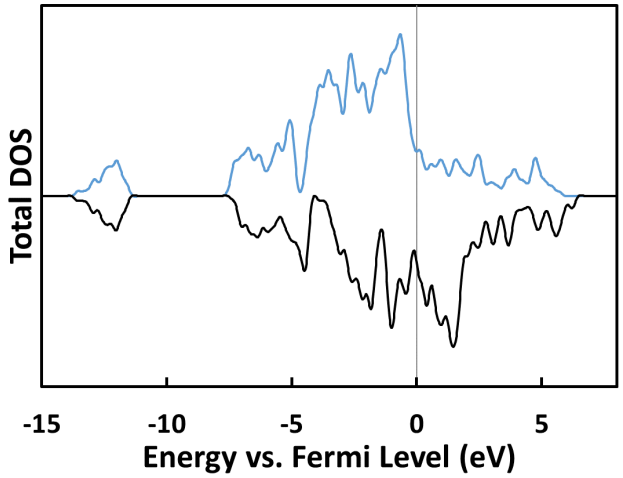


Figure S4. Density of states (DOS) of bulk Fe_3C. The blue and black line represent two different spin states. The vertical line is the Fermi level.

3 Detailed geometries

The detailed adsorption geometries of the most stable configuration along with the transition states on the surfaces of Fe, Fe_3C, and Pt are shown with Figure S5-S11.

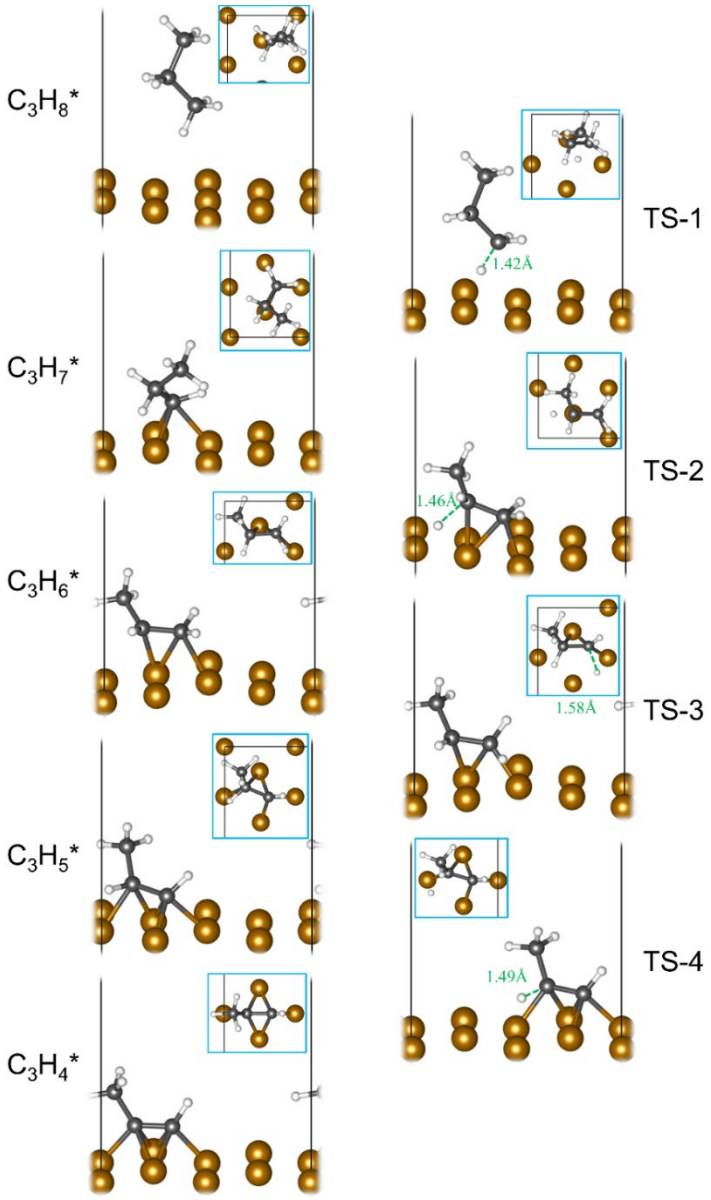


Figure S5. Adsorption configurations and transition state structures on Fe(110). The top views are shown as insets on top of each side view. The unit cell is shown with black line. Brown: Fe; Gray: C; White: H. The breaking bonds in transition states are labeled with green dashed lines with their bond lengths.

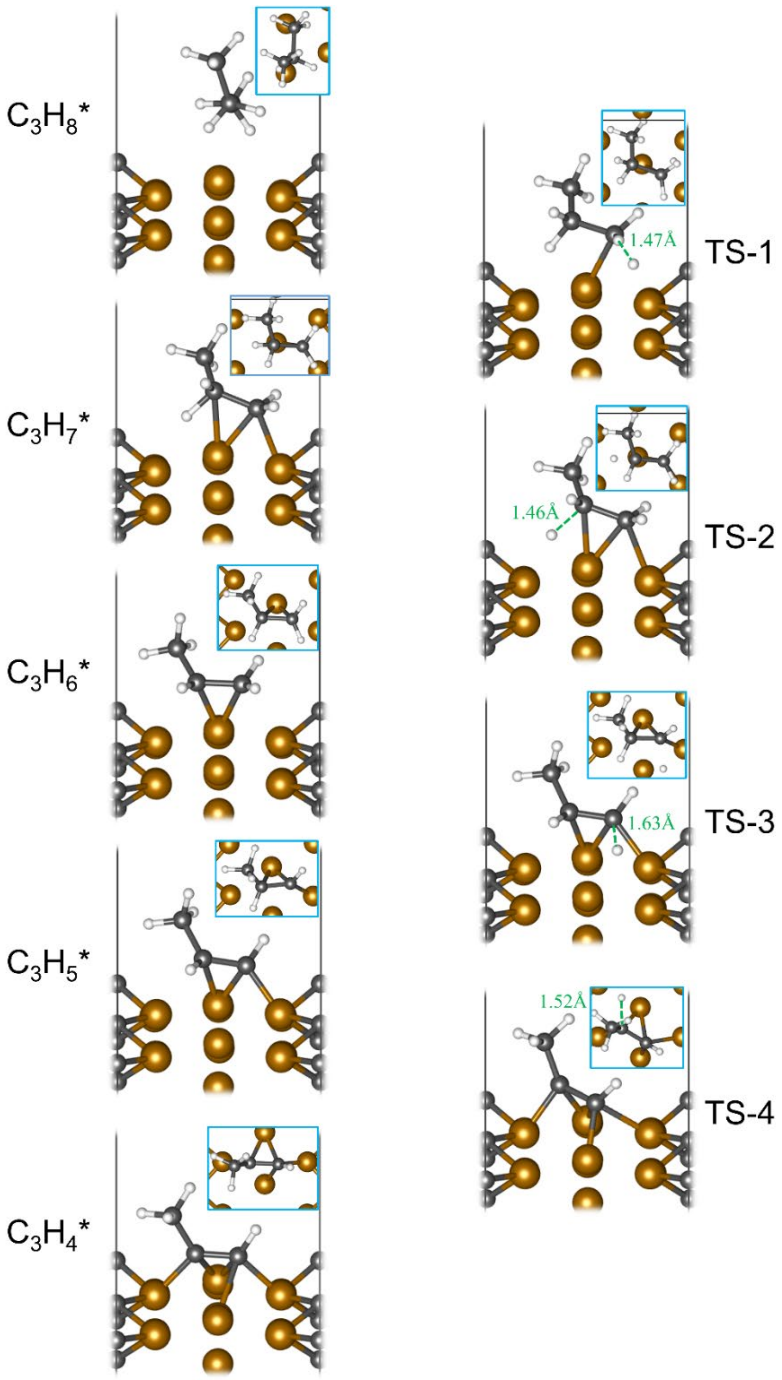


Figure S6. Adsorption configurations and transition state structures on $Fe_3C(001)$-ST-1.

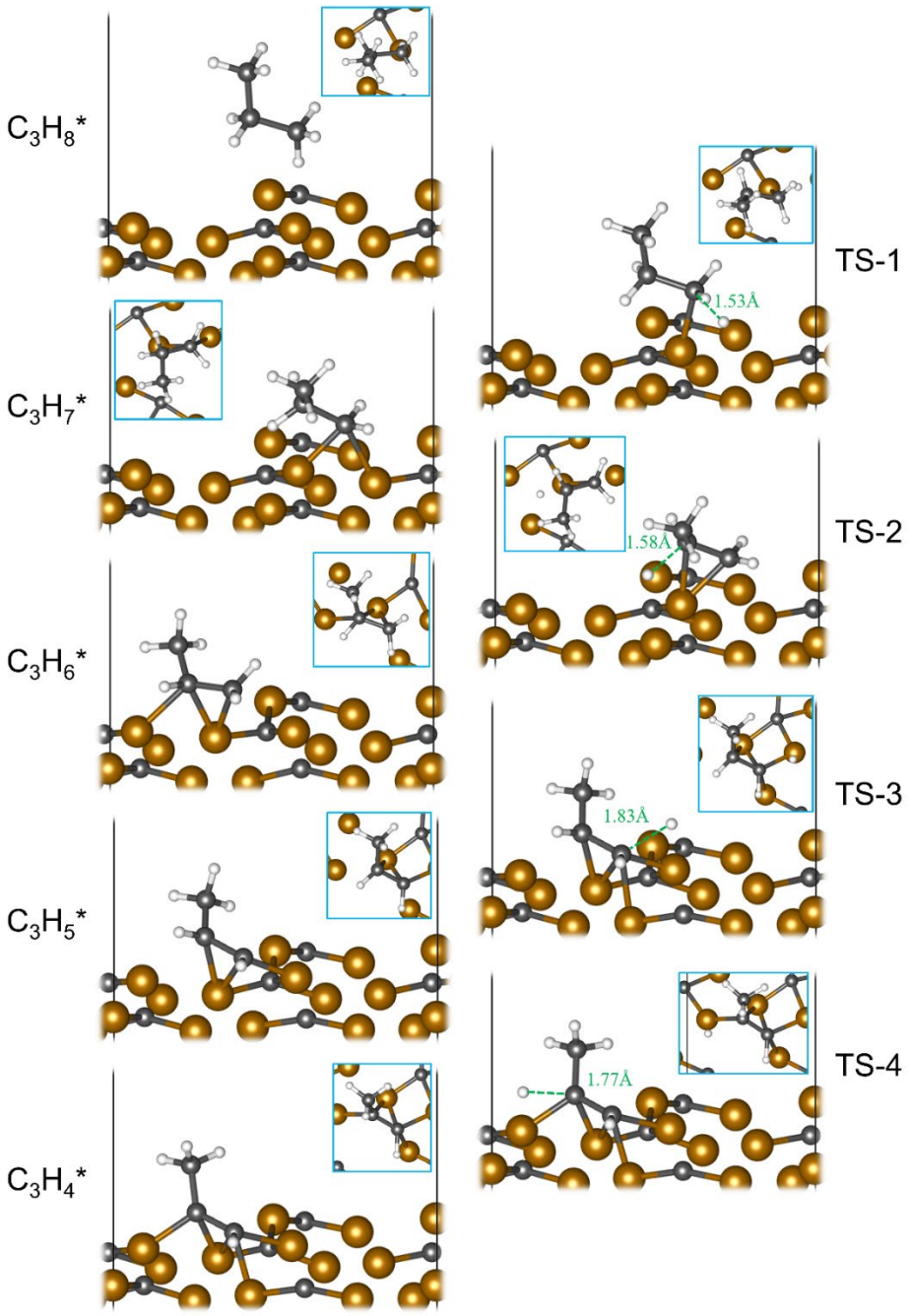


Figure S7. Adsorption configurations and transition state structures on $Fe_3C(011)$-ST-1.

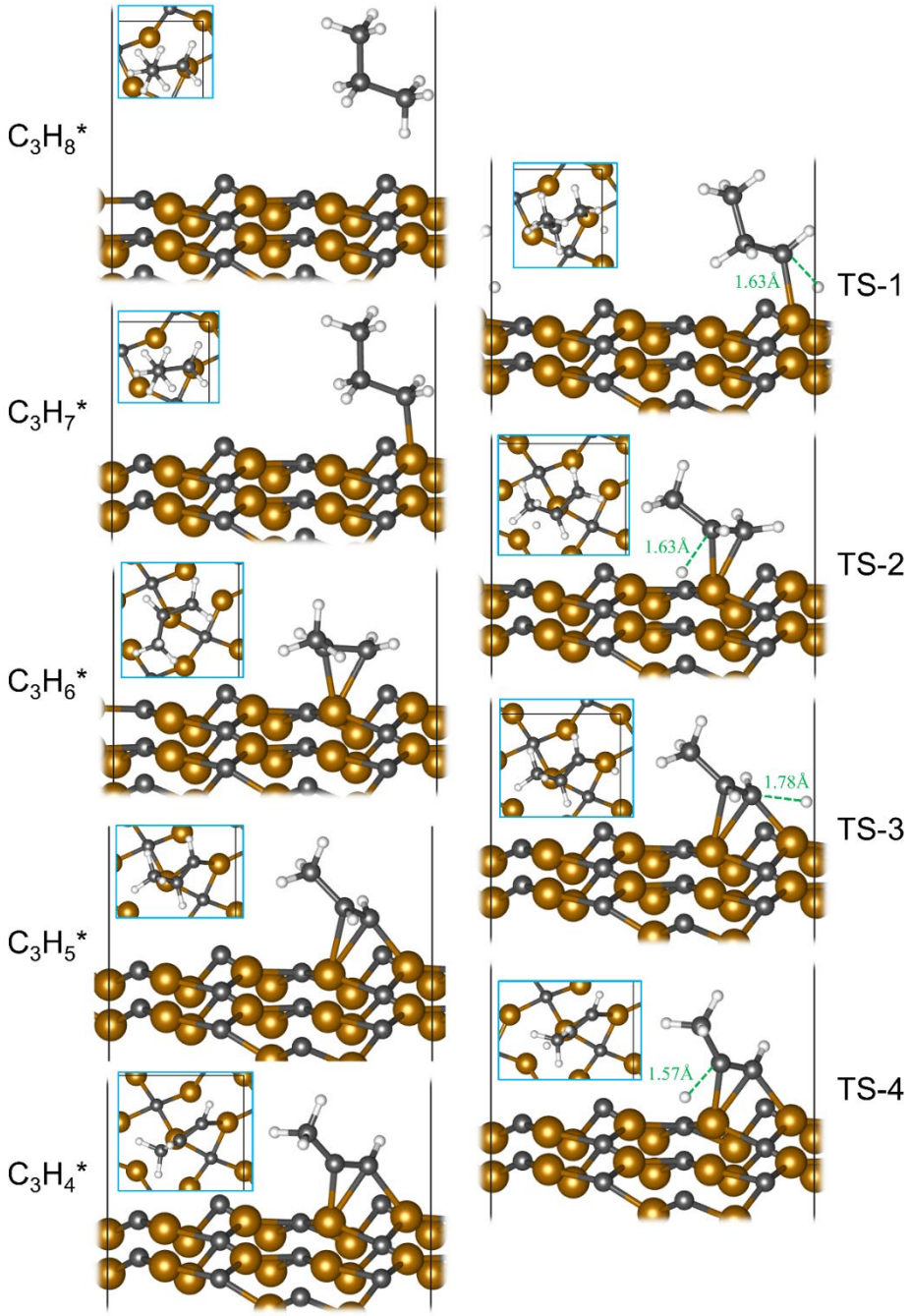


Figure S8. Adsorption configurations and transition state structures on $Fe_3C(010)$-CR.

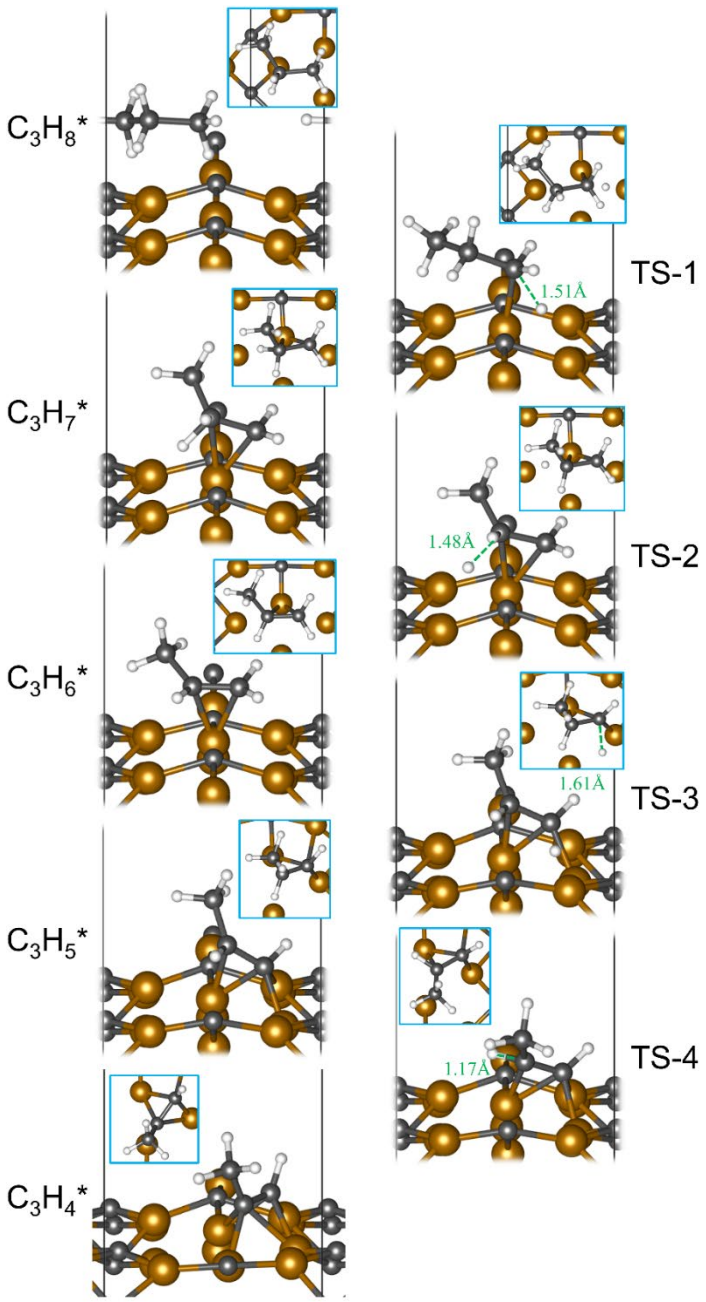


Figure S9. Adsorption configurations and transition state structures on $Fe_3C(001)$-CR.

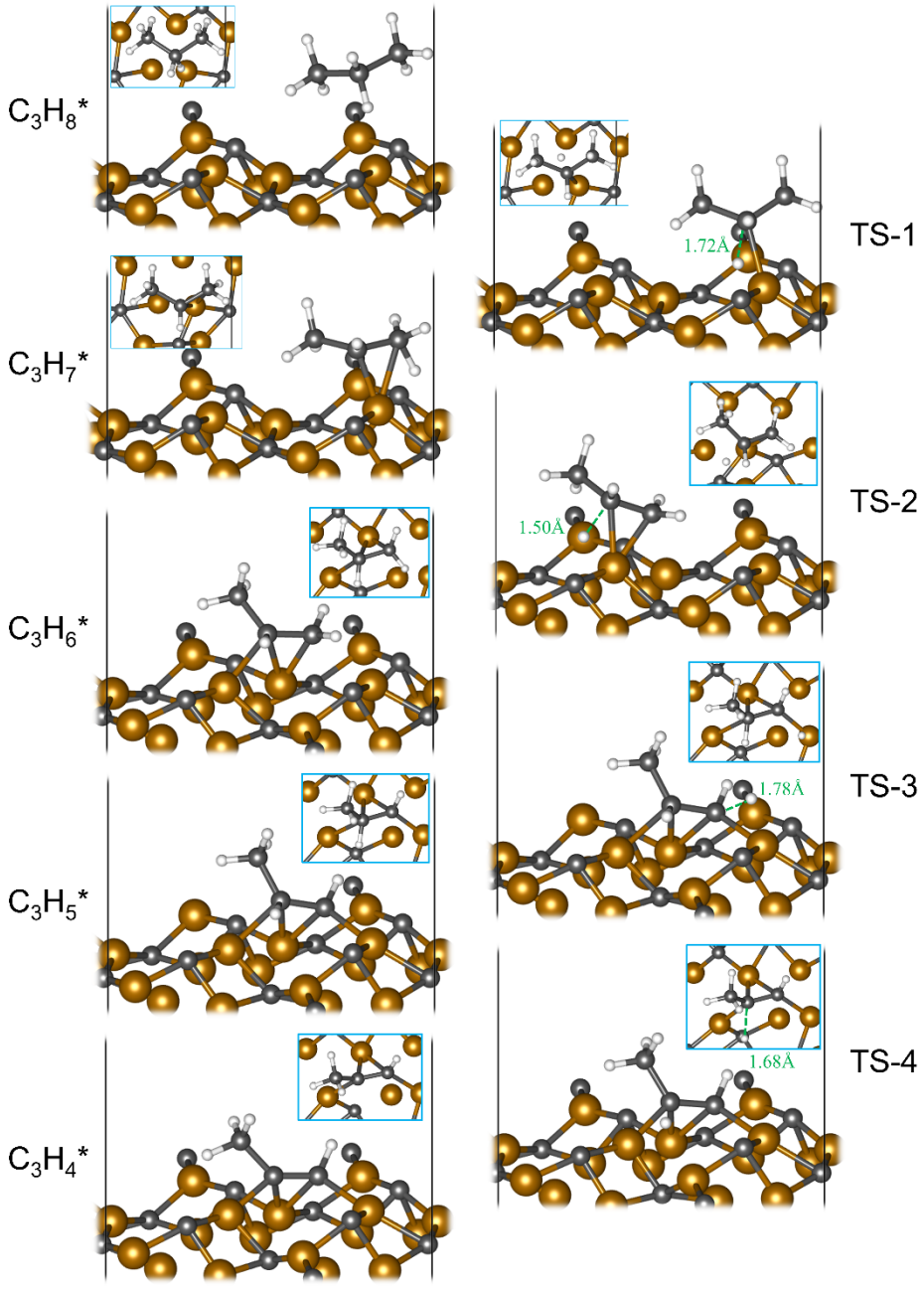


Figure S10. Adsorption configurations and transition state structures on $Fe_3C(011)$-CR-3.

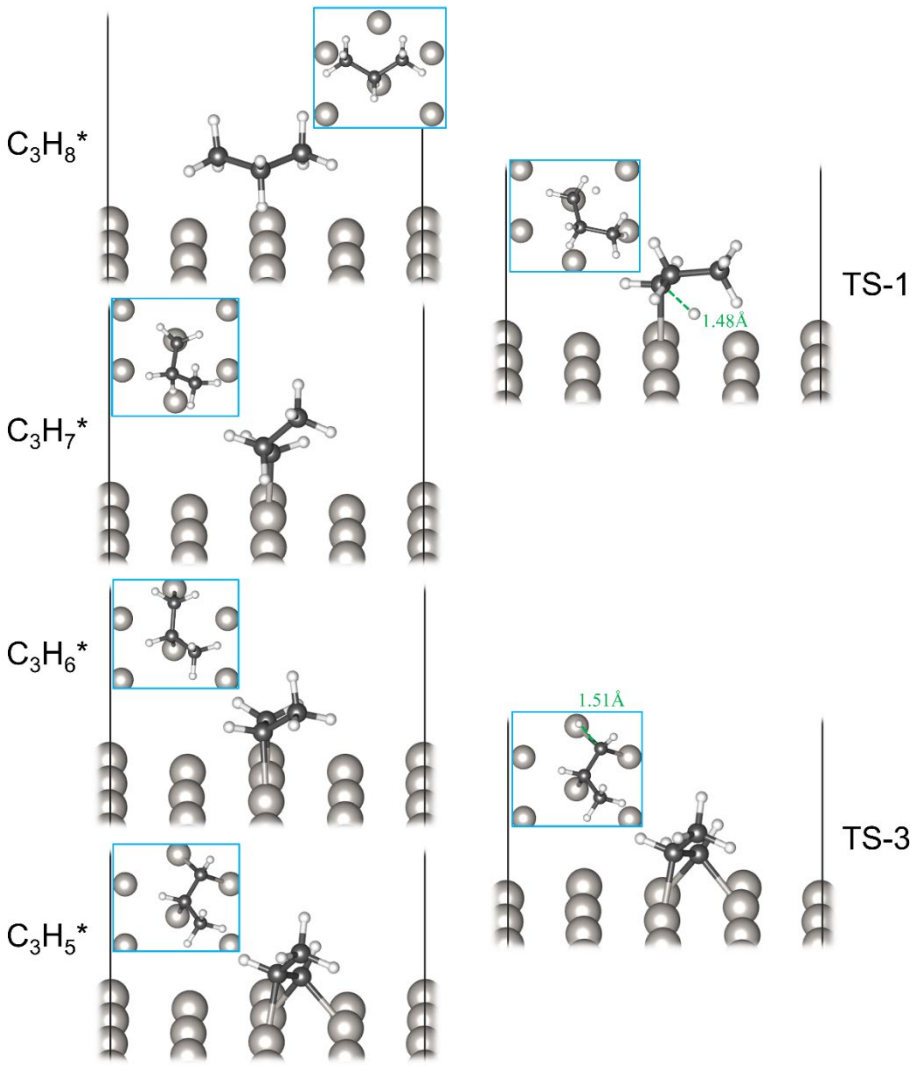


Figure S11. Adsorption configurations and transition state structures on Pt(111).

All final structures of stable adsorption and transition states in VASP format, and the script used to generate the plot in Figure 2 are supplied online at *https://github.com/tsenftle/PDH-Fe3C*.

4 Data in figures

The data needed to generate the plot in Figure 2 are shown in Table S6. Through the equations discussed in the main text, only the number of atoms and the total energies of the slabs is needed to determine their relative stability. The total DFT energy of Fe_3C per formula unit is -34.824 eV. The free energies of propane and hydrogen at 873.15 K and 1 atm were -57.010 eV and -7.660 eV, respectively.

Table S6. The slab models and corresponding energies used in Figure 2

Terminations	Number of Fe	Number of C	E (eV)	Area ($Å^2$)
(011)-ST-1	48	16	-543.072	40.009
(011)-CR-1	44	16	-506.633	40.009
(011)-IR-1	44	12	-469.516	40.009
(011)-IR-2	40	12	-436.389	40.009
(011)-ST-2	36	12	-402.318	40.009
(011)-CR-2	32	12	-367.605	40.009
(011)-CR-3	28	12	-333.903	40.009
(011)-IR-3	28	8	-298.340	40.009
(001)-CR	42	16	-493.609	33.240
(001)-ST-1	42	14	-475.885	33.240
(001)-IR	42	12	-456.102	33.240
(001)-ST-2	36	12	-403.946	33.240
(010)-ST	48	16	-548.679	22.267
(010)-CR	44	16	-516.233	22.267
(010)-IR	40	12	-442.862	22.267

All the energies of adsorption configurations and transition states used to generate Figure 7 and Figure 8 are summarized in Table S7.

Table S7. DFT and Gibbs free energies of intermediates adsorption and transition states

surface	Transition states / Adsorbed species	DFT energy E (eV)	Gibbs free energy G (eV)	Imaginary Frequency (cm^{-1})
Fe	C_3H_8*	-382.231	-380.705	-
	TS(C_3H_8*-C_3H_7*)	-381.621	-380.339	872.987
	C_3H_7*	-378.767	-377.409	-
	TS(C_3H_7*-C_3H_6*)	-378.689	-377.380	763.623
	C_3H_6*	-375.077	-373.981	-
	TS(C_3H_6*-C_3H_5*)	-374.624	-373.641	964.418
	C_3H_5*	-371.349	-370.476	-
	TS(C_3H_5*-C_3H_4*)	-371.254	-370.335	835.381
	C_3H_4*	-368.190	-367.478	-
	H*	-329.053	-329.029	-
	Clean surface	-324.869	-	-
Fe_3C(001)-ST-1	C_3H_8*	-590.313	-588.789	-
	TS(C_3H_8*-C_3H_7*)	-589.729	-588.136	862.987
	C_3H_7*	-586.728	-585.398	-
	TS(C_3H_7*-C_3H_6*)	-586.693	-585.394	712.511
	C_3H_6*	-583.249	-582.082	-
	TS(C_3H_6*-C_3H_5*)	-582.393	-581.329	733.047
	C_3H_5*	-579.046	-578.154	-
	TS(C_3H_5*-C_3H_4*)	-578.778	-578.006	741.219
	C_3H_4*	-575.612	-574.892	-
	H*	-536.840	-536.712	-
	Clean surface	-532.654	-	-
Fe_3C(011)-ST-1	C_3H_8*	-586.081	-584.673	-
	TS(C_3H_8*-C_3H_7*)	-585.531	-584.104	720.044
	C_3H_7*	-582.471	-581.186	-
	TS(C_3H_7*-C_3H_6*)	-582.243	-580.936	842.665

	C_3H_6*	-578.861	-577.679	-
	TS(C_3H_6*-C_3H_5*)	-577.913	-576.879	650.353
	C_3H_5*	-574.552	-573.611	-
	TS(C_3H_5*-C_3H_4*)	-573.616	-572.810	650.600
	C_3H_4*	-570.385	-569.762	-
	H*	-532.643	-532.543	-
	Clean surface	-528.606	-	-
Fe_3C(010)-CR	C_3H_8*	-725.917	-724.397	-
	TS(C_3H_8*-C_3H_7*)	-725.162	-723.728	837.558
	C_3H_7*	-721.928	-720.546	-
	TS(C_3H_7*-C_3H_6*)	-721.833	-720.485	699.207
	C_3H_6*	-718.454	-717.320	-
	TS(C_3H_6*-C_3H_5*)	-717.663	-716.636	650.996
	C_3H_5*	-714.184	-713.251	-
	TS(C_3H_5*-C_3H_4*)	-713.060	-712.327	654.533
	C_3H_4*	-709.709	-709.183	-
	H*	-672.098	-671.999	-
	Clean surface	-668.528	-	-
Fe_3C(001)-CR	C_3H_8*	-588.945	-587.412	-
	TS(C_3H_8*-C_3H_7*)	-588.073	-586.383	819.175
	C_3H_7*	-584.841	-583.440	-
	TS(C_3H_7*-C_3H_6*)	-584.803	-583.432	716.748
	C_3H_6*	-581.177	-580.001	-
	TS(C_3H_6*-C_3H_5*)	-580.055	-578.931	900.835
	C_3H_5*	-577.053	-576.049	-
	TS(C_3H_5*-C_3H_4*)	-576.205	-575.272	245.408
	C_3H_4*	-573.351	-572.581	-
	H*	-535.534	-535.397	-
	Clean surface	-531.372	-	-
Fe_3C(011)-CR-3	C_3H_8*	-549.371	-547.833	-
	TS(C_3H_8*-C_3H_7*)	-548.601	-546.958	659.618
	C_3H_7*	-545.112	-543.810	-

	TS(C_3H_7*-C_3H_6*)	-544.954	-543.607	1028.981
	C_3H_6*	-541.354	-540.147	-
	TS(C_3H_6*-C_3H_5*)	-540.750	-539.581	393.150
	C_3H_5*	-537.544	-536.528	-
	TS(C_3H_5*-C_3H_4*)	-536.926	-536.038	654.454
	C_3H_4*	-533.673	-532.886	-
	H*	-495.477	-495.356	-
	Clean surface	-491.493	-	-
Pt(111)	C_3H_8*	-354.147	-352.427	-
	TS(C_3H_8*-C_3H_7*)	-353.672	-352.256	885.778
	C_3H_7*	-350.419	-349.141	-
	C_3H_6*	-347.096	-345.809	-
	TS(C_3H_6*-C_3H_5*)	-346.341	-345.126	709.733
	C_3H_5*	-343.162	-342.078	-
	H*	-300.364	-329.029	-
	Clean surface	-296.412	-	-