Supporting Information

Theoretical Insight into h-Fe_7C_3 Catalyzed Fischer-Tropsch Synthesis: Unraveling C_{2+} Product Formation Mechanism and Surface-specific Electronic Descriptors

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Fig. S2 The structures of the transition states for coupling reactions under (a) CO insertion mechanism and (b) Carbide mechanism on different h-Fe_7C_3 surfaces. (purple: Fe atoms; gray: C atoms; red: O atoms; yellow: H atoms).

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Fig. S4 Structures of the intermediate products for (a) CsH_4 formation and (b) C_dH_4 formation on h-Fe_7C_3 surfaces (purple: Fe atoms; gray: C atoms; red: O atoms; yellow: H atoms).

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Computational details

Method. All spin-polarized DFT calculations were performed using the Material Studio CASTEP package. The Perdew-Burke-Ernzerh (PBE) functional together with the generalized gradient approximation (GGA) are adopt to describe the electron exchange correlation energy. [1-4] The cutoff energy of 400 eV was used for the plane wave basis set, and the k point mesh was set to 2×3×1 with sampling density of 0.25 $Å^{-1}$. The convergence criteria for energy and the self-consistent field were set to 2×10^{-5} eV/atom and 2×10^{-6} eV/atom, respectively. Zero point energy correction could be ignored. [5-10] Moreover, Mulliken charge is adopted to analyze the electron interaction between atoms in the model. [11] Mulliken population analysis is based the electron-ion interactions described by ultra-soft pseudopotentials, and the exchange-correlation effects described by the GGA-PBE functional. The convergence parameters, including the plane-wave cutoff energy, k-point grid density, and SCF tolerance, were set to the "Fine" quality (400 eV, 0.04 $Å^{-1}$, and 2.0×10^{-6} eV/atom, respectively). The Mulliken population analysis was performed based on the optimized structure to quantify the charge transfer. The reactant charge, $q_{M(IS)}$, is defined as the total charge of the reactant species. For instance, on the (101) surface, the value of -1.21 eV for CO and Cs coupling route under CO insertion mechanism is derived from the sum of the Mulliken charges for constituent atoms of the reactant (C, O, and Cs). While the value of -1.29 eV for Cs and C_dH coupling route under carbide mechanism is derived from the sum of the Mulliken charges for its constituent atoms (Cs, C_d and H). It is properly considered the charge of the vacant surface site (*) in the calculation of $q_{M(IS)}$. However, since the vacant surface site is not an individual atom, no explicit charge is assigned to it in the Mulliken population analysis.We therefore used the Mulliken charges of the corresponding surface atoms to characterize its electronic state.

For evaluating the energy pathways, the transition states were located using the LST/QST method in CASTEP. [12] The reaction energy and the energy barrier are calculated by $\Delta E_r = E(FS) - E(IS)$ and $E_a = E(TS) - E(IS)$, where E(IS), E(TS), and E(FS) are the energies of the corresponding initial state (IS), transition state (TS), and final state (FS), respectively. Recently, for a series of consecutive reactions, the effective energy barriers ($_{Eeff}$) has been used as a descriptor to evaluate FTS selectivity. [13-22] The E_{eff} of the k^{th} elementary reaction in a consecutive reactions is calculated by

the following formula: $E_{eff,k} = E_{a,k} + \sum_{i}^{k-1} \Delta E_{r,i} + \sum_{i}^{k-1} \Delta E_{m,i}$, where the $E_{eff,k}$ is the effective energy barrier of the k[th] elementary reaction, the $E_{a,k}$ is the intrinsic energy barrier of the k[th] step elementary reaction, $\sum_{i}^{k-1} \Delta E_{r,i}$ and $\sum_{i}^{k-1} \Delta E_{m,i}$ are the sum of the reaction energy and the sum of the migration energy from the i[th] step elementary reaction to the (k-1)[th] step elementary reaction, in which the i[th] step elementary reaction represents the elementary reaction whose initial state is the most stable in the consecutive reactions. From the energy profile, E_{eff} represents the overall energy barrier defined as the energy difference between the highest-energy TS and the most stable C_1 species.

Reaction route. The reaction route for C-C coupling under carbide mechanism and CO-insertion mechanism and CH_4 formation are respectively illustrated in Figure S1. Four typical carbon-containing facets of (101), $(1\bar{1}\bar{1})$, $(1\bar{1}0)$ and $(1\bar{1}1)$ on h-Fe_7C_3 are systematically investigated. Based on previous calculation results, [23-24] the $(1\bar{1}0)$ and $(1\bar{1}1)$ surfaces are not considered for carbide coupling process, as it is difficult to activate CO to obtain dissociated carbon atom (C_d).

There are two kinds of carbon atoms on h-Fe_7C_3 surface, one is the surface carbon (Cs) atom of the iron carbide, and the other is the dissociated carbon (C_d) atom from CO adsorbed on the surface, both of which may be gradually hydrogenated to CH_4. Therefore, they are respectively considered in this paper.

As a rich source of C_1 key raw materials, the synthesis of C_{2+} compounds through C-C coupling reaction is a highly attractive and challenging reaction in Fischer-Tropsch synthesis. This article explores the coupling intermediates and reaction pathways in the generation process of C_{2+} compounds from the perspectives of carbide mechanism and CO insertion mechanism, in order to deeply understand the chemical process of C-C coupling and provide reference for rational regulation of product selectivity.

For the reaction of C-C coupling involving catalyst surface carbon atoms, Cs atoms with weak adsorption energy are preferentially selected. The adsorption energy of Cs atom on the surface can be calculated by the following formula: $E_{ads,CS} = E_{slab} - E_{slab-CS} - E_{CS}$, where E_{slab} is the energy of the pristine crystal slab, E_{Cs} is the energy of an isolated C_S atom which escaped from crystal slab, and $E_{slab-Cs}$ is the

energy of the crystal slab with a carbon vacancy.

Table S1 Size of the slabs and k-points test for the surface energy calculation [23-24]

Surface	Supercell size	k-point	Vacuum space(Å)	n(atoms)	Energy(J/m^2)
$(1\bar{1}1)$	p(1×1×2)	3×5×1	10	C12Fe28	2.693
	p(2×2×2)	2×1×1	10	C48Fe112	2.679
	p(2×2×3)	2×1×1	10	C72Fe168	2.616
	p(2×2×3)	2×2×1	10	C72Fe168	2.613
	p(2×2×3)	2×3×1	10	C72Fe168	2.613
	p(2×2×3)	2×3×1	15	C72Fe168	2.615
$(1\bar{1}0)$	p(1×1×2)	3×5×1	10	C12Fe28	2.972
	p(1×1×9)	3×5×1	10	C54Fe126	2.864
	p(2×2×2)	2×3×1	10	C48Fe112	2.787
	p(2×2×3)	2×3×1	10	C72Fe168	2.760
	p(2×2×3)	2×3×1	15	C72Fe168	2.764
$(1\bar{1}\bar{1})$	p(2×2×3)	1×2×1	10	C72Fe168	2.702
	p(2×2×3)	2×3×1	10	C72Fe168	2.703
	p(2×2×3)	2×3×1	15	C72Fe168	2.709
(101)	p(2×2×3)	1×2×1	10	C72Fe168	2.702
	p(2×2×3)	2×2×1	10	C72Fe168	2.703
	p(2×2×3)	2×3×1	10	C72Fe168	2.703
	p(2×2×3)	2×3×1	15	C72Fe168	2.697

Table S2 Parameters test of surface energy, adsorption energy, reaction energy barrier (E_a) and reaction energy (ΔE_r) of CO=C+O on the most stable sites [23-24]

Surface	Energy cut-off	Force (eV/Å)	Energy convergence(Å)	Surface Energy(J/m^2)	E_{ads}-CO (eV)	E_{ads}-C+O(eV)	E_a (eV)	ΔE_r (eV)
(101)	400	0.05	2 x 10^{-5}	2.70	-3.51	-4.57	1.48	-1.06
	450	0.05	2 x 10^{-5}	2.70	-3.48	-4.49	1.46	-1.01
	400	0.03	2 x 10^{-5}	2.70	-3.50	-4.47	1.45	-0.97
	400	0.1	2 x 10^{-5}	2.71	-3.47	-4.46	1.49	-0.99
	400	0.05	1 x 10^{-5}	2.70	-3.53	-4.57	1.47	-1.04
	400	0.05	1 x 10^{-6}	2.70	-3.48	-4.53	1.46	-1.05
$(1\bar{1}\bar{1})$	400	0.05	2 x 10^{-5}	2.70	-3.73	-2.74	2.93	0.99
	450	0.05	2 x 10^{-5}	2.70	-3.68	-2.65	2.91	1.03
	400	0.03	2 x 10^{-5}	2.70	-3.71	-2.66	2.88	1.05
	400	0.1	2 x 10^{-5}	2.71	-3.67	-2.69	2.94	0.98
	400	0.05	1 x 10^{-5}	2.70	-3.74	-2.75	2.85	0.99
	400	0.05	1 x 10^{-6}	2.70	-3.74	-2.72	2.89	1.02
$(1\bar{1}0)$	400	0.05	2 x 10^{-5}	2.76	-2.49	-2.16	3.21	0.33
	450	0.05	2 x 10^{-5}	2.76	-2.08	-1.92	3.05	0.16
	400	0.03	2 x 10^{-5}	2.76	-2.47	-2.12	3.24	0.35
	400	0.1	2 x 10^{-5}	2.76	-2.40	-2.33	3.16	0.07
	400	0.05	1 x 10^{-5}	2.76	-2.48	-2.13	3.29	0.35
	400	0.05	1 x 10^{-6}	2.76	-2.49	-2.17	3.18	0.32
$(1\bar{1}1)$	400	0.05	2 x 10^{-5}	2.61	-3.03	-4.35	0.97	-1.32
	450	0.05	2 x 10^{-5}	2.61	-2.96	-4.33	0.86	-1.37
	400	0.03	2 x 10^{-5}	2.61	-3.00	-4.31	0.95	-1.31
	400	0.1	2 x 10^{-5}	2.61	-3.05	-4.31	0.99	-1.26
	400	0.05	1 x 10^{-5}	2.61	-2.95	-4.22	1.02	-1.27
	400	0.05	1 x 10^{-6}	2.61	-3.02	-4.32	0.90	-1.30

Table S3 Calculated surface energies for different surfaces of h-Fe_7C_3 [23-24]

Possible exposed surface	This work Surface energy (J/m^2)	Ref. 25 Surface energy (J/m^2)
$(1\bar{1}1)$	2.613	--
(101)	2.703	2.87
(011)	2.804	2.87
$(1\bar{1}\bar{1})$	2.703	--
$(0\bar{1}\bar{1})$	2.796	--
$(10\bar{1})$	2.812	--
$(1\bar{1}0)$	2.760	--
(100)	2.916	2.92
(110)	3.123	3.19
$(\bar{1}\bar{1}0)$	3.142	--
(001)	3.255	3.41
(111)	3.301	3.43

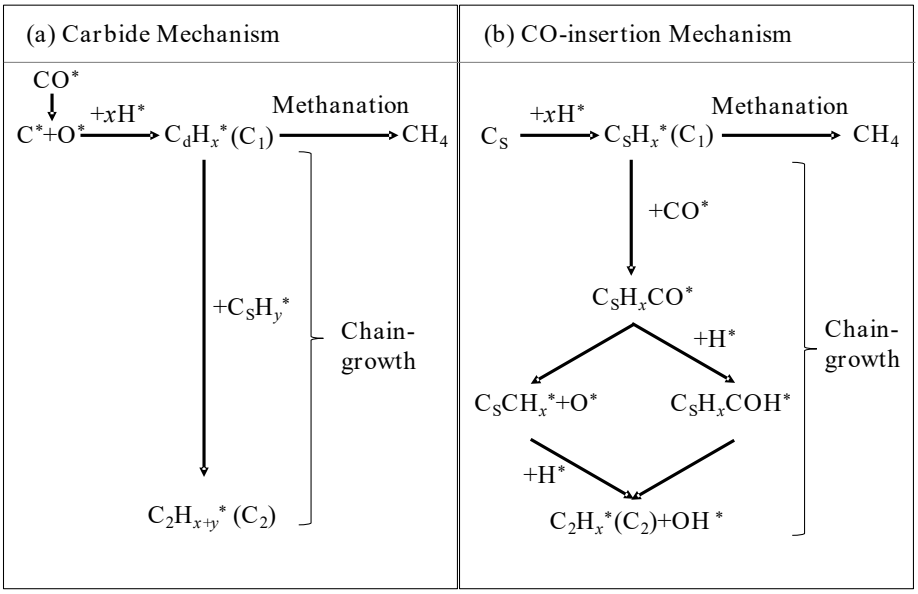


Fig. S1 The reaction route for C-C coupling under (a) carbide mechanism and (b) CO-insertion mechanism and CH_4 formation

Table S4 Schematic top view of h-Fe_7C_3 surfaces and adsorption energies of surface carbons [24]

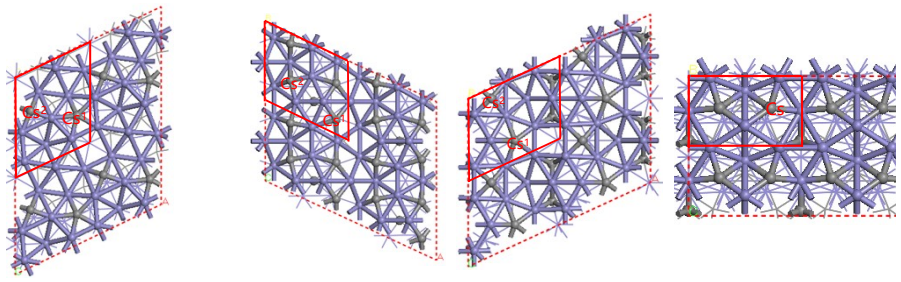
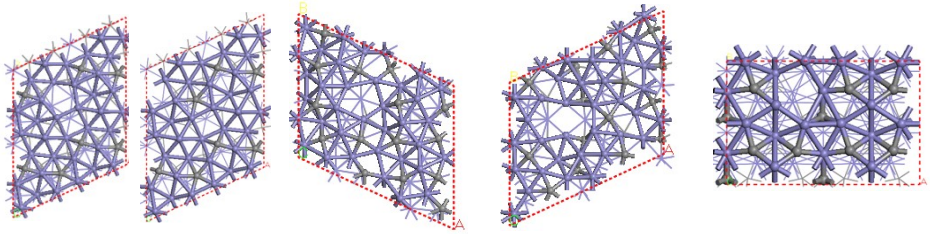
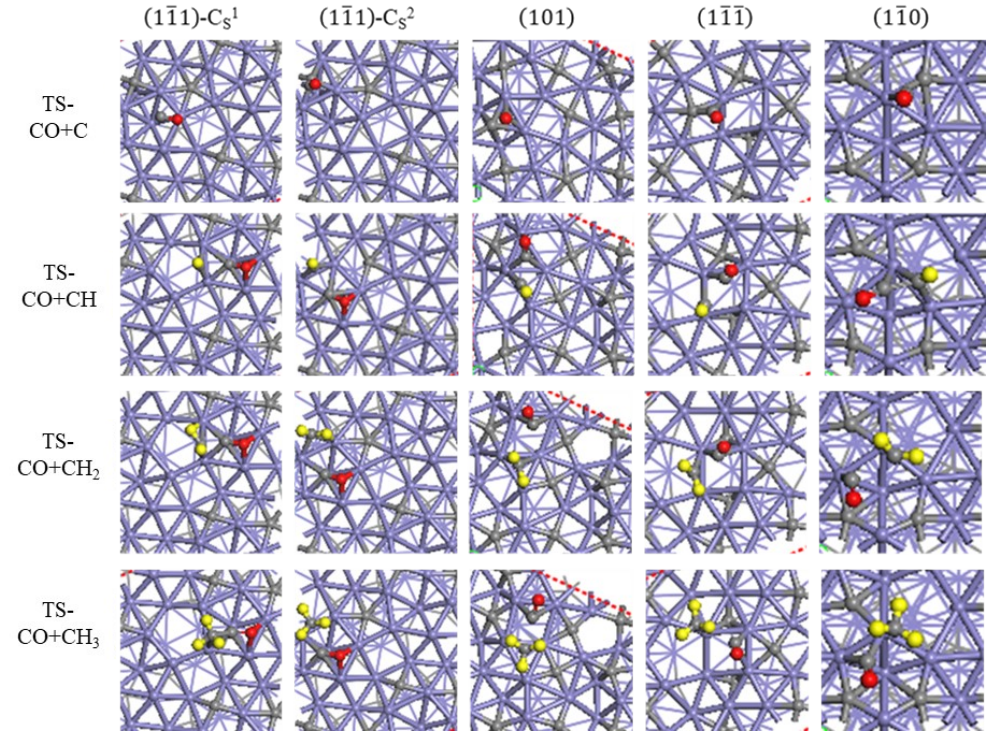
Perfect surfaces	$(1\bar{1}1)$	(101)	$(1\bar{1}\bar{1})$	$(1\bar{1}0)$
Lattice parameters (Å)	a=13.5118, b=16.0530, c=19.4845	a=16.0530, b=13.5118, c=20.0028	a=16.0530, b=13.5118, c=20.0028	a=13.5118, b=8.6678, c=26.5543
Schematic top view				
	C_s^1	C_s^2	C_s^1	C_s^2	C_s^1	C_s^2	C_s
$E_{ads(Cs)}$(eV)	-10.196	-10.273	-8.802	-9.049	-8.415	-9.575	-12.642
Defective surface	$(1\bar{1}1)_{VCs1}$	$(1\bar{1}1)_{VCs2}$	$(101)_{VCs1}$		$(1\bar{1}\bar{1})_{VCs1}$		$(1\bar{1}0)_{VCs}$
Schematic top view							

Table S5 The elemental reaction barrier (E_a, in eV) and reaction energy (ΔE_r, in eV) for coupling reactions on h-Fe_7C_3 surfaces

Reactions steps	$(1\bar{1}1)$				(101)		$(1\bar{1}\bar{1})$		$(1\bar{1}0)$	
	C_s^1		C_s^2		C_s^1		C_s^1		E_a	ΔE_r
	E_a	ΔE_r	E_a	ΔE_r	E_a	ΔE_r	E_a	ΔE_r		
CO insertion mechanism										
$CO^*+C_s=C_sCO^*$	3.43	2.07	4.05	2.07	1.35	1.18	**0.97**	**0.99**	**1.64**	**1.53**
$CO^*+C_sH^*=C_sHCO^*+*$	2.12	0.82	2.27	0.81	0.64	2.03	2.17	1.21	1.87	0.99
$CO^*+C_sH_2^*=C_sH_2CO^*+*$	**1.79**	**0.86**	**1.39**	**0.56**	**0.31**	**1.28**	2.38	1.52	2.10	1.06
$CO^*+C_sH_3^*=C_sH_3CO^*+*$	2.05	1.23	1.53	0.67	0.63	2.85	1.90	-0.01	1.78	1.08
Carbide mechanism										
$C_s + C_d^* = C_sC_d^*$	3.51	1.65	3.36	1.33	1.66	0.88	--	--	--	--
$C_s + C_dH^* = C_sC_dH^*$	2.79	0.45	2.28	-0.13	1.68	0.52	--	--	--	--
$C_s + C_dH_2^* = C_sC_dH_2^*$	2.12	0.75	2.23	0.93	1.48	0.29	--	--	--	--
$C_s + C_dH_3^* = C_sC_dH_3^*$	2.00	0.98	1.62	0.60	1.32	0.31	--	--	--	--
$C_sH^* + C_dH^* = C_sHC_dH^*+*$	2.47	1.04	2.33	0.86	2.06	1.03	--	--	--	--
$C_sH^* + C_dH_2^*= C_sHC_dH_2^*+*$	2.72	0.35	1.94	0.95	1.74	0.69	--	--	--	--
$C_sH^* + C_dH_3^*= C_sHC_dH_3^*+*$	3.84	0.76	2.25	0.95	2.24	0.56	--	--	--	--
$C_sH_2^* +C_dH_2^*=C_sH_2C_dH_2^*+*$	1.27	-0.24	1.01	-0.34	2.27	0.61	--	--	--	--
$C_sH_2^* +C_dH_3^*=C_sH_2C_dH_3^*+*$	3.20	0.51	1.75	0.33	2.76	0.92	--	--	--	--

$C_sH_3^*+C_dH_3^*=C_sH_3C_dH_3^*+*$	2.81	0.93	2.35	0.79	4.30	1.14	--	--	--	--

(a) CO insertion mechanism



(b) Carbide mechanism

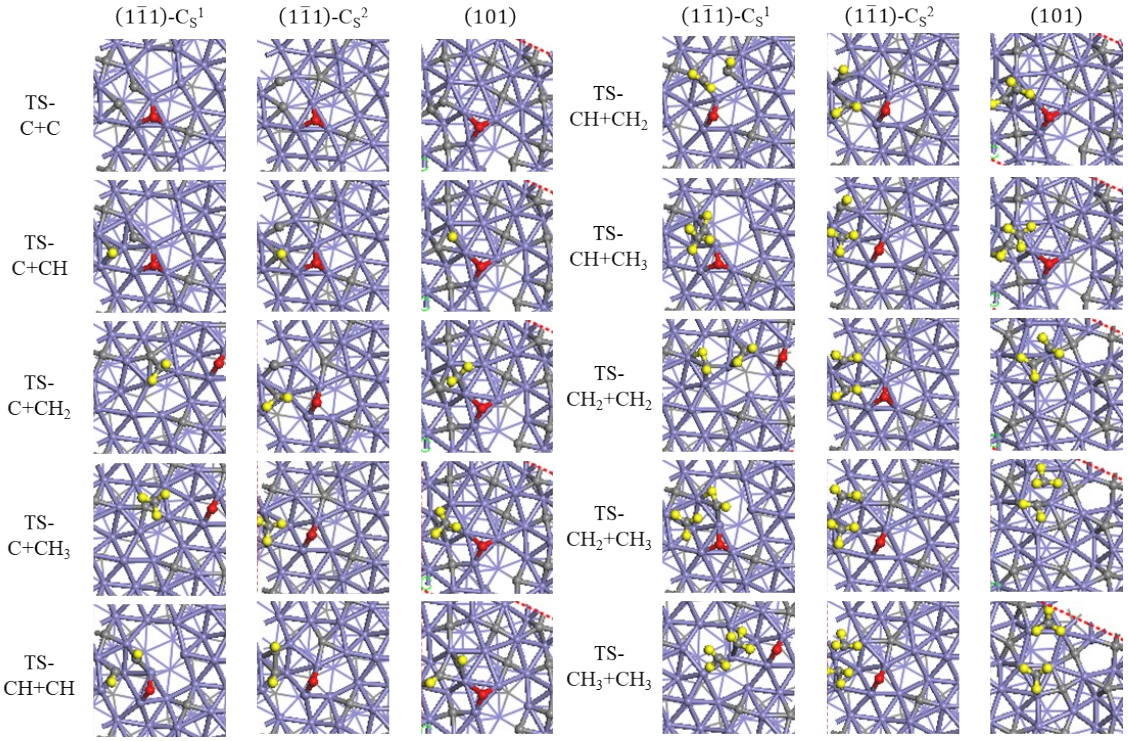


Fig. S2 The structures of the transition states for coupling reactions under (a) CO insertion

mechanism and (b) Carbide mechanism on different h-Fe_7C_3 surfaces. (purple: Fe atoms; gray: C atoms; red: O atoms; yellow: H atoms).

Table S6 The elemental reaction barrier (E_a, in eV) and reaction energy (ΔE_r, in eV) for C_{2+} formation on h-Fe_7C_3 (101), $(1\bar{1}\bar{1})$ and $(1\bar{1}0)$ surfaces

Reactions steps	(101)		$(1\bar{1}\bar{1})$		$(1\bar{1}0)$	
	E_a	ΔE_r	E_a	ΔE_r	E_a	ΔE_r
$CsCO^* + H^* = CsCOH^* + *$	2.04	0.48	3.15	0.02	1.75	-0.59
$CsCOH^* + * = CsC^* + OH^*$	1.48	-0.54	1.57	-0.15	1.48	-0.10
$CsCO^* + * = CsC^* + O^*$	1.63	-1.97	0.91	-0.96	1.44	-0.17
$CsC^* + O^* + H^* = CsC^* + OH^* + *$	0.77	1.61	1.72	0.49	0.87	-0.80

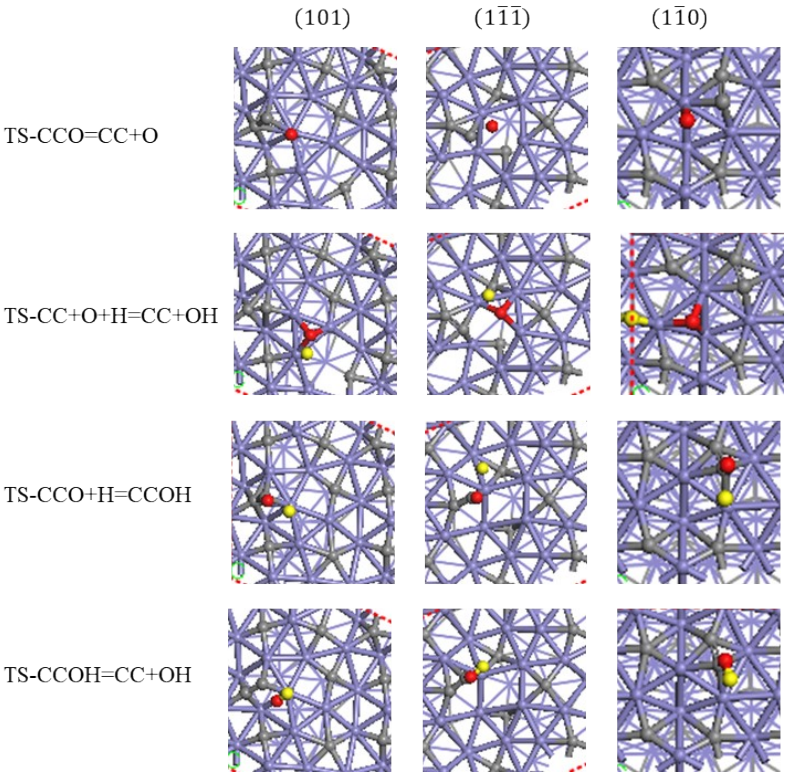


Fig. S3 Structures of the transition states for C_{2+} formation on h-Fe_7C_3 surfaces.

Table S7 The elemental reaction barrier (E_a, in eV) and reaction energy (Δ_rE, in eV) for CH_4 formation on h-Fe_7C_3 surfaces

Reactions steps	$(1\bar{1}1)$				(101)		$(1\bar{1}\bar{1})$		$(1\bar{1}0)$	
C_sH_4 formation	C_s^1		C_s^2		C_s^1		C_s^1		C_s	
	E_a	ΔE_r	E_a	ΔE_r	E_a	ΔE_r	E_a	ΔE_r	E_a	ΔE_r
$C_s+H^*=C_sH^*$	1.07	0.55	1.28	0.78	0.91	0.77	0.72	0.04	0.82	0.69
$C_sH^*+H^*=C_sH_2^*+*$	1.24	0.41	1.24	1.06	1.49	0.66	0.78	0.69	1.48	0.83
$C_sH_2^*+H^*=C_sH_3^*+*$	0.87	0.38	1.17	0.42	0.89	0.23	1.74	0.22	0.34	-0.21
$C_sH_3^*+H^*=C_sH_4+2*$	1.90	0.91	1.48	1.02	0.87	0.42	1.18	0.19	1.45	0.48
C_dH_4 formation	E_a		ΔE_r		E_a	ΔE_r				
$C_d^*+O^*+H^*=C_dH^*+O^*+*$	1.32		1.20		1.54	-0.24				
$C_dH^*+O^*+H^*=C_dH_2^*+O^*+*$	1.36		1.06		1.45	0.67				
$C_dH_2^*+O^*+H^*=C_dH_3^*+O^*+*$	0.90		-0.15		1.34	0.41				
$C_dH_3^*+O^*+H^*=C_dH_4+O^*+2*$	0.62		0.87		2.82	0.32				

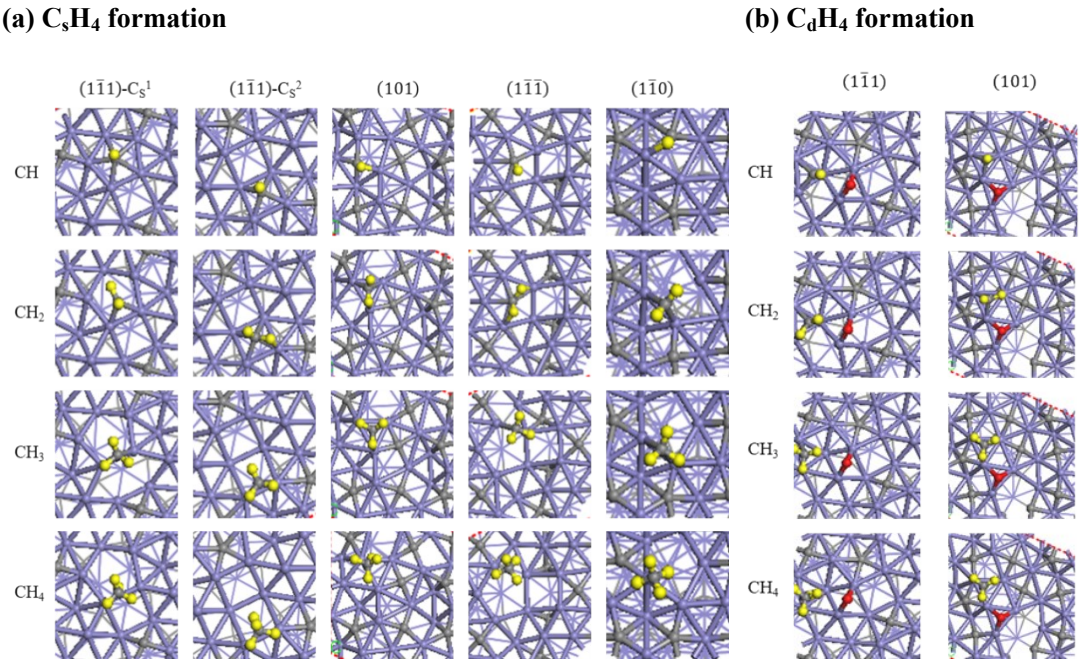


Fig. S4 Structures of the intermediate products for (a) CsH_4 formation and (b) C_dH_4 formation on h-Fe_7C_3 surfaces (purple: Fe atoms; gray: C atoms; red: O atoms; yellow: H atoms).

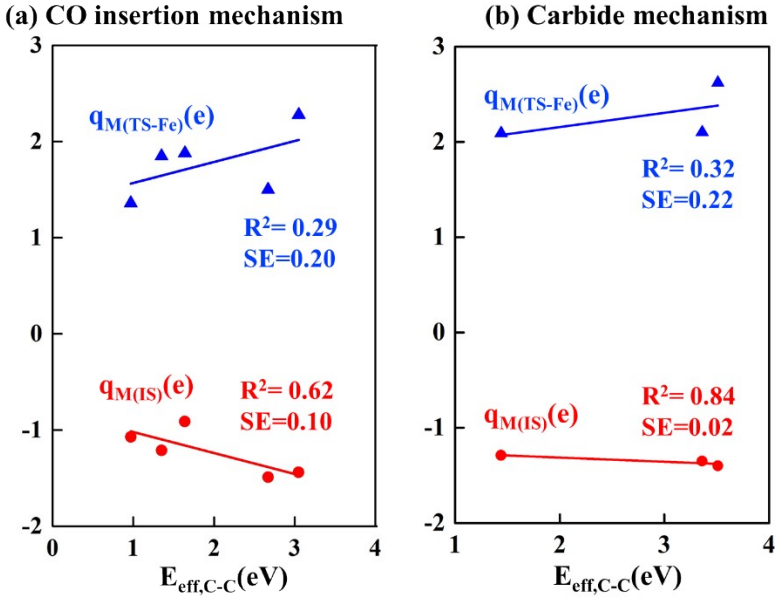


Fig. S5 The relationships between E_{eff} for C-C coupling and $q_{M(IS)}$ and $q_{M(TS-Fe)}$ on different h-

Fe_7C_3 Surfaces.

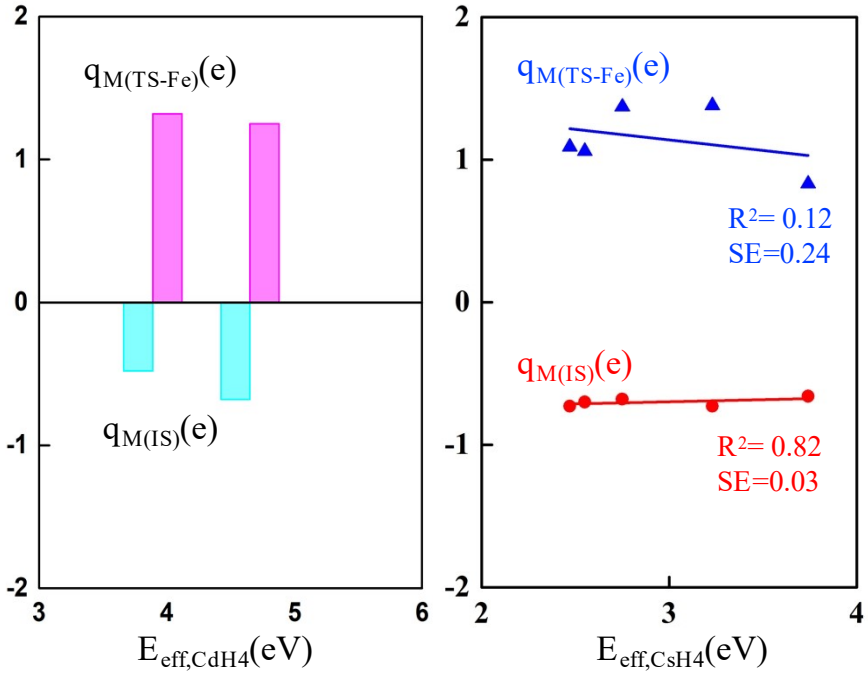


Fig. S6 The relationships between $E_{eff,CH4}$ and $q_{M(IS)}$ and $q_{M(TS-Fe)}$ on different h-Fe_7C_3 Surfaces.

Table S8 E_{eff} for direct CO dissociation(*+CO*→C*+O*), $E_{ads(CO)}$, $d_{(C-O)}$, $q_{M(IS-CO)}$ and $q_{M(TS-Fe)}$ on h-Fe_7C_3 surfaces.

Surface	E_{eff} (eV)	$E_{ads(CO)}$ (eV)	$d_{(C-O)}$ (eV)	$q_{M(IS)}$ (eV)	$q_{M(TS-Fe)}$ (eV)
Perfect surfaces					
(001)	0.92	-2.67	1.32	-0.77	1.15
$(1\bar{1}1)$	0.97	-3.03	1.36	-0.78	1.92
(101)	1.48	-3.51	1.21	-0.52	1.83
$(1\bar{1}\bar{1})$	2.93	-3.73	1.19	-0.38	0.60
$(1\bar{1}0)$	3.21	-2.49	1.18	-0.22	0.47
Carbon-defective surfaces					
$(101)_{VCs1}$	1.02	-2.46	1.21	-0.58	3.16
$(1\bar{1}\bar{1})_{VCs1}$	0.89	-2.86	1.29	-0.67	1.70
$(1\bar{1}1)_{VCs1}$	0.85	-2.90	1.36	-0.79	2.68
$(1\bar{1}1)_{VCs2}$	0.78	-3.09	1.37	-0.80	2.53

$(1\bar{1}0)_{VCs}$	0.74	-2.95	1.41	-0.86	2.23

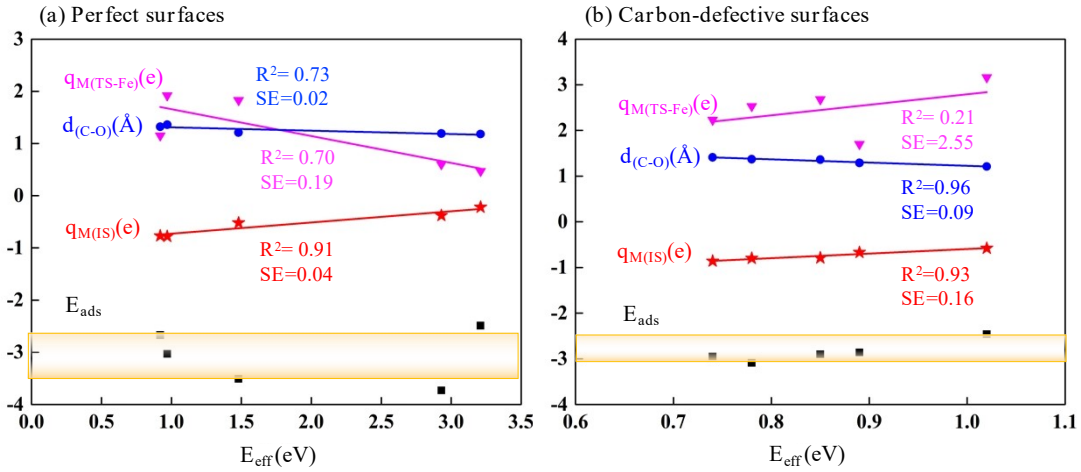


Fig. S7 The relationships between E_{eff} for direct CO dissociation and $E_{ads(CO)}$, $d_{(C-O)}$, $q_{M(IS)}$, $q_{M(TS-Fe)}$ on h-Fe_7C_3 (a) perfect surfaces and (b) carbon-defective surfaces.

Table S9 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for CO + Cs^1H = Cs^1HCO on h-Fe_7C_3 $(1\bar{1}1)$ surface

IS-CO+Cs^1H					TS-CO + Cs^1H= Cs^1HCO					FS-Cs^1HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
H	1	0.419984	0.661920	0.553423	H	1	0.513559	0.640381	0.588940	H	1	0.576864	0.626257	0.594392
C	1	0.102233	0.294153	0.461959	C	1	0.103086	0.292612	0.462952	C	1	0.103721	0.291508	0.463493
C	2	0.138050	0.498781	0.375619	C	2	0.138599	0.498224	0.375968	C	2	0.138814	0.497937	0.376305
C	3	0.359148	0.496311	0.377279	C	3	0.359053	0.498327	0.375365	C	3	0.357855	0.499761	0.374090
C	4	0.424698	0.147265	0.451309	C	4	0.425706	0.147845	0.452279	C	4	0.426276	0.148110	0.452947
C	5	0.484158	0.264522	0.368640	C	5	0.482899	0.265908	0.369065	C	5	0.481667	0.267399	0.369819
C	6	0.249198	0.266701	0.368268	C	6	0.250491	0.267208	0.369413	C	6	0.251405	0.267485	0.370244
C	7	0.602088	0.293932	0.462338	C	7	0.603724	0.293282	0.462439	C	7	0.604722	0.292915	0.463518
C	8	0.636755	0.502576	0.372655	C	8	0.638035	0.501608	0.372179	C	8	0.636809	0.502190	0.377568
C	9	0.852960	0.503268	0.374781	C	9	0.854844	0.500954	0.380194	C	9	0.856208	0.499109	0.383222
C	10	0.923680	0.151857	0.452573	C	10	0.925639	0.148585	0.451061	C	10	0.926681	0.146709	0.450043
C	11	0.980919	0.267527	0.367054	C	11	0.983294	0.266072	0.367037	C	11	0.984609	0.265070	0.366499
C	12	0.750024	0.266319	0.369190	C	12	0.750755	0.265943	0.367821	C	12	0.750328	0.266721	0.367753
C	13	0.105563	0.786974	0.465992	C	13	0.103737	0.790674	0.464336	C	13	0.101460	0.793495	0.462920
C	14	0.158612	0.981844	0.389759	C	14	0.149169	0.991715	0.380663	C	14	0.142456	0.998976	0.375226
C	15	0.358905	1.005379	0.368234	C	15	0.359522	1.002660	0.371551	C	15	0.359439	1.000098	0.374290
C	16	0.458679	0.787756	0.370712	C	16	0.472701	0.773612	0.368367	C	16	0.480526	0.765425	0.368057
C	17	0.261332	0.757790	0.377222	C	17	0.255402	0.759949	0.373859	C	17	0.250810	0.761492	0.370840
C	18	0.605025	0.797066	0.471492	C	18	0.601795	0.799008	0.465865	C	18	0.599526	0.798284	0.464840

IS-CO+Cs[1]H					TS-CO + Cs[1]H= Cs[1]HCO					FS-Cs[1]HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	19	0.641704	1.000973	0.375458	C	19	0.642116	1.000175	0.374477	C	19	0.642081	0.999090	0.374603
C	20	0.863839	0.996890	0.380768	C	20	0.861407	0.998641	0.375567	C	20	0.859499	0.999684	0.372251
C	21	0.922305	0.647337	0.449456	C	21	0.923967	0.647206	0.451237	C	21	0.925277	0.647237	0.452294
C	22	0.984132	0.765723	0.367729	C	22	0.981383	0.766860	0.367254	C	22	0.978878	0.767511	0.366839
C	23	0.743423	0.766844	0.371041	C	23	0.747135	0.765209	0.369706	C	23	0.747705	0.764586	0.369843
C	24	0.425187	0.654412	0.496387	C	24	0.526361	0.628774	0.534709	C	24	0.595320	0.615770	0.539391
C	25	0.680330	0.585043	0.497880	C	25	0.688229	0.572776	0.502044	C	25	0.699032	0.564008	0.511745
O	1	0.770457	0.538074	0.536112	O	1	0.779967	0.528616	0.540795	O	1	0.798735	0.516309	0.542900
Fe	1	0.212958	0.072413	0.395415	Fe	1	0.213078	0.074692	0.398773	Fe	1	0.212889	0.076318	0.401414
Fe	2	0.356473	0.285478	0.417399	Fe	2	0.357318	0.285558	0.420120	Fe	2	0.357697	0.285601	0.421995
Fe	3	0.286069	0.422783	0.354816	Fe	3	0.287151	0.421912	0.356291	Fe	3	0.288207	0.421593	0.357539
Fe	4	0.133732	0.230321	0.370192	Fe	4	0.134857	0.230600	0.370750	Fe	4	0.135604	0.230834	0.370995
Fe	5	0.252060	0.209188	0.461134	Fe	5	0.252855	0.208599	0.462552	Fe	5	0.253307	0.208369	0.463478
Fe	6	0.072300	0.048945	0.465546	Fe	6	0.071535	0.044647	0.462459	Fe	6	0.071621	0.041990	0.460445
Fe	7	0.036356	0.211267	0.462707	Fe	7	0.038120	0.208760	0.462646	Fe	7	0.039082	0.207327	0.462565
Fe	8	0.382775	0.041144	0.458732	Fe	8	0.385027	0.042176	0.459443	Fe	8	0.386213	0.043135	0.460440
Fe	9	0.280957	0.439321	0.469200	Fe	9	0.280648	0.442625	0.469942	Fe	9	0.279716	0.445203	0.470722
Fe	10	-0.002446	0.494781	0.369947	Fe	10	-0.001388	0.494189	0.372247	Fe	10	-0.000562	0.493632	0.373215
Fe	11	0.343764	0.135857	0.364099	Fe	11	0.342956	0.136718	0.365092	Fe	11	0.342565	0.137059	0.365769
Fe	12	0.468929	0.373884	0.416423	Fe	12	0.470184	0.372863	0.417247	Fe	12	0.470679	0.372879	0.419219
Fe	13	0.021840	0.137825	0.366389	Fe	13	0.022633	0.135758	0.365624	Fe	13	0.022785	0.135034	0.364951
Fe	14	0.156428	0.373959	0.419144	Fe	14	0.156862	0.373110	0.419970	Fe	14	0.156960	0.372716	0.420419

IS-CO+Cs[1]H					TS-CO + Cs[1]H= Cs[1]HCO					FS-Cs[1]HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	15	0.714663	0.075159	0.405470	Fe	15	0.713451	0.075806	0.401238	Fe	15	0.712225	0.076337	0.398707
Fe	16	0.856126	0.286237	0.419118	Fe	16	0.858374	0.283109	0.417651	Fe	16	0.859410	0.281520	0.417205
Fe	17	0.784463	0.425726	0.354098	Fe	17	0.784950	0.425450	0.355793	Fe	17	0.784304	0.425641	0.357853
Fe	18	0.635636	0.229633	0.371441	Fe	18	0.634724	0.231172	0.370337	Fe	18	0.633813	0.232709	0.370256
Fe	19	0.751517	0.211083	0.463654	Fe	19	0.752593	0.209076	0.462224	Fe	19	0.753132	0.207749	0.461790
Fe	20	0.570602	0.042228	0.461434	Fe	20	0.571995	0.043041	0.460457	Fe	20	0.572738	0.043637	0.460385
Fe	21	0.535831	0.210248	0.462405	Fe	21	0.538187	0.209320	0.462474	Fe	21	0.539455	0.209027	0.462816
Fe	22	0.888856	0.045200	0.464670	Fe	22	0.886282	0.043179	0.461293	Fe	22	0.884700	0.042183	0.458985
Fe	23	0.773528	0.441603	0.470791	Fe	23	0.782513	0.434642	0.473305	Fe	23	0.791018	0.428755	0.475050
Fe	24	0.502325	0.496522	0.368126	Fe	24	0.503430	0.494594	0.367153	Fe	24	0.502685	0.493024	0.368891
Fe	25	0.844393	0.135076	0.367821	Fe	25	0.843586	0.135115	0.365310	Fe	25	0.842345	0.136003	0.363826
Fe	26	0.966956	0.373288	0.416757	Fe	26	0.968533	0.371171	0.417701	Fe	26	0.970100	0.369447	0.417776
Fe	27	0.523090	0.133663	0.366144	Fe	27	0.522267	0.135640	0.365598	Fe	27	0.521475	0.137169	0.365429
Fe	28	0.657404	0.374566	0.419422	Fe	28	0.659411	0.373459	0.419568	Fe	28	0.661042	0.373252	0.422058
Fe	29	0.210922	0.574452	0.403184	Fe	29	0.208796	0.575825	0.399639	Fe	29	0.207647	0.577017	0.397527
Fe	30	0.365815	0.772292	0.437496	Fe	30	0.359167	0.782994	0.424651	Fe	30	0.355980	0.786164	0.416171
Fe	31	0.318594	0.906542	0.361765	Fe	31	0.299717	0.916733	0.357044	Fe	31	0.288735	0.923517	0.354237
Fe	32	0.135501	0.729673	0.373512	Fe	32	0.132959	0.730408	0.371275	Fe	32	0.130257	0.731317	0.369129
Fe	33	0.255810	0.699157	0.466938	Fe	33	0.251038	0.703915	0.463462	Fe	33	0.248220	0.707110	0.461126
Fe	34	0.068475	0.543265	0.461318	Fe	34	0.072070	0.543762	0.462067	Fe	34	0.074297	0.544002	0.462567
Fe	35	0.036292	0.706741	0.463526	Fe	35	0.036048	0.708668	0.463209	Fe	35	0.035844	0.709968	0.462586
Fe	36	0.389878	0.547194	0.462791	Fe	36	0.385073	0.543825	0.461181	Fe	36	0.381780	0.543034	0.460971

IS-CO+Cs[1]H					TS-CO + Cs[1]H= Cs[1]HCO					FS-Cs[1]HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	37	0.274346	0.942878	0.470558	Fe	37	0.277266	0.940677	0.469773	Fe	37	0.278871	0.938110	0.468616
Fe	38	0.010845	0.990693	0.376131	Fe	38	0.007416	0.991191	0.370872	Fe	38	0.004406	0.992162	0.367559
Fe	39	0.341133	0.631645	0.364523	Fe	39	0.342428	0.632134	0.365602	Fe	39	0.342754	0.632659	0.365425
Fe	40	0.468883	0.873846	0.439140	Fe	40	0.467705	0.873722	0.425604	Fe	40	0.466689	0.873379	0.419555
Fe	41	0.021372	0.635243	0.365250	Fe	41	0.019406	0.635808	0.366023	Fe	41	0.017382	0.636356	0.366358
Fe	42	0.165597	0.863206	0.421753	Fe	42	0.160600	0.868647	0.420359	Fe	42	0.157227	0.871995	0.419257
Fe	43	0.701949	0.581365	0.400652	Fe	43	0.704550	0.578280	0.407707	Fe	43	0.708306	0.575550	0.412960
Fe	44	0.857381	0.783035	0.416310	Fe	44	0.856552	0.783897	0.417818	Fe	44	0.855601	0.784786	0.418782
Fe	45	0.788833	0.924097	0.356253	Fe	45	0.790149	0.922961	0.354975	Fe	45	0.789536	0.922044	0.354518
Fe	46	0.614610	0.746825	0.374390	Fe	46	0.625919	0.737513	0.371212	Fe	46	0.630487	0.730542	0.375223
Fe	47	0.748646	0.710078	0.462623	Fe	47	0.748579	0.712199	0.464632	Fe	47	0.748475	0.713796	0.466169
Fe	48	0.564454	0.550136	0.463931	Fe	48	0.568455	0.542523	0.467976	Fe	48	0.568292	0.539402	0.467763
Fe	49	0.558799	0.698955	0.476124	Fe	49	0.547619	0.705798	0.475148	Fe	49	0.537761	0.713400	0.472435
Fe	50	0.875544	0.546307	0.463591	Fe	50	0.879872	0.545954	0.467714	Fe	50	0.883700	0.545222	0.469647
Fe	51	0.785800	0.938212	0.470599	Fe	51	0.782030	0.939843	0.469530	Fe	51	0.778974	0.940880	0.468944
Fe	52	0.506314	0.987414	0.369683	Fe	52	0.504635	0.991942	0.368425	Fe	52	0.503665	0.993375	0.368391
Fe	53	0.838203	0.637304	0.365426	Fe	53	0.838197	0.635622	0.368434	Fe	53	0.837517	0.634351	0.370848
Fe	54	0.973149	0.869577	0.419663	Fe	54	0.970223	0.871514	0.418959	Fe	54	0.967590	0.872924	0.418303
Fe	55	0.512104	0.650867	0.369657	Fe	55	0.515822	0.642922	0.370297	Fe	55	0.518377	0.636535	0.373459
Fe	56	0.662000	0.874613	0.425848	Fe	56	0.659387	0.874554	0.420097	Fe	56	0.656964	0.873455	0.418504

Table S10 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for CO + Cs^2H = Cs^2HCO on h-Fe_7C_3 $(1\bar{1}1)$ surface

IS-CO+Cs^2H					TS-CO + Cs^2H= Cs^2HCO					FS-Cs^2HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
H	1	0.085437	0.833941	0.540710	H	1	0.114346	0.736323	0.584284	H	1	0.133679	0.681461	0.589552
C	1	0.103864	0.293312	0.464945	C	1	0.104686	0.292078	0.465318	C	1	0.104726	0.292023	0.465391
C	2	0.139257	0.498973	0.371983	C	2	0.141650	0.498282	0.379188	C	2	0.142535	0.498828	0.383022
C	3	0.358787	0.499036	0.373940	C	3	0.359100	0.500983	0.374913	C	3	0.359112	0.502077	0.375967
C	4	0.427614	0.145922	0.452466	C	4	0.426656	0.146094	0.451726	C	4	0.426090	0.146332	0.451634
C	5	0.482469	0.266052	0.369910	C	5	0.482526	0.266427	0.368149	C	5	0.482122	0.266972	0.367400
C	6	0.251046	0.266503	0.370880	C	6	0.250530	0.265964	0.370476	C	6	0.249831	0.266428	0.370484
C	7	0.603526	0.292279	0.465443	C	7	0.603899	0.291661	0.464038	C	7	0.603983	0.291402	0.463602
C	8	0.640055	0.499173	0.379660	C	8	0.641748	0.499378	0.376596	C	8	0.642071	0.499691	0.374861
C	9	0.858275	0.498963	0.377611	C	9	0.859454	0.499192	0.378328	C	9	0.859994	0.499347	0.378899
C	10	0.925757	0.149185	0.454507	C	10	0.926307	0.148122	0.452900	C	10	0.926370	0.147799	0.452070
C	11	0.982628	0.266225	0.371074	C	11	0.981474	0.268288	0.370556	C	11	0.980292	0.269703	0.370391
C	12	0.751210	0.267236	0.371190	C	12	0.751063	0.267545	0.370197	C	12	0.750865	0.267955	0.369667
C	13	0.095824	0.810241	0.486808	C	13	0.130211	0.714814	0.531651	C	13	0.145396	0.663691	0.534749
C	14	0.145358	0.993210	0.381992	C	14	0.143852	0.994967	0.375871	C	14	0.142465	0.996618	0.372771
C	15	0.359918	0.998788	0.375680	C	15	0.359131	0.998485	0.375155	C	15	0.358436	0.998476	0.375063
C	16	0.420924	0.647658	0.452181	C	16	0.428012	0.644998	0.450818	C	16	0.430944	0.643682	0.451077
C	17	0.481241	0.767544	0.371964	C	17	0.478633	0.768741	0.372139	C	17	0.476242	0.769488	0.372252

IS-CO+Cs²H					TS-CO + Cs²H= Cs²HCO					FS-Cs²HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	18	0.248371	0.765681	0.370032	C	18	0.247899	0.765608	0.367906	C	18	0.247883	0.765065	0.368818
C	19	0.605044	0.789983	0.467582	C	19	0.603481	0.792429	0.466027	C	19	0.602529	0.793760	0.465196
C	20	0.642526	0.997531	0.375169	C	20	0.639453	1.000814	0.373640	C	20	0.637534	1.002387	0.372998
C	21	0.861944	0.991514	0.384055	C	21	0.858901	0.997724	0.374629	C	21	0.857066	1.000878	0.370218
C	22	0.931369	0.647158	0.453645	C	22	0.927209	0.651161	0.451969	C	22	0.924721	0.652813	0.451789
C	23	0.981435	0.767809	0.370221	C	23	0.982869	0.766751	0.364236	C	23	0.982149	0.766841	0.362328
C	24	0.751750	0.766484	0.372458	C	24	0.749472	0.767281	0.370193	C	24	0.748373	0.767739	0.369053
C	25	0.182435	0.591717	0.493825	C	25	0.207989	0.587845	0.501405	C	25	0.227124	0.581197	0.509325
O	1	0.270487	0.540740	0.534218	O	1	0.292060	0.524530	0.540091	O	1	0.309895	0.510375	0.542683
Fe	1	0.211995	0.074817	0.401596	Fe	1	0.210895	0.074495	0.399790	Fe	1	0.210461	0.074546	0.398956
Fe	2	0.359313	0.281482	0.422562	Fe	2	0.359528	0.281992	0.420584	Fe	2	0.359380	0.282502	0.419787
Fe	3	0.289526	0.419980	0.356807	Fe	3	0.290112	0.422219	0.357295	Fe	3	0.289760	0.424213	0.358207
Fe	4	0.134491	0.230958	0.372415	Fe	4	0.133286	0.231696	0.372216	Fe	4	0.132440	0.232391	0.372148
Fe	5	0.251929	0.208074	0.464414	Fe	5	0.252917	0.207642	0.463561	Fe	5	0.253016	0.207829	0.463346
Fe	6	0.070893	0.044786	0.464781	Fe	6	0.071174	0.041955	0.460809	Fe	6	0.071333	0.040866	0.458717
Fe	7	0.038989	0.209267	0.464857	Fe	7	0.039676	0.207796	0.464598	Fe	7	0.040318	0.207064	0.464450
Fe	8	0.384994	0.041865	0.462245	Fe	8	0.383205	0.042362	0.461386	Fe	8	0.382492	0.042845	0.460939
Fe	9	0.278361	0.439071	0.473046	Fe	9	0.283819	0.433572	0.474769	Fe	9	0.287253	0.430039	0.475638
Fe	10	0.002750	0.492049	0.368055	Fe	10	0.003851	0.492356	0.373510	Fe	10	0.003993	0.494355	0.375340
Fe	11	0.342558	0.135481	0.367055	Fe	11	0.341065	0.135204	0.365908	Fe	11	0.340246	0.135664	0.365511
Fe	12	0.470376	0.370639	0.419367	Fe	12	0.470173	0.371410	0.418672	Fe	12	0.470282	0.371613	0.418514
Fe	13	0.021356	0.136309	0.368287	Fe	13	0.020264	0.138086	0.366448	Fe	13	0.020008	0.139382	0.365575

IS-CO+Cs²H					TS-CO + Cs²H= Cs²HCO					FS-Cs²HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	14	0.159070	0.373436	0.422157	Fe	14	0.161127	0.372517	0.423061	Fe	14	0.160910	0.373000	0.423290
Fe	15	0.713573	0.074092	0.400579	Fe	15	0.712117	0.075983	0.399682	Fe	15	0.711302	0.077148	0.399257
Fe	16	0.857544	0.285332	0.422722	Fe	16	0.858003	0.284418	0.422727	Fe	16	0.857978	0.283907	0.423002
Fe	17	0.787285	0.422136	0.358669	Fe	17	0.789569	0.421688	0.358876	Fe	17	0.790270	0.421395	0.359088
Fe	18	0.635253	0.230879	0.372809	Fe	18	0.634430	0.231871	0.371297	Fe	18	0.633763	0.232622	0.370713
Fe	19	0.752787	0.208568	0.465162	Fe	19	0.753161	0.207236	0.463546	Fe	19	0.753179	0.206631	0.462914
Fe	20	0.574841	0.041178	0.462038	Fe	20	0.573056	0.042127	0.460751	Fe	20	0.572088	0.042951	0.460125
Fe	21	0.540294	0.207288	0.464529	Fe	21	0.539392	0.207711	0.463216	Fe	21	0.538751	0.208135	0.462819
Fe	22	0.883829	0.045724	0.465339	Fe	22	0.885831	0.042479	0.460052	Fe	22	0.886809	0.041232	0.457235
Fe	23	0.781735	0.440031	0.472898	Fe	23	0.779314	0.442298	0.472571	Fe	23	0.777848	0.443651	0.472508
Fe	24	0.502203	0.492049	0.371129	Fe	24	0.503271	0.493065	0.370742	Fe	24	0.503744	0.493963	0.370725
Fe	25	0.841266	0.136854	0.368065	Fe	25	0.841380	0.137359	0.365295	Fe	25	0.840741	0.138130	0.363797
Fe	26	0.968930	0.373170	0.421301	Fe	26	0.970268	0.372581	0.422235	Fe	26	0.970369	0.372897	0.422733
Fe	27	0.522553	0.135390	0.366989	Fe	27	0.520582	0.136195	0.365816	Fe	27	0.519520	0.136850	0.365406
Fe	28	0.657758	0.373068	0.422717	Fe	28	0.658151	0.372305	0.421545	Fe	28	0.658110	0.372044	0.421073
Fe	29	0.209607	0.576608	0.396433	Fe	29	0.211440	0.576777	0.405573	Fe	29	0.213266	0.575241	0.410491
Fe	30	0.357916	0.778957	0.422734	Fe	30	0.354869	0.777691	0.422635	Fe	30	0.354186	0.777189	0.424026
Fe	31	0.293173	0.918803	0.358649	Fe	31	0.293244	0.917726	0.357294	Fe	31	0.292982	0.917579	0.357143
Fe	32	0.132052	0.731638	0.362270	Fe	32	0.132302	0.731902	0.363237	Fe	32	0.130714	0.733434	0.367900
Fe	33	0.236548	0.706805	0.460400	Fe	33	0.228092	0.704705	0.466750	Fe	33	0.227498	0.707395	0.467676
Fe	34	0.076507	0.544588	0.462017	Fe	34	0.073075	0.548949	0.466003	Fe	34	0.067245	0.550559	0.467765
Fe	35	0.059354	0.703757	0.465937	Fe	35	0.043030	0.712037	0.462846	Fe	35	0.039229	0.714763	0.463764

IS-CO+Cs²H					TS-CO + Cs²H= Cs²HCO					FS-Cs²HCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	36	0.377301	0.544684	0.463329	Fe	36	0.383510	0.543575	0.463983	Fe	36	0.387471	0.541757	0.465817
Fe	37	0.280209	0.940282	0.471813	Fe	37	0.275627	0.939039	0.471107	Fe	37	0.273554	0.938849	0.470839
Fe	38	0.003256	0.992236	0.374147	Fe	38	0.002710	0.995234	0.367116	Fe	38	0.001757	0.996497	0.364015
Fe	39	0.345006	0.635828	0.365599	Fe	39	0.345008	0.635609	0.366245	Fe	39	0.341308	0.636884	0.370753
Fe	40	0.469822	0.871395	0.424099	Fe	40	0.467817	0.871987	0.423857	Fe	40	0.466752	0.872696	0.423612
Fe	41	0.016642	0.637586	0.366694	Fe	41	0.021835	0.633849	0.363430	Fe	41	0.023814	0.636292	0.368203
Fe	42	0.155928	0.869484	0.418622	Fe	42	0.156996	0.871805	0.411497	Fe	42	0.155576	0.872804	0.410005
Fe	43	0.711186	0.575761	0.404836	Fe	43	0.711689	0.577232	0.401601	Fe	43	0.711480	0.578113	0.399962
Fe	44	0.863127	0.777653	0.425154	Fe	44	0.859512	0.783428	0.418405	Fe	44	0.858382	0.785028	0.415960
Fe	45	0.790218	0.916167	0.359612	Fe	45	0.785270	0.922000	0.354666	Fe	45	0.782477	0.924923	0.352300
Fe	46	0.633743	0.731714	0.374530	Fe	46	0.631606	0.733261	0.372690	Fe	46	0.630114	0.734376	0.371836
Fe	47	0.754383	0.705776	0.465988	Fe	47	0.752526	0.709013	0.464178	Fe	47	0.751554	0.710786	0.463053
Fe	48	0.566537	0.544836	0.463913	Fe	48	0.574243	0.542097	0.462291	Fe	48	0.578195	0.540743	0.461830
Fe	49	0.538295	0.707656	0.466245	Fe	49	0.539549	0.707472	0.465256	Fe	49	0.540107	0.707697	0.464833
Fe	50	0.887824	0.543377	0.462355	Fe	50	0.884097	0.545932	0.463222	Fe	50	0.880890	0.547070	0.464125
Fe	51	0.780054	0.940632	0.472181	Fe	51	0.783206	0.939456	0.469025	Fe	51	0.784665	0.938439	0.467164
Fe	52	0.504689	0.991223	0.371196	Fe	52	0.503063	0.991806	0.369880	Fe	52	0.501829	0.992381	0.369176
Fe	53	0.840352	0.635685	0.366731	Fe	53	0.842019	0.636609	0.366660	Fe	53	0.841962	0.637061	0.366496
Fe	54	0.976339	0.867515	0.419759	Fe	54	0.966457	0.873830	0.409318	Fe	54	0.965053	0.875200	0.405202
Fe	55	0.521363	0.636523	0.367950	Fe	55	0.520935	0.637387	0.367205	Fe	55	0.520695	0.637684	0.367016
Fe	56	0.659987	0.870491	0.424400	Fe	56	0.658298	0.872829	0.422148	Fe	56	0.657332	0.874006	0.421013

Table S11 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for $Cs^1 + C_d = Cs^1C_d$ on h-Fe_7C_3 $(1\bar{1}1)$ surface

IS-Cs^1 + Cd					TS-$Cs^1 + C_d = Cs^1C_d$					FS-Cs^1C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	1	0.110168	0.283129	0.460527	C	1	0.108160	0.282103	0.462749	C	1	0.106666	0.282667	0.462753
C	2	0.161990	0.477394	0.385331	C	2	0.156348	0.482020	0.395576	C	2	0.153367	0.483277	0.395809
C	3	0.342372	0.525265	0.355539	C	3	0.343347	0.522314	0.366739	C	3	0.344880	0.521035	0.370299
C	4	0.436192	0.155461	0.474083	C	4	0.436643	0.151387	0.469874	C	4	0.435482	0.151450	0.470205
C	5	0.453428	0.300401	0.378443	C	5	0.450722	0.300204	0.376691	C	5	0.449467	0.300244	0.376675
C	6	0.276533	0.246320	0.378618	C	6	0.269675	0.249837	0.379589	C	6	0.267808	0.250123	0.379718
C	7	0.612620	0.293197	0.473530	C	7	0.613830	0.289639	0.472727	C	7	0.610748	0.291844	0.473363
C	8	0.632851	0.497923	0.377853	C	8	0.631500	0.499858	0.375491	C	8	0.631593	0.500395	0.371866
C	9	0.864739	0.488100	0.391919	C	9	0.862422	0.488189	0.390774	C	9	0.861522	0.487686	0.388443
C	10	0.920939	0.146775	0.445094	C	10	0.920859	0.145938	0.441932	C	10	0.920205	0.147217	0.443882
C	11	0.993585	0.257755	0.362521	C	11	0.991592	0.258974	0.362775	C	11	0.990622	0.258090	0.364036
C	12	0.739938	0.268841	0.367403	C	12	0.738020	0.272387	0.366287	C	12	0.737015	0.273515	0.367443
C	13	0.103462	0.802162	0.473171	C	13	0.099346	0.807755	0.468779	C	13	0.103421	0.803784	0.471349
C	14	0.132195	0.995495	0.372534	C	14	0.129138	0.998141	0.364275	C	14	0.129076	0.997293	0.368790
C	15	0.362521	0.986358	0.391303	C	15	0.362408	0.987954	0.386606	C	15	0.361784	0.988826	0.388457
C	16	0.413766	0.645478	0.447008	C	16	0.301424	0.628921	0.518959	C	16	0.238360	0.615993	0.503702
C	17	0.489702	0.758207	0.366477	C	17	0.494634	0.755564	0.365136	C	17	0.497467	0.755278	0.362150
C	18	0.239105	0.763735	0.369076	C	18	0.241251	0.757900	0.365216	C	18	0.240062	0.755930	0.371043

IS-Cs^1 + Cd					TS-Cs^1 + C_d = Cs^1C_d					FS-Cs^1C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	19	0.608874	0.783815	0.463560	C	19	0.610282	0.787157	0.460021	C	19	0.612653	0.787951	0.456005
C	20	0.660790	0.980805	0.389305	C	20	0.661728	0.981960	0.384280	C	20	0.659766	0.984556	0.383609
C	21	0.837310	1.027889	0.352418	C	21	0.835209	1.032750	0.345701	C	21	0.833128	1.035821	0.345447
C	22	0.936827	0.660902	0.472258	C	22	0.935249	0.663606	0.472783	C	22	0.934361	0.665283	0.470975
C	23	0.946920	0.805318	0.372531	C	23	0.948372	0.814143	0.367658	C	23	0.951862	0.820437	0.365395
C	24	0.771583	0.749874	0.379519	C	24	0.774940	0.750124	0.376205	C	24	0.777940	0.749813	0.372215
C	25	0.199217	0.601702	0.480001	C	25	0.178190	0.583346	0.501363	C	25	0.170726	0.572441	0.515834
O	1	0.384666	0.449661	0.521769	O	1	0.393283	0.437752	0.526003	O	1	0.391408	0.441787	0.527684
Fe	1	0.203461	0.070525	0.413139	Fe	1	0.201463	0.071228	0.413285	Fe	1	0.202449	0.071138	0.416624
Fe	2	0.361549	0.283285	0.444338	Fe	2	0.362297	0.279018	0.443518	Fe	2	0.360891	0.279146	0.442958
Fe	3	0.325180	0.416065	0.365485	Fe	3	0.318615	0.417283	0.370972	Fe	3	0.316417	0.416914	0.371094
Fe	4	0.143894	0.222613	0.371315	Fe	4	0.141508	0.223915	0.372305	Fe	4	0.141227	0.222877	0.372602
Fe	5	0.261226	0.198623	0.465639	Fe	5	0.259791	0.196564	0.465864	Fe	5	0.257793	0.196998	0.466600
Fe	6	0.055750	0.037625	0.457244	Fe	6	0.056294	0.032795	0.450229	Fe	6	0.054053	0.034017	0.454506
Fe	7	0.036183	0.204081	0.458531	Fe	7	0.035454	0.202521	0.459203	Fe	7	0.034721	0.201906	0.459426
Fe	8	0.396497	0.045457	0.468975	Fe	8	0.397221	0.042721	0.465714	Fe	8	0.398015	0.042671	0.467002
Fe	9	0.260614	0.460090	0.475555	Fe	9	0.265486	0.453587	0.484185	Fe	9	0.268331	0.445149	0.483576
Fe	10	0.015701	0.491828	0.375681	Fe	10	0.014097	0.490114	0.381617	Fe	10	0.011655	0.488924	0.380212
Fe	11	0.340104	0.116489	0.366404	Fe	11	0.338629	0.119420	0.365339	Fe	11	0.339276	0.119684	0.366799
Fe	12	0.473159	0.376688	0.452946	Fe	12	0.475011	0.369771	0.452942	Fe	12	0.470597	0.373874	0.452923
Fe	13	0.022865	0.128068	0.361341	Fe	13	0.023038	0.128270	0.359125	Fe	13	0.023216	0.127831	0.360571
Fe	14	0.173582	0.358931	0.414774	Fe	14	0.171431	0.359976	0.421842	Fe	14	0.169685	0.360029	0.421971

IS-Cs^1 + Cd					TS-Cs^1 + C_d = Cs^1C_d					FS-Cs^1C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	15	0.691391	0.087333	0.390445	Fe	15	0.689816	0.089677	0.385618	Fe	15	0.690475	0.090584	0.386469
Fe	16	0.859989	0.282676	0.405225	Fe	16	0.858983	0.282603	0.406409	Fe	16	0.857213	0.283574	0.408427
Fe	17	0.780259	0.430035	0.354016	Fe	17	0.777715	0.429012	0.353968	Fe	17	0.777658	0.427129	0.352895
Fe	18	0.606985	0.254338	0.376092	Fe	18	0.605277	0.257196	0.373862	Fe	18	0.603454	0.258816	0.375171
Fe	19	0.755207	0.209628	0.456974	Fe	19	0.754620	0.207752	0.454380	Fe	19	0.752509	0.209547	0.455795
Fe	20	0.572735	0.046960	0.466328	Fe	20	0.574217	0.046047	0.463030	Fe	20	0.574941	0.046197	0.462634
Fe	21	0.554749	0.201991	0.474894	Fe	21	0.555508	0.199138	0.471761	Fe	21	0.553646	0.200559	0.472924
Fe	22	0.867762	0.044257	0.449311	Fe	22	0.869044	0.045270	0.442454	Fe	22	0.865853	0.047234	0.445495
Fe	23	0.806766	0.433514	0.467011	Fe	23	0.802587	0.434864	0.467073	Fe	23	0.799311	0.436853	0.466222
Fe	24	0.495138	0.484069	0.368817	Fe	24	0.496952	0.482230	0.369714	Fe	24	0.498349	0.481804	0.369246
Fe	25	0.838984	0.142375	0.355914	Fe	25	0.836948	0.146631	0.351033	Fe	25	0.836809	0.148014	0.353157
Fe	26	0.981697	0.363613	0.412280	Fe	26	0.979124	0.363113	0.413837	Fe	26	0.978027	0.362650	0.414276
Fe	27	0.488453	0.159575	0.378550	Fe	27	0.489125	0.159783	0.374431	Fe	27	0.490500	0.159539	0.375156
Fe	28	0.665508	0.375167	0.423722	Fe	28	0.663537	0.376056	0.425578	Fe	28	0.661587	0.377457	0.426534
Fe	29	0.194296	0.581930	0.386273	Fe	29	0.197962	0.582272	0.405565	Fe	29	0.201129	0.579785	0.408241
Fe	30	0.358631	0.777594	0.411925	Fe	30	0.356116	0.784066	0.399112	Fe	30	0.358387	0.783445	0.396453
Fe	31	0.282162	0.923973	0.353721	Fe	31	0.281565	0.928703	0.346791	Fe	31	0.279273	0.930998	0.348090
Fe	32	0.099711	0.758457	0.373856	Fe	32	0.099658	0.753924	0.374947	Fe	32	0.100085	0.752830	0.379527
Fe	33	0.241328	0.705393	0.460366	Fe	33	0.240749	0.719284	0.464107	Fe	33	0.246433	0.719979	0.467855
Fe	34	0.074781	0.550765	0.464279	Fe	34	0.066406	0.549937	0.475300	Fe	34	0.061715	0.546344	0.475909
Fe	35	0.059218	0.703823	0.478331	Fe	35	0.064475	0.699551	0.481655	Fe	35	0.062448	0.698535	0.482817
Fe	36	0.366191	0.543556	0.459990	Fe	36	0.380005	0.533778	0.468865	Fe	36	0.381566	0.535636	0.468038

IS-Cs^1 + Cd					TS-Cs^1 + C_d = Cs^1C_d					FS-Cs^1C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	37	0.299744	0.934291	0.467164	Fe	37	0.299161	0.932307	0.460474	Fe	37	0.304276	0.928947	0.461443
Fe	38	-0.006204	0.983160	0.363070	Fe	38	-0.008405	0.986384	0.354685	Fe	38	-0.011349	0.986204	0.358300
Fe	39	0.342190	0.640481	0.358099	Fe	39	0.346427	0.638029	0.365287	Fe	39	0.346747	0.636763	0.367912
Fe	40	0.477341	0.863836	0.414616	Fe	40	0.478906	0.865435	0.411029	Fe	40	0.480519	0.865623	0.408183
Fe	41	-0.013682	0.663468	0.378353	Fe	41	-0.001835	0.651519	0.382947	Fe	41	0.003533	0.646439	0.383191
Fe	42	0.164242	0.872991	0.421597	Fe	42	0.162140	0.877390	0.409883	Fe	42	0.165357	0.874587	0.413876
Fe	43	0.704231	0.573073	0.419813	Fe	43	0.703906	0.575089	0.415656	Fe	43	0.703946	0.575267	0.410203
Fe	44	0.858225	0.790330	0.441850	Fe	44	0.863757	0.789632	0.435261	Fe	44	0.867902	0.789006	0.430531
Fe	45	0.818640	0.921444	0.361279	Fe	45	0.817992	0.925568	0.357611	Fe	45	0.819695	0.927725	0.356264
Fe	46	0.641341	0.724332	0.374179	Fe	46	0.645246	0.724495	0.370711	Fe	46	0.648131	0.724861	0.366703
Fe	47	0.763793	0.699390	0.466417	Fe	47	0.765289	0.701792	0.464189	Fe	47	0.766388	0.702726	0.461152
Fe	48	0.555080	0.541339	0.461883	Fe	48	0.561344	0.537573	0.460748	Fe	48	0.561014	0.539084	0.458940
Fe	49	0.535703	0.705338	0.462370	Fe	49	0.540201	0.708044	0.459502	Fe	49	0.542466	0.708453	0.456064
Fe	50	0.898292	0.547649	0.468839	Fe	50	0.889248	0.547141	0.470747	Fe	50	0.885985	0.546423	0.468633
Fe	51	0.765131	0.956140	0.470095	Fe	51	0.765070	0.956712	0.466905	Fe	51	0.766546	0.955760	0.465029
Fe	52	0.514766	0.990512	0.376097	Fe	52	0.514657	0.990836	0.371272	Fe	52	0.514149	0.992652	0.372067
Fe	53	0.838896	0.619482	0.366948	Fe	53	0.842151	0.619047	0.366824	Fe	53	0.844403	0.618497	0.364806
Fe	54	0.966380	0.880621	0.446642	Fe	54	0.964037	0.885666	0.442460	Fe	54	0.968507	0.884737	0.444813
Fe	55	0.523061	0.628570	0.365122	Fe	55	0.519456	0.629125	0.365461	Fe	55	0.518773	0.629480	0.362871
Fe	56	0.668261	0.859867	0.419268	Fe	56	0.671967	0.861039	0.414707	Fe	56	0.674978	0.861069	0.410646
Fe	56	0.00119	-0.01641	0.00390	Fe	56	-0.00332	-0.03228	0.00472	Fe	56	0.00479	-0.00252	0.00874

Table S12 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for $Cs^2 + C_d = Cs^2C_d$ on h-Fe_7C_3 $(1\bar{1}1)$ surface

IS-Cs^2 + Cd					TS-$Cs^2 + C_d = Cs^2C_d$					FS-Cs^2C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	1	0.110168	0.283129	0.460527	C	1	0.107411	0.282729	0.462222	C	1	0.104610	0.282864	0.464144
C	2	0.161990	0.477394	0.385331	C	2	0.157149	0.479765	0.388311	C	2	0.151860	0.482436	0.393325
C	3	0.342372	0.525265	0.355539	C	3	0.341926	0.523381	0.364341	C	3	0.342578	0.521267	0.370275
C	4	0.436192	0.155461	0.474083	C	4	0.434051	0.154249	0.473021	C	4	0.432084	0.153170	0.471646
C	5	0.453428	0.300401	0.378443	C	5	0.450026	0.300916	0.378792	C	5	0.447214	0.301132	0.378449
C	6	0.276533	0.246320	0.378618	C	6	0.271188	0.248521	0.380059	C	6	0.265943	0.251120	0.381309
C	7	0.612620	0.293197	0.473530	C	7	0.610219	0.294004	0.474020	C	7	0.608820	0.293868	0.474152
C	8	0.632851	0.497923	0.377853	C	8	0.632021	0.498758	0.375418	C	8	0.631187	0.499724	0.374056
C	9	0.864739	0.488100	0.391919	C	9	0.862367	0.487853	0.390465	C	9	0.859545	0.487961	0.389645
C	10	0.920939	0.146775	0.445094	C	10	0.919808	0.145286	0.444140	C	10	0.919170	0.143866	0.443012
C	11	0.993585	0.257755	0.362521	C	11	0.991568	0.257567	0.364199	C	11	0.989388	0.258163	0.365385
C	12	0.739938	0.268841	0.367403	C	12	0.737570	0.270672	0.368101	C	12	0.735888	0.271892	0.368414
C	13	0.103462	0.802162	0.473171	C	13	0.155909	0.716985	0.516711	C	13	0.223717	0.630495	0.501786
C	14	0.132195	0.995495	0.372534	C	14	0.130342	0.997639	0.369162	C	14	0.128174	1.000486	0.364784
C	15	0.362521	0.986358	0.391303	C	15	0.364793	0.988377	0.389938	C	15	0.365478	0.990079	0.389862
C	16	0.413766	0.645478	0.447008	C	16	0.419318	0.648267	0.445551	C	16	0.419474	0.652085	0.446282
C	17	0.489702	0.758207	0.366477	C	17	0.494662	0.758440	0.359969	C	17	0.497168	0.758762	0.356930
C	18	0.239105	0.763735	0.369076	C	18	0.236300	0.762640	0.367352	C	18	0.237080	0.759917	0.368960

IS-Cs^2 + Cd					TS-Cs^2 + C_d = Cs^2C_d					FS-Cs^2C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	19	0.608874	0.783815	0.463560	C	19	0.610334	0.785840	0.458762	C	19	0.610478	0.787670	0.456201
C	20	0.660790	0.980805	0.389305	C	20	0.664162	0.982081	0.390413	C	20	0.665833	0.983218	0.391586
C	21	0.837310	1.027889	0.352418	C	21	0.835291	1.034347	0.347701	C	21	0.833601	1.038810	0.343517
C	22	0.936827	0.660902	0.472258	C	22	0.930942	0.660593	0.470519	C	22	0.932757	0.662483	0.470592
C	23	0.946920	0.805318	0.372531	C	23	0.953245	0.811209	0.373369	C	23	0.958211	0.816037	0.373330
C	24	0.771583	0.749874	0.379519	C	24	0.775724	0.750011	0.377126	C	24	0.777689	0.750428	0.375664
C	25	0.199217	0.601702	0.480001	C	25	0.179185	0.587722	0.495592	C	25	0.169846	0.574983	0.513467
O	1	0.384666	0.449661	0.521769	O	1	0.387498	0.450297	0.524679	O	1	0.389980	0.450395	0.527441
Fe	1	0.203461	0.070525	0.413139	Fe	1	0.203345	0.070992	0.418147	Fe	1	0.202665	0.072009	0.422153
Fe	2	0.361549	0.283285	0.444338	Fe	2	0.359848	0.282249	0.444703	Fe	2	0.358487	0.281431	0.444544
Fe	3	0.325180	0.416065	0.365485	Fe	3	0.319496	0.416644	0.368583	Fe	3	0.314153	0.417153	0.371195
Fe	4	0.143894	0.222613	0.371315	Fe	4	0.142043	0.222726	0.372686	Fe	4	0.139588	0.223943	0.374156
Fe	5	0.261226	0.198623	0.465639	Fe	5	0.259019	0.197896	0.466839	Fe	5	0.256748	0.197674	0.468095
Fe	6	0.055750	0.037625	0.457244	Fe	6	0.056689	0.032226	0.455789	Fe	6	0.057226	0.028658	0.453133
Fe	7	0.036183	0.204081	0.458531	Fe	7	0.034677	0.201968	0.459302	Fe	7	0.032917	0.201169	0.460349
Fe	8	0.396497	0.045457	0.468975	Fe	8	0.397969	0.044253	0.469144	Fe	8	0.398072	0.043734	0.469472
Fe	9	0.260614	0.460090	0.475555	Fe	9	0.264304	0.455896	0.480741	Fe	9	0.269231	0.449033	0.484290
Fe	10	0.015701	0.491828	0.375681	Fe	10	0.012941	0.488691	0.374665	Fe	10	0.009927	0.488338	0.379032
Fe	11	0.340104	0.116489	0.366404	Fe	11	0.339932	0.118159	0.367824	Fe	11	0.338994	0.120102	0.368778
Fe	12	0.473159	0.376688	0.452946	Fe	12	0.470138	0.378012	0.453859	Fe	12	0.467863	0.379290	0.453386
Fe	13	0.022865	0.128068	0.361341	Fe	13	0.022997	0.127737	0.361251	Fe	13	0.022777	0.127875	0.361252
Fe	14	0.173582	0.358931	0.414774	Fe	14	0.170360	0.359885	0.419035	Fe	14	0.167473	0.360712	0.423482

IS-Cs^2 + Cd					TS-Cs^2 + C_d = Cs^2C_d					FS-Cs^2C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	15	0.691391	0.087333	0.390445	Fe	15	0.691287	0.090045	0.389759	Fe	15	0.690994	0.092174	0.389101
Fe	16	0.859989	0.282676	0.405225	Fe	16	0.857613	0.283280	0.407547	Fe	16	0.855619	0.283798	0.409267
Fe	17	0.780259	0.430035	0.354016	Fe	17	0.778931	0.428050	0.353644	Fe	17	0.777348	0.426888	0.353583
Fe	18	0.606985	0.254338	0.376092	Fe	18	0.603211	0.258147	0.376317	Fe	18	0.600272	0.261022	0.376165
Fe	19	0.755207	0.209628	0.456974	Fe	19	0.752548	0.208420	0.456474	Fe	19	0.750564	0.207104	0.455613
Fe	20	0.572735	0.046960	0.466328	Fe	20	0.574769	0.048821	0.466838	Fe	20	0.575977	0.050561	0.467084
Fe	21	0.554749	0.201991	0.474894	Fe	21	0.551321	0.204254	0.474977	Fe	21	0.548819	0.205569	0.474609
Fe	22	0.867762	0.044257	0.449311	Fe	22	0.869018	0.042875	0.446537	Fe	22	0.870746	0.040865	0.443265
Fe	23	0.806766	0.433514	0.467011	Fe	23	0.800941	0.435730	0.466776	Fe	23	0.796002	0.437386	0.466900
Fe	24	0.495138	0.484069	0.368817	Fe	24	0.494989	0.483586	0.370471	Fe	24	0.496352	0.482640	0.370582
Fe	25	0.838984	0.142375	0.355914	Fe	25	0.839414	0.145859	0.354089	Fe	25	0.839548	0.148442	0.352281
Fe	26	0.981697	0.363613	0.412280	Fe	26	0.978984	0.362891	0.414176	Fe	26	0.976328	0.362840	0.416030
Fe	27	0.488453	0.159575	0.378550	Fe	27	0.488648	0.160662	0.378176	Fe	27	0.488817	0.161375	0.377381
Fe	28	0.665508	0.375167	0.423722	Fe	28	0.663258	0.375986	0.425652	Fe	28	0.661268	0.376425	0.427145
Fe	29	0.194296	0.581930	0.386273	Fe	29	0.194537	0.582351	0.399333	Fe	29	0.197468	0.579640	0.406150
Fe	30	0.358631	0.777594	0.411925	Fe	30	0.359780	0.782354	0.400179	Fe	30	0.359587	0.784936	0.393282
Fe	31	0.282162	0.923973	0.353721	Fe	31	0.279808	0.932181	0.349238	Fe	31	0.278666	0.938792	0.346126
Fe	32	0.099711	0.758457	0.373856	Fe	32	0.104554	0.752949	0.376773	Fe	32	0.106847	0.746669	0.377510
Fe	33	0.241328	0.705393	0.460366	Fe	33	0.259623	0.711624	0.459172	Fe	33	0.258622	0.720419	0.463986
Fe	34	0.074781	0.550765	0.464279	Fe	34	0.066946	0.547428	0.467155	Fe	34	0.062538	0.545582	0.473737
Fe	35	0.059218	0.703823	0.478331	Fe	35	0.054859	0.699254	0.476777	Fe	35	0.059372	0.697963	0.478688
Fe	36	0.366191	0.543556	0.459990	Fe	36	0.368299	0.545500	0.464842	Fe	36	0.372876	0.546520	0.467910

IS-Cs^2 + Cd					TS-Cs^2 + C_d = Cs^2C_d					FS-Cs^2C_d				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	37	0.299744	0.934291	0.467164	Fe	37	0.302659	0.930672	0.463036	Fe	37	0.302393	0.928148	0.459953
Fe	38	-0.006204	0.983160	0.363070	Fe	38	-0.006867	0.981076	0.360030	Fe	38	-0.008036	0.980971	0.356043
Fe	39	0.342190	0.640481	0.358099	Fe	39	0.342522	0.638052	0.359102	Fe	39	0.342546	0.637014	0.363967
Fe	40	0.477341	0.863836	0.414616	Fe	40	0.479885	0.865163	0.409529	Fe	40	0.480779	0.866191	0.407584
Fe	41	-0.013682	0.663468	0.378353	Fe	41	-0.005790	0.653751	0.374102	Fe	41	-0.000290	0.648228	0.381210
Fe	42	0.164242	0.872991	0.421597	Fe	42	0.167152	0.875986	0.414737	Fe	42	0.168352	0.877280	0.407839
Fe	43	0.704231	0.573073	0.419813	Fe	43	0.703686	0.574588	0.414759	Fe	43	0.702720	0.576031	0.411515
Fe	44	0.858225	0.790330	0.441850	Fe	44	0.864124	0.789312	0.437976	Fe	44	0.868527	0.788614	0.435786
Fe	45	0.818640	0.921444	0.361279	Fe	45	0.825298	0.925826	0.365343	Fe	45	0.829170	0.930078	0.369005
Fe	46	0.641341	0.724332	0.374179	Fe	46	0.645365	0.724574	0.369888	Fe	46	0.646826	0.725367	0.367759
Fe	47	0.763793	0.699390	0.466417	Fe	47	0.764823	0.700676	0.464321	Fe	47	0.764331	0.702231	0.463157
Fe	48	0.555080	0.541339	0.461883	Fe	48	0.557799	0.543483	0.459731	Fe	48	0.559757	0.545195	0.458976
Fe	49	0.535703	0.705338	0.462370	Fe	49	0.535165	0.707905	0.456929	Fe	49	0.533906	0.710198	0.454363
Fe	50	0.898292	0.547649	0.468839	Fe	50	0.892934	0.546100	0.468062	Fe	50	0.887125	0.545907	0.468812
Fe	51	0.765131	0.956140	0.470095	Fe	51	0.764140	0.957670	0.472260	Fe	51	0.762249	0.959187	0.474407
Fe	52	0.514766	0.990512	0.376097	Fe	52	0.517164	0.992976	0.376190	Fe	52	0.518134	0.994553	0.376502
Fe	53	0.838896	0.619482	0.366948	Fe	53	0.841738	0.618705	0.366051	Fe	53	0.842507	0.619461	0.366151
Fe	54	0.966380	0.880621	0.446642	Fe	54	0.976683	0.879386	0.446687	Fe	54	0.985610	0.878488	0.446316
Fe	55	0.523061	0.628570	0.365122	Fe	55	0.522588	0.629094	0.361241	Fe	55	0.520793	0.630478	0.359511
Fe	56	0.668261	0.859867	0.419268	Fe	56	0.672504	0.860734	0.415673	Fe	56	0.675391	0.861230	0.413897

Table S13 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for CO + Cs= CsCO on h-Fe_7C_3 (101) surface

IS-CO + Cs					TS-CO + Cs= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	1	0.109293	0.408949	0.453063	C	1	0.103211	0.401480	0.465858	C	1	0.100804	0.398421	0.470735
C	2	0.166937	0.229424	0.453213	C	2	0.162647	0.224332	0.454369	C	2	0.161125	0.222902	0.455130
C	3	0.451707	0.476232	0.377698	C	3	0.451076	0.474836	0.375686	C	3	0.450592	0.474300	0.375501
C	4	0.401311	0.071915	0.473646	C	4	0.400933	0.073285	0.474055	C	4	0.400772	0.073796	0.474173
C	5	0.430237	0.311967	0.469054	C	5	0.428255	0.314046	0.468853	C	5	0.427490	0.314633	0.469078
C	6	0.328677	0.162038	0.360001	C	6	0.324897	0.161379	0.360793	C	6	0.323665	0.161416	0.361149
C	7	0.656367	0.453538	0.463911	C	7	0.655531	0.451890	0.462606	C	7	0.655189	0.451301	0.462202
C	8	0.622759	0.196290	0.449893	C	8	0.622118	0.196708	0.449969	C	8	0.621803	0.196794	0.449981
C	9	0.941738	0.469366	0.362987	C	9	0.947010	0.470925	0.366839	C	9	0.948699	0.471435	0.368074
C	10	0.937254	0.127802	0.460391	C	10	0.932304	0.122108	0.461912	C	10	0.930630	0.120245	0.462369
C	11	0.879089	0.297607	0.471684	C	11	0.876909	0.295849	0.473423	C	11	0.876297	0.295446	0.473918
C	12	0.815235	0.160717	0.351765	C	12	0.815410	0.160310	0.351771	C	12	0.815430	0.160237	0.351723
C	13	0.153780	0.948553	0.458361	C	13	0.152311	0.946687	0.459960	C	13	0.151847	0.945847	0.460390
C	14	0.149196	0.699525	0.460226	C	14	0.152733	0.698987	0.460771	C	14	0.154196	0.698318	0.461939
C	15	0.442371	0.960259	0.361916	C	15	0.443327	0.964763	0.360959	C	15	0.443387	0.966115	0.360595
C	16	0.446085	0.627212	0.464154	C	16	0.439230	0.621941	0.463186	C	16	0.437588	0.620692	0.462950
C	17	0.389759	0.799812	0.478162	C	17	0.390773	0.803297	0.475436	C	17	0.391515	0.804847	0.474404
C	18	0.314643	0.650980	0.359420	C	18	0.317485	0.654658	0.357140	C	18	0.318055	0.655575	0.356576

IS-CO + Cs					TS-CO + Cs= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	19	0.609898	0.913023	0.458645	C	19	0.609012	0.912925	0.456389	C	19	0.608803	0.912989	0.455609
C	20	0.661753	0.728322	0.450736	C	20	0.659777	0.726186	0.449655	C	20	0.659183	0.725566	0.449298
C	21	0.952859	0.986416	0.372396	C	21	0.950589	0.984099	0.372454	C	21	0.949865	0.983287	0.372481
C	22	0.918232	0.594190	0.464789	C	22	0.919533	0.594785	0.465819	C	22	0.919783	0.594819	0.466201
C	23	0.923079	0.832083	0.468381	C	23	0.921949	0.829846	0.468818	C	23	0.921624	0.829049	0.468929
C	24	0.826597	0.669493	0.355645	C	24	0.827047	0.668651	0.355903	C	24	0.827087	0.668315	0.356005
C	25	0.252999	0.562977	0.538205	C	25	0.166289	0.474699	0.541597	C	25	0.141884	0.445935	0.535209
O	1	0.255122	0.561465	0.598625	O	1	0.161037	0.458873	0.600989	O	1	0.134829	0.430392	0.595517
Fe	1	0.301436	0.404399	0.379963	Fe	1	0.300369	0.402541	0.377336	Fe	1	0.299113	0.402713	0.378491
Fe	2	0.340907	0.160027	0.456792	Fe	2	0.340637	0.161553	0.457875	Fe	2	0.340416	0.162221	0.458387
Fe	3	0.294584	0.299478	0.472159	Fe	3	0.290510	0.298157	0.471866	Fe	3	0.288966	0.297769	0.472284
Fe	4	0.232145	0.023257	0.380957	Fe	4	0.230688	0.022342	0.382342	Fe	4	0.230153	0.022148	0.382896
Fe	5	0.234851	0.435711	0.477963	Fe	5	0.244985	0.448906	0.476109	Fe	5	0.248979	0.452954	0.476676
Fe	6	0.228277	0.209322	0.374515	Fe	6	0.224427	0.207560	0.374960	Fe	6	0.222958	0.207207	0.375546
Fe	7	0.139571	0.318149	0.392949	Fe	7	0.140105	0.324091	0.399234	Fe	7	0.140547	0.325553	0.401169
Fe	8	0.412714	0.475744	0.464629	Fe	8	0.411408	0.471258	0.462790	Fe	8	0.411116	0.470074	0.462829
Fe	9	0.396475	0.312213	0.380432	Fe	9	0.394005	0.311340	0.380115	Fe	9	0.393145	0.311260	0.380313
Fe	10	0.048590	0.128059	0.422177	Fe	10	0.046170	0.125599	0.423505	Fe	10	0.045337	0.124530	0.423834
Fe	11	0.399727	0.079378	0.375811	Fe	11	0.399181	0.082569	0.376014	Fe	11	0.398826	0.083508	0.376087
Fe	12	0.053488	0.452229	0.383770	Fe	12	0.054275	0.444936	0.390654	Fe	12	0.053970	0.442879	0.392908
Fe	13	-0.009820	0.281841	0.451258	Fe	13	-0.013597	0.276146	0.454620	Fe	13	-0.016369	0.272682	0.454686
Fe	14	0.178144	0.096709	0.468344	Fe	14	0.177549	0.095155	0.469771	Fe	14	0.177257	0.094425	0.470375

IS-CO + Cs					TS-CO + Cs= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	15	0.801505	0.400801	0.376287	Fe	15	0.803460	0.401010	0.376353	Fe	15	0.803961	0.400937	0.376366
Fe	16	0.823125	0.147844	0.452357	Fe	16	0.820523	0.146812	0.452084	Fe	16	0.819311	0.146254	0.451923
Fe	17	0.757752	0.284629	0.472717	Fe	17	0.756340	0.284735	0.472790	Fe	17	0.755757	0.284768	0.472772
Fe	18	0.720886	0.022703	0.370766	Fe	18	0.720629	0.021580	0.369582	Fe	18	0.720460	0.021178	0.369176
Fe	19	0.782474	0.478126	0.475166	Fe	19	0.781313	0.477696	0.474585	Fe	19	0.780896	0.477530	0.474383
Fe	20	0.716635	0.203406	0.371464	Fe	20	0.717343	0.203433	0.370802	Fe	20	0.717550	0.203429	0.370682
Fe	21	0.651431	0.336648	0.414227	Fe	21	0.651924	0.336108	0.412075	Fe	21	0.651978	0.335938	0.411388
Fe	22	0.917301	0.446611	0.456372	Fe	22	0.915668	0.445213	0.458654	Fe	22	0.915013	0.445012	0.459323
Fe	23	0.893108	0.307522	0.372008	Fe	23	0.893285	0.307250	0.373408	Fe	23	0.893222	0.307097	0.373749
Fe	24	0.555506	0.105539	0.380017	Fe	24	0.555967	0.108275	0.378948	Fe	24	0.555967	0.109134	0.378613
Fe	25	0.900581	0.096974	0.369077	Fe	25	0.900126	0.095994	0.369839	Fe	25	0.899874	0.095716	0.370147
Fe	26	0.539128	0.430747	0.435665	Fe	26	0.538930	0.429287	0.434074	Fe	26	0.538571	0.428860	0.433716
Fe	27	0.502826	0.216630	0.452314	Fe	27	0.503159	0.217047	0.451885	Fe	27	0.503240	0.217245	0.451771
Fe	28	0.651831	0.070747	0.460080	Fe	28	0.650835	0.070633	0.458962	Fe	28	0.650418	0.070646	0.458601
Fe	29	0.304931	0.895298	0.379597	Fe	29	0.306068	0.898163	0.380624	Fe	29	0.306244	0.898734	0.381025
Fe	30	0.331962	0.642729	0.463844	Fe	30	0.331550	0.649984	0.457117	Fe	30	0.330938	0.651542	0.456274
Fe	31	0.273259	0.793897	0.479219	Fe	31	0.274802	0.797392	0.480897	Fe	31	0.275630	0.798863	0.481791
Fe	32	0.221242	0.515688	0.379369	Fe	32	0.222910	0.518360	0.377798	Fe	32	0.223061	0.519061	0.378793
Fe	33	0.275925	0.963370	0.479804	Fe	33	0.275861	0.965407	0.481487	Fe	33	0.275737	0.965960	0.482049
Fe	34	0.215761	0.693730	0.380798	Fe	34	0.221085	0.700180	0.380399	Fe	34	0.222137	0.701055	0.381520
Fe	35	0.147330	0.822321	0.415827	Fe	35	0.148124	0.821255	0.417630	Fe	35	0.148347	0.820250	0.418742
Fe	36	0.435201	0.954562	0.456914	Fe	36	0.436814	0.958047	0.455994	Fe	36	0.437408	0.959426	0.455642

IS-CO + Cs					TS-CO + Cs= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	37	0.389554	0.795072	0.379864	Fe	37	0.393252	0.800732	0.376343	Fe	37	0.394102	0.802162	0.375301
Fe	38	0.041118	0.608843	0.421349	Fe	38	0.042205	0.607953	0.423238	Fe	38	0.042734	0.607294	0.425019
Fe	39	0.400879	0.589492	0.374463	Fe	39	0.400943	0.588615	0.372488	Fe	39	0.400623	0.588173	0.372095
Fe	40	0.041625	0.944080	0.428648	Fe	40	0.040948	0.943488	0.429367	Fe	40	0.040655	0.942909	0.429610
Fe	41	-0.006391	0.751152	0.445203	Fe	41	-0.005461	0.751057	0.446171	Fe	41	-0.005233	0.750803	0.446543
Fe	42	0.162982	0.564883	0.472507	Fe	42	0.163183	0.562365	0.472908	Fe	42	0.164376	0.563998	0.472796
Fe	43	0.800385	0.911196	0.374192	Fe	43	0.799443	0.909547	0.373784	Fe	43	0.799105	0.909062	0.373672
Fe	44	0.836363	0.666118	0.452170	Fe	44	0.836512	0.665369	0.452575	Fe	44	0.836490	0.665148	0.452662
Fe	45	0.788914	0.805394	0.469241	Fe	45	0.786513	0.802213	0.468659	Fe	45	0.785733	0.801249	0.468487
Fe	46	0.730266	0.529681	0.378904	Fe	46	0.730792	0.529471	0.377943	Fe	46	0.730993	0.529438	0.377635
Fe	47	0.737690	0.950507	0.469725	Fe	47	0.736483	0.949794	0.468811	Fe	47	0.736162	0.949644	0.468542
Fe	48	0.727212	0.714282	0.372506	Fe	48	0.726149	0.712929	0.371377	Fe	48	0.725672	0.712490	0.371054
Fe	49	0.641775	0.826204	0.392171	Fe	49	0.639939	0.824251	0.391253	Fe	49	0.639411	0.823632	0.390924
Fe	50	0.909751	0.977986	0.459292	Fe	50	0.907982	0.973888	0.459634	Fe	50	0.907409	0.972610	0.459734
Fe	51	0.897069	0.821386	0.376850	Fe	51	0.896588	0.820003	0.377254	Fe	51	0.896408	0.819520	0.377351
Fe	52	0.549590	0.620489	0.421900	Fe	52	0.547098	0.618674	0.421699	Fe	52	0.546264	0.618026	0.421640
Fe	53	0.897816	0.588327	0.371332	Fe	53	0.898508	0.587453	0.372402	Fe	53	0.898816	0.587151	0.372767
Fe	54	0.550357	0.931737	0.381241	Fe	54	0.551327	0.934267	0.379363	Fe	54	0.551479	0.935048	0.378742
Fe	55	0.496554	0.782270	0.460854	Fe	55	0.495987	0.779316	0.457005	Fe	55	0.496042	0.778735	0.455869
Fe	56	0.676897	0.598304	0.469008	Fe	56	0.675873	0.596645	0.467619	Fe	56	0.675569	0.596049	0.467218

Table S14 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for Cs + CdH= CsCdH on h-Fe_7C_3 (101) surface

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
H	1	0.255501	0.581361	0.586930	H	1	0.171053	0.492312	0.595207	H	1	0.117961	0.428806	0.583506
C	1	0.110685	0.410937	0.444566	C	1	0.101081	0.400889	0.462694	C	1	0.092417	0.390978	0.472133
C	2	0.165068	0.218627	0.445652	C	2	0.162914	0.216902	0.444904	C	2	0.160942	0.216216	0.444915
C	3	0.451407	0.475059	0.394380	C	3	0.452667	0.475247	0.390895	C	3	0.453051	0.475328	0.389684
C	4	0.389858	0.058678	0.477462	C	4	0.389758	0.060694	0.476162	C	4	0.389399	0.062264	0.475666
C	5	0.509113	0.301905	0.427909	C	5	0.510188	0.302560	0.424149	C	5	0.510638	0.303211	0.422401
C	6	0.340307	0.166104	0.361630	C	6	0.338370	0.165800	0.359612	C	6	0.336831	0.166123	0.359225
C	7	0.667662	0.468090	0.470399	C	7	0.667518	0.466218	0.468820	C	7	0.667313	0.465219	0.468003
C	8	0.630900	0.195994	0.447474	C	8	0.630237	0.194904	0.449533	C	8	0.629372	0.194278	0.451041
C	9	0.935038	0.467761	0.361221	C	9	0.942588	0.469647	0.364091	C	9	0.947429	0.470910	0.366454
C	10	0.939289	0.132463	0.454894	C	10	0.933833	0.126195	0.456628	C	10	0.929756	0.122097	0.457726
C	11	0.881738	0.299697	0.471192	C	11	0.877680	0.297562	0.471885	C	11	0.874642	0.296144	0.472191
C	12	0.812376	0.163995	0.348154	C	12	0.812823	0.163620	0.347966	C	12	0.812642	0.163407	0.347850
C	13	0.143162	0.936303	0.448697	C	13	0.141610	0.935414	0.446670	C	13	0.140297	0.933944	0.446078
C	14	0.144203	0.696421	0.453089	C	14	0.149126	0.696269	0.454137	C	14	0.153829	0.694255	0.458417
C	15	0.441404	0.953982	0.361124	C	15	0.443938	0.958187	0.360124	C	15	0.444945	0.960960	0.358840
C	16	0.451767	0.641438	0.469134	C	16	0.447781	0.640031	0.465732	C	16	0.445832	0.639754	0.463267
C	17	0.387000	0.799162	0.480449	C	17	0.386359	0.801076	0.478390	C	17	0.387291	0.803808	0.476591

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	18	0.313623	0.647062	0.361353	C	18	0.317786	0.650225	0.358082	C	18	0.320625	0.652743	0.355711
C	19	0.610623	0.916420	0.464116	C	19	0.610103	0.913979	0.463441	C	19	0.610174	0.913204	0.462100
C	20	0.661392	0.735033	0.454116	C	20	0.661277	0.733435	0.453454	C	20	0.661285	0.732733	0.452887
C	21	0.946039	0.985150	0.368171	C	21	0.944547	0.984495	0.367301	C	21	0.943867	0.984058	0.366642
C	22	0.923551	0.601482	0.466327	C	22	0.926151	0.603015	0.465934	C	22	0.927706	0.603818	0.465860
C	23	0.923088	0.835391	0.466383	C	23	0.923112	0.834629	0.465243	C	23	0.923193	0.833848	0.464423
C	24	0.818764	0.666455	0.360794	C	24	0.820101	0.665096	0.360424	C	24	0.820843	0.664001	0.360204
C	25	0.247461	0.567698	0.532627	C	25	0.178495	0.494175	0.538808	C	25	0.137223	0.443266	0.530872
O	1	0.317664	0.401898	0.537030	O	1	0.321618	0.402793	0.535315	O	1	0.322254	0.404596	0.535404
Fe	1	0.304634	0.404445	0.386025	Fe	1	0.304971	0.404050	0.383605	Fe	1	0.304166	0.404810	0.385029
Fe	2	0.334156	0.149295	0.455523	Fe	2	0.332480	0.150026	0.453785	Fe	2	0.330819	0.150614	0.453602
Fe	3	0.281736	0.286916	0.481936	Fe	3	0.280591	0.287264	0.480271	Fe	3	0.278906	0.288441	0.480526
Fe	4	0.236931	0.023132	0.375517	Fe	4	0.236425	0.022299	0.374352	Fe	4	0.235675	0.022112	0.374373
Fe	5	0.232705	0.439201	0.485531	Fe	5	0.240431	0.445359	0.483150	Fe	5	0.245187	0.451371	0.483448
Fe	6	0.244406	0.214103	0.373897	Fe	6	0.244218	0.215364	0.373072	Fe	6	0.244198	0.216756	0.373532
Fe	7	0.142661	0.315557	0.392347	Fe	7	0.140888	0.323758	0.399082	Fe	7	0.140681	0.328692	0.402789
Fe	8	0.402134	0.492413	0.477234	Fe	8	0.404636	0.491383	0.474488	Fe	8	0.405616	0.491422	0.473462
Fe	9	0.405463	0.316784	0.396684	Fe	9	0.406278	0.317008	0.394072	Fe	9	0.406360	0.317483	0.393744
Fe	10	0.044992	0.124433	0.416612	Fe	10	0.043049	0.124411	0.417249	Fe	10	0.041583	0.124244	0.417391
Fe	11	0.400852	0.072674	0.374999	Fe	11	0.401310	0.075464	0.374032	Fe	11	0.401078	0.077411	0.373894
Fe	12	0.051278	0.453465	0.378116	Fe	12	0.053257	0.446189	0.386705	Fe	12	0.055398	0.443567	0.391368
Fe	13	-0.009660	0.285290	0.446105	Fe	13	-0.015243	0.278004	0.450002	Fe	13	-0.020245	0.271961	0.449227

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	14	0.174165	0.086481	0.460946	Fe	14	0.172728	0.085785	0.459176	Fe	14	0.171360	0.085373	0.458792
Fe	15	0.793461	0.398380	0.376957	Fe	15	0.794626	0.397125	0.378259	Fe	15	0.794939	0.396144	0.379161
Fe	16	0.823907	0.149678	0.449686	Fe	16	0.820343	0.148450	0.449216	Fe	16	0.817353	0.147475	0.448924
Fe	17	0.761455	0.287018	0.471763	Fe	17	0.759291	0.288469	0.474800	Fe	17	0.757259	0.289388	0.476831
Fe	18	0.719857	0.026374	0.368203	Fe	18	0.719613	0.025008	0.367397	Fe	18	0.718982	0.024036	0.366800
Fe	19	0.792131	0.488660	0.473578	Fe	19	0.792313	0.489161	0.474103	Fe	19	0.792163	0.489442	0.474476
Fe	20	0.715148	0.207854	0.368587	Fe	20	0.716765	0.207358	0.370805	Fe	20	0.717335	0.207013	0.372410
Fe	21	0.641118	0.338373	0.425105	Fe	21	0.641984	0.337021	0.423036	Fe	21	0.642179	0.336099	0.421936
Fe	22	0.918087	0.447875	0.454503	Fe	22	0.916730	0.446649	0.456278	Fe	22	0.915449	0.445821	0.457434
Fe	23	0.890732	0.309406	0.369627	Fe	23	0.891815	0.309665	0.370313	Fe	23	0.892081	0.309774	0.370682
Fe	24	0.559059	0.095879	0.373869	Fe	24	0.560097	0.098043	0.374245	Fe	24	0.560245	0.099751	0.374631
Fe	25	0.897002	0.098951	0.364345	Fe	25	0.896164	0.097911	0.364871	Fe	25	0.895110	0.097174	0.365174
Fe	26	0.557089	0.454287	0.426252	Fe	26	0.558846	0.454917	0.422368	Fe	26	0.559898	0.455534	0.420523
Fe	27	0.506850	0.173940	0.457686	Fe	27	0.506682	0.175745	0.457198	Fe	27	0.506263	0.177105	0.457343
Fe	28	0.655938	0.071345	0.459349	Fe	28	0.654171	0.068797	0.459407	Fe	28	0.652540	0.067260	0.459365
Fe	29	0.303116	0.891385	0.375074	Fe	29	0.305918	0.894135	0.375586	Fe	29	0.306959	0.895240	0.376603
Fe	30	0.333867	0.643485	0.466493	Fe	30	0.331782	0.647563	0.460349	Fe	30	0.331249	0.651287	0.456194
Fe	31	0.268329	0.785642	0.472524	Fe	31	0.269541	0.792116	0.474976	Fe	31	0.271446	0.796732	0.477908
Fe	32	0.222014	0.510157	0.380698	Fe	32	0.224707	0.512589	0.378416	Fe	32	0.226599	0.514300	0.378472
Fe	33	0.263712	0.951294	0.475455	Fe	33	0.263064	0.954860	0.475702	Fe	33	0.262604	0.957126	0.476481
Fe	34	0.212318	0.686850	0.374923	Fe	34	0.219950	0.692437	0.375299	Fe	34	0.224377	0.694564	0.378027
Fe	35	0.144768	0.816639	0.404616	Fe	35	0.148442	0.815942	0.405532	Fe	35	0.150644	0.813118	0.409018

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	36	0.428587	0.948852	0.456537	Fe	36	0.430793	0.952083	0.455635	Fe	36	0.432768	0.955043	0.454496
Fe	37	0.388520	0.791323	0.381336	Fe	37	0.393159	0.795995	0.378140	Fe	37	0.396091	0.799296	0.375543
Fe	38	0.038481	0.609102	0.411931	Fe	38	0.040530	0.609494	0.414709	Fe	38	0.041947	0.608107	0.421424
Fe	39	0.400157	0.588386	0.377695	Fe	39	0.402299	0.589202	0.374842	Fe	39	0.403860	0.589872	0.372875
Fe	40	0.035444	0.944127	0.421589	Fe	40	0.034510	0.945497	0.420038	Fe	40	0.033692	0.944734	0.419112
Fe	41	-0.002489	0.756172	0.448971	Fe	41	0.000482	0.759639	0.445334	Fe	41	0.002634	0.760519	0.444436
Fe	42	0.159879	0.565409	0.470381	Fe	42	0.159994	0.563309	0.468661	Fe	42	0.161639	0.561421	0.470663
Fe	43	0.798431	0.912595	0.371497	Fe	43	0.797570	0.910891	0.370515	Fe	43	0.797183	0.909824	0.369657
Fe	44	0.839929	0.674559	0.456104	Fe	44	0.842394	0.674857	0.455545	Fe	44	0.843925	0.675170	0.455101
Fe	45	0.789531	0.811220	0.468007	Fe	45	0.788567	0.808207	0.466865	Fe	45	0.788100	0.806375	0.465976
Fe	46	0.719972	0.527023	0.383136	Fe	46	0.721983	0.526276	0.382096	Fe	46	0.723170	0.525856	0.381540
Fe	47	0.739346	0.954111	0.467947	Fe	47	0.738742	0.952644	0.466986	Fe	47	0.738641	0.951970	0.466033
Fe	48	0.720409	0.713701	0.374498	Fe	48	0.719972	0.711361	0.373225	Fe	48	0.719604	0.709709	0.372279
Fe	49	0.640075	0.830078	0.393682	Fe	49	0.639151	0.827980	0.392977	Fe	49	0.638822	0.826762	0.392065
Fe	50	0.907709	0.982265	0.456207	Fe	50	0.906289	0.978501	0.455767	Fe	50	0.905519	0.976053	0.455350
Fe	51	0.890644	0.818505	0.375783	Fe	51	0.890051	0.817309	0.374644	Fe	51	0.889663	0.816334	0.373755
Fe	52	0.548604	0.627909	0.426314	Fe	52	0.548351	0.627510	0.425890	Fe	52	0.548347	0.627490	0.425712
Fe	53	0.889918	0.584446	0.375397	Fe	53	0.891350	0.582265	0.375614	Fe	53	0.892228	0.580390	0.375740
Fe	54	0.548492	0.926866	0.384531	Fe	54	0.550112	0.928357	0.383404	Fe	54	0.551106	0.929744	0.381760
Fe	55	0.497294	0.791616	0.468979	Fe	55	0.495913	0.790573	0.466947	Fe	55	0.495750	0.790653	0.464912
Fe	56	0.681516	0.610253	0.475928	Fe	56	0.682356	0.608664	0.474438	Fe	56	0.682973	0.607877	0.473551

Table S15 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for Cs + CdH= CsCdH on h-Fe_7C_3 (101) surface

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
H	1	0.255501	0.581361	0.586930	H	1	0.171053	0.492312	0.595207	H	1	0.117961	0.428806	0.583506
C	1	0.110685	0.410937	0.444566	C	1	0.101081	0.400889	0.462694	C	1	0.092417	0.390978	0.472133
C	2	0.165068	0.218627	0.445652	C	2	0.162914	0.216902	0.444904	C	2	0.160942	0.216216	0.444915
C	3	0.451407	0.475059	0.394380	C	3	0.452667	0.475247	0.390895	C	3	0.453051	0.475328	0.389684
C	4	0.389858	0.058678	0.477462	C	4	0.389758	0.060694	0.476162	C	4	0.389399	0.062264	0.475666
C	5	0.509113	0.301905	0.427909	C	5	0.510188	0.302560	0.424149	C	5	0.510638	0.303211	0.422401
C	6	0.340307	0.166104	0.361630	C	6	0.338370	0.165800	0.359612	C	6	0.336831	0.166123	0.359225
C	7	0.667662	0.468090	0.470399	C	7	0.667518	0.466218	0.468820	C	7	0.667313	0.465219	0.468003
C	8	0.630900	0.195994	0.447474	C	8	0.630237	0.194904	0.449533	C	8	0.629372	0.194278	0.451041
C	9	0.935038	0.467761	0.361221	C	9	0.942588	0.469647	0.364091	C	9	0.947429	0.470910	0.366454
C	10	0.939289	0.132463	0.454894	C	10	0.933833	0.126195	0.456628	C	10	0.929756	0.122097	0.457726
C	11	0.881738	0.299697	0.471192	C	11	0.877680	0.297562	0.471885	C	11	0.874642	0.296144	0.472191
C	12	0.812376	0.163995	0.348154	C	12	0.812823	0.163620	0.347966	C	12	0.812642	0.163407	0.347850
C	13	0.143162	0.936303	0.448697	C	13	0.141610	0.935414	0.446670	C	13	0.140297	0.933944	0.446078
C	14	0.144203	0.696421	0.453089	C	14	0.149126	0.696269	0.454137	C	14	0.153829	0.694255	0.458417
C	15	0.441404	0.953982	0.361124	C	15	0.443938	0.958187	0.360124	C	15	0.444945	0.960960	0.358840
C	16	0.451767	0.641438	0.469134	C	16	0.447781	0.640031	0.465732	C	16	0.445832	0.639754	0.463267
C	17	0.387000	0.799162	0.480449	C	17	0.386359	0.801076	0.478390	C	17	0.387291	0.803808	0.476591

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	18	0.313623	0.647062	0.361353	C	18	0.317786	0.650225	0.358082	C	18	0.320625	0.652743	0.355711
C	19	0.610623	0.916420	0.464116	C	19	0.610103	0.913979	0.463441	C	19	0.610174	0.913204	0.462100
C	20	0.661392	0.735033	0.454116	C	20	0.661277	0.733435	0.453454	C	20	0.661285	0.732733	0.452887
C	21	0.946039	0.985150	0.368171	C	21	0.944547	0.984495	0.367301	C	21	0.943867	0.984058	0.366642
C	22	0.923551	0.601482	0.466327	C	22	0.926151	0.603015	0.465934	C	22	0.927706	0.603818	0.465860
C	23	0.923088	0.835391	0.466383	C	23	0.923112	0.834629	0.465243	C	23	0.923193	0.833848	0.464423
C	24	0.818764	0.666455	0.360794	C	24	0.820101	0.665096	0.360424	C	24	0.820843	0.664001	0.360204
C	25	0.247461	0.567698	0.532627	C	25	0.178495	0.494175	0.538808	C	25	0.137223	0.443266	0.530872
O	1	0.317664	0.401898	0.537030	O	1	0.321618	0.402793	0.535315	O	1	0.322254	0.404596	0.535404
Fe	1	0.304634	0.404445	0.386025	Fe	1	0.304971	0.404050	0.383605	Fe	1	0.304166	0.404810	0.385029
Fe	2	0.334156	0.149295	0.455523	Fe	2	0.332480	0.150026	0.453785	Fe	2	0.330819	0.150614	0.453602
Fe	3	0.281736	0.286916	0.481936	Fe	3	0.280591	0.287264	0.480271	Fe	3	0.278906	0.288441	0.480526
Fe	4	0.236931	0.023132	0.375517	Fe	4	0.236425	0.022299	0.374352	Fe	4	0.235675	0.022112	0.374373
Fe	5	0.232705	0.439201	0.485531	Fe	5	0.240431	0.445359	0.483150	Fe	5	0.245187	0.451371	0.483448
Fe	6	0.244406	0.214103	0.373897	Fe	6	0.244218	0.215364	0.373072	Fe	6	0.244198	0.216756	0.373532
Fe	7	0.142661	0.315557	0.392347	Fe	7	0.140888	0.323758	0.399082	Fe	7	0.140681	0.328692	0.402789
Fe	8	0.402134	0.492413	0.477234	Fe	8	0.404636	0.491383	0.474488	Fe	8	0.405616	0.491422	0.473462
Fe	9	0.405463	0.316784	0.396684	Fe	9	0.406278	0.317008	0.394072	Fe	9	0.406360	0.317483	0.393744
Fe	10	0.044992	0.124433	0.416612	Fe	10	0.043049	0.124411	0.417249	Fe	10	0.041583	0.124244	0.417391
Fe	11	0.400852	0.072674	0.374999	Fe	11	0.401310	0.075464	0.374032	Fe	11	0.401078	0.077411	0.373894
Fe	12	0.051278	0.453465	0.378116	Fe	12	0.053257	0.446189	0.386705	Fe	12	0.055398	0.443567	0.391368
Fe	13	-0.009660	0.285290	0.446105	Fe	13	-0.015243	0.278004	0.450002	Fe	13	-0.020245	0.271961	0.449227

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	14	0.174165	0.086481	0.460946	Fe	14	0.172728	0.085785	0.459176	Fe	14	0.171360	0.085373	0.458792
Fe	15	0.793461	0.398380	0.376957	Fe	15	0.794626	0.397125	0.378259	Fe	15	0.794939	0.396144	0.379161
Fe	16	0.823907	0.149678	0.449686	Fe	16	0.820343	0.148450	0.449216	Fe	16	0.817353	0.147475	0.448924
Fe	17	0.761455	0.287018	0.471763	Fe	17	0.759291	0.288469	0.474800	Fe	17	0.757259	0.289388	0.476831
Fe	18	0.719857	0.026374	0.368203	Fe	18	0.719613	0.025008	0.367397	Fe	18	0.718982	0.024036	0.366800
Fe	19	0.792131	0.488660	0.473578	Fe	19	0.792313	0.489161	0.474103	Fe	19	0.792163	0.489442	0.474476
Fe	20	0.715148	0.207854	0.368587	Fe	20	0.716765	0.207358	0.370805	Fe	20	0.717335	0.207013	0.372410
Fe	21	0.641118	0.338373	0.425105	Fe	21	0.641984	0.337021	0.423036	Fe	21	0.642179	0.336099	0.421936
Fe	22	0.918087	0.447875	0.454503	Fe	22	0.916730	0.446649	0.456278	Fe	22	0.915449	0.445821	0.457434
Fe	23	0.890732	0.309406	0.369627	Fe	23	0.891815	0.309665	0.370313	Fe	23	0.892081	0.309774	0.370682
Fe	24	0.559059	0.095879	0.373869	Fe	24	0.560097	0.098043	0.374245	Fe	24	0.560245	0.099751	0.374631
Fe	25	0.897002	0.098951	0.364345	Fe	25	0.896164	0.097911	0.364871	Fe	25	0.895110	0.097174	0.365174
Fe	26	0.557089	0.454287	0.426252	Fe	26	0.558846	0.454917	0.422368	Fe	26	0.559898	0.455534	0.420523
Fe	27	0.506850	0.173940	0.457686	Fe	27	0.506682	0.175745	0.457198	Fe	27	0.506263	0.177105	0.457343
Fe	28	0.655938	0.071345	0.459349	Fe	28	0.654171	0.068797	0.459407	Fe	28	0.652540	0.067260	0.459365
Fe	29	0.303116	0.891385	0.375074	Fe	29	0.305918	0.894135	0.375586	Fe	29	0.306959	0.895240	0.376603
Fe	30	0.333867	0.643485	0.466493	Fe	30	0.331782	0.647563	0.460349	Fe	30	0.331249	0.651287	0.456194
Fe	31	0.268329	0.785642	0.472524	Fe	31	0.269541	0.792116	0.474976	Fe	31	0.271446	0.796732	0.477908
Fe	32	0.222014	0.510157	0.380698	Fe	32	0.224707	0.512589	0.378416	Fe	32	0.226599	0.514300	0.378472
Fe	33	0.263712	0.951294	0.475455	Fe	33	0.263064	0.954860	0.475702	Fe	33	0.262604	0.957126	0.476481
Fe	34	0.212318	0.686850	0.374923	Fe	34	0.219950	0.692437	0.375299	Fe	34	0.224377	0.694564	0.378027
Fe	35	0.144768	0.816639	0.404616	Fe	35	0.148442	0.815942	0.405532	Fe	35	0.150644	0.813118	0.409018

IS-Cs + CdH					TS-Cs + CdH= CsCdH					FS-CsCdH				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	36	0.428587	0.948852	0.456537	Fe	36	0.430793	0.952083	0.455635	Fe	36	0.432768	0.955043	0.454496
Fe	37	0.388520	0.791323	0.381336	Fe	37	0.393159	0.795995	0.378140	Fe	37	0.396091	0.799296	0.375543
Fe	38	0.038481	0.609102	0.411931	Fe	38	0.040530	0.609494	0.414709	Fe	38	0.041947	0.608107	0.421424
Fe	39	0.400157	0.588386	0.377695	Fe	39	0.402299	0.589202	0.374842	Fe	39	0.403860	0.589872	0.372875
Fe	40	0.035444	0.944127	0.421589	Fe	40	0.034510	0.945497	0.420038	Fe	40	0.033692	0.944734	0.419112
Fe	41	-0.002489	0.756172	0.448971	Fe	41	0.000482	0.759639	0.445334	Fe	41	0.002634	0.760519	0.444436
Fe	42	0.159879	0.565409	0.470381	Fe	42	0.159994	0.563309	0.468661	Fe	42	0.161639	0.561421	0.470663
Fe	43	0.798431	0.912595	0.371497	Fe	43	0.797570	0.910891	0.370515	Fe	43	0.797183	0.909824	0.369657
Fe	44	0.839929	0.674559	0.456104	Fe	44	0.842394	0.674857	0.455545	Fe	44	0.843925	0.675170	0.455101
Fe	45	0.789531	0.811220	0.468007	Fe	45	0.788567	0.808207	0.466865	Fe	45	0.788100	0.806375	0.465976
Fe	46	0.719972	0.527023	0.383136	Fe	46	0.721983	0.526276	0.382096	Fe	46	0.723170	0.525856	0.381540
Fe	47	0.739346	0.954111	0.467947	Fe	47	0.738742	0.952644	0.466986	Fe	47	0.738641	0.951970	0.466033
Fe	48	0.720409	0.713701	0.374498	Fe	48	0.719972	0.711361	0.373225	Fe	48	0.719604	0.709709	0.372279
Fe	49	0.640075	0.830078	0.393682	Fe	49	0.639151	0.827980	0.392977	Fe	49	0.638822	0.826762	0.392065
Fe	50	0.907709	0.982265	0.456207	Fe	50	0.906289	0.978501	0.455767	Fe	50	0.905519	0.976053	0.455350
Fe	51	0.890644	0.818505	0.375783	Fe	51	0.890051	0.817309	0.374644	Fe	51	0.889663	0.816334	0.373755
Fe	52	0.548604	0.627909	0.426314	Fe	52	0.548351	0.627510	0.425890	Fe	52	0.548347	0.627490	0.425712
Fe	53	0.889918	0.584446	0.375397	Fe	53	0.891350	0.582265	0.375614	Fe	53	0.892228	0.580390	0.375740
Fe	54	0.548492	0.926866	0.384531	Fe	54	0.550112	0.928357	0.383404	Fe	54	0.551106	0.929744	0.381760
Fe	55	0.497294	0.791616	0.468979	Fe	55	0.495913	0.790573	0.466947	Fe	55	0.495750	0.790653	0.464912
Fe	56	0.681516	0.610253	0.475928	Fe	56	0.682356	0.608664	0.474438	Fe	56	0.682973	0.607877	0.473551

Table S16 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for Cs + CO= CsCO on h-Fe_7C_3 $(1\bar{1}\bar{1})$ surface

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	1	0.267451	0.103081	0.480205	C	1	0.254417	0.112914	0.488093	C	1	0.252676	0.112620	0.488599
C	2	0.439823	0.172661	0.392787	C	2	0.431956	0.172274	0.400246	C	2	0.431681	0.170508	0.403623
C	3	0.480035	0.391907	0.382059	C	3	0.477809	0.393560	0.374064	C	3	0.478002	0.392257	0.370844
C	4	0.140124	0.418617	0.486308	C	4	0.134213	0.419651	0.486853	C	4	0.133539	0.419529	0.488436
C	5	0.248280	0.468687	0.381271	C	5	0.244217	0.471193	0.384004	C	5	0.243129	0.471335	0.385328
C	6	0.220911	0.264951	0.371410	C	6	0.219875	0.262988	0.374828	C	6	0.217886	0.263911	0.375996
C	7	0.753392	0.126599	0.491210	C	7	0.753678	0.132587	0.488003	C	7	0.754118	0.131736	0.488181
C	8	0.981125	0.127363	0.368287	C	8	0.977715	0.130392	0.364659	C	8	0.976244	0.131716	0.363243
C	9	0.930612	0.399024	0.405624	C	9	0.927237	0.400003	0.403166	C	9	0.928540	0.399312	0.402381
C	10	0.642102	0.437432	0.494149	C	10	0.639845	0.440010	0.492698	C	10	0.639721	0.440071	0.492308
C	11	0.715968	0.515800	0.379211	C	11	0.717407	0.516554	0.377632	C	11	0.717516	0.516566	0.377084
C	12	0.742547	0.282394	0.385823	C	12	0.742397	0.286801	0.383434	C	12	0.742590	0.286410	0.383539
C	13	0.268564	0.605421	0.479480	C	13	0.252608	0.612330	0.495321	C	13	0.250667	0.615188	0.498101
C	14	0.436815	0.674635	0.387787	C	14	0.434881	0.671427	0.406267	C	14	0.434767	0.669675	0.409360
C	15	0.477145	0.890291	0.380029	C	15	0.481280	0.889874	0.374661	C	15	0.480348	0.889765	0.371621
C	16	0.137774	0.920519	0.486412	C	16	0.134547	0.923514	0.492016	C	16	0.133913	0.923751	0.491830
C	17	0.246511	0.968988	0.380332	C	17	0.247854	0.967255	0.386840	C	17	0.247322	0.966975	0.386151
C	18	0.217422	0.767609	0.370574	C	18	0.219613	0.766616	0.379920	C	18	0.219905	0.765898	0.380351

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	19	0.753932	0.630892	0.491375	C	19	0.755935	0.630948	0.489742	C	19	0.756207	0.631416	0.488800
C	20	0.983167	0.625347	0.370496	C	20	0.983232	0.623905	0.369528	C	20	0.982350	0.625610	0.371386
C	21	0.929486	0.899240	0.405124	C	21	0.930876	0.899645	0.401871	C	21	0.931127	0.899542	0.401399
C	22	0.636449	0.940945	0.493280	C	22	0.637867	0.943568	0.490057	C	22	0.638161	0.942714	0.490361
C	23	0.713707	1.015573	0.377677	C	23	0.715337	1.018802	0.374608	C	23	0.716262	1.017466	0.374943
C	24	0.744021	0.783921	0.386291	C	24	0.744007	0.786408	0.383592	C	24	0.743894	0.786169	0.383581
C	25	0.441172	0.616530	0.540118	C	25	0.348938	0.575717	0.547385	C	25	0.330033	0.581270	0.545593
O	1	0.437493	0.624954	0.599481	O	1	0.358370	0.550703	0.605034	O	1	0.346130	0.557521	0.603689
Fe	1	0.125112	0.176730	0.463422	Fe	1	0.118029	0.178710	0.464713	Fe	1	0.117319	0.177943	0.464806
Fe	2	0.154442	0.411380	0.390073	Fe	2	0.151539	0.410816	0.391287	Fe	2	0.151305	0.411343	0.392937
Fe	3	0.473135	0.275709	0.430169	Fe	3	0.474772	0.274692	0.423793	Fe	3	0.476042	0.273919	0.421755
Fe	4	0.243211	0.119624	0.386242	Fe	4	0.240727	0.117521	0.392470	Fe	4	0.239265	0.117938	0.392445
Fe	5	0.096394	0.279572	0.362349	Fe	5	0.096487	0.276643	0.362691	Fe	5	0.094647	0.278454	0.363569
Fe	6	0.037452	0.057811	0.459896	Fe	6	0.037889	0.059016	0.461735	Fe	6	0.037885	0.059007	0.461932
Fe	7	0.106062	0.097833	0.365556	Fe	7	0.101970	0.097192	0.365740	Fe	7	0.100039	0.097723	0.365390
Fe	8	0.045238	0.372793	0.462574	Fe	8	0.040238	0.373323	0.461573	Fe	8	0.039848	0.373321	0.463035
Fe	9	0.320606	0.304247	0.398473	Fe	9	0.317087	0.303316	0.403142	Fe	9	0.317044	0.300653	0.405304
Fe	10	0.488269	0.023202	0.374837	Fe	10	0.487556	0.025424	0.373282	Fe	10	0.487834	0.024581	0.373463
Fe	11	0.219935	0.265067	0.469852	Fe	11	0.216152	0.266381	0.473059	Fe	11	0.214908	0.265993	0.474231
Fe	12	0.365080	0.462815	0.418805	Fe	12	0.364810	0.455332	0.411566	Fe	12	0.364590	0.453231	0.408346
Fe	13	0.211177	0.498644	0.470508	Fe	13	0.206332	0.498907	0.473606	Fe	13	0.205267	0.498695	0.474999
Fe	14	0.377131	0.122885	0.458733	Fe	14	0.372043	0.113468	0.460444	Fe	14	0.370982	0.109621	0.460899

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	15	0.619400	0.196677	0.472721	Fe	15	0.618580	0.201509	0.467968	Fe	15	0.618833	0.201146	0.467572
Fe	16	0.653091	0.431848	0.397286	Fe	16	0.650460	0.436414	0.395204	Fe	16	0.651034	0.435779	0.395103
Fe	17	0.981058	0.248569	0.417594	Fe	17	0.976999	0.250123	0.416169	Fe	17	0.976483	0.250026	0.416413
Fe	18	0.738904	0.135021	0.395272	Fe	18	0.737280	0.141314	0.391373	Fe	18	0.737717	0.140405	0.391593
Fe	19	0.604097	0.294819	0.375830	Fe	19	0.601554	0.300967	0.370417	Fe	19	0.602457	0.300285	0.369829
Fe	20	0.539884	0.079855	0.469369	Fe	20	0.540669	0.083282	0.466060	Fe	20	0.541477	0.082780	0.466111
Fe	21	0.587835	0.126034	0.371032	Fe	21	0.589629	0.128302	0.366860	Fe	21	0.591327	0.126443	0.366556
Fe	22	0.542296	0.397837	0.469733	Fe	22	0.539559	0.403065	0.466281	Fe	22	0.539759	0.403136	0.465478
Fe	23	0.818694	0.379828	0.406790	Fe	23	0.816173	0.379297	0.404030	Fe	23	0.816585	0.380168	0.403714
Fe	24	0.987076	-0.014365	0.369995	Fe	24	0.989997	-0.013207	0.370388	Fe	24	0.989838	-0.012371	0.370547
Fe	25	0.715609	0.286013	0.477316	Fe	25	0.715457	0.289772	0.474865	Fe	25	0.715328	0.289481	0.474972
Fe	26	0.874596	0.521707	0.461033	Fe	26	0.875422	0.522139	0.459809	Fe	26	0.874849	0.520737	0.459891
Fe	27	0.719351	0.512633	0.477691	Fe	27	0.718990	0.513630	0.476437	Fe	27	0.718550	0.514603	0.475935
Fe	28	0.866627	0.179592	0.405529	Fe	28	0.866013	0.178930	0.404417	Fe	28	0.865665	0.179457	0.404327
Fe	29	0.125033	0.680715	0.464880	Fe	29	0.116051	0.683220	0.468813	Fe	29	0.114428	0.684385	0.470812
Fe	30	0.151822	0.914117	0.388917	Fe	30	0.152744	0.915237	0.394766	Fe	30	0.152505	0.915226	0.394316
Fe	31	0.473251	0.772215	0.427633	Fe	31	0.477660	0.773578	0.426684	Fe	31	0.478067	0.773416	0.424756
Fe	32	0.243084	0.622394	0.386551	Fe	32	0.239185	0.623294	0.397249	Fe	32	0.238345	0.623468	0.399064
Fe	33	0.093428	0.782236	0.362649	Fe	33	0.096780	0.781101	0.366746	Fe	33	0.096401	0.780861	0.368711
Fe	34	0.038096	0.556165	0.460963	Fe	34	0.033079	0.556820	0.460260	Fe	34	0.032532	0.557363	0.462407
Fe	35	0.108394	0.597305	0.369245	Fe	35	0.108506	0.596427	0.370951	Fe	35	0.107594	0.597300	0.373311
Fe	36	0.042870	0.875784	0.462728	Fe	36	0.040067	0.878195	0.464560	Fe	36	0.038790	0.879220	0.465464

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	37	0.317902	0.805133	0.394403	Fe	37	0.318519	0.801699	0.407817	Fe	37	0.318326	0.801484	0.408344
Fe	38	0.490833	0.524869	0.378166	Fe	38	0.488768	0.526325	0.376071	Fe	38	0.488696	0.525094	0.375350
Fe	39	0.219020	0.769551	0.469327	Fe	39	0.214051	0.770664	0.478704	Fe	39	0.214158	0.772474	0.478938
Fe	40	0.365287	0.963056	0.419276	Fe	40	0.368703	0.955654	0.413796	Fe	40	0.368196	0.954400	0.410905
Fe	41	0.213870	0.993512	0.470711	Fe	41	0.214112	0.994944	0.477125	Fe	41	0.215114	0.993140	0.476866
Fe	42	0.378063	0.626908	0.460232	Fe	42	0.371931	0.608196	0.464581	Fe	42	0.371822	0.605358	0.461635
Fe	43	0.618974	0.698462	0.472944	Fe	43	0.622068	0.699090	0.471143	Fe	43	0.621896	0.699873	0.469614
Fe	44	0.650047	0.932625	0.395531	Fe	44	0.650860	0.936970	0.393235	Fe	44	0.651110	0.935803	0.393368
Fe	45	0.980457	0.748920	0.418844	Fe	45	0.977822	0.750501	0.416667	Fe	45	0.976430	0.751400	0.418967
Fe	46	0.739024	0.637763	0.395931	Fe	46	0.741100	0.638110	0.393894	Fe	46	0.740747	0.638675	0.392904
Fe	47	0.601034	0.794699	0.374630	Fe	47	0.606313	0.796456	0.373547	Fe	47	0.604803	0.797192	0.371446
Fe	48	0.543054	0.576110	0.476702	Fe	48	0.544932	0.580639	0.469318	Fe	48	0.545138	0.580867	0.468515
Fe	49	0.589446	0.624569	0.372557	Fe	49	0.593275	0.626585	0.369811	Fe	49	0.593255	0.625611	0.368838
Fe	50	0.538622	0.900389	0.467761	Fe	50	0.538758	0.904990	0.465619	Fe	50	0.539613	0.903896	0.464870
Fe	51	0.816997	0.879979	0.404708	Fe	51	0.817105	0.882622	0.402483	Fe	51	0.817273	0.881824	0.402549
Fe	52	0.989191	0.483782	0.370449	Fe	52	0.987657	0.482723	0.368430	Fe	52	0.988132	0.483832	0.369773
Fe	53	0.713358	0.789639	0.476939	Fe	53	0.713780	0.792241	0.474358	Fe	53	0.714820	0.791751	0.474619
Fe	54	0.874445	1.022641	0.460693	Fe	54	0.872158	1.022781	0.457801	Fe	54	0.872949	1.022364	0.457941
Fe	55	0.718316	1.009332	0.477056	Fe	55	0.716833	1.016222	0.473833	Fe	55	0.717359	1.015462	0.474051
Fe	56	0.867732	0.678307	0.407149	Fe	56	0.867292	0.680429	0.405560	Fe	56	0.866857	0.679844	0.407573

Table S17 Fractional coordinates of the initial (IS), transition (TS) and final (FS) geometries of the preferred coupling route for Cs + CO= CsCO on h-Fe_7C_3 $(1\bar{1}0)$ surface

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	1	0.250000	0.309107	0.507843	C	1	0.250000	0.309105	0.507843	C	1	0.250000	0.309107	0.507843
C	2	0.134733	0.274506	0.613960	C	2	0.134733	0.276026	0.614701	C	2	0.134774	0.276352	0.614926
C	3	0.367204	0.267508	0.614475	C	3	0.363971	0.278715	0.613798	C	3	0.363511	0.280124	0.613584
C	4	-0.000010	0.038179	0.562923	C	4	-0.001298	0.041553	0.562770	C	4	-0.001452	0.041901	0.562790
C	5	0.108797	0.048481	0.462343	C	5	0.108797	0.048479	0.462342	C	5	0.108797	0.048481	0.462343
C	6	0.391203	0.048481	0.462342	C	6	0.391203	0.048480	0.462342	C	6	0.391203	0.048481	0.462342
C	7	0.750001	0.309105	0.507846	C	7	0.750001	0.309103	0.507845	C	7	0.750001	0.309105	0.507846
C	8	0.635525	0.276488	0.614211	C	8	0.632288	0.265415	0.615083	C	8	0.631814	0.263943	0.615315
C	9	0.865586	0.274904	0.614424	C	9	0.865732	0.277200	0.614531	C	9	0.865700	0.277421	0.614547
C	10	0.501895	0.037008	0.563055	C	10	0.496959	0.031880	0.564193	C	10	0.496520	0.032080	0.563925
C	11	0.608796	0.048482	0.462342	C	11	0.608797	0.048481	0.462341	C	11	0.608796	0.048482	0.462342
C	12	0.891203	0.048481	0.462342	C	12	0.891204	0.048480	0.462341	C	12	0.891203	0.048481	0.462342
C	13	0.250000	0.809100	0.507842	C	13	0.250000	0.809096	0.507841	C	13	0.250000	0.809100	0.507842
C	14	0.136435	0.774925	0.613076	C	14	0.137656	0.775740	0.613006	C	14	0.137316	0.776733	0.612256
C	15	0.362976	0.780182	0.612171	C	15	0.386251	0.760345	0.633239	C	15	0.392726	0.753697	0.637953
C	16	0.001150	0.536197	0.563518	C	16	0.001818	0.535228	0.563668	C	16	0.001833	0.534540	0.563732
C	17	0.108792	0.548480	0.462343	C	17	0.108793	0.548477	0.462342	C	17	0.108792	0.548480	0.462343
C	18	0.391207	0.548480	0.462343	C	18	0.391208	0.548477	0.462342	C	18	0.391207	0.548480	0.462343

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
C	19	0.750001	0.809106	0.507841	C	19	0.750001	0.809102	0.507841	C	19	0.750001	0.809106	0.507841
C	20	0.632810	0.768898	0.614635	C	20	0.636319	0.778767	0.613495	C	20	0.636516	0.779424	0.613667
C	21	0.865877	0.774443	0.613985	C	21	0.866656	0.771367	0.614280	C	21	0.866647	0.770942	0.614245
C	22	0.497836	0.535382	0.563659	C	22	0.501124	0.535380	0.563472	C	22	0.501855	0.535874	0.563215
C	23	0.608794	0.548479	0.462344	C	23	0.608794	0.548476	0.462343	C	23	0.608794	0.548479	0.462344
C	24	0.891206	0.548477	0.462344	C	24	0.891207	0.548474	0.462343	C	24	0.891206	0.548477	0.462344
C	25	0.263659	0.608534	0.695740	C	25	0.320777	0.686792	0.685618	C	25	0.346393	0.712526	0.684195
O	1	0.273159	0.581233	0.740496	O	1	0.338154	0.697730	0.731584	O	1	0.335384	0.706981	0.731136
Fe	1	0.249470	0.403921	0.578546	Fe	1	0.252375	0.407040	0.578715	Fe	1	0.252269	0.408400	0.578959
Fe	2	-0.000002	0.160254	0.496298	Fe	2	-0.000002	0.160252	0.496297	Fe	2	-0.000002	0.160254	0.496298
Fe	3	0.249473	0.153962	0.625593	Fe	3	0.250190	0.155983	0.625604	Fe	3	0.250400	0.156712	0.625840
Fe	4	0.250000	0.501648	0.473826	Fe	4	0.250000	0.501646	0.473825	Fe	4	0.250000	0.501648	0.473826
Fe	5	0.341181	0.170100	0.544750	Fe	5	0.340646	0.169358	0.545937	Fe	5	0.340179	0.169594	0.545870
Fe	6	0.097370	0.499699	0.613925	Fe	6	0.099954	0.501432	0.613732	Fe	6	0.100452	0.501911	0.613427
Fe	7	0.158558	0.170074	0.545053	Fe	7	0.159128	0.169959	0.545773	Fe	7	0.158678	0.170616	0.545933
Fe	8	0.401979	0.493837	0.613872	Fe	8	0.406194	0.503147	0.615066	Fe	8	0.406010	0.505168	0.614722
Fe	9	-0.000001	0.421430	0.440913	Fe	9	-0.000001	0.421428	0.440912	Fe	9	-0.000001	0.421430	0.440913
Fe	10	-0.000056	0.260859	0.589865	Fe	10	0.000203	0.263011	0.590251	Fe	10	0.000633	0.263586	0.590346
Fe	11	0.403472	0.417422	0.520530	Fe	11	0.403472	0.417419	0.520529	Fe	11	0.403472	0.417422	0.520530
Fe	12	0.159576	0.249565	0.449789	Fe	12	0.159576	0.249563	0.449788	Fe	12	0.159576	0.249565	0.449789
Fe	13	0.096528	0.417421	0.520530	Fe	13	0.096528	0.417418	0.520529	Fe	13	0.096528	0.417421	0.520530
Fe	14	0.340425	0.249565	0.449789	Fe	14	0.340425	0.249563	0.449788	Fe	14	0.340425	0.249565	0.449789

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	15	0.749989	0.405762	0.578550	Fe	15	0.750939	0.406156	0.578106	Fe	15	0.751070	0.406234	0.578085
Fe	16	0.500002	0.160256	0.496298	Fe	16	0.500002	0.160254	0.496297	Fe	16	0.500002	0.160256	0.496298
Fe	17	0.750061	0.155487	0.626055	Fe	17	0.751413	0.156089	0.626055	Fe	17	0.751548	0.156236	0.625964
Fe	18	0.750000	0.501647	0.473827	Fe	18	0.750000	0.501645	0.473827	Fe	18	0.750000	0.501647	0.473827
Fe	19	0.841167	0.170077	0.545525	Fe	19	0.841768	0.170672	0.545615	Fe	19	0.841740	0.170819	0.545677
Fe	20	0.596412	0.501105	0.613293	Fe	20	0.598334	0.491277	0.613521	Fe	20	0.598005	0.490147	0.613518
Fe	21	0.659056	0.169815	0.545614	Fe	21	0.659575	0.170256	0.545006	Fe	21	0.659666	0.170005	0.544990
Fe	22	0.903552	0.499823	0.613464	Fe	22	0.903556	0.501485	0.613518	Fe	22	0.903776	0.501403	0.613576
Fe	23	0.500001	0.421430	0.440913	Fe	23	0.500002	0.421428	0.440912	Fe	23	0.500001	0.421430	0.440913
Fe	24	0.501541	0.259662	0.589581	Fe	24	0.497995	0.255906	0.589919	Fe	24	0.497448	0.254214	0.590372
Fe	25	0.903472	0.417422	0.520531	Fe	25	0.903473	0.417420	0.520530	Fe	25	0.903472	0.417422	0.520531
Fe	26	0.659575	0.249568	0.449791	Fe	26	0.659575	0.249566	0.449791	Fe	26	0.659575	0.249568	0.449791
Fe	27	0.596527	0.417424	0.520531	Fe	27	0.596528	0.417421	0.520530	Fe	27	0.596527	0.417424	0.520531
Fe	28	0.840426	0.249566	0.449791	Fe	28	0.840426	0.249564	0.449791	Fe	28	0.840426	0.249566	0.449791
Fe	29	0.249916	0.905019	0.579112	Fe	29	0.245903	0.912462	0.576767	Fe	29	0.246285	0.912912	0.576274
Fe	30	-0.000002	0.660246	0.496298	Fe	30	-0.000002	0.660243	0.496297	Fe	30	-0.000002	0.660246	0.496298
Fe	31	0.251735	0.656579	0.629537	Fe	31	0.256152	0.669783	0.625864	Fe	31	0.255697	0.666747	0.626408
Fe	32	0.250000	1.001645	0.473828	Fe	32	0.250000	1.001641	0.473827	Fe	32	0.250000	1.001645	0.473828
Fe	33	0.341722	0.668877	0.544701	Fe	33	0.340896	0.671419	0.545676	Fe	33	0.339915	0.668815	0.545188
Fe	34	0.095937	0.999874	0.613366	Fe	34	0.094143	0.999897	0.613164	Fe	34	0.094169	1.000024	0.613254
Fe	35	0.158463	0.669040	0.544751	Fe	35	0.159593	0.669516	0.544262	Fe	35	0.158308	0.670816	0.543635
Fe	36	0.404538	1.003026	0.613051	Fe	36	0.399790	0.982738	0.615062	Fe	36	0.400458	0.986398	0.613936

IS-Cs + CO					TS-Cs + CO= CsCO					FS-CsCO				
Atom	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**	**Atom**	**No.**	**x**	**y**	**z**
Fe	37	0.000001	0.921427	0.440911	Fe	37	0.000001	0.921423	0.440910	Fe	37	0.000001	0.921427	0.440911
Fe	38	0.000960	0.759330	0.589604	Fe	38	0.001378	0.758489	0.589589	Fe	38	0.001198	0.758101	0.589791
Fe	39	0.403473	0.917414	0.520530	Fe	39	0.403474	0.917410	0.520529	Fe	39	0.403473	0.917414	0.520530
Fe	40	0.159575	0.749566	0.449790	Fe	40	0.159575	0.749563	0.449789	Fe	40	0.159575	0.749566	0.449790
Fe	41	0.096527	0.917414	0.520530	Fe	41	0.096527	0.917409	0.520529	Fe	41	0.096527	0.917414	0.520530
Fe	42	0.340425	0.749567	0.449790	Fe	42	0.340426	0.749563	0.449789	Fe	42	0.340425	0.749567	0.449790
Fe	43	0.750646	0.905750	0.578431	Fe	43	0.749846	0.906220	0.578468	Fe	43	0.749764	0.906380	0.578506
Fe	44	0.500002	0.660248	0.496297	Fe	44	0.500002	0.660245	0.496297	Fe	44	0.500002	0.660248	0.496297
Fe	45	0.750445	0.654852	0.625700	Fe	45	0.749603	0.654845	0.625848	Fe	45	0.749414	0.655345	0.625686
Fe	46	0.750000	1.001648	0.473828	Fe	46	0.750001	1.001643	0.473827	Fe	46	0.750000	1.001648	0.473828
Fe	47	0.841357	0.670472	0.545143	Fe	47	0.841035	0.669859	0.545160	Fe	47	0.841138	0.669940	0.545236
Fe	48	0.597163	0.994669	0.613720	Fe	48	0.597037	1.001748	0.613036	Fe	48	0.596264	1.002481	0.613068
Fe	49	0.658795	0.670419	0.545036	Fe	49	0.658954	0.669598	0.545458	Fe	49	0.658986	0.669443	0.545440
Fe	50	0.904281	0.998734	0.613583	Fe	50	0.903943	0.996480	0.613597	Fe	50	0.904114	0.995906	0.613606
Fe	51	0.500000	0.921428	0.440911	Fe	51	0.500000	0.921423	0.440910	Fe	51	0.500000	0.921428	0.440911
Fe	52	0.498398	0.758494	0.589416	Fe	52	0.500947	0.756189	0.590800	Fe	52	0.502485	0.755886	0.589824
Fe	53	0.903469	0.917416	0.520531	Fe	53	0.903470	0.917412	0.520530	Fe	53	0.903469	0.917416	0.520531
Fe	54	0.659576	0.749567	0.449791	Fe	54	0.659576	0.749564	0.449791	Fe	54	0.659576	0.749567	0.449791
Fe	55	0.596530	0.917418	0.520531	Fe	55	0.596531	0.917414	0.520530	Fe	55	0.596530	0.917418	0.520531
Fe	56	0.840424	0.749566	0.449791	Fe	56	0.840425	0.749562	0.449791	Fe	56	0.840424	0.749566	0.449791

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