Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Suppression of Pt on CO Adsorption Dissociation and the Methane Formation on $Fe_5C_2(100)$ Surfaces

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Table S1 Computed adsorption energies (E_{ads}/eV) and bond lengths (d(C-O)/Å) of CO on perfect Fe_5C_2(100) surface

Surface	Site	E_{ads}/eV	d(C-O)/Å
Perfect (100)	Fe-T1	-1.74	1.170
	C-T	-0.73	1.182
	2F1	-0.82	1.214
	2F2	-0.86	1.209

Table S2 Computed adsorption energies (E_{ads}/eV) and bond lengths (d(C-O)/Å) of CO on Pt_{12} adsorbed perfect Fe_5C_2(100) surface

Surface	Site	E_{ads}/eV	d(C-O)/Å
Perfect (100)-Pt_{12}	Pt-T1	-1.82	1.162
	PF1	-1.70	1.183
	PF2	-1.53	1.184
	2P1	-1.71	1.183
	2P2	-1.72	1.186
	2P3	-1.62	1.180
	3P	-1.59	1.196
	2PF	-1.52	1.193
	2P2F	-1.41	1.206
	2F	-0.67	1.200

Table S3 Computed adsorption energies (E_{ads}/eV) and bond lengths (d(C-O)/Å) of CO on defect Fe_5C_2(100) surface

Surface	Site	E_{ads}/eV	d(C-O)/Å
Defect (100)	Fe-T1	-1.90	1.182
	C-T	-0.88	1.186
	2F1	-1.90	1.185
	2F2	-0.88	1.212
	3F1	-0.73	1.221
	4F1	-1.89	1.248
	4F2	-1.04	1.283
	5F1	-1.93	1.291
	5F2	-1.35	1.287
	6F1	-2.26	1.332

Table S4 Computed adsorption energies (E_{ads}/eV) and bond lengths (d(C-O)/Å) of CO on Pt_{12} adsorbed defect Fe_5C_2(100) surface

Surface	Site	E_{ads}/eV	d(C-O)/Å
Defect (100)-Pt_{12}	Pt-T1	-1.75	1.162
	PF1	-1.57	1.188
	2P1	-1.45	1.183
	2P2	-1.65	1.183
	2P3	-1.68	1.180
	2P4	-1.69	1.185
	2F	-1.74	1.180
	Fe-T1	-1.66	1.174
	5F1	-1.78	1.286
	6F1	-2.13	1.321

Table S5 Computed adsorption energies (E_{ads}/eV) and bond lengths (d(C-O)/Å) of CO on C*-free Fe_5C_2(100) surface

Surface	Site	E_{ads}/eV	d(C-O)/Å
C*-free (100)	5F1	-2.02	1.309
	5F2	-2.20	1.328
	Fe-T1	-1.76	1.176
	Fe-T2	-1.89	1.200

Table S6 Computed adsorption energies (E_{ads}/eV) and bond lengths (d(C-O)/Å) of CO on Pt_{12} adsorbed C*-free Fe_5C_2(100) surface

Surface	Site	E_{ads}/eV	d(C-O)/Å
C*-free (100)-Pt_{12}	Pt-T1	-1.40	1.162
	PF1	-1.47	1.186
	Fe-T1	-1.60	1.179
	2P1	-1.35	1.187
	2P2	-1.69	1.184
	3P1	-1.40	1.195
	P2F	-1.44	1.200
	2PF	-1.32	1.198
	2P2F	-1.39	1.218
	5F1	-2.13	1.307
	5F2	-2.18	1.318

Figure S1 Configurations of CO adsorption on perfect $Fe_5C_2(100)$ surface (blue: Fe, black: C, red: O, purple: C from CO)

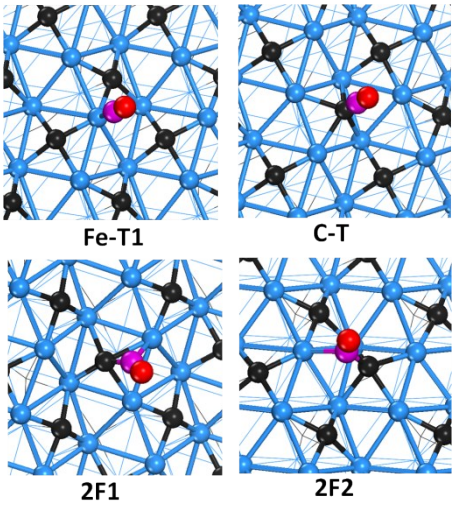

Figure S2 Configurations of CO adsorption on Pt_{12} adsorbed perfect $Fe_5C_2(100)$ surface (blue: Fe, black: C, red: O, purple: C from CO, green: Pt)

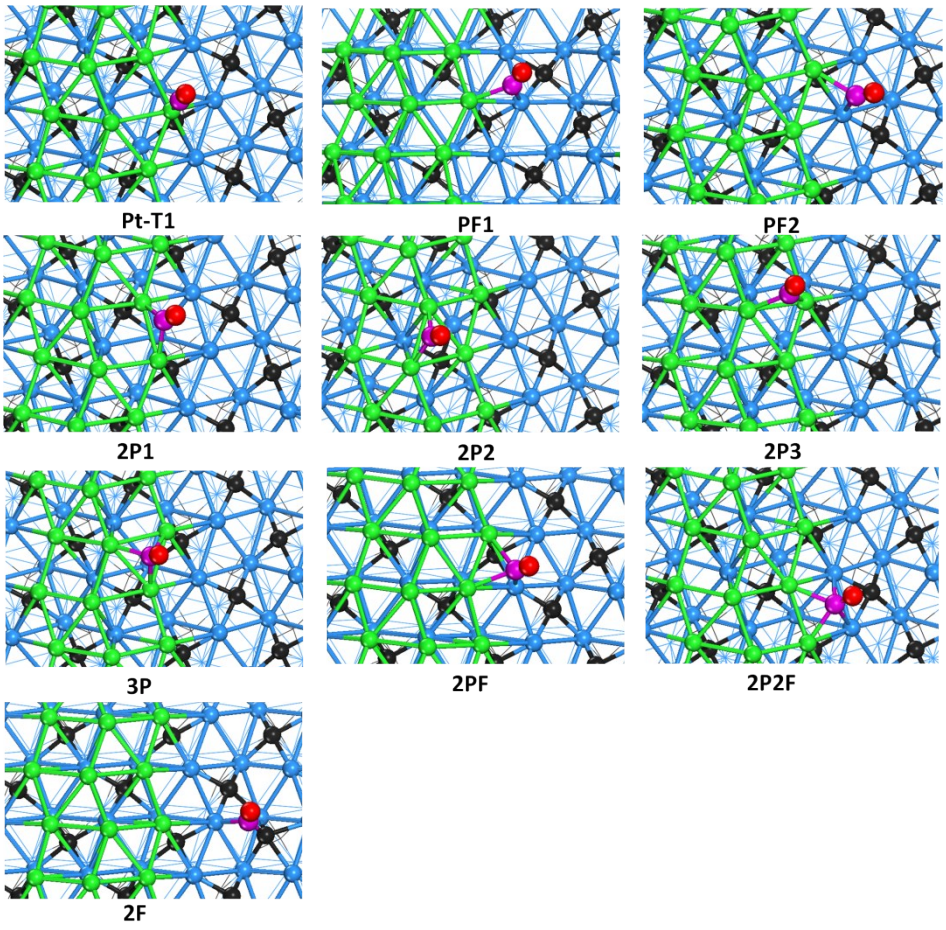

Figure S3 Configurations of CO adsorption on defect $Fe_5C_2(100)$ surface (blue: Fe, black: C, red: O, purple: C from CO)

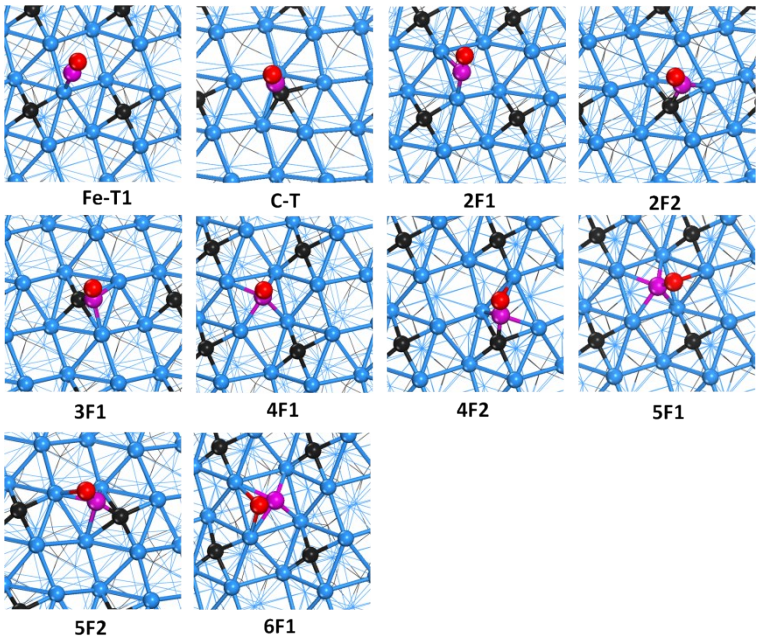

Figure S4 Configurations of CO adsorption on Pt_{12} adsorbed defect $Fe_5C_2(100)$ surface (blue: Fe, black: C, red: O, purple: C from CO, green: Pt)

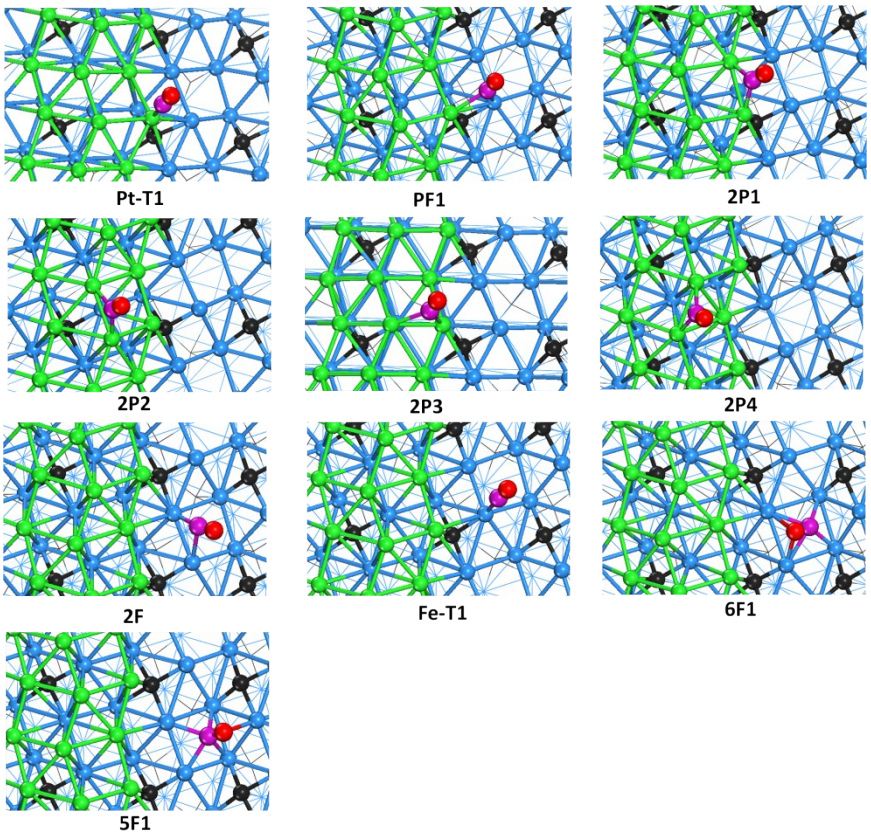

Figure S5 Configurations of CO adsorption on C*-free $Fe_5C_2(100)$ surface (blue: Fe, black: C, red: O, purple: C from CO)

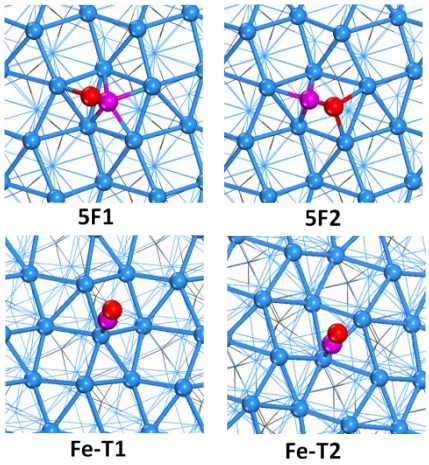

Figure S6 Configurations of CO adsorption on Pt_{12} adsorbed C*-free $Fe_5C_2(100)$ surface (blue: Fe, black: C, red: O, purple: C from CO, green: Pt)

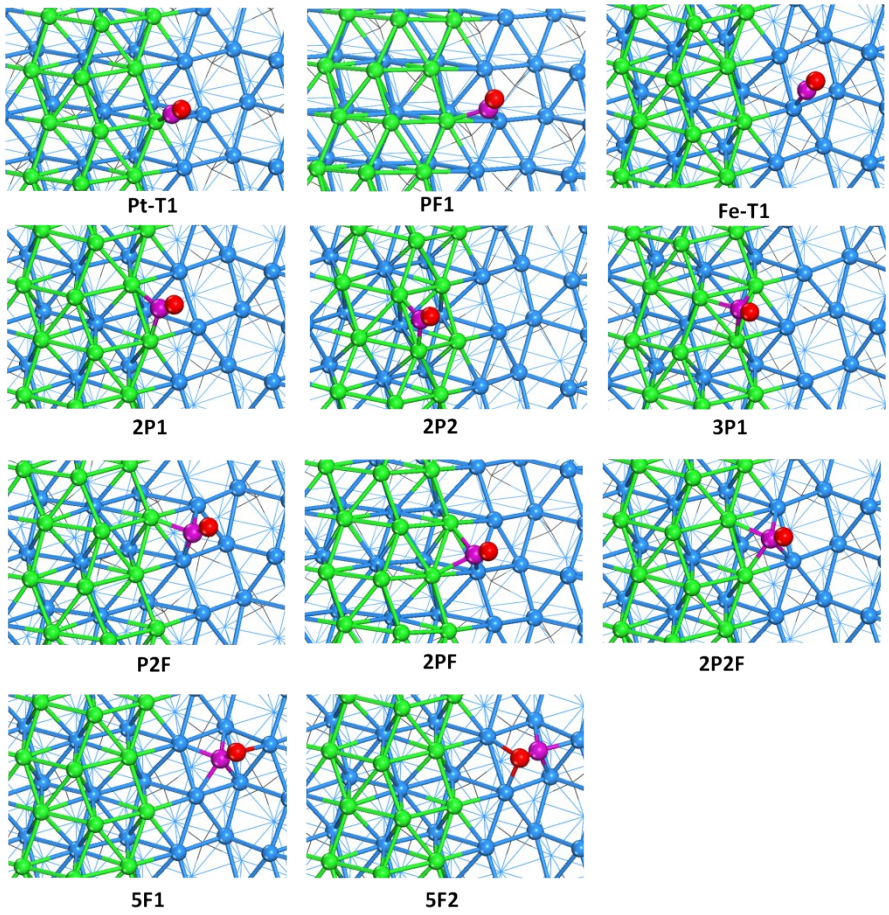

Figure S7 Structures and energies for direct (**D**) CO dissociation on perfect $Fe_5C_2(100)$ surfaces with Pt_{12} adsorption, dis1 is the dissociation pathway initiated from 2PF site, dis2, dis3, and dis4 are dissociation pathways from the 4-fold 2P2F site, dis5 is from the Fe-C 2F site, values without parentheses are the calculated adsorption energy originated from bare surface and free CO molecule, while the values in the parentheses represent the corresponding energy barriers, all the energy data have the unit of eV (Blue: Fe atoms; black: surface C atoms; red: O atoms; green: Pt atoms, purple: C atoms from CO)

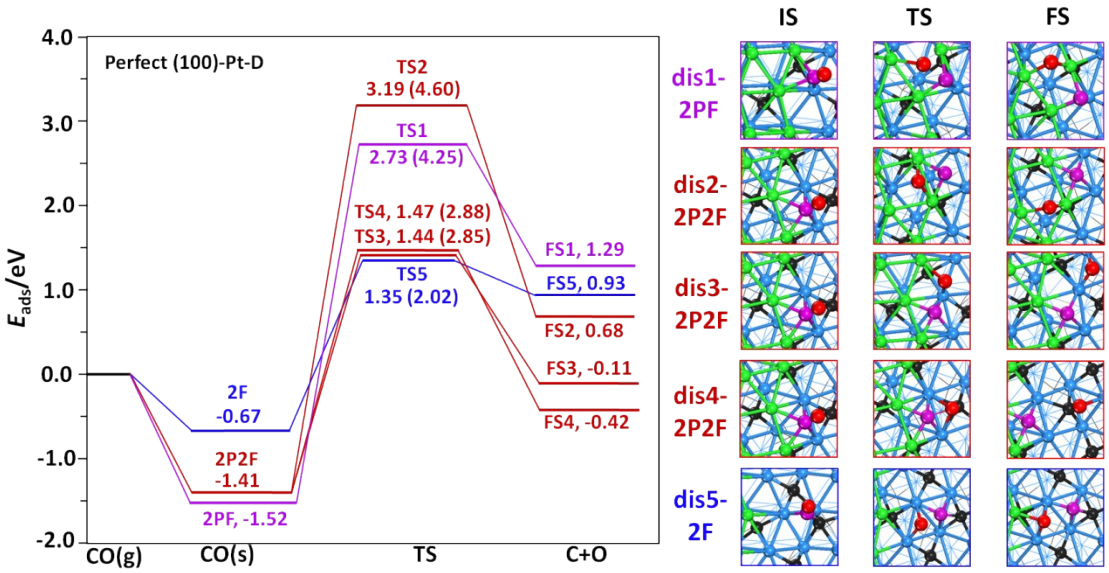

Figure S8 Structures and energies for H-assisted (**H**) CO dissociation on perfect $Fe_5C_2(100)$ surfaces with Pt_{12} adsorption, dis1 is the dissociation pathway initiated from 2PF site, dis2 is the dissociation pathway initiated from 2P site, dis3 is from the 4-fold 2P2F site, dis4 is from the Fe-C 2F site, values without parentheses are the calculated adsorption energy originated from bare surface and free CO molecule, while the values in the parentheses represent the corresponding energy barriers, all the energy data have the unit of eV (Blue: Fe; black: surface C; red: O; yellow: H, green: Pt, purple: C atoms from CO)

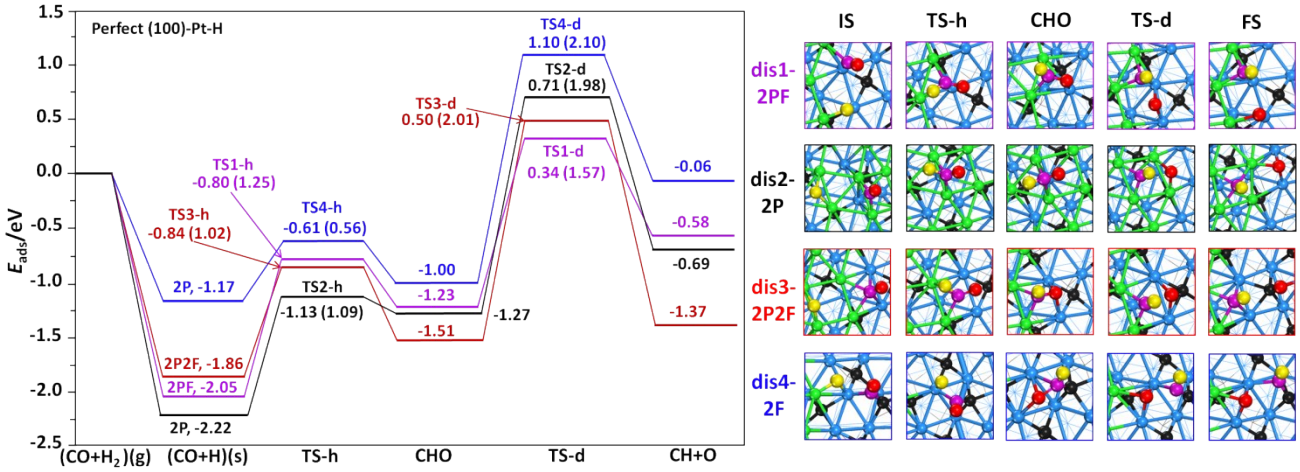

Figure S9 Structures and energies for direct (**D**) and H-assisted (**H**) CO dissociation on defect $Fe_5C_2(100)$ surfaces initiating from 6F1 (purple, dis1) and 5F1 (black, dis2) sites. (blue: Fe; black: surface C; red: O; yellow: H, purple: C atoms from CO)

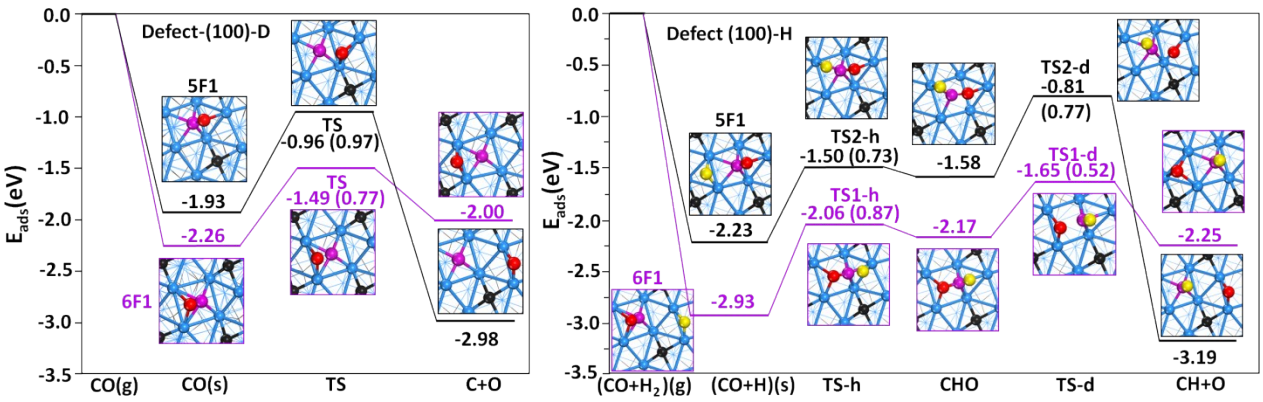

Figure S10 Structures and energies for direct (**D**) CO dissociation on defect $Fe_5C_2(100)$ surfaces with Pt_{12} adsorption, dis1-dis4 represent the dissociation from 6F1, 5F1, 2P1, and PF1 sites, respectively (Blue: Fe; black: surface C; red: O; yellow: H; green: Pt; purple: C atoms from CO)

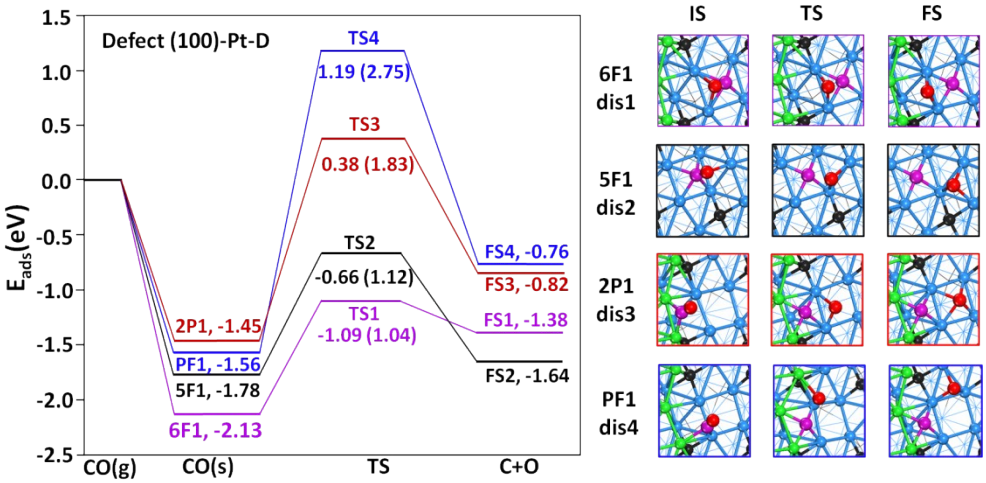

Figure S11 Structures and energies for H-assisted (**H**) CO dissociation on defect $Fe_5C_2(100)$ surfaces with Pt_{12} adsorption, dis1-dis4 represent the dissociation from 6F1, 5F1, 2P1, and PF1 sites, respectively (Blue: Fe; black: surface C; red: O; yellow: H, green: Pt, purple: C atoms from CO)

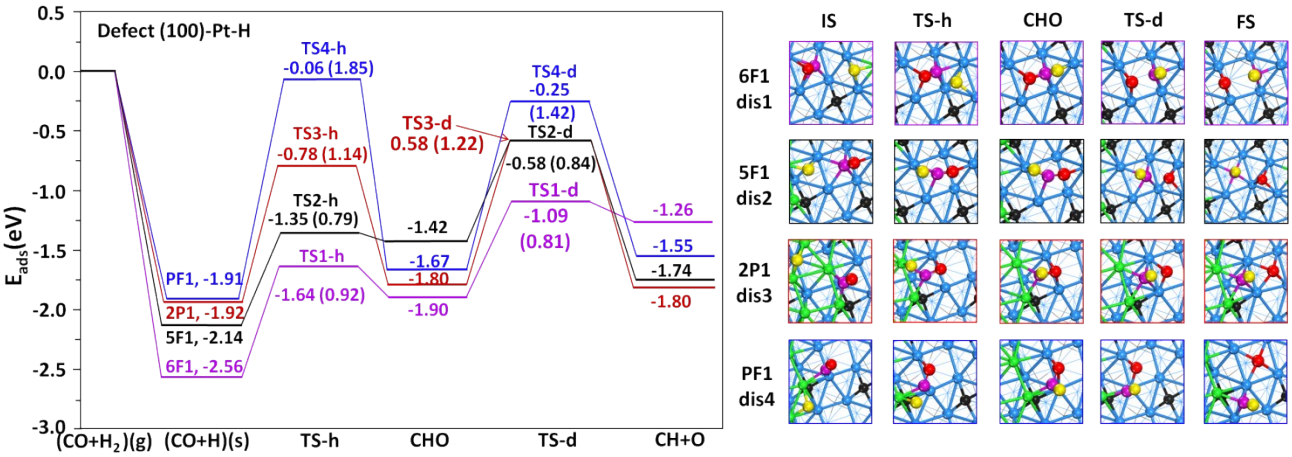

Figure S12 Structures and energies for direct (**D**) and H-assisted (**H**) CO dissociation initiating from 5F1 (black, dis2) and 5F2 (purple, dis1) sites on the C*-free Fe_5C_2(100) surfaces (Blue: Fe; black: surface C; red: O; yellow: H, purple: C atoms from CO)

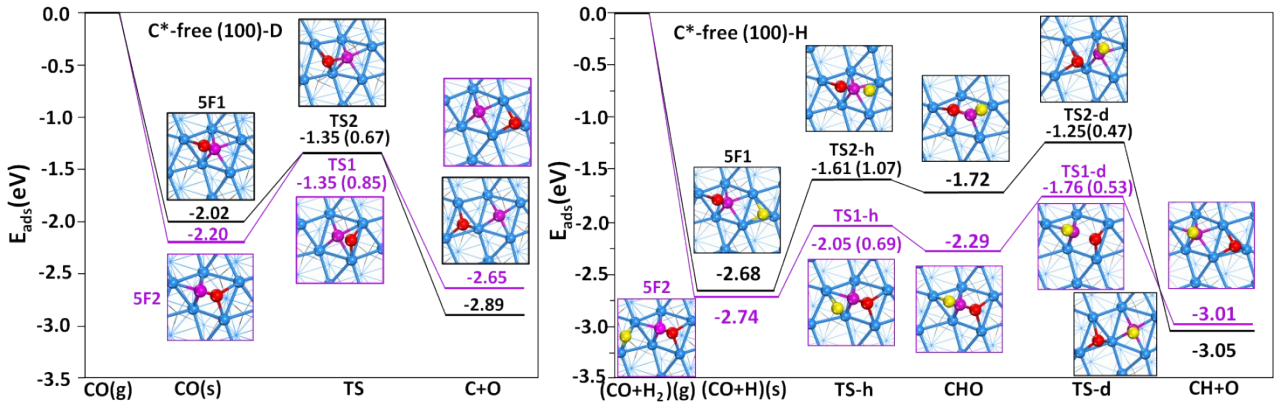

Figure S13 Structures and energies for direct (**D**) CO dissociation on C-free Fe_5C_2(100) surfaces with Pt_{12} adsorption, dis1, dis2, and dis3 represent the dissociation from 5F2, 5F1, and 2P2F sites, respectively (Blue: Fe; black: surface C; red: O; yellow: H; green: Pt; purple: C from CO)

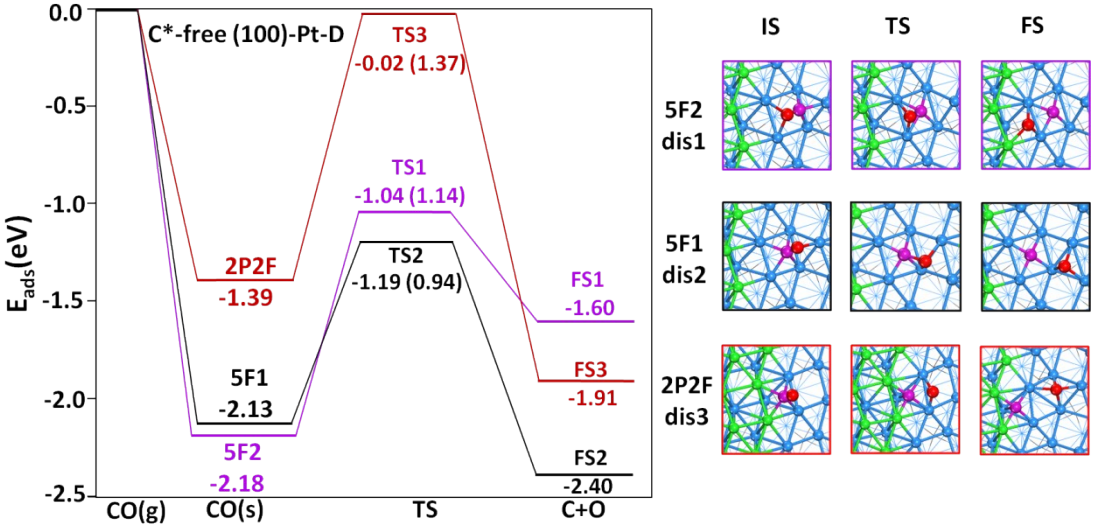

Figure S14 Structures and energies for H-assisted (**H**) CO dissociation on C-free $Fe_5C_2(100)$ surfaces with Pt_{12} adsorption, dis1, dis2, and dis3 represent the dissociation from 5F2, 5F1, and 2P2F sites, respectively (Blue: Fe; black: surface C; red: O; yellow: H, green: Pt, purple: C atoms from CO)