Supporting Information

Mechanistic Insight into Hydrocarbons Synthesis via CO_2 Hydrogenation on χ-Fe_5C_2 Catalysts

Haozhi Wang[a,b,c], Xiaowa Nie[a*], Yuan Liu[c], Michael J. Janik[d], Xiaopeng Han[c*], Yida Deng[c], Wenbin Hu[b,c], Chunshan Song[a,e], and Xinwen Guo[a*]

[a]*State Key Laboratory of Fine Chemicals, PSU-DUT Joint Center for Energy Research, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, China*

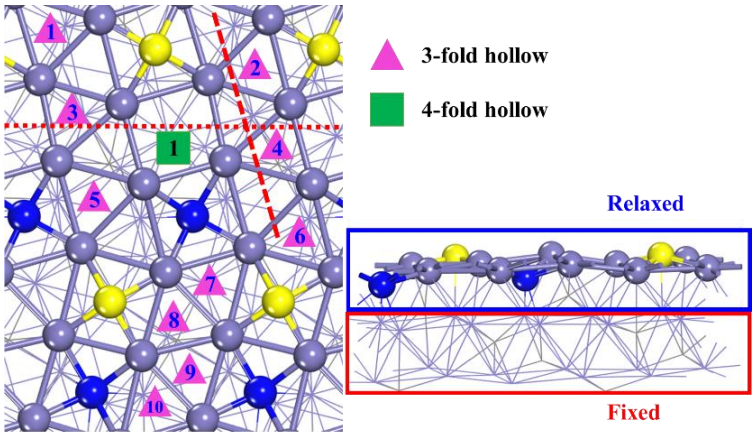
[b]*Joint School of National University of Singapore and Tianjin University International Campus of Tianjin University, Binhai New City, Fuzhou 350207, China*

[c]*School of Materials Science and Engineering Tianjin Key Laboratory of Composite and Functional Materials Key Laboratory of Advanced Ceramics and Machining Technology (Ministry of Education), Tianjin University, Tianjin 300072, China*

[d]*EMS Energy Institute, PSU-DUT Joint Center for Energy Research, and Department of Energy & Mineral Engineering, Pennsylvania State University, University Park, Pennsylvania 16802, USA.*

[e]*Department of Chemistry, Faculty of Science, The Chinese University of Hong Kong, Shatin, NT 999077, Hong Kong, China.*

Authors to whom all correspondence should be addressed:
Email: niexiaowa@dlut.edu.cn; xphan@tju.edu.cn; guoxw@dlut.edu.cn.



(a) (b)

Figure S1. (a) Possible active sites examined for CO_2 hydrogenation to hydrocarbons on χ-Fe_5C_2(510) and (b) Side view of the χ-Fe_5C_2(510) model to show the fixed and relaxed atomic layers in structural optimization. (purple: Fe; yellow: top-layer carbon; blue: sub-layer carbon.)

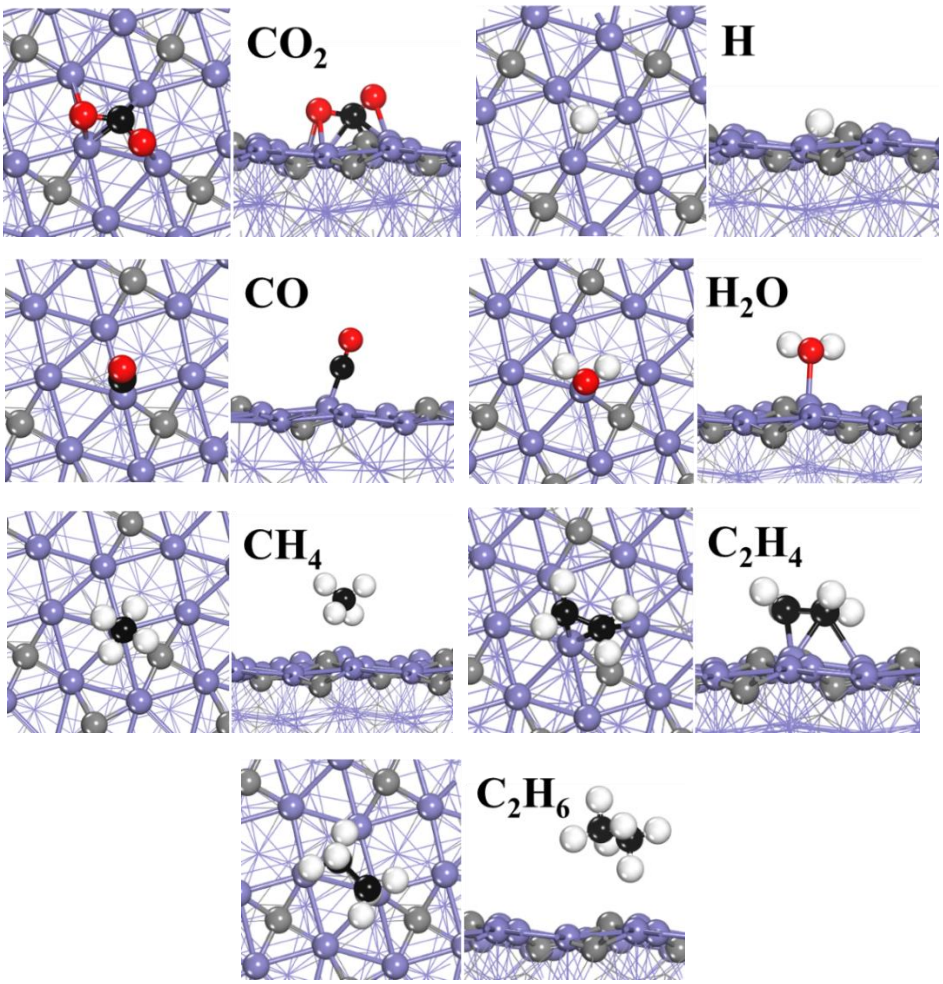


Figure S2. Top and side views of the most stable adsorption configurations of CO_2, H, CO, H_2O, CH_4, C_2H_4 and C_2H_6 on the χ-Fe_5C_2(510) surface. (purple: Fe; black: C of adsorbates; red: O; white: H; gray: C of χ-Fe_5C_2 catalyst.)

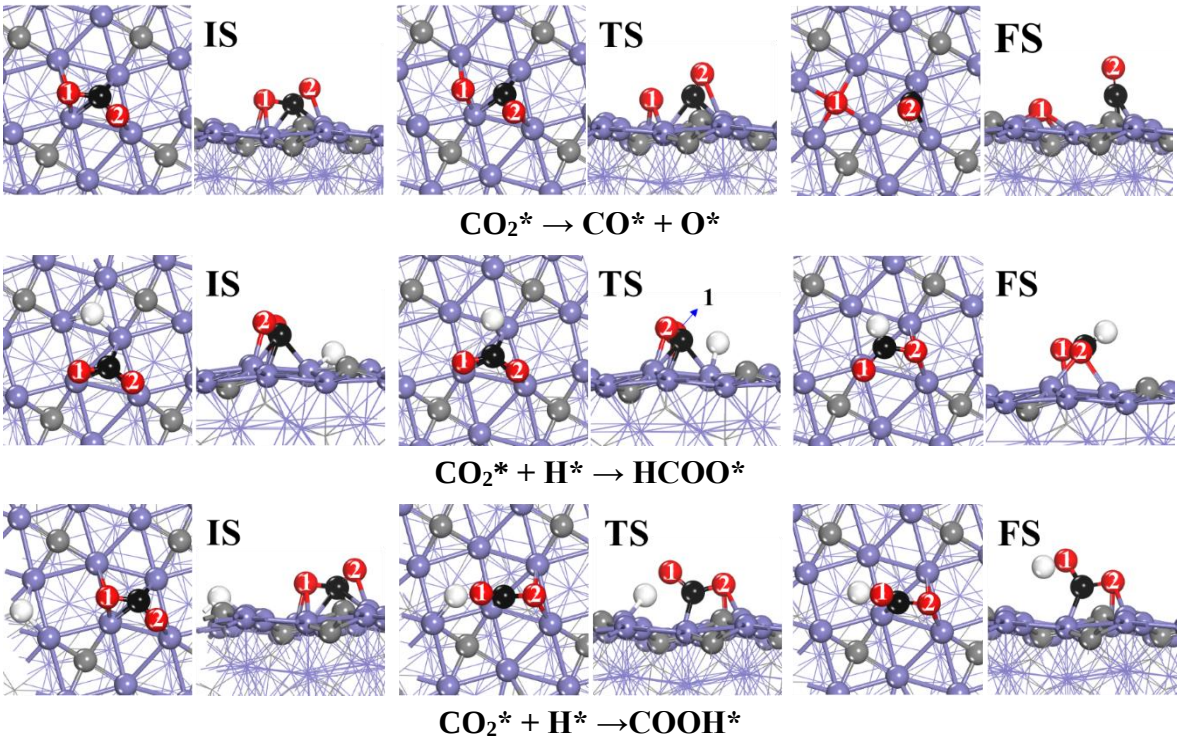
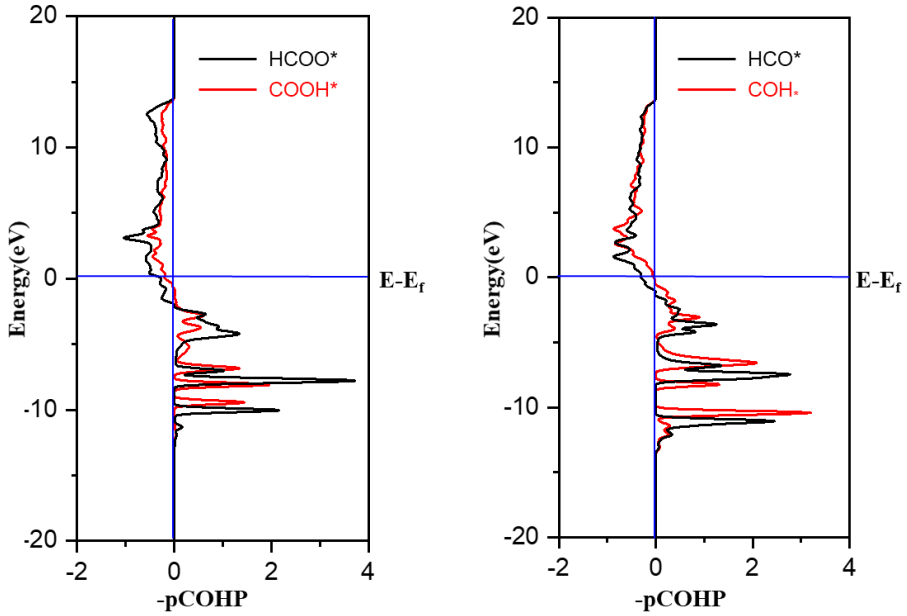


Figure S3. The initial, transition, and final states associated with CO_2 direct dissociation and initial hydrogenation on the χ-Fe_5C_2(510) surface. (purple: Fe; black: C of adsorbates; red: O; white: H; gray: C of χ-Fe_5C_2 catalyst.)



(a) (b)

Figure S4. The COHP analysis for the interaction of the bonds between the adsorbates and substrate in the transition states for (a) CO_2 and (b) CO hydrogenation over χ-Fe_5C_2(510).

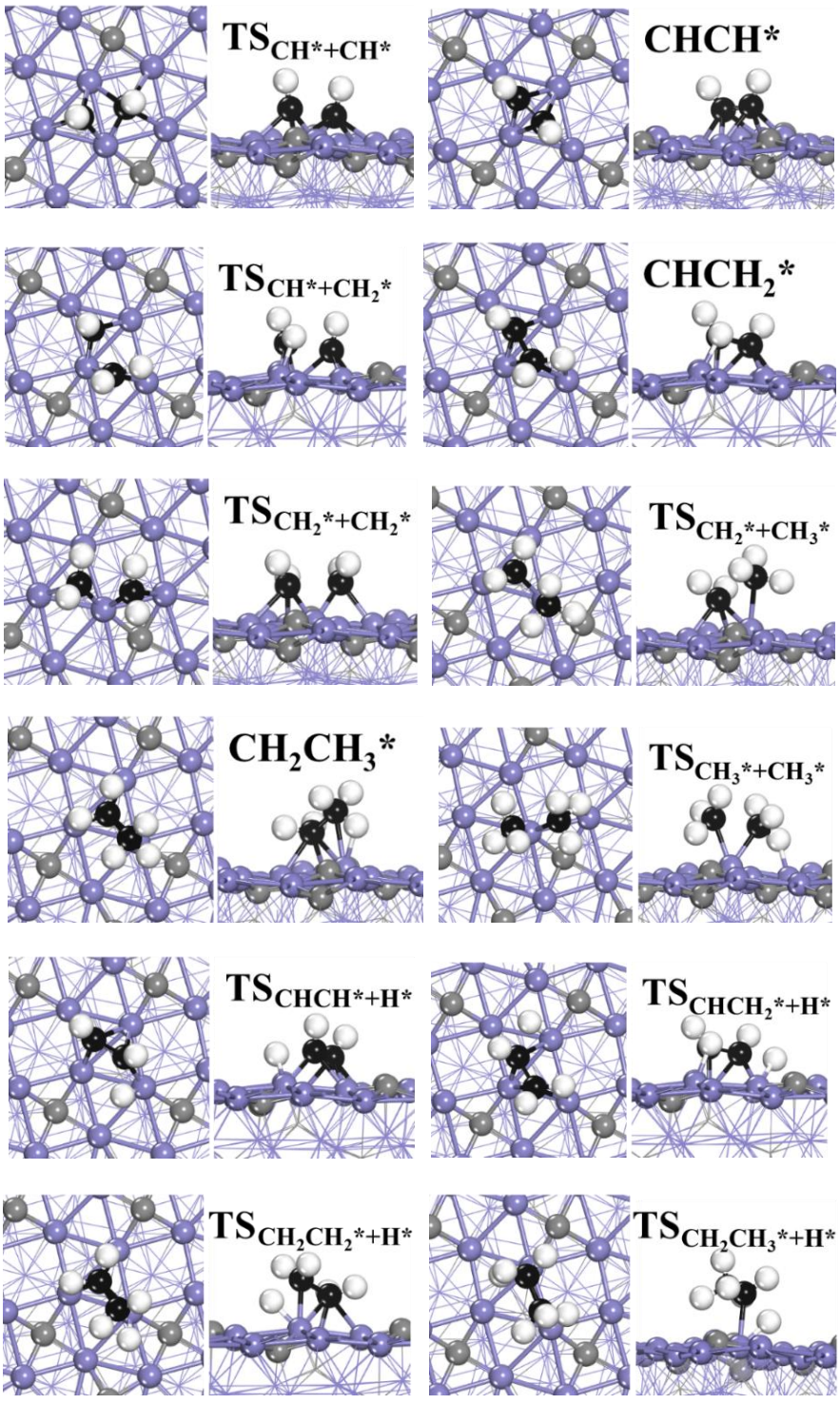
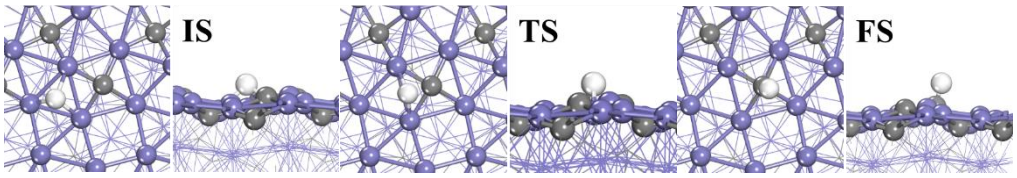
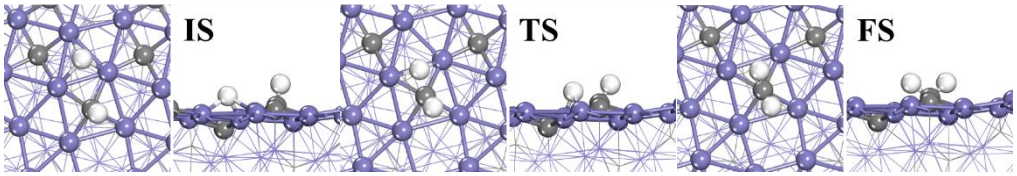


Figure S5. Corresponding structures of transition states and intermediates for C_2 hydrocarbons formation on the χ-Fe_5C_2(510) surface. (purple: Fe; black: C of adsorbates; white: H; gray: C of χ-Fe_5C_2 catalyst.)

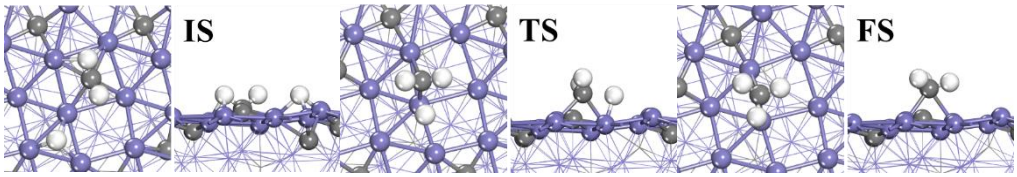
(a) States involved in C-vacancy formation



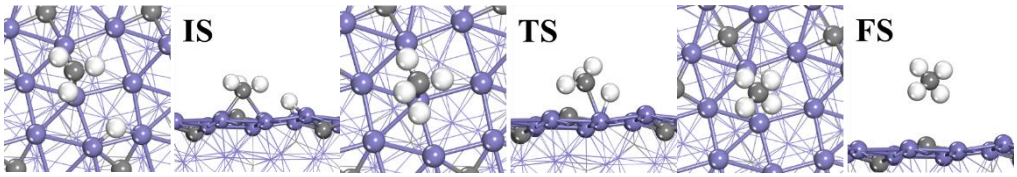
(1) C_{surf} + H* → CH*



(2) CH* + H* → CH_2*

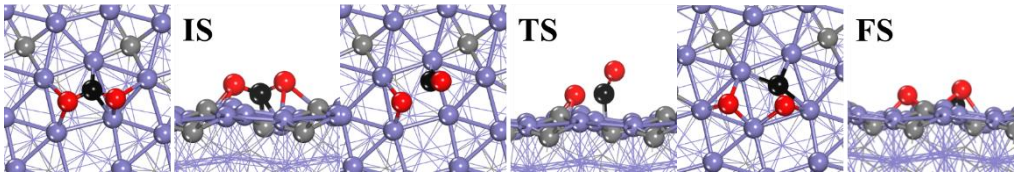


(3) CH_2* + H* → CH_3*

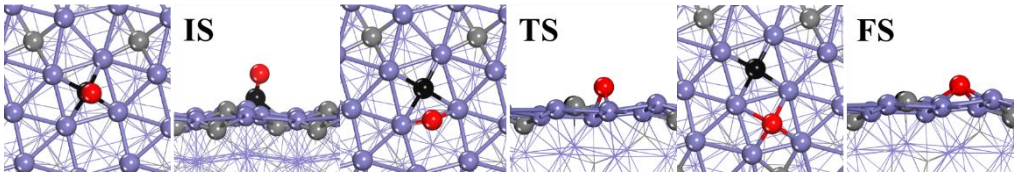


CH_3* + H* → CH_4(g)

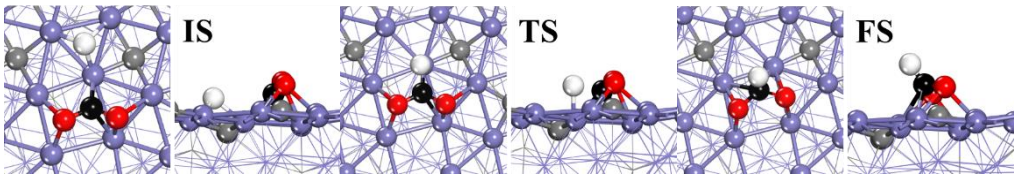
(b) CO_2 chemistry on the surface with a C-vacancy



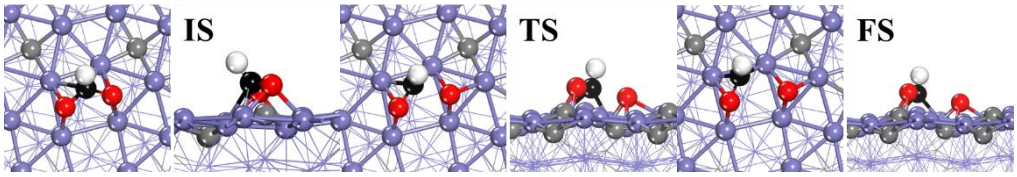
CO_2* → CO* + O*



CO* → C* + O*

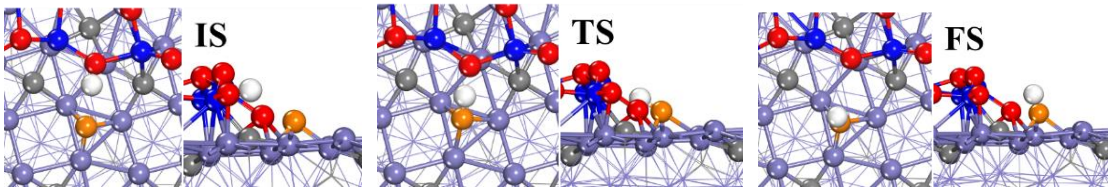


CO_2* + H* → HCOO*

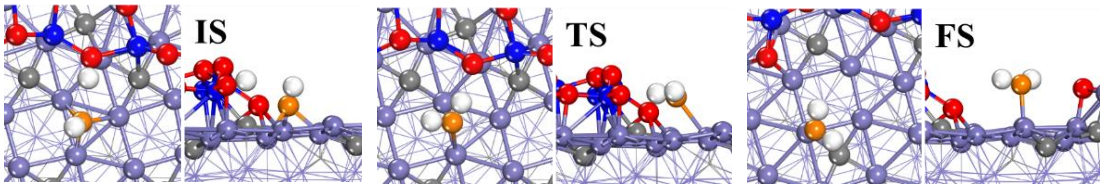


HCOO* →HCO* + O*

Figure S6. The initial, transition, and final states associated with (a) C vacancy formation on the χ-Fe_5C_2(510) surface and (b) CO_2 dissociation and hydrogenation on the χ-Fe_5C_2(510) surface with a C-vacancy. (purple: Fe; black: C of adsorbates; red: O; white: H; gray: C of χ-Fe_5C_2 catalyst.)



O* + H* → OH*



OH* + H* → H_2O*

Figure S7. The initial, transition, and final states associated for OH* and H_2O* formation on the interfacial site of χ-Fe_5C_2(510) and iron oxide. (purple: Fe; red: O of iron oxide catalyst; orange: O of adsorbates; white: H; gray: C of χ-Fe_5C_2 catalyst.)

Table S1. Impact of *k*-point on CO_2 adsorption energy and initial hydrogenation energetics.

	***k*-point**	
	3×3×1	**1×1×1**
CO_2 adsorption energy/eV	-0.68	-0.68
E_{act} (eV) for CO_2 to HCOO*	0.80	0.84
E_{act} (eV) for CO_2 to COOH*	1.26	1.28

Table S2. The calculated lattice parameter of Fe_5C_2 unit cell.

bulk	*a*	*b*	*c*	*α*	*β*	*γ*
Fe_5C_2	11.46 Å	4.47 Å	4.96 Å	90°	97.59°	90°
Ref [30]	11.55 Å	4.51 Å	4.99 Å	90°	97.63°	90°

Table S3. Key structural parameters for initial, transition, and final states involved in the "CO" pathway for methane synthesis from CO_2 hydrogenation on the χ-Fe_5C_2(510) surface. (Distances are in Angstroms, and angles are in degrees.)

CO_2* → CO* + O*				**CO* → C* + O***			
parameters	IS	TS	FS	parameters	IS	TS	FS
C-O_1	1.34	1.77	3.25	C-O_1	1.21	1.81	2.49
C-O_2	1.30	1.23	1.19				
∠O_1-C-O_2	124.1	115.6	96.1				
C* + H* → CH*				**CH* + H* → CH_2***			
parameters	IS	TS	FS	parameters	IS	TS	FS
C-H_{surf}	2.49	1.49	1.11	C-H_1	1.11	1.11	1.11
				C-H_{surf}	2.51	1.45	1.28
				∠H_1-C-H_{surf}	91.5	91.5	92.8
CH_2* + H* → CH_3*				**CH_3* + H* → CH_4***			
parameters	IS	TS	FS	parameters	IS	TS	FS
C-H_{1surf}	2.65	1.64	1.13	C-H_{1surf}	2.73	1.41	1.12
∠H_2-C-H_{surf}	83.40	96.31	104.43	∠H_2-C-H_{surf}	79.57	90.28	107.47
∠H_1-C-H_{surf}	135.3	93.3	105.2	∠H_1-C-H_{surf}	63.2	99.5	108.0

Table S4. Key structural parameters for initial, transition, and final states involved in the "HCOO" pathway for methane synthesis from CO_2 hydrogenation on the χ-Fe_5C_2(510) surface. (Distances are in Angstroms, and angles are in degrees.)

CO_2* + H* → HCOO*				**HCOO* → HCO* + O***			
parameters	IS	TS	FS	parameters	IS	TS	FS
C-H_{surf}	2.47	1.56	1.10	C-O_1	1.30	1.31	1.33
∠H-C-O_1	86.92	102.27	119.07	C-O_2	1.33	1.88	3.52
∠H-C-O_2	141.8	120.6	115.5	∠O_1-C-O_2	123.1	109.3	90.7
HCO* → CH* + O*				**HCOO* + H* → H_2COO***			
parameters	IS	TS	FS	parameters	IS	TS	FS
C-O	1.39	1.92	4.07	C-H_{surf}	2.98	1.24	1.11
C-H	1.11	1.10	1.10	∠H-C-O_1	54.19	104.94	109.39
∠H-C-O	109.9	90.3	80.5	∠H-C-O_2	89.3	109.4	108.0
HCO* + H* → H_2CO*				**H_2COO* → H_2CO* + O***			
parameters	IS	TS	FS	parameters	IS	TS	FS
C-H_1	1.11	1.11	1.14	C-O_1	1.42	1.28	1.37
C-H_{surf}	2.57	1.54	1.11	C-O_2	1.43	2.20	3.62
∠H_1-C-H_{surf}	73.7	90.3	104.8	∠O_1-C-O_2	111.9	102.2	98.3
H_2CO* → CH_2* + O*							
parameters	IS	TS	FS				
C-O	1.42	1.98	2.31				
∠H_1-C-O	109.99	88.66	77.63				
∠H_2-C-O	110.8	95.7	139.8				

Table S5. Key structural parameters for initial, transition, and final states involved in the "COOH" pathway for methane synthesis from CO_2 hydrogenation on the χ-Fe_5C_2(510) surface. (Distances are in Angstroms, and angles are in degrees.)

CO_2* + H* → COOH*				**COOH* → CO* + OH***			
parameters	IS	TS	FS	parameters	IS	TS	FS
O-H_{surf}	3.71	1.44	0.98	C-O_1	1.32	1.24	1.18
∠H-O_1-C	156.58	95.80	106.61	C-O_2	1.35	1.84	4.04
∠O_1-C-O_2	124.1	123.7	112.1	∠O_1-C-O_2	112.1	106.8	91.5

Table S6. Relative stabilities of adsorbed CH_x* (x = 1-3, E_x) species with respect to surface C* species.

Relative stabilities	**χ-Fe_5C_2(510)**
E_1	0.29
E_2	1.19
E_3	1.54