Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Insight into the Fischer-Tropsch mechanism on hcp-Fe_7C_3(211) by Density function theory : the role of surface carbon and vacancy

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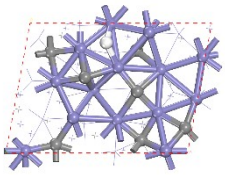
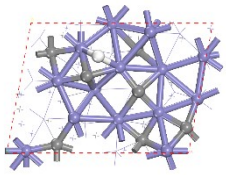
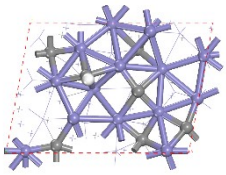
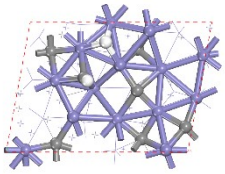
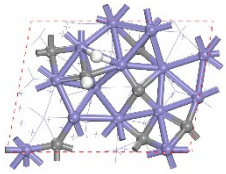
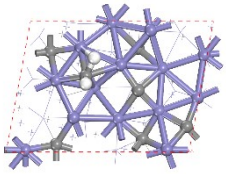
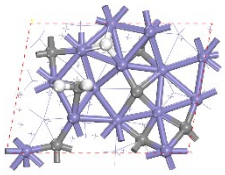
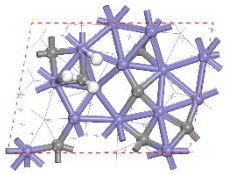
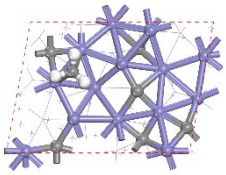
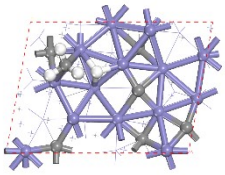
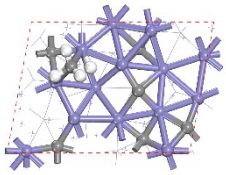
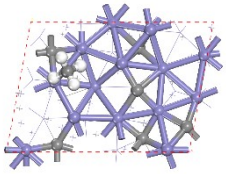
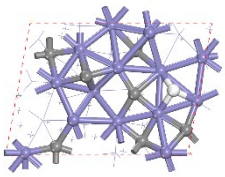
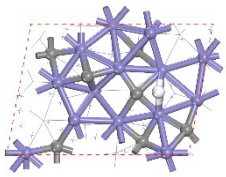
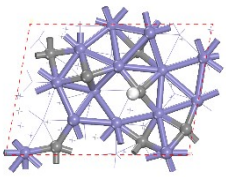
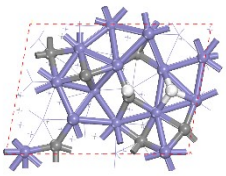
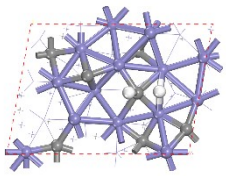
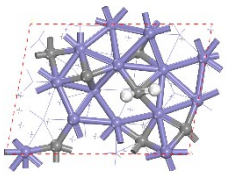
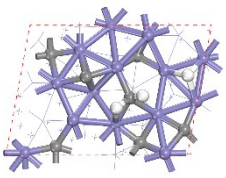
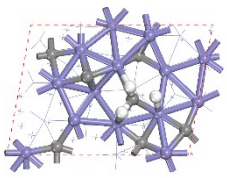
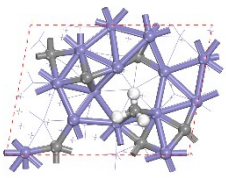
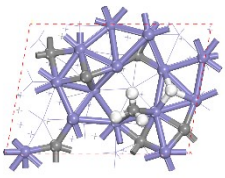
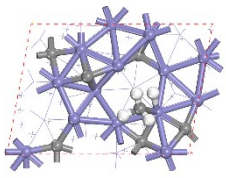
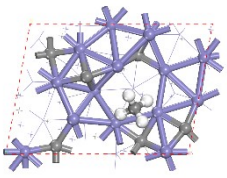
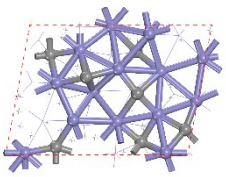
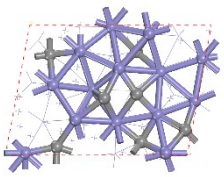
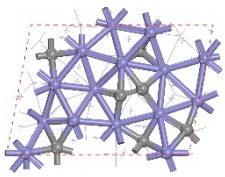
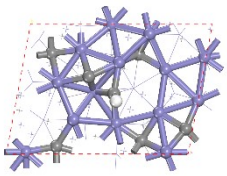
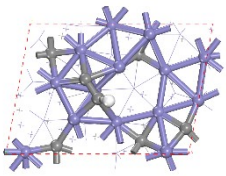
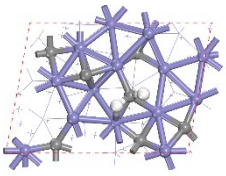
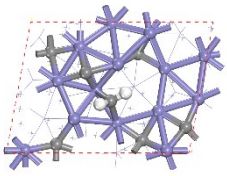
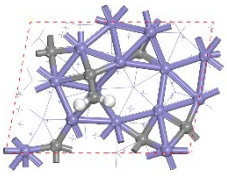
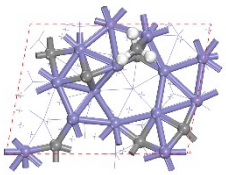
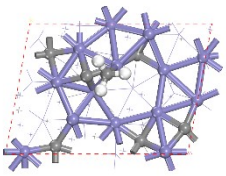
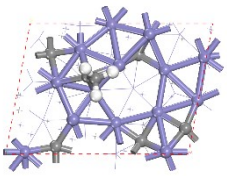
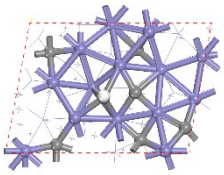
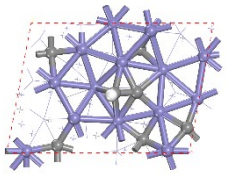
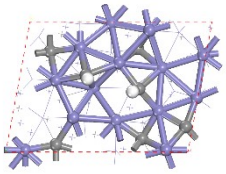
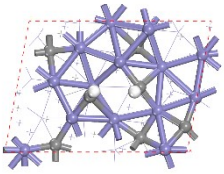
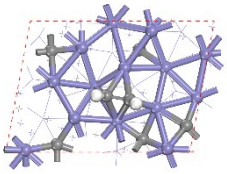
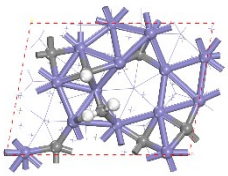
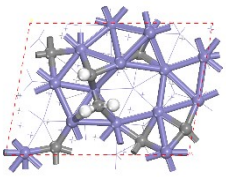
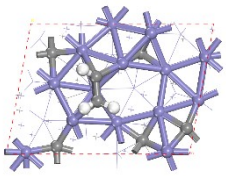
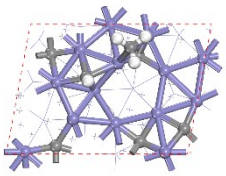
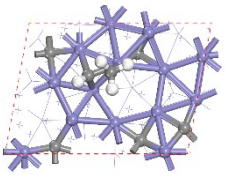
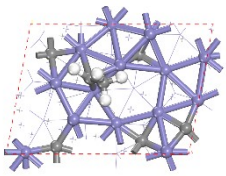
The structures of the elementary reactions in the C^1-C^2 coupling pathway

Elementary reactions	Initial states	Transition states	Final states
1. $C^1+H=HC^1$			
2. $HC^1+H=H_2C^1$			
3. $H_2C^1+H=H_3C^1$			
4. $H_3C^1+H=H_4C^1$			
5. $C^2+H=HC^2$			
6. $HC^2+H=H_2C^2$			
7. $H_2C^2+H=H_3C^2$			
8. $H_3C^2+H=H_4C^2$			

9. C^1+C^2 $=C^1C^2$			
10. C^1+HC^2 $=C^1HC^2$			
11. $C^1+H_2C^2$ $=C^1H_2C^2$			
12. $C^1+H_3C^2$ $=C^1H_3C^2$			
13. HC^1+C^2 $=HC^1C^2$			
14. HC^1+HC^2 $=HC^1HC^2$			
15. $HC^1+H_2C^2$ $=HC^1H_2C^2$			
16. $HC^1+H_3C^2$ $=HC^1H_3C^2$			

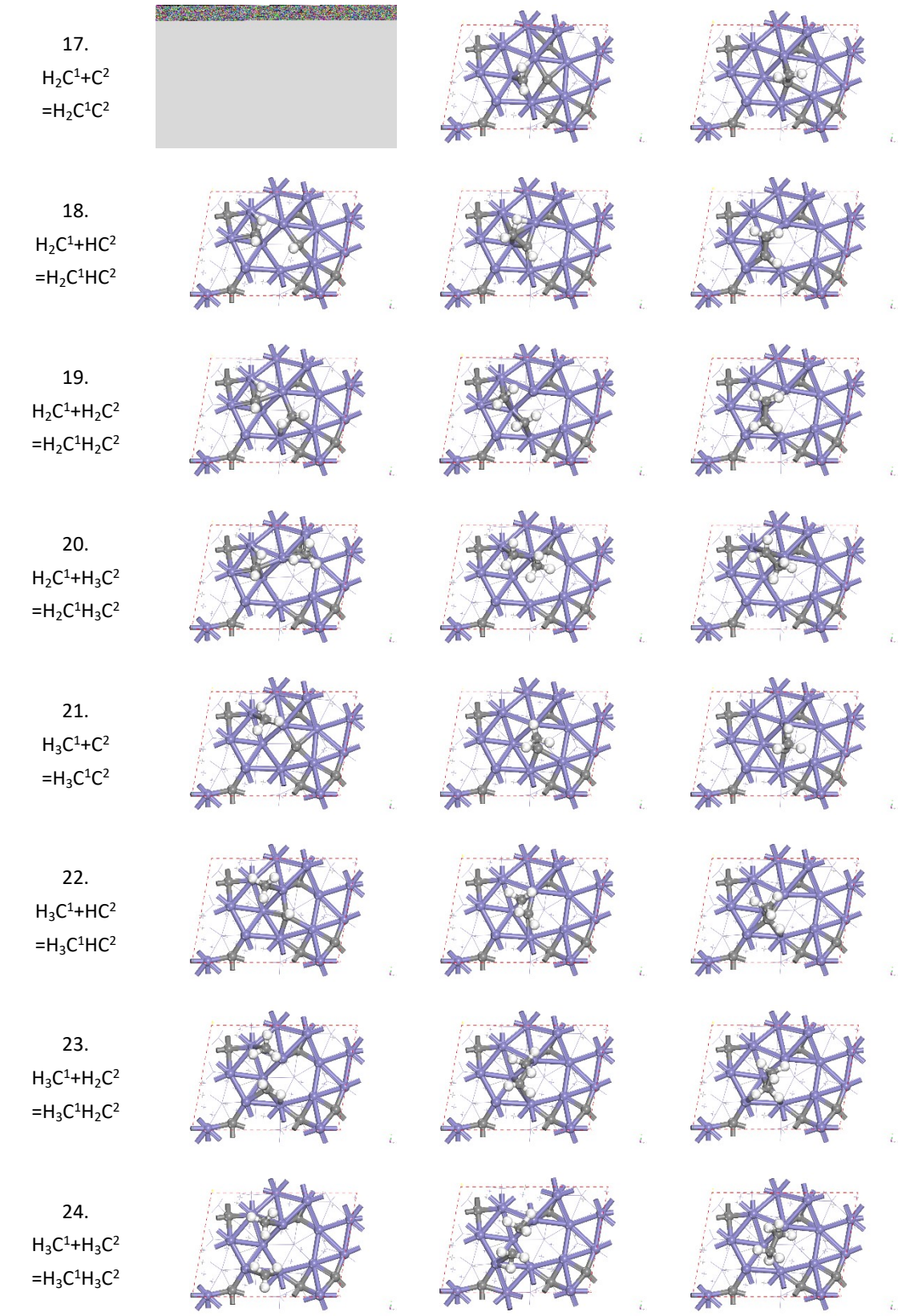
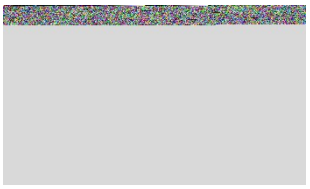
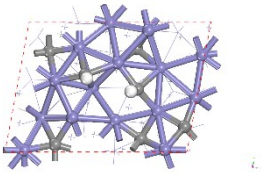
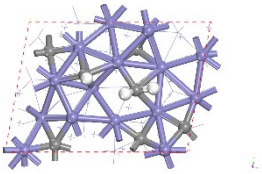
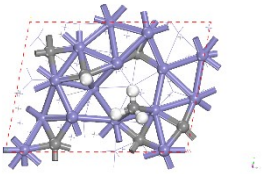
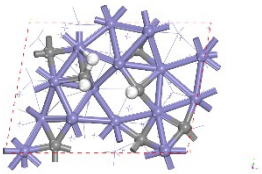
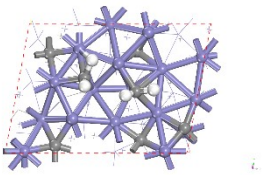
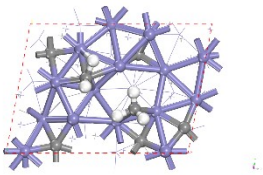


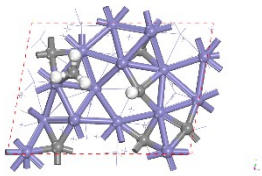
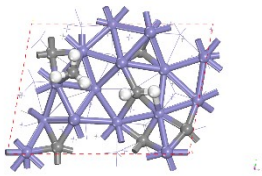
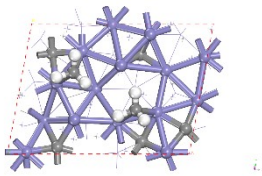
Figure S1. The structures of initial states, transition states, and final states about the C^1-C^2 coupling pathway on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; red: O atoms; white: H atoms.

The energy barrier and structures of the migration reactions in the C^1-C^2 coupling pathway

Elementary reactions	reactant structure	Reference structure*	Highest barrier energy of Migration reaction (eV)	Total reaction energy of Migration reaction (eV)
1. $C^1+H=HC^1$			0	0
2. $HC^1+H=H_2C^1$			0	0
3. $H_2C^1+H=H_3C^1$			0.11	0.09
4. $H_3C^1+H=H_4C^1$			0	0
5. $C^2+H=HC^2$			0	0
6. $HC^2+H=H_2C^2$			0	0

7. $H_2C^2+H=H_3C^2$			0.01	-0.09
8. $H_3C^2+H=H_4C^2$			0	0
9. $C^1+C^2=C^1C^2$			0	0
10. $C^1+HC^2=C^1HC^2$			0	0
11. $C^1+H_2C^2=C^1H_2C^2$			0.01	-0.09
12. $C^1+H_3C^2=C^1H_3C^2$			0.29	-0.45
13. $HC^1+C^2=HC^1C^2$			0	0

14. HC^1+HC^2 $=HC^1HC^2$			0	0
15. $HC^1+H_2C^2$ $=HC^1H_2C^2$			0.67	0.39
16. $HC^1+H_3C^2$ $=HC^1H_3C^2$			0.29	-0.46
17. $H_2C^1+C^2$ $=H_2C^1C^2$			0	0
18. $H_2C^1+HC^2$ $=H_2C^1HC^2$			0	0
19. $H_2C^1+H_2C^2$ $=H_2C^1H_2C^2$			0.01	-0.09
20. $H_2C^1+H_3C^2$ $=H_2C^1H_3C^2$			0.29	-0.46

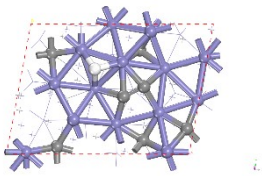
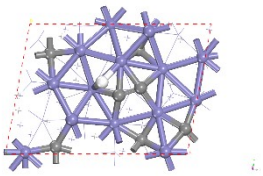
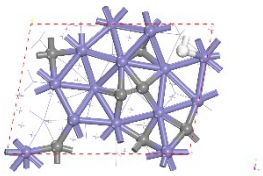
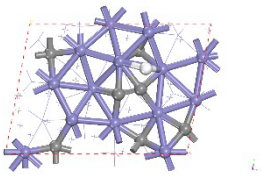
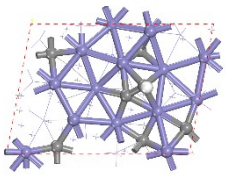
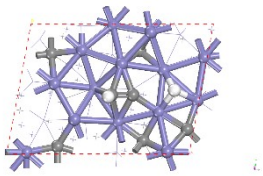
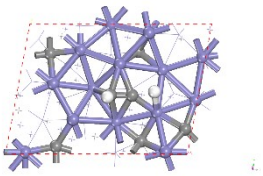
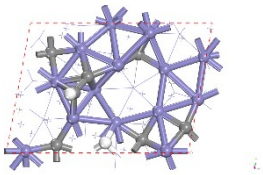
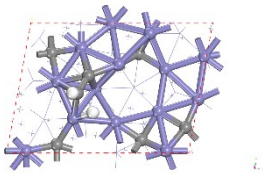
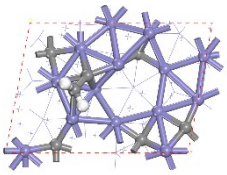
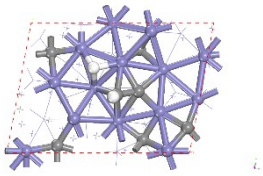
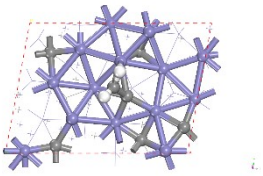
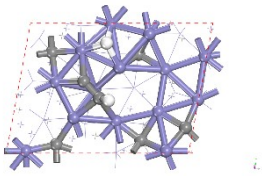
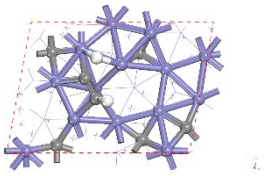
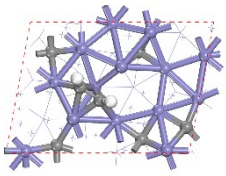
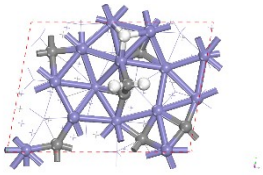
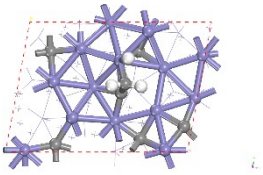
21. $H_3C^1+C^2$ $=H_3C^1C^2$			0.10	-0.13
22. $H_3C^1+HC^2$ $=H_3C^1HC^2$			0.10	-0.17
23. $H_3C^1+H_2C^2$ $=H_3C^1H_2C^2$			0.30	-0.34
24. $H_3C^1+H_3C^2$ $=H_3C^1H_3C^2$			0.10	-0.62

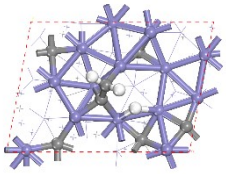
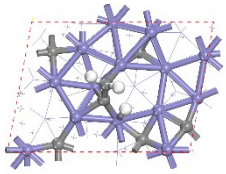
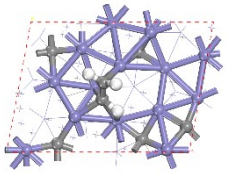
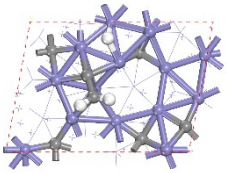
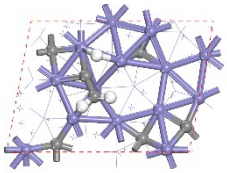
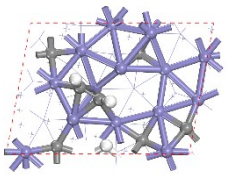
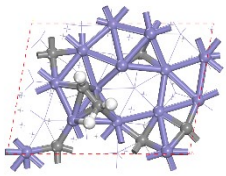
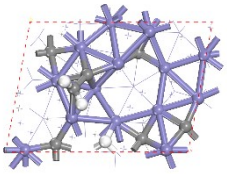
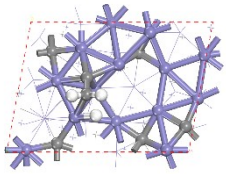
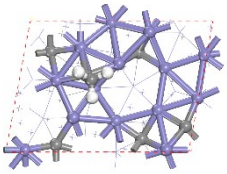
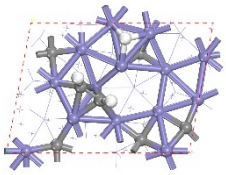
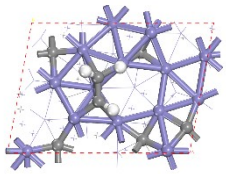
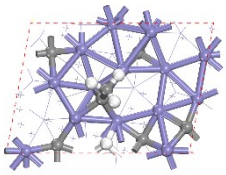
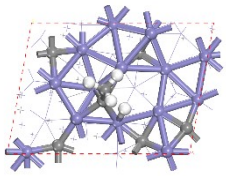
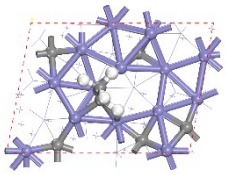
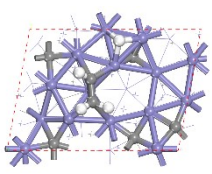
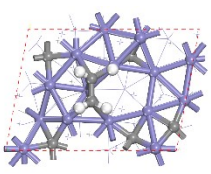
*The reference structure of the C-C coupling reaction is the final structure of the stepwise hydrogenation reaction.

*The reference structure of the stepwise hydrogenation reaction is the final structure of the stepwise hydrogenation reaction in the former hydrogenation elementary reaction.

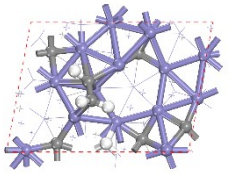
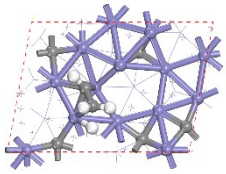
Figure S2. The reactant structure, reference structure and the migration energy about the C^1-C^2 coupling pathway on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; red: O atoms; white: H atoms.

The structures of the elementary reactions in the stepwise hydrogenation pathway of C_2 species

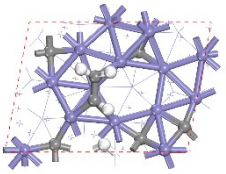
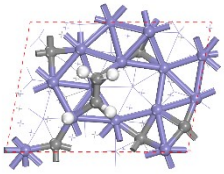
Elementary reactions	Initial states	Transition states	Final states
1. $H+C^1C^2=HC^1C^2$			
2. $C^1C^2+H=C^1HC^2$			
3. $HC^1C^2+H=HC^1HC^2$			
4. $C^1HC^2+H=C^1H_2C^2$			
5. $H+HC^1C^2=H_2C^1C^2$			
6. $H+C^1HC^2=HC^1HC^2$			
7. $H+H_2C^1C^2=H_3C^1C^2$			

8. $H_2C^1C^2+H=H_2C^1HC^2$			
9. $H+C^1H_2C^2=HC^1H_2C^2$			
10. $HC^1HC^2+H=HC^1H_2C^2$			
11. $C^1H_2C^2+H=C^1H_3C^2$			
12. $H+HC^1HC^2=H_2C^1HC^2$			
13. $H_3C^1C^2+H=H_3C^1HC^2$			
14. $H+HC^1H_2C^2=H_2C^1H_2C^2$			

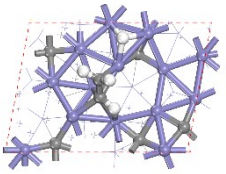
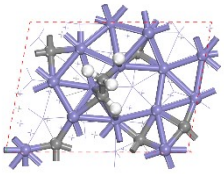
15.
$HC^1H_2C^2+H$
$=HC^1H_3C^2$

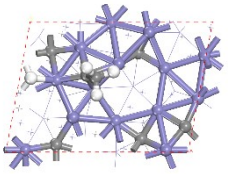
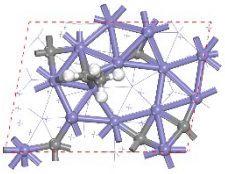
16.
$H_2C^1HC^2+H$
$=H_2C^1H_2C^2$

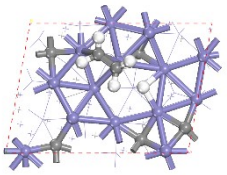
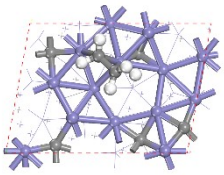
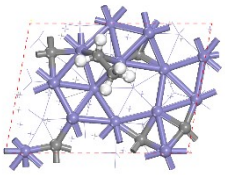
17.
$H+H_2C^1HC^2$
$=H_3C^1HC^2$

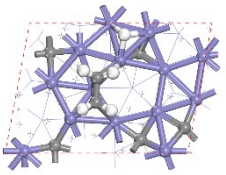
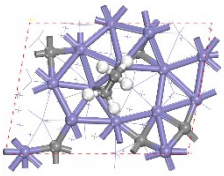
18
$H+C^1H_3C^2$
$=HC^1H_3C^2$

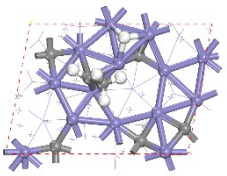
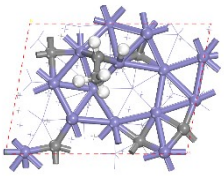
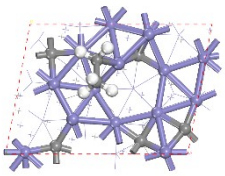
19.
$H_2C^1H_2C^2+H$
$=H_2C^1H_3C^2$

20.
$H+H_2C^1H_2C^2$
$=H_3C^1H_2C^2$

21.
$H+HC^1H_3C^2$
$=H_2C^1H_3C^2$

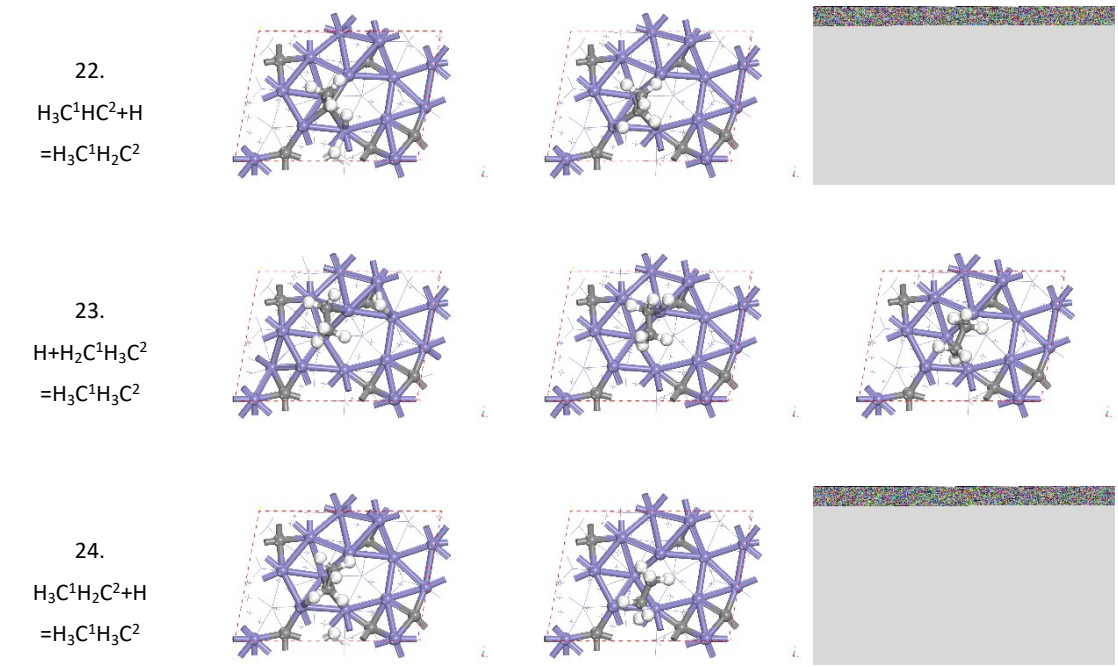
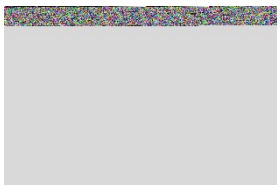
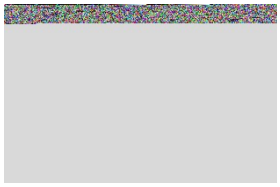
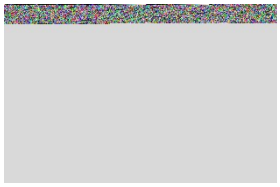


Figure S3. The structures of initial states, transition states, and final states about the stepwise hydrogenation pathway of C_2 species on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; white: H atoms.

The barrier energy and structures of the stepwise hydrogenation pathway of C_2 species

Elementary reactions	reactant structure	Reference structure*	Highest barrier energy of Migration reaction (eV)	Total reaction energy of Migration reaction (eV)
1. $H+C^1C^2=HC^1C^2$			0	0
2. $C^1C^2+H=C^1HC^2$			0	0
3. $HC^1C^2+H=HC^1HC^2$			0	0
4. $C^1HC^2+H=C^1H_2C^2$			0.80	0.11
5. $H+HC^1C^2=H_2C^1C^2$			0	0
6. $H+C^1HC^2=HC^1HC^2$			0.80	0.29

7. $H+H_2C^1C^2=H_3C^1C^2$			0	0
8. $H_2C^1C^2+H=H_2C^1HC^2$			0.09	-0.10
9. $H+C^1H_2C^2=HC^1H_2C^2$			0.46	0.42
10. $HC^1HC^2+H=HC^1H_2C^2$			0	0
11. $C^1H_2C^2+H=C^1H_3C^2$			0	0
12. $H+HC^1HC^2=H_2C^1HC^2$			0	0
13. $H_3C^1C^2+H=H_3C^1HC^2$			0.67	0.02

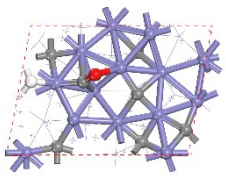
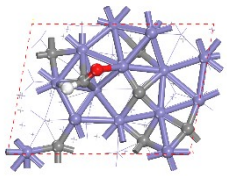
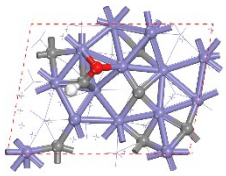
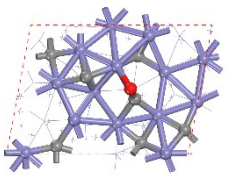
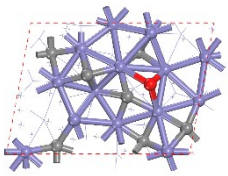
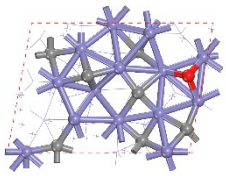
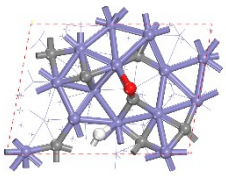
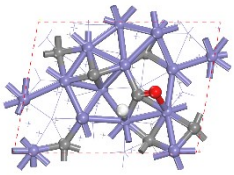
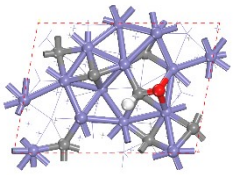
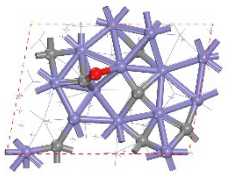
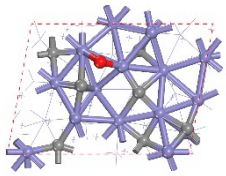
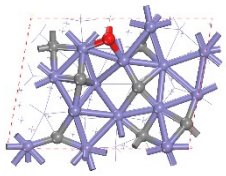
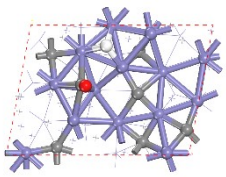
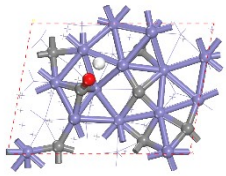
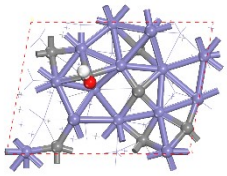
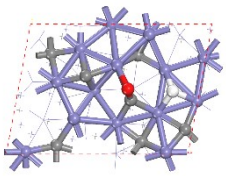
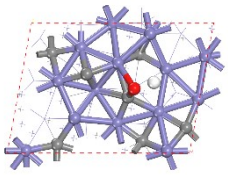
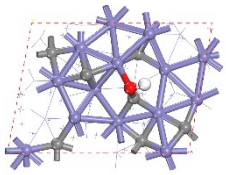
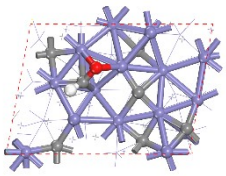
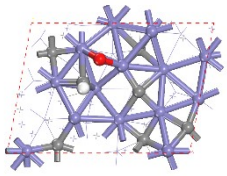
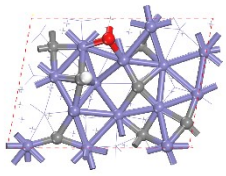
14. $H+HC^1H_2C^2=H_2C^1H_2C^2$			0	0
15. $HC^1H_2C^2+H=HC^1H_3C^2$			0.13	0.10
16. $H_2C^1HC^2+H=H_2C^1H_2C^2$			0.06	0
17. $H+H_2C^1HC^2=H_3C^1HC^2$			0	0
18 $H+C^1H_3C^2=HC^1H_3C^2$			0	0
19. $H_2C^1H_2C^2+H=H_2C^1H_3C^2$			0.55	0.10
20. $H+H_2C^1H_2C^2=H_3C^1H_2C^2$			0	0

21. $H+HC^1H_3C^2$ $=H_2C^1H_3C^2$			0	0
22. $H_3C^1HC^2+H$ $=H_3C^1H_2C^2$			0	0
23. $H+H_2C^1H_3C^2$ $=H_3C^1H_3C^2$			0	0
24. $H_3C^1H_2C^2+H$ $=H_3C^1H_3C^2$			0	0

*The reference structure of the C_2 stepwise hydrogenation pathway is the final structure of C-C coupling reaction.

Figure S4. The reactant structure, reference structure and the migration energy about the stepwise hydrogenation pathway of C_2 species on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; white: H atoms.

The structures of the elementary reactions in the carbon vacancy recover pathway

Elementary reactions	Initial states	Transition states	Final states
1. $H+C^1O=HC^1O$			
2. $C^2O=C^2+O$			
3. $H+C^2O=HC^2O$			
4. $C^1O=C^1+O$			
5. $C^1O+H=C^1OH$			
6. $C^2O+H=C^2OH$			
7. $HC^1O=C^1H+O$			

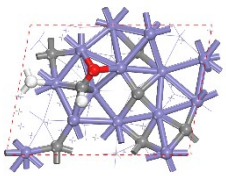
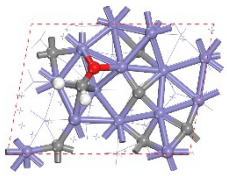
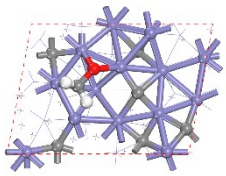
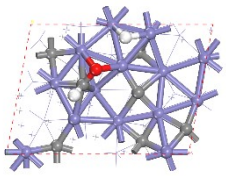
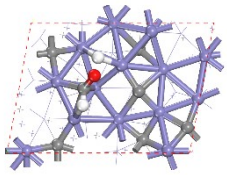
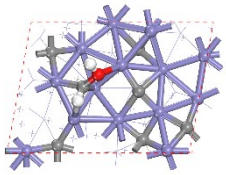
8. $H+HC^1O=H_2C^1O$			
9. $HC^1O+H=HC^1OH$			

Figure S5. The structures of initial states, transition states, and final states about carbon vacancy recover pathway on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; red: O atoms; white: H atoms.

The structures of the elementary reactions in oxygen remove pathway

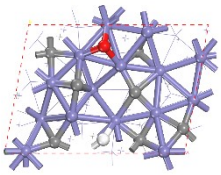
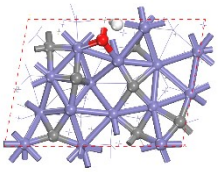
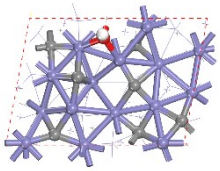
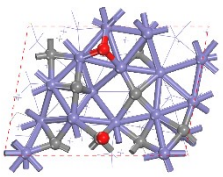
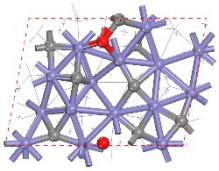
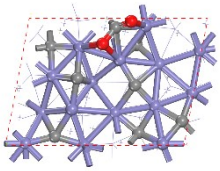
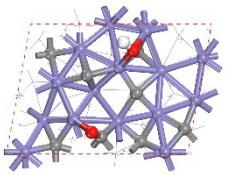
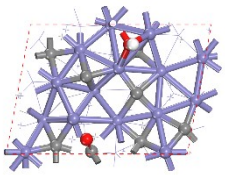
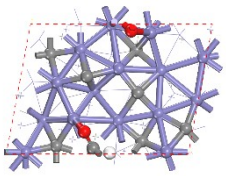
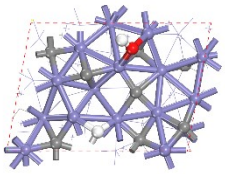
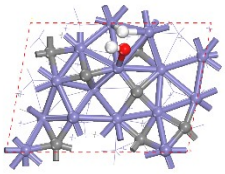
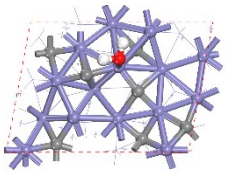
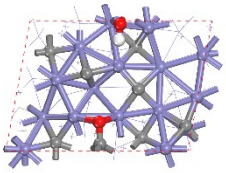
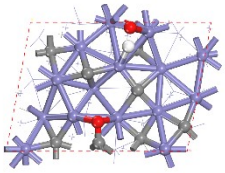
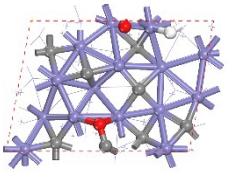
Elementary reactions	Initial states	Transition states	Final states
1. O+H =OH			
2. O+CO =CO_2			
3. OH+CO =COOH			
4. OH+H =H_2O			
5. COOH =CO_2+H			

Figure S6. The structures of initial states, transition states, and final states about the oxygen remove pathway on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; red: O atoms; white: H atoms.

The barrier energy and structures of the migration reactions in the oxygen remove pathway

Elementary reactions	reactant structure	Reference structure*	Highest barrier energy of migration reaction (eV)	Total reaction energy of migration reaction (eV)
1. O+H =OH			0	0
2. O+CO =CO_2			0	0
3. OH+CO =COOH			0.07	-0.01
4. OH+H =H_2O			0.07	-0.01
5. COOH =CO_2+H			0.27	-0.02

*The reference structure of the O remove pathway is the final structure of the former elementary reaction.

Figure S7. The reactant structure, reference structure and the migration energy about the oxygen remove pathway on hcp-Fe_7C_3 (211) surface. Blue: Fe atoms; gray: C atoms; red: O atoms; white: H atoms.