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Supporting Information

Structures and Energies of Cu_n Clusters on Fe and Fe_3C Surfaces from Density Functional Theory Computation

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Table S1: Benchmark of slab thickness and relaxation thickness of single Cu atom adsorption on Fe(100) and Fe(111) surfaces. (L represents total layers, R represents relaxed layers.)

Test	Fe(100)		Fe(111)	
		E_{ads}(eV)		E_{ads}(eV)
Slab thickness	p(3×3)-3LR2	-3.20	p(3×3)-6LR4	-3.77
	p(3×3)-4LR2	-3.15	p(3×3)-7LR4	-3.81
	p(3×3)-5LR2	-3.11	p(3×3)-8LR4	-3.78
	p(3×3)-6LR2	-3.17	p(3×3)-9LR4	-3.84
	p(3×3)-7LR2	-3.16		
Relaxation thickness	p(3×3)-5LR2	-3.11	p(3×3)-6LR3	-3.74
	p(3×3)-5LR3	-3.13	p(3×3)-6LR4	-3.77
	p(3×3)-5LR4	-3.13	p(3×3)-6LR5	-3.78

Table S2: Benchmark of slab thickness and relaxation thickness of single Cu atom adsorption on $Fe_3C(100)$ and $Fe_3C(010)$ surfaces. (L represents total layers, R represents relaxed layers.)

Test	$Fe_3C(100)$		$Fe_3C(010)$	
		E_{ads}(eV)		E_{ads}(eV)
Slab thickness	p(2×2)-10LR6	-3.16	p(1×1)-6LR3	-3.16
	p(2×2)-12LR6	-3.22	p(1×1)-7LR3	-3.17
	p(2×2)-13LR6	-3.19	p(1×1)-8LR3	-3.19
	p(2×2)-15LR6	-3.19	p(1×1)-9LR3	-3.17
Relaxation thickness	p(1×1)-12LR6	-3.16	p(1×1)-6LR3	-3.16
	p(1×1)-12LR7	-3.17	p(1×1)-6LR4	-3.16
	p(1×1)-12LR8	-3.18	p(1×1)-6LR5	-3.18

Table S3. Adsorption energies [$E(Cu_{n/ads})$; eV], coordination numbers (CN) with surface Fe(C) atoms, numbers of Cu–Cu bond (NB) for Cu_n (n = 1–6) on the $Fe_3C(100)$ surface

	$E(Cu_{n/ads})$	CN-Fe	CN-C	NB		$E(Cu_{n/ads})$	CN-Fe	CN-C	NB
Cu_1-6F	-3.58	5	1	0	Cu_4-3	-14.08	17	3	3
Cu_1-4F1	-3.22	3	1	0	Cu_4-4	-14.06	16	4	5
Cu_1-4F2	-3.16	3	1	0	Cu_4-5	-13.99	15	3	4
Cu_1-4F3	-3.09	3	1	0	Cu_4-6	-13.81	13	3	5
Cu_1-4F4	-3.08	4	0	0	Cu_4-7	-13.26	13	2	2
Cu_1-2F	-2.54	2	0	0	Cu_4-8	-13.18	12	3	3
Cu_1-1F	-1.74	1	0	0	Cu_4-9	-12.94	10	2	6
Cu_2-1	-7.17	10	2	0	Cu_4-10	-12.69	11	3	6
Cu_2-2	-7.13	10	2	0	Cu_4-11	-12.61	10	2	3
Cu_2-3	-7.06	10	2	0	Cu_5-1	-17.28	24	4	0
Cu_2-4	-6.76	8	2	0	Cu_5-2	-17.71	18	4	7
Cu_2-5	-6.71	9	1	0	Cu_5-3	-17.62	21	5	4
Cu_2-6	-6.71	8	2	0	Cu_5-4	-17.61	20	4	5
Cu_2-7	-6.66	8	2	0	Cu_5-5	-17.59	23	4	2
Cu_2-8	-6.65	9	1	0	Cu_5-6	-17.53	19	5	7
Cu_2-9	-6.39	6	2	0	Cu_5-7	-17.40	18	4	6
Cu_2-10	-6.38	7	1	0	Cu_5-8	-16.98	16	3	7
Cu_2-11	-6.35	6	2	0	Cu_5-9	-16.86	16	4	8
Cu_2-12	-6.98	8	2	1	Cu_5-10	-16.64	16	4	8
Cu_2-13	-6.92	8	2	1	Cu_5-11	-16.47	13	3	8
Cu_2-14	-6.60	7	1	1	Cu_5-12	-16.30	15	4	4
Cu_2-15	-6.33	6	2	1	Cu_6-1	-20.40	28	4	0
Cu_3-1	-10.63	15	3	0	Cu_6-2	-21.20	20	4	10
Cu_3-2	-10.29	14	2	0	Cu_6-3	-21.12	23	5	7
Cu_3-3	-10.28	13	3	0	Cu_6-4	-21.12	22	4	8
Cu_3-4	-10.24	14	2	0	Cu_6-5	-21.09	21	5	10
Cu_3-5	-10.00	12	2	0	Cu_6-6	-21.06	24	5	5
Cu_3-6	-10.71	13	3	2	Cu_6-7	-21.05	26	6	4
Cu_3-7	-10.34	12	2	2	Cu_6-8	-21.05	21	5	10
Cu_3-8	-10.31	11	3	3	Cu_6-9	-21.05	26	6	4
Cu_3-9	-10.29	12	2	2	Cu_6-10	-20.96	26	6	4
Cu_3-10	-10.29	10	2	3	Cu_6-11	-20.96	26	4	5
Cu_3-11	-10.26	11	3	2	Cu_6-12	-20.67	23	4	4
Cu_3-12	-10.08	11	3	3	Cu_6-13	-20.52	20	4	8
Cu_3-13	-10.01	9	2	2	Cu_6-14	-20.33	18	4	10
Cu_3-14	-9.74	10	2	2	Cu_6-15	-20.32	19	5	9
Cu_4-1	-14.11	20	4	0	Cu_6-16	-20.06	18	4	6
Cu_4-2	-14.21	16	4	4					

Table S4. Adsorption energies [$E(Cu_{n/ads})$; eV], coordination numbers (CN) with surface Fe(C) atoms, numbers of Cu–Cu bond (NB) for Cu_n (n = 1–6) on the $Fe_3C(010)$ surface

	$E(Cu_{n/ads})$	CN-Fe	CN-C	NB		$E(Cu_{n/ads})$	CN-Fe	CN-C	NB
Cu_1-5F	-3.39	5	0	0	Cu_4-9	-13.39	12	0	5
Cu_1-4F	-3.18	4	0	0	Cu_4-10	-13.24	14	0	5
Cu_1-2F	-2.60	2	0	0	Cu_4-11	-13.20	13	0	5
Cu_1-1F	-2.14	1	0	0	Cu_4-12	-13.16	14	0	3
Cu_2-1	-6.79	10	0	0	Cu_5-1	-16.61	22	0	0
Cu_2-2	-6.79	10	0	0	Cu_5-2	-17.77	25	0	4
Cu_2-3	-6.76	10	0	0	Cu_5-3	-17.67	22	0	6
Cu_2-4	-6.62	9	0	0	Cu_5-4	-17.55	22	0	5
Cu_2-5	-6.57	9	0	0	Cu_5-5	-17.50	22	0	5
Cu_2-6	-6.57	9	0	0	Cu_5-6	-17.32	25	0	2
Cu_2-7	-6.37	8	0	0	Cu_5-7	-17.19	19	0	6
Cu_2-8	-6.36	8	0	0	Cu_5-8	-17.08	19	0	6
Cu_2-9	-6.34	8	0	0	Cu_5-9	-17.06	19	0	6
Cu_2-10	-6.98	10	0	1	Cu_5-10	-16.86	18	0	6
Cu_2-11	-6.61	8	0	1	Cu_5-11	-16.71	16	0	6
Cu_3-1	-10.17	15	0	0	Cu_5-12	-15.97	14	0	8
Cu_3-2	-10.57	15	0	2	Cu_6-1	-19.75	22	0	4
Cu_3-3	-10.16	12	0	3	Cu_6-2	-19.63	24	0	2
Cu_3-4	-10.16	12	0	2	Cu_6-3	-19.63	24	0	2
Cu_3-5	-10.08	12	0	2	Cu_6-4	-21.39	27	0	7
Cu_3-6	-10.07	12	0	2	Cu_6-5	-21.33	30	0	5
Cu_3-7	-10.03	11	0	3	Cu_6-6	-21.16	27	0	6
Cu_3-8	-9.92	12	0	2	Cu_6-7	-21.15	24	0	8
Cu_3-9	-9.90	10	0	3	Cu_6-8	-21.11	27	0	6
Cu_3-10	-9.58	10	0	2	Cu_6-9	-21.10	30	0	4
Cu_4-1	-13.55	20	0	0	Cu_6-10	-21.10	30	0	4
Cu_4-2	-14.42	20	0	4	Cu_6-11	-21.01	24	0	8
Cu_4-3	-13.94	17	0	4	Cu_6-12	-20.97	24	0	8
Cu_4-4	-13.81	17	0	4	Cu_6-13	-20.91	24	0	8
Cu_4-5	-13.68	17	0	3	Cu_6-14	-20.70	23	0	8
Cu_4-6	-13.51	14	0	4	Cu_6-15	-20.60	21	0	8
Cu_4-7	-13.46	14	0	5	Cu_6-16	-20.19	21	0	7
Cu_4-8	-13.42	14	0	4	Cu_6-17	-19.81	19	0	10

Table S5. Adsorption energies [$E(Cu_{n/ads})$; eV] of Cu_n on Fe(110) and $Fe_3C(001)$ surfaces with respect to Cu atom and bulk fcc-Cu energy.

Fe(110)	$E(Cu_{n/ads})$-Cu_{atom}	$E(Cu_{ads/av})$-Cu_{bulk}	$Fe_3C(001)$	$E(Cu_{n/ads})$-Cu_{atom}	$E(Cu_{ads/av})$-Cu_{bulk}
Cu_1	-3.30	0.20	Cu1	-3.28	0.22
Cu_2-a	-6.77	0.23	Cu2-a	-6.56	0.44
Cu_3-a	-10.26	0.25	Cu3-a	-9.82	0.69
Cu_4-a	-13.99	0.02	Cu4-a	-13.10	0.91
Cu_5-a	-17.43	0.09	Cu5-a	-16.15	1.37
Cu_6-a	-20.95	0.07	Cu6-a	-19.16	1.86
Cu_7-a	-24.55	-0.04			
Cu_2-b	-6.76	0.24	Cu2-b	-6.36	0.65
Cu_3-b	-10.25	0.26	Cu3-b	-9.82	0.69
Cu_4-b	-13.77	0.24	Cu4-b	-13.16	0.85
Cu_5-b	-17.28	0.24	Cu5-b	-16.46	1.05
Cu_6-b	-20.79	0.23	Cu6-b	-20.06	0.96
Cu_7-b	-24.49	0.03			
Cu_4-c	-12.78	1.23	Cu4-c	-12.46	1.56
Cu_5-c	-16.53	0.98	Cu5-c	-15.91	1.60
Cu_6-c	-20.06	0.96	Cu6-c	-19.37	1.65
Cu_7-c	-23.76	0.76	Cu7	-23.35	1.17
Cu_{13}-a	-46.96	-1.43	Cu13-a	-43.50	2.04
Cu_{13}-c1	-45.84	-0.30	Cu13-b	-42.91	2.63
Cu_{13}-c2	-43.71	1.83	Cu13-c	-41.59	3.95

Fig. S1. Various optimized Cu_{1-4} configurations on the p(4×4) Fe(100) surface (adsorption energy in eV)

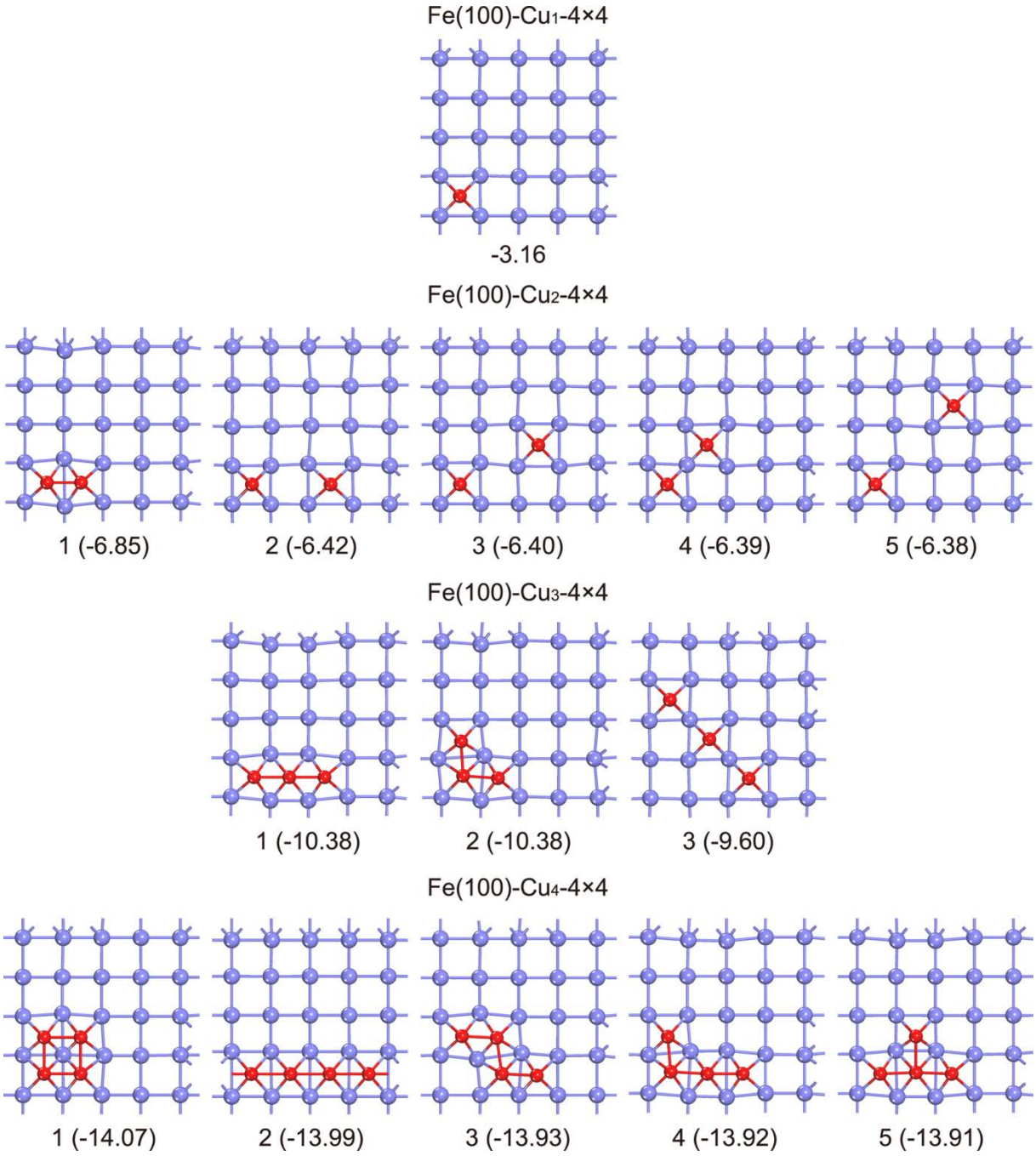


Fig. S2. Various optimized Cu_5 configurations on the p(4×4) Fe(100) surface (adsorption energy in eV)

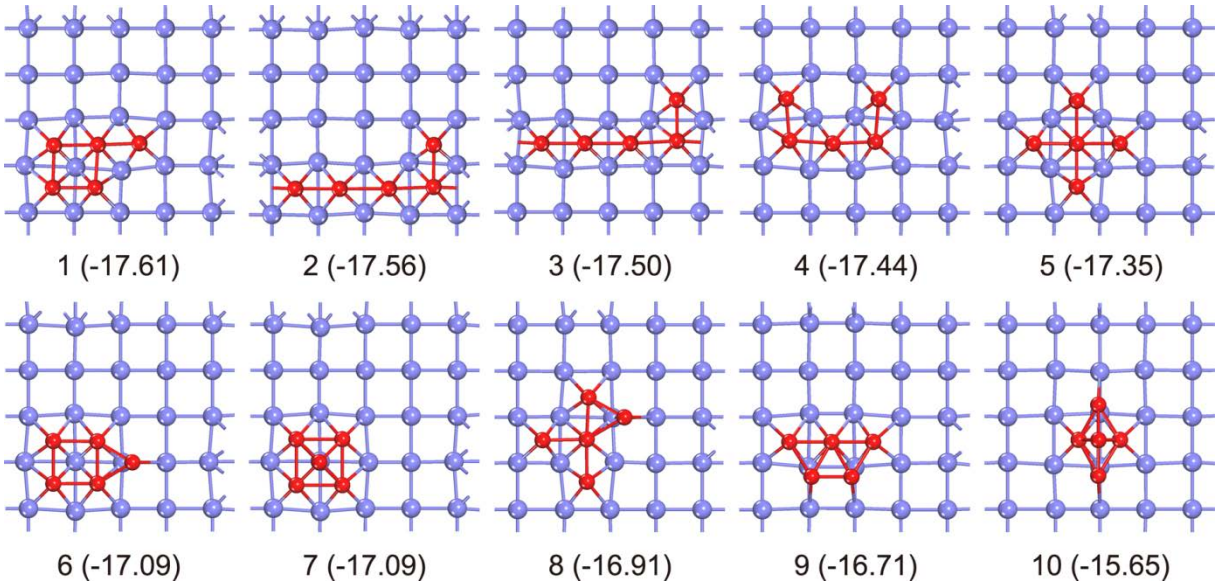


Fig. S3. Various optimized Cu_6 configurations on the p(4×4) Fe(100) surface (adsorption energy in eV)

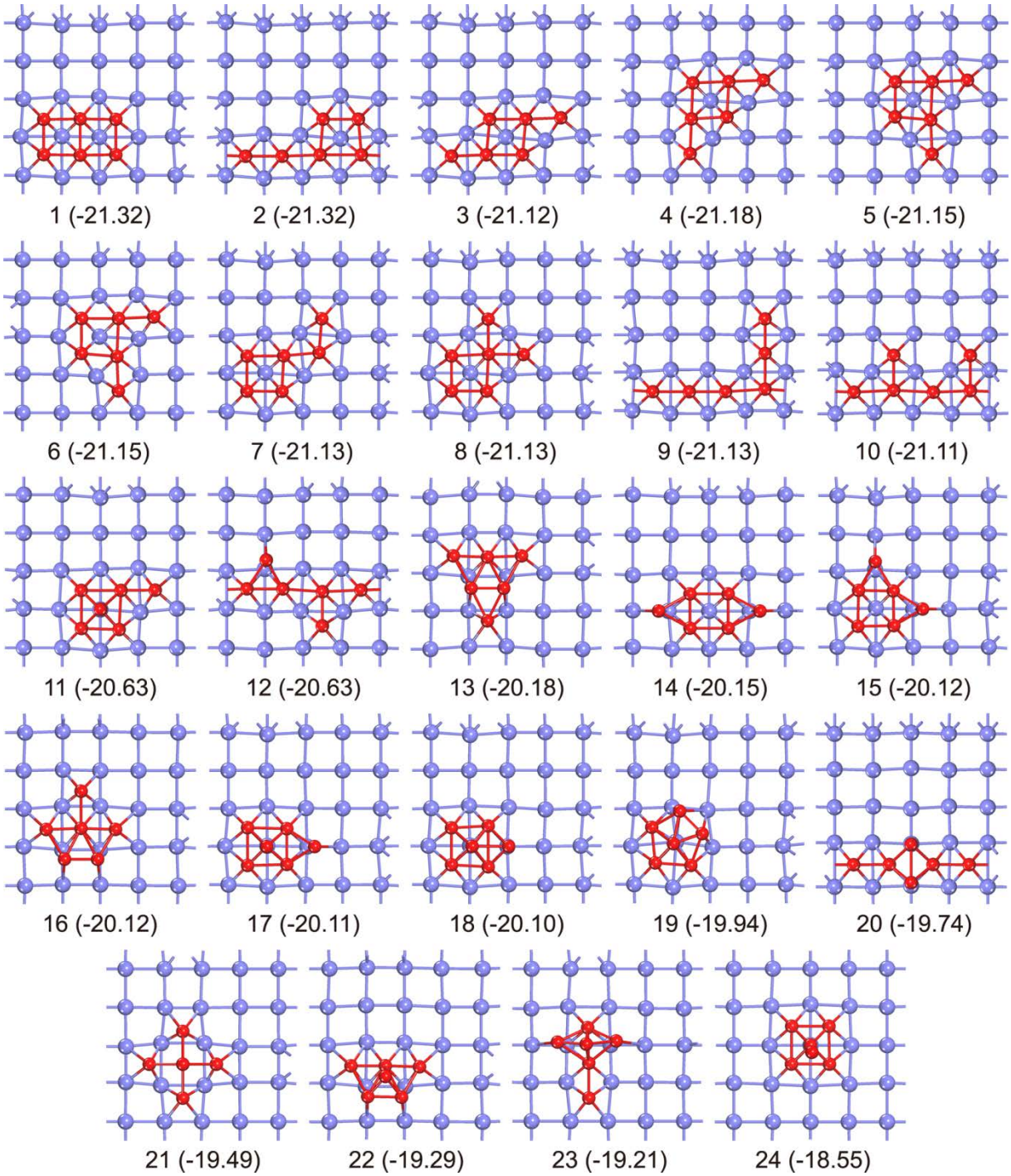


Fig. S4. Various optimized Cu_7 configurations on the p(4×4) Fe(100) surface (adsorption energy in eV)

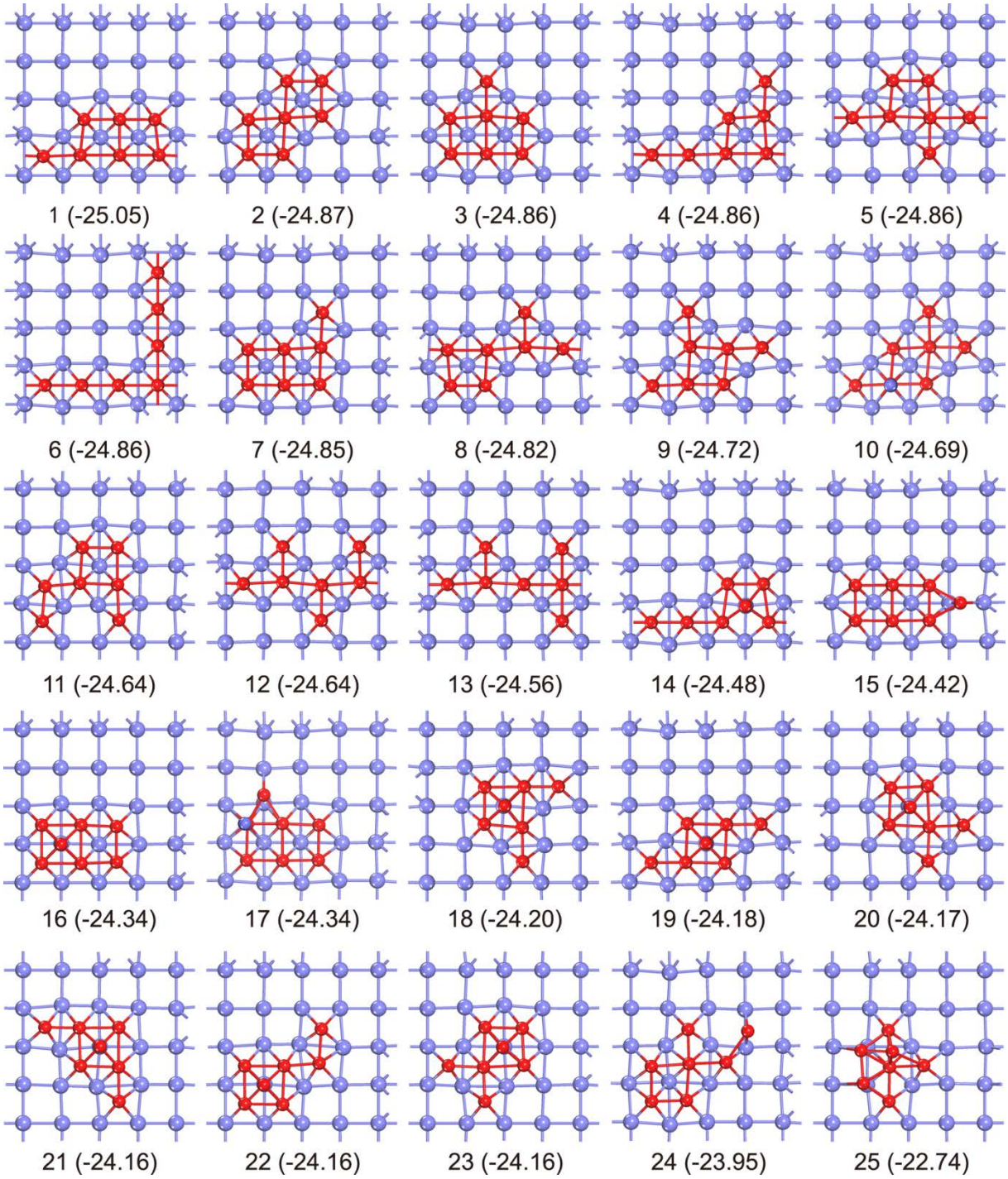
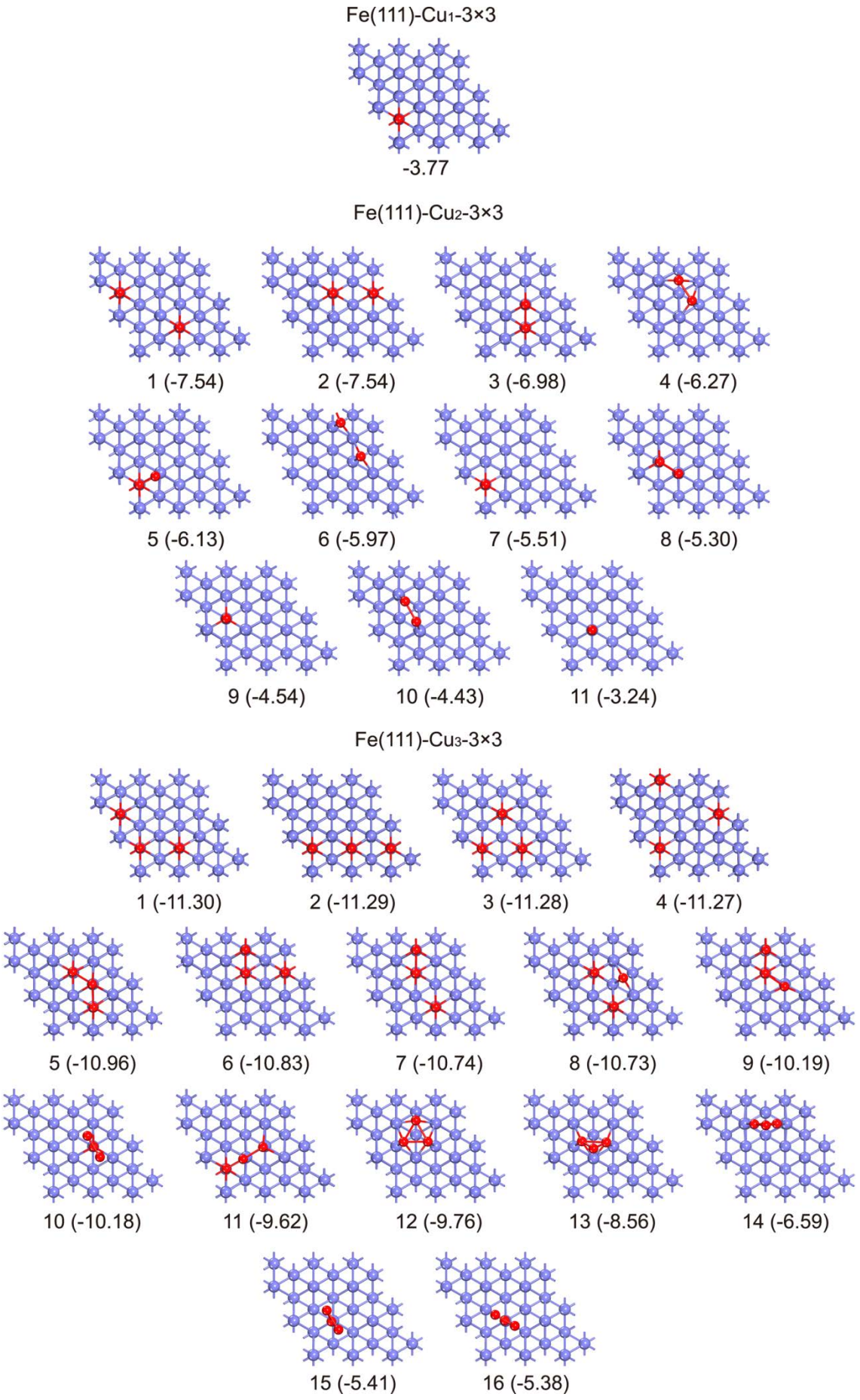
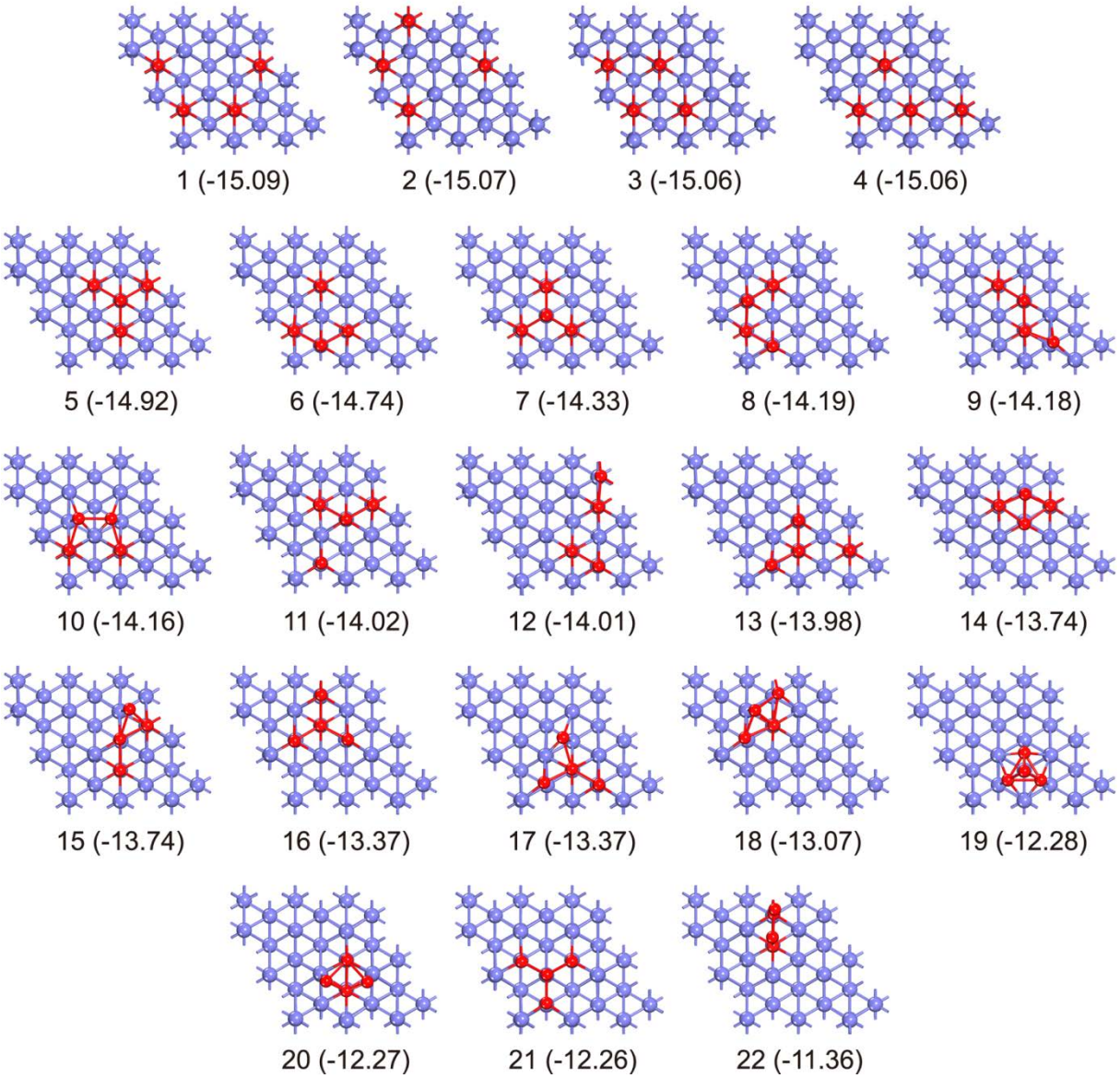


Fig. S5. Various optimized Cu_{2-4} configurations on the p(3×3) Fe(111) surface (adsorption energy in eV)



Fe(111)-Cu_4-3×3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7 (-14.33)
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9 (-14.18)
10 (-14.16)
11 (-14.02)
12 (-14.01)
13 (-13.98)
14 (-13.74)
15 (-13.74)
16 (-13.37)
17 (-13.37)
18 (-13.07)
19 (-12.28)
20 (-12.27)
21 (-12.26)
22 (-11.36)

Fig. S6. Various optimized Cu_5 configurations on the p(3×3) Fe(111) surface (adsorption energy in eV)

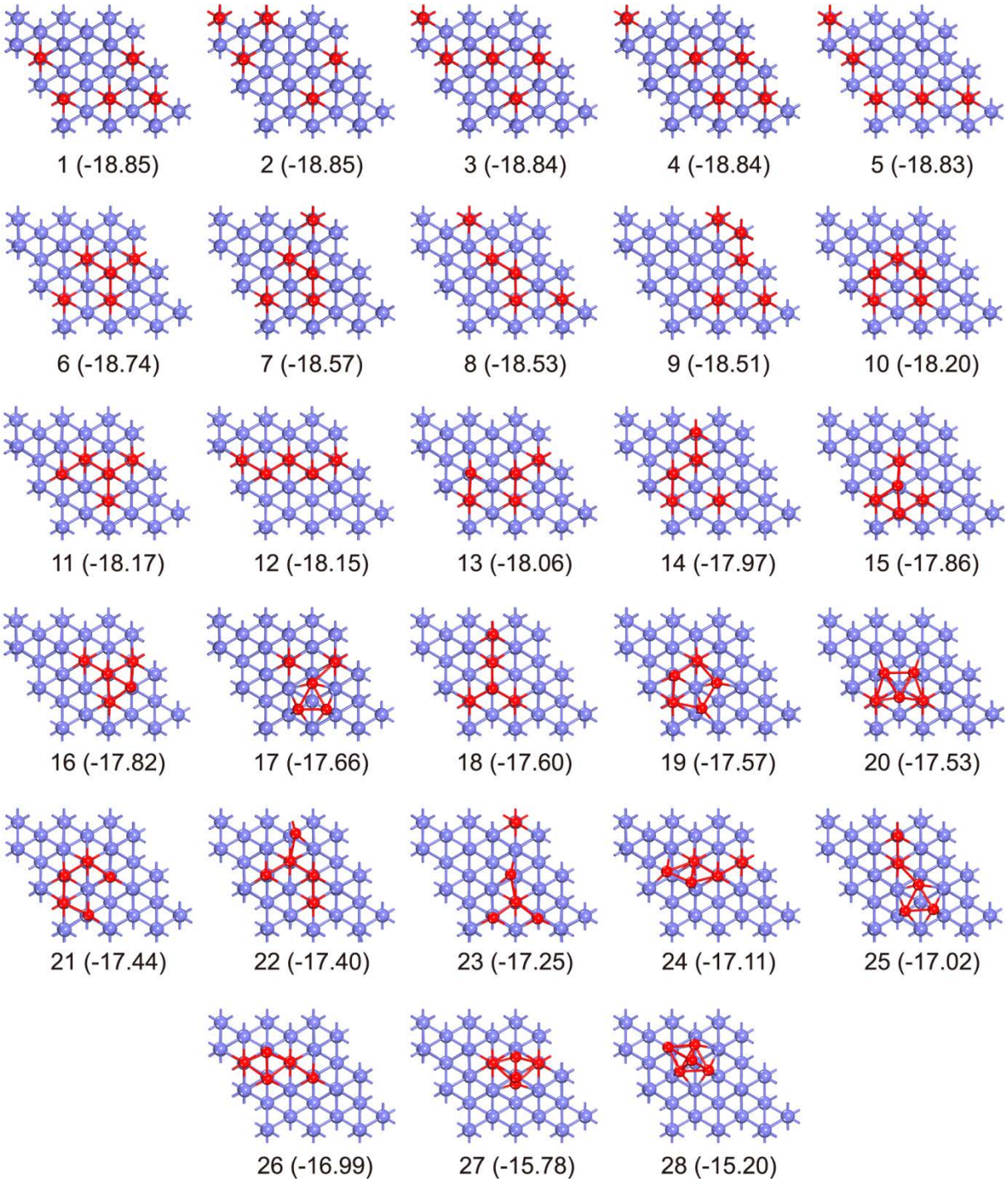
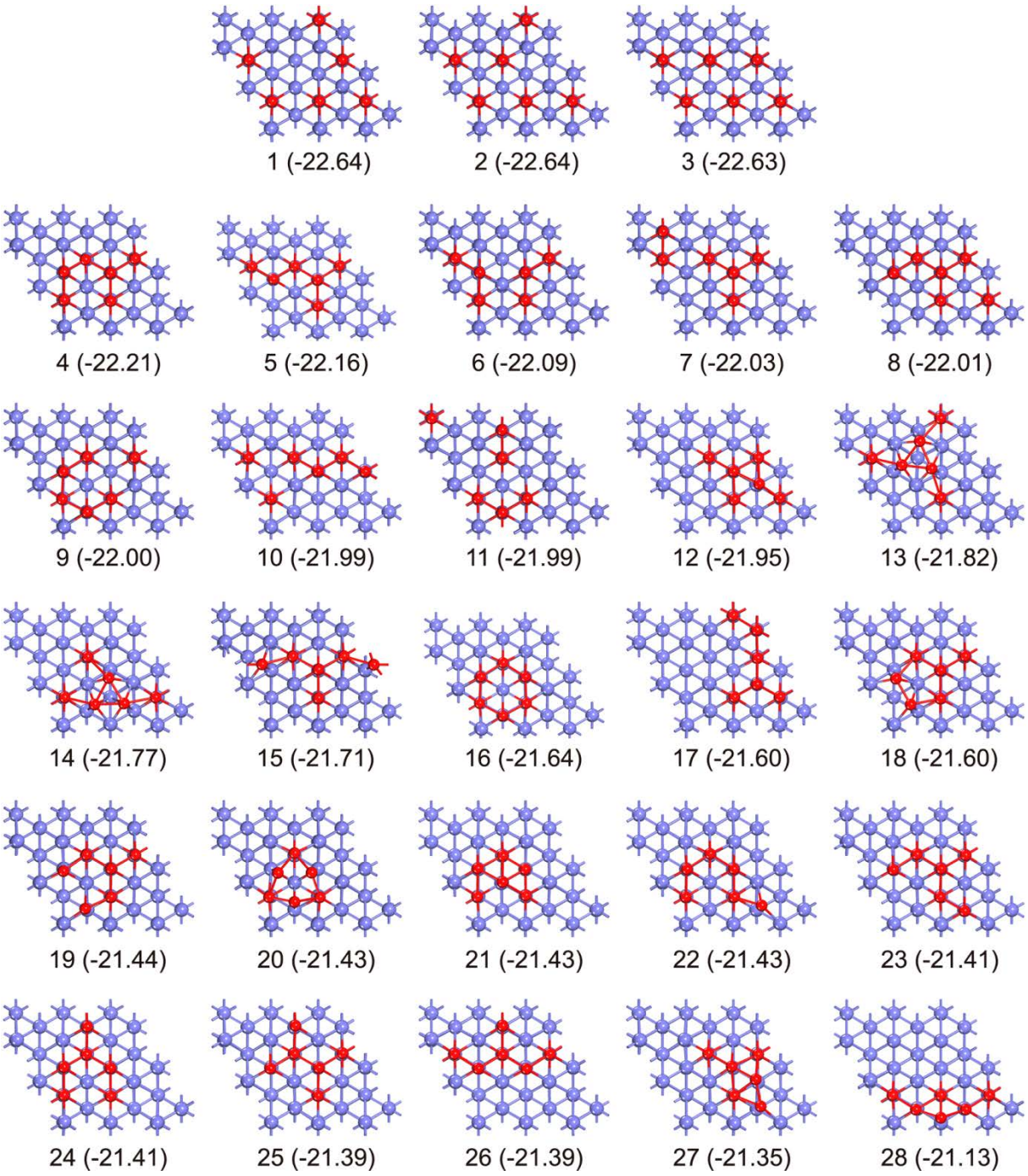
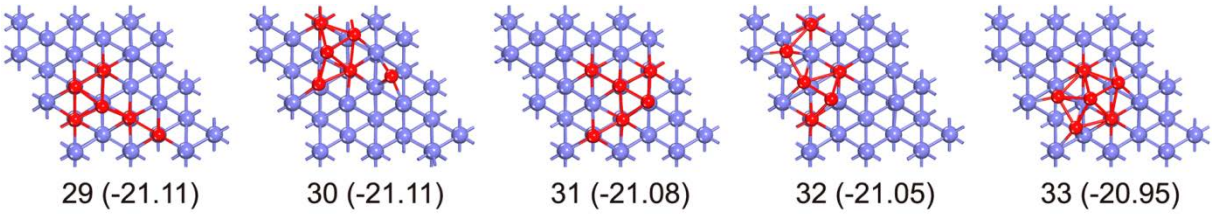


Fig. S7. Various optimized Cu_6 configurations on the p(3×3) Fe(111) surface (adsorption energy in eV)

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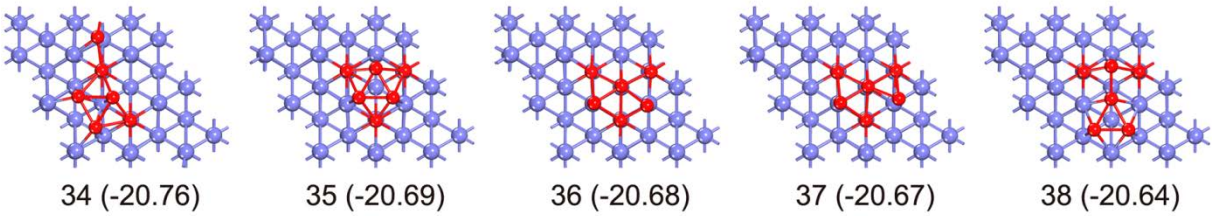
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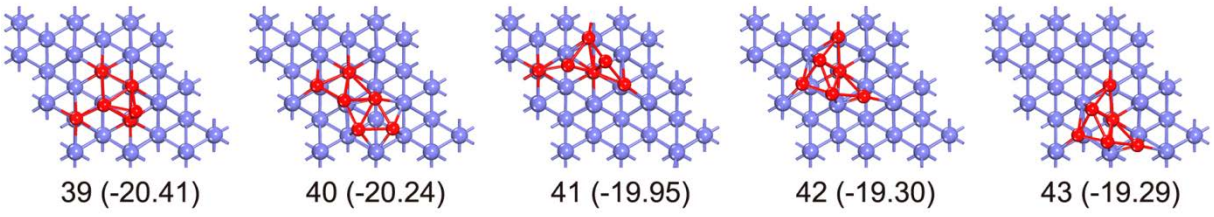

39 (-20.41) 40 (-20.24) 41 (-19.95) 42 (-19.30) 43 (-19.29)

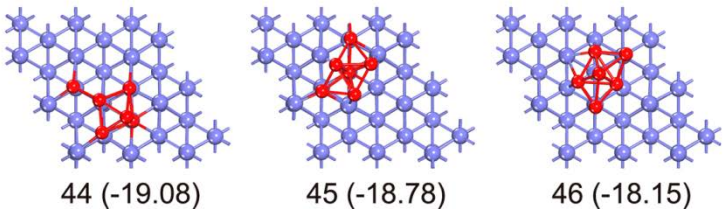

44 (-19.08) 45 (-18.78) 46 (-18.15)

Fig. S8. Various optimized Cu_7 configurations on the p(3×3) Fe(111) surface (adsorption energy in eV)

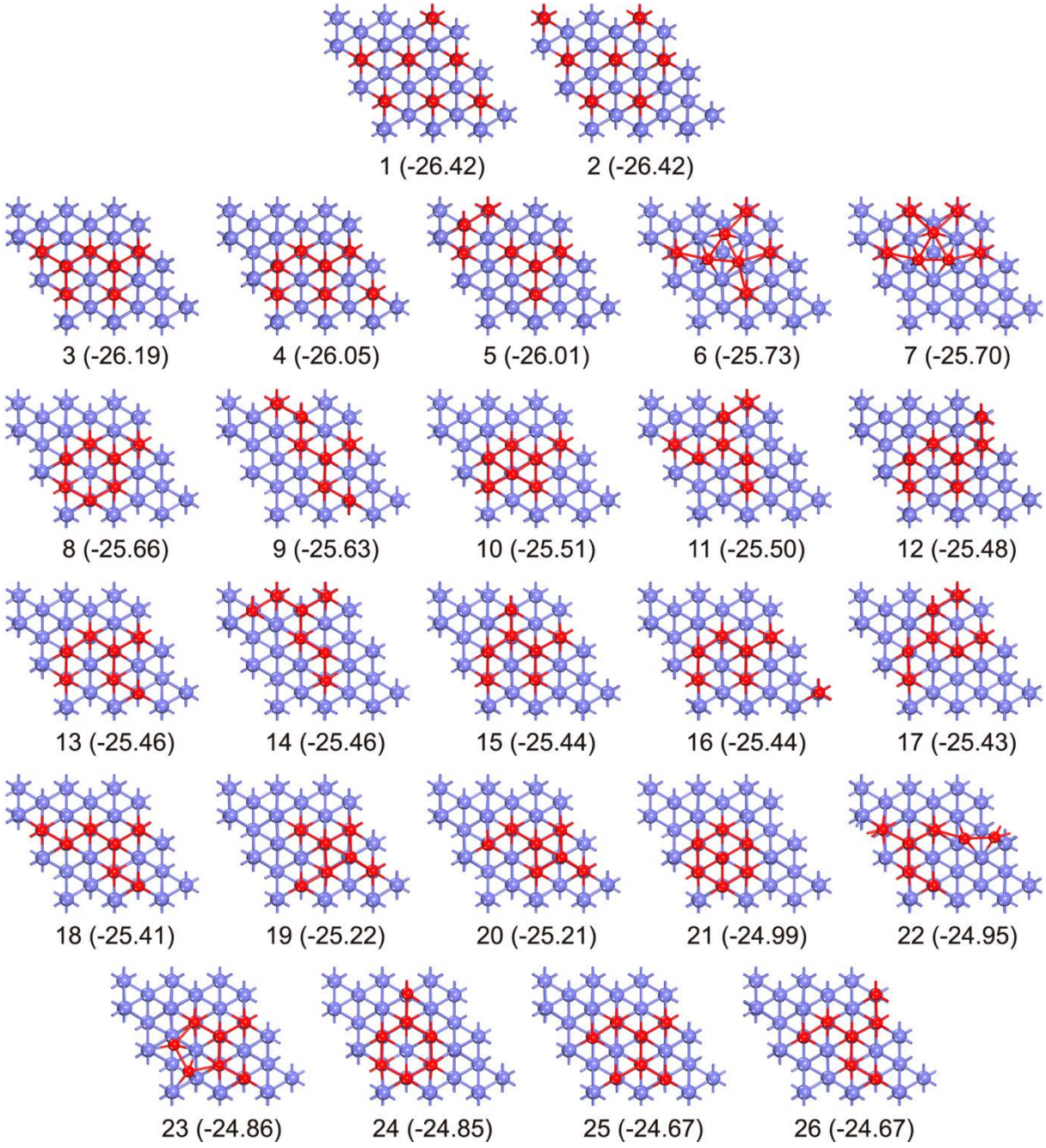


Fig. S9. Various optimized Cu_1 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

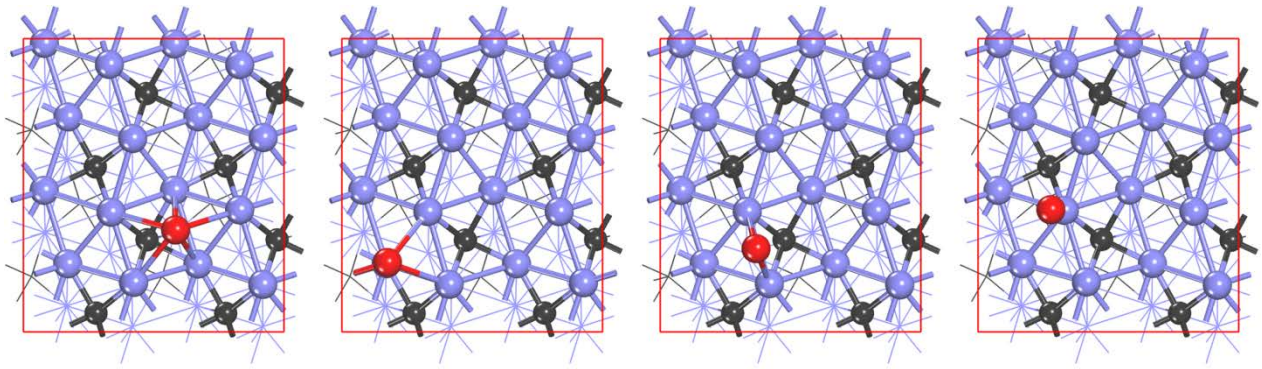


Fig. S10. Various optimized Cu_2 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

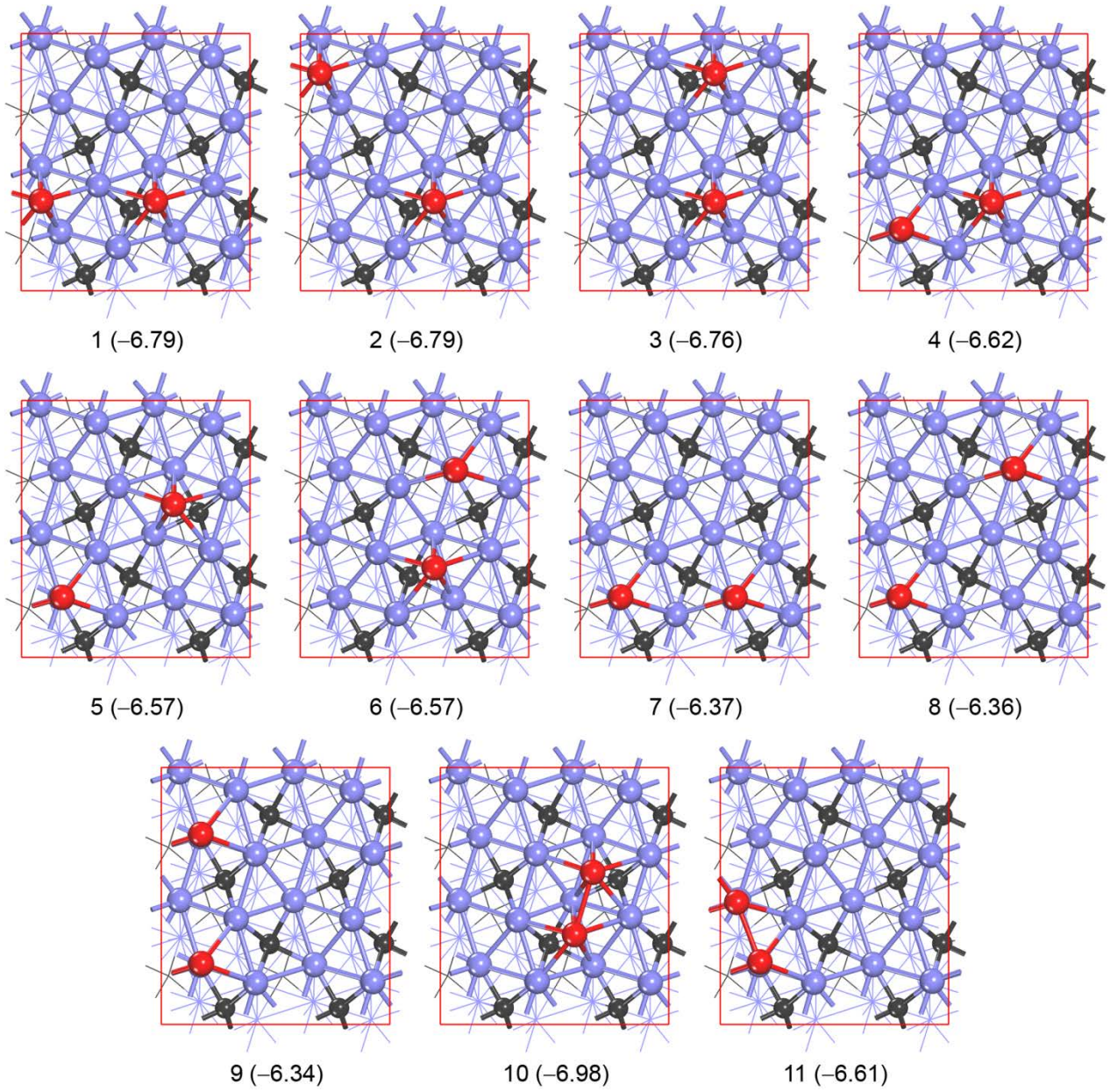


Fig. S11. Various optimized Cu_3 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

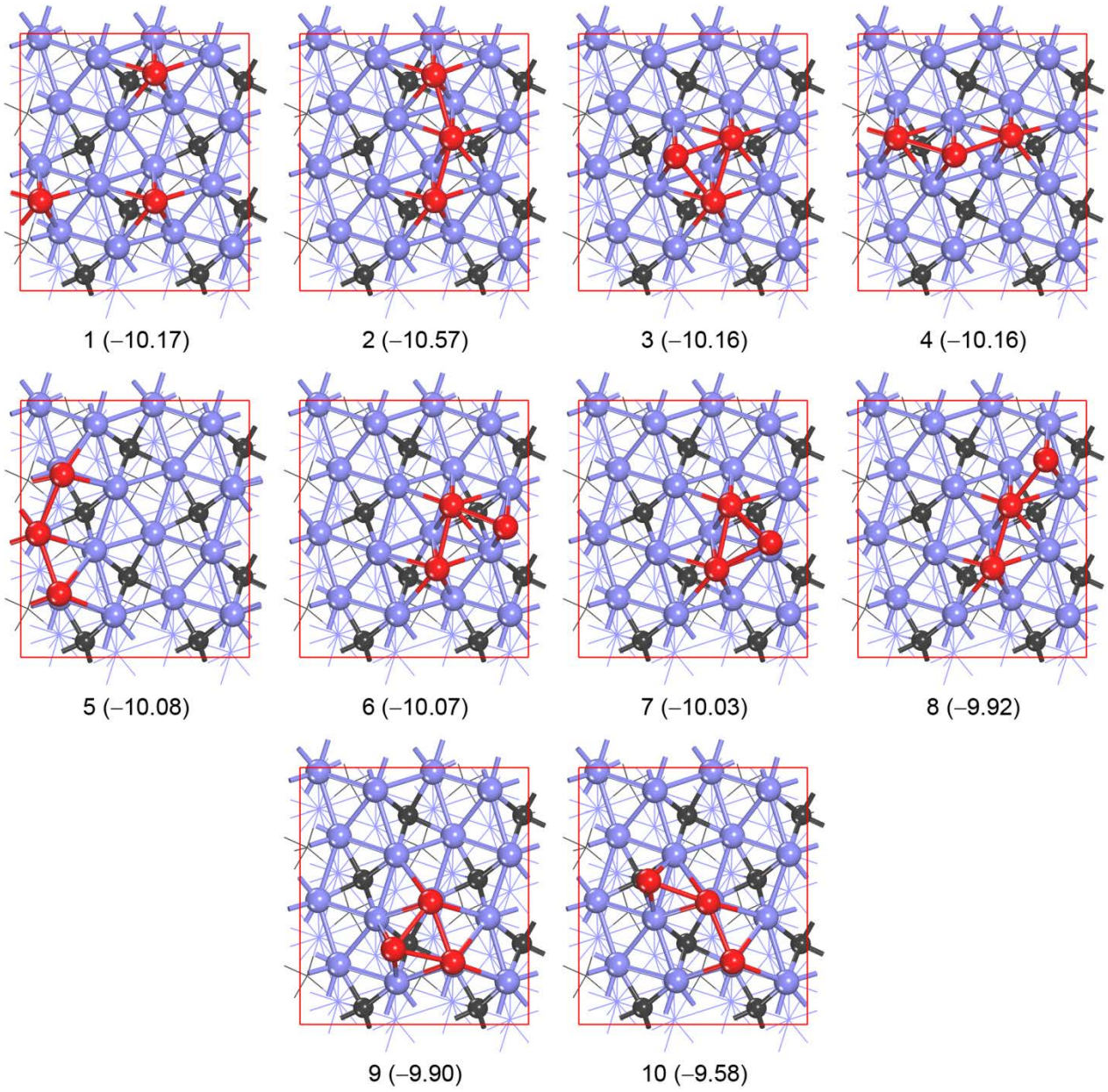


Fig. S12. Various optimized Cu_4 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

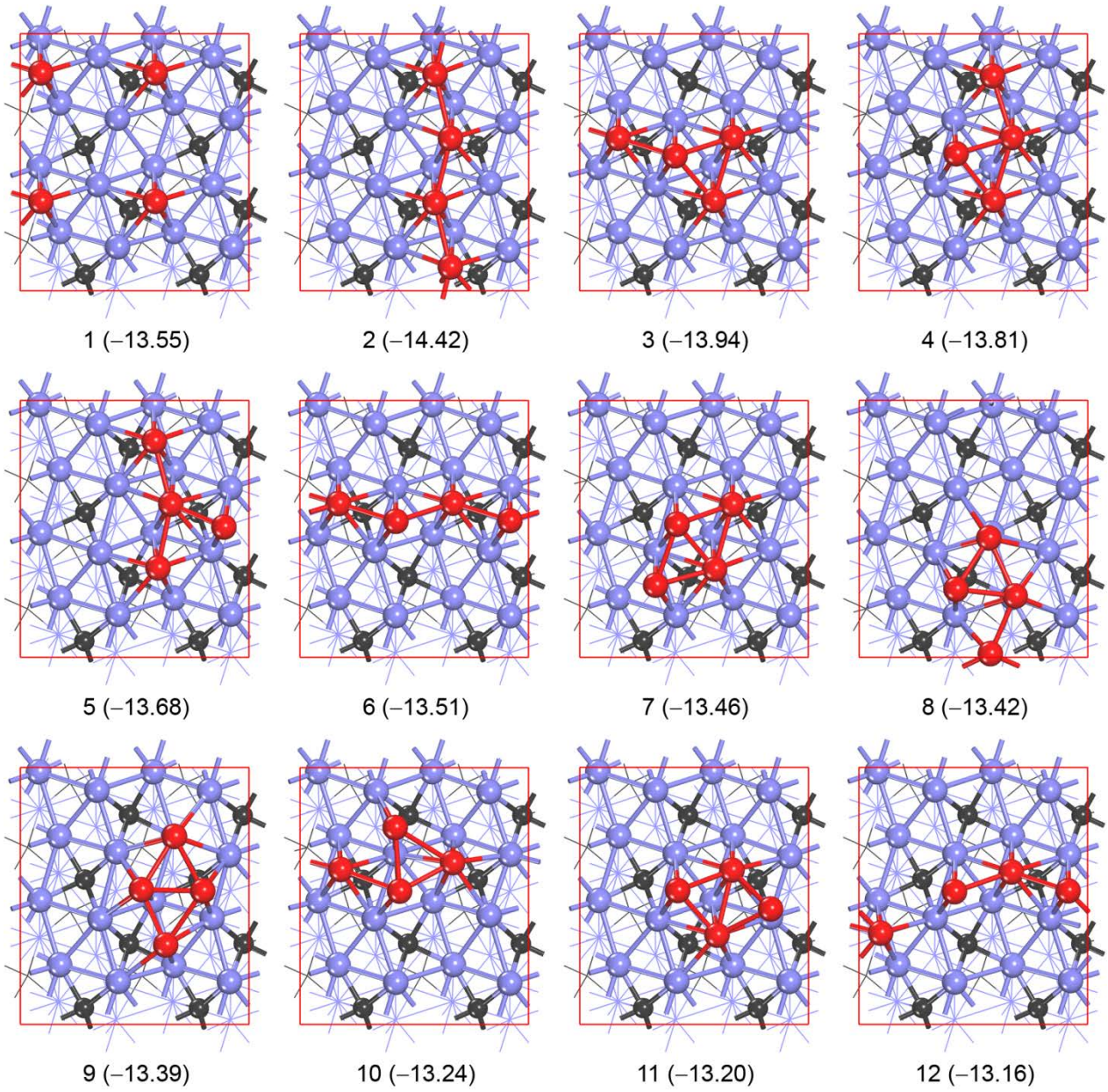


Fig. S13. Various optimized Cu_5 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

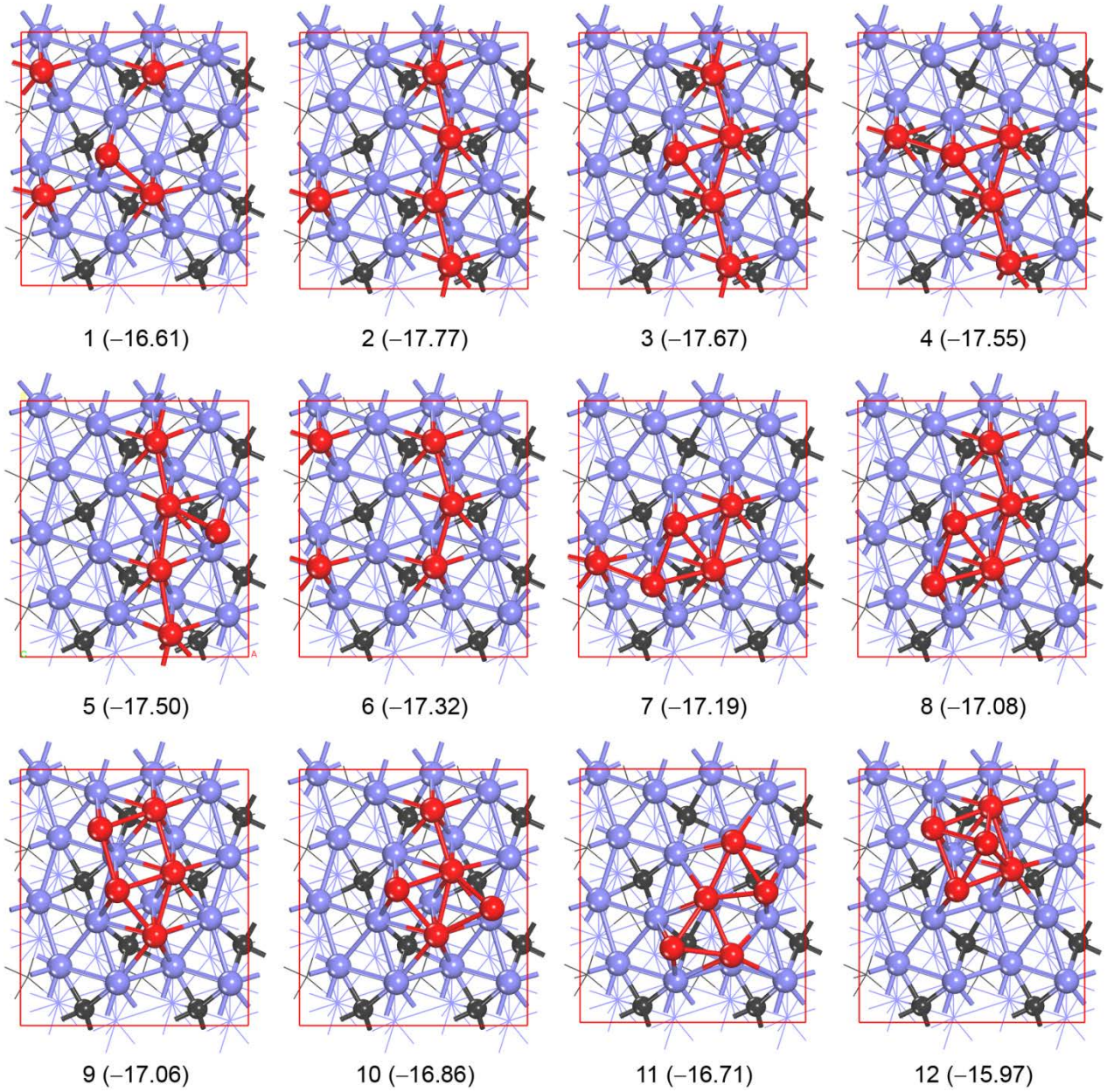
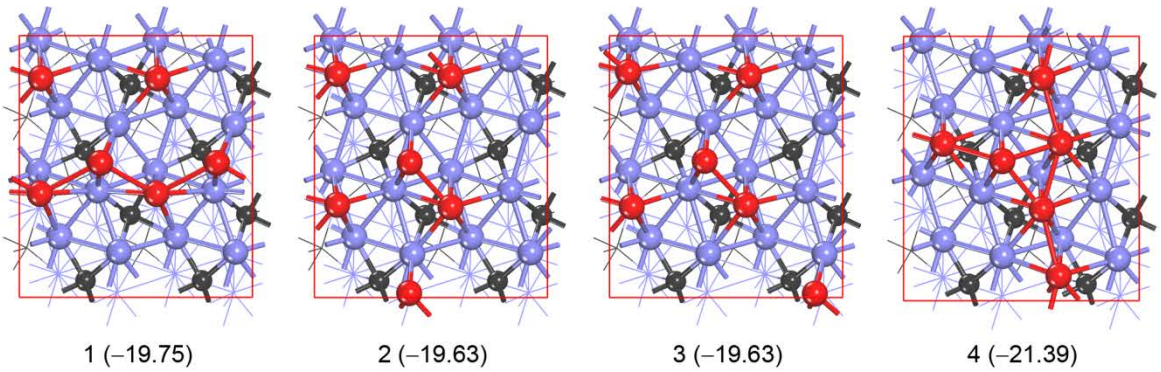


Fig. S14. Various optimized Cu_6 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)



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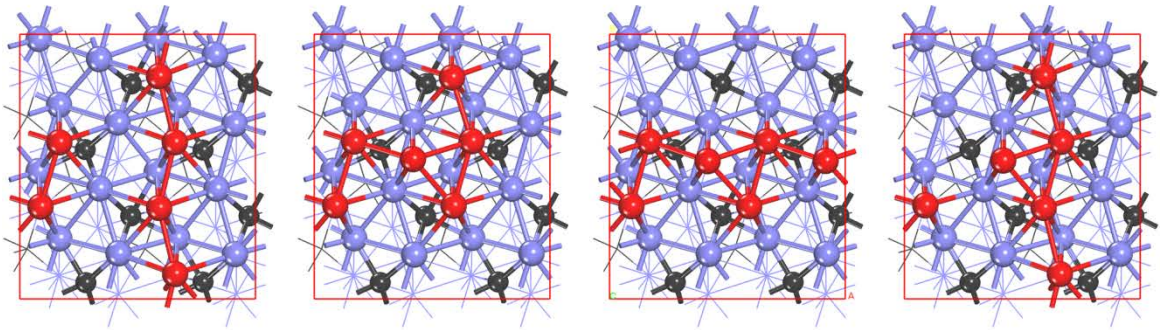

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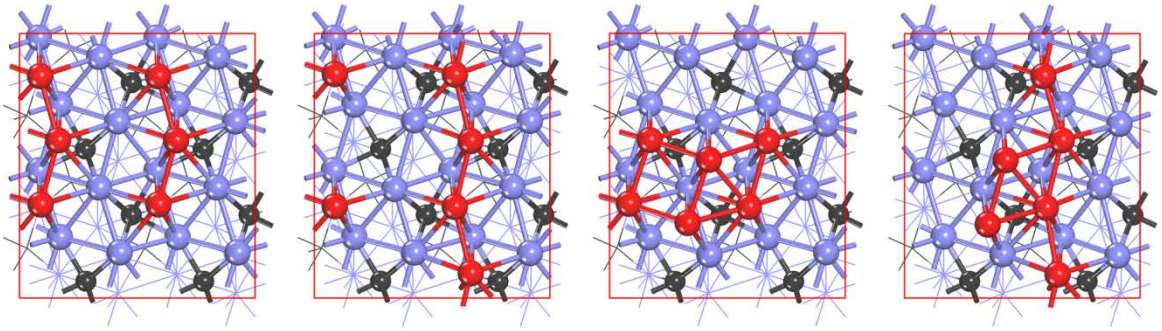
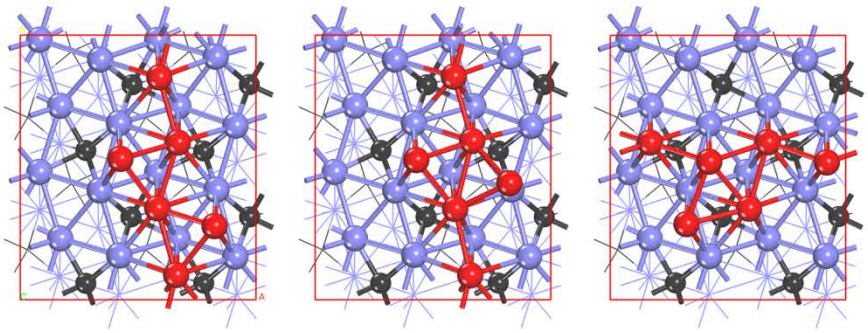
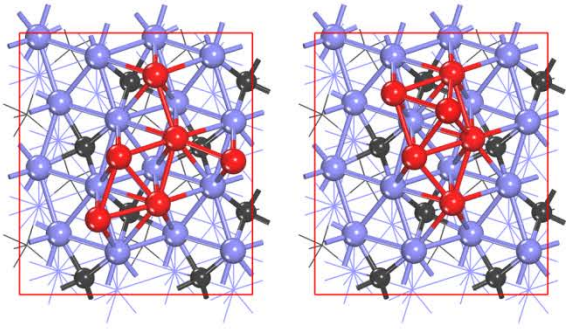


9 (–21.10) 10 (–21.10) 11 (–21.01) 12 (–20.97)



13 (–20.91) 14 (–20.70) 15 (–20.60)



16 (–20.19) 17 (–19.81)

Fig. S15. Various optimized Cu_7 configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

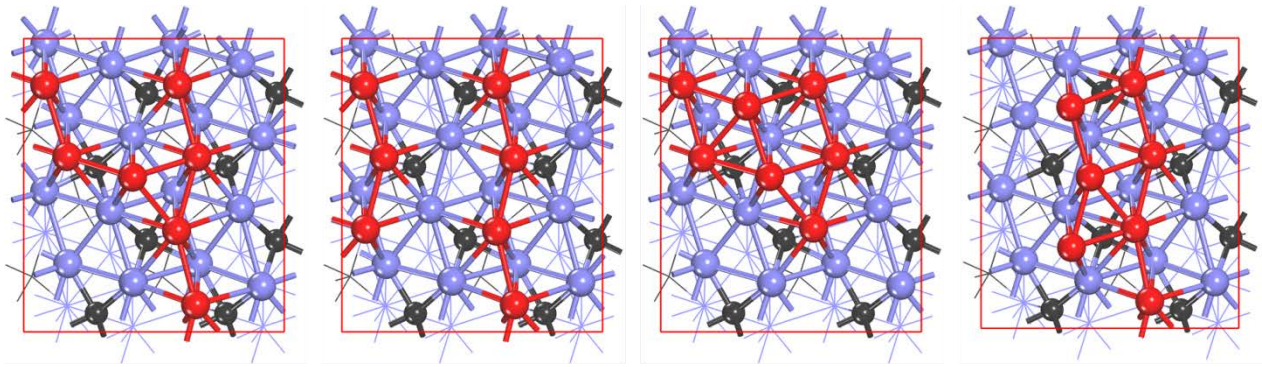


Fig. S16. Various optimized Cu_{13} configurations on the $Fe_3C(010)$ surface (adsorption energy in eV)

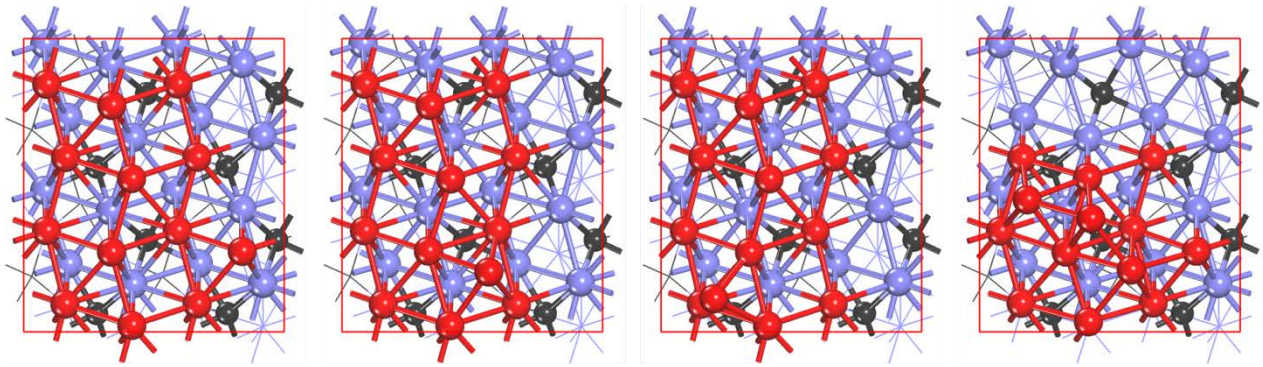


Fig. S17. Various optimized Cu_1 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

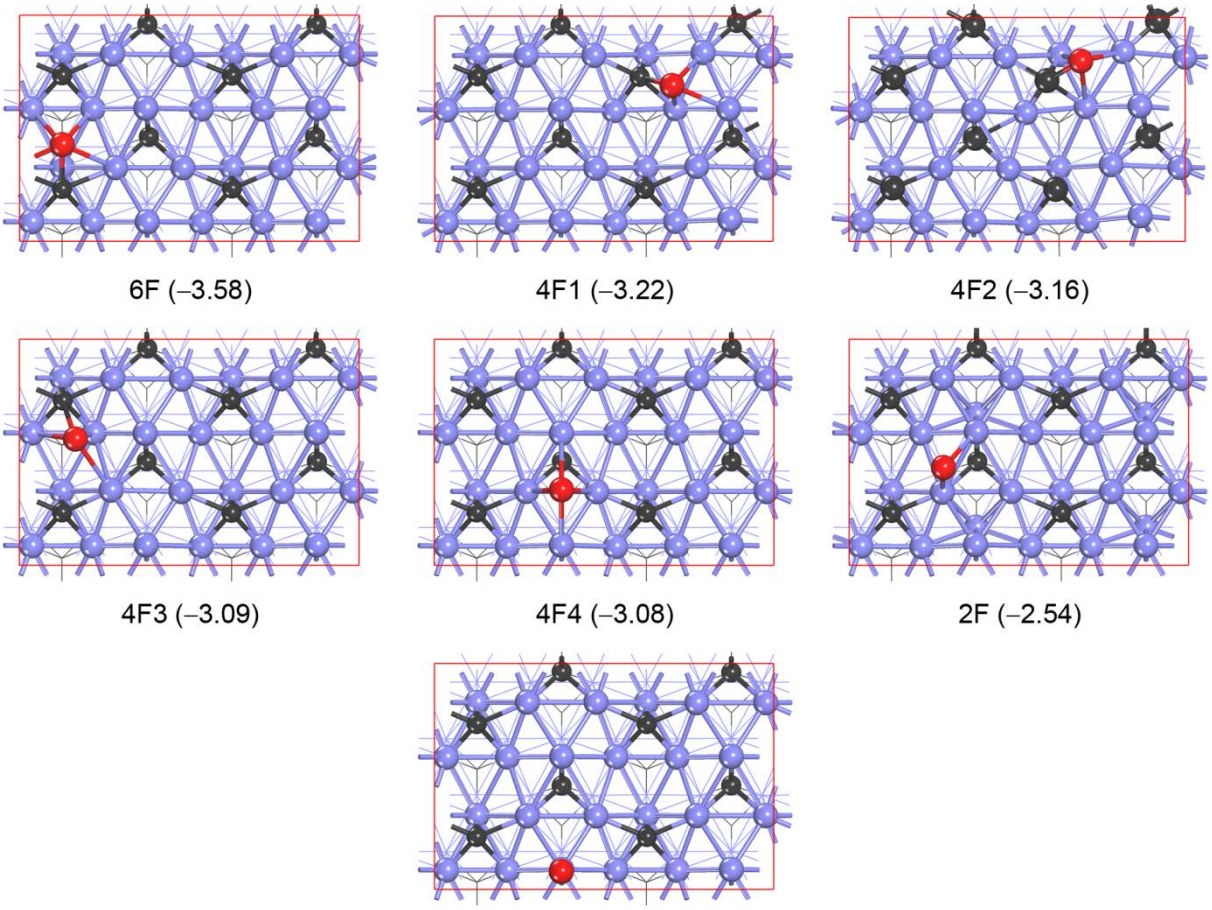


Fig. S18. Various optimized Cu_2 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

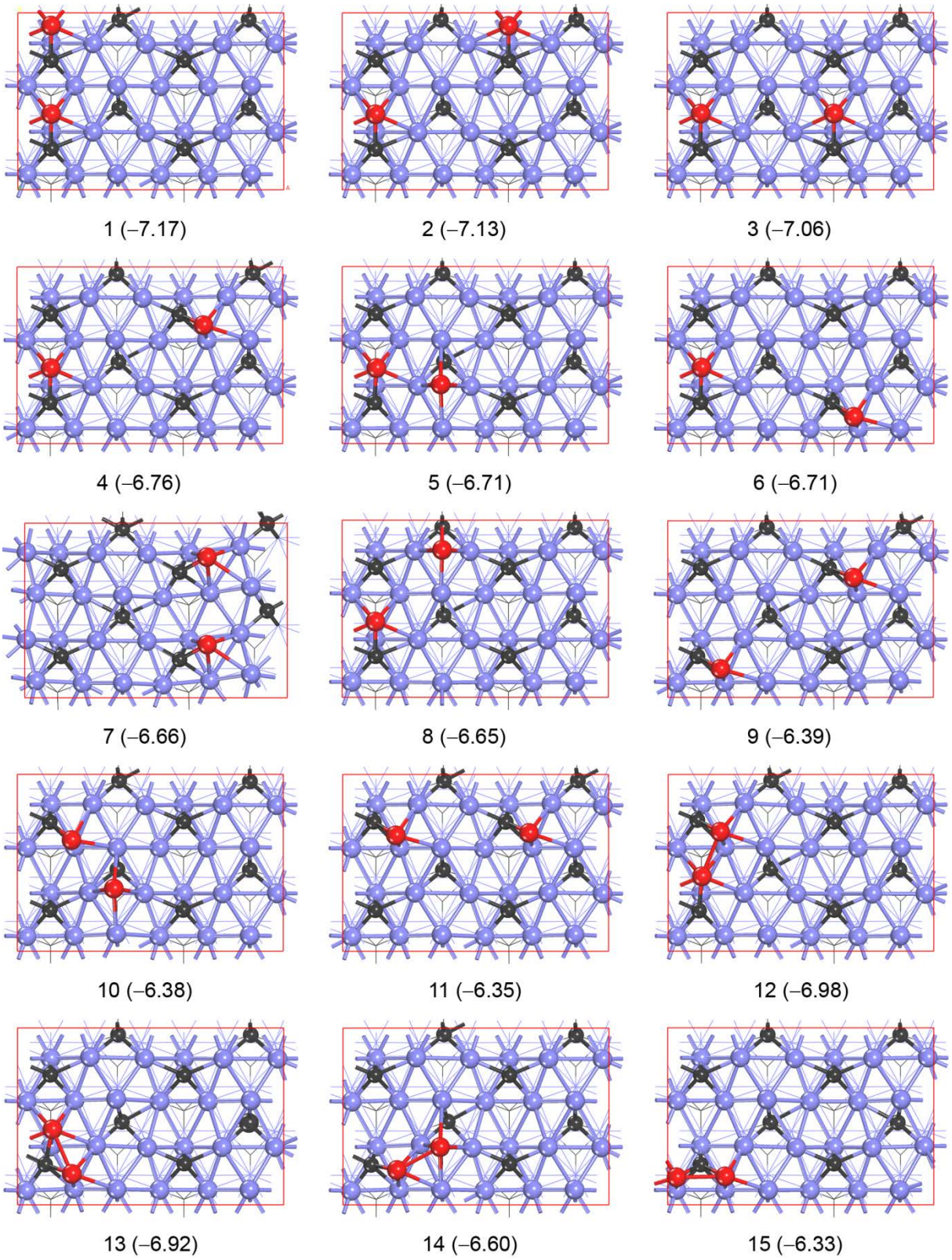


Fig. S19. Various optimized Cu_3 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

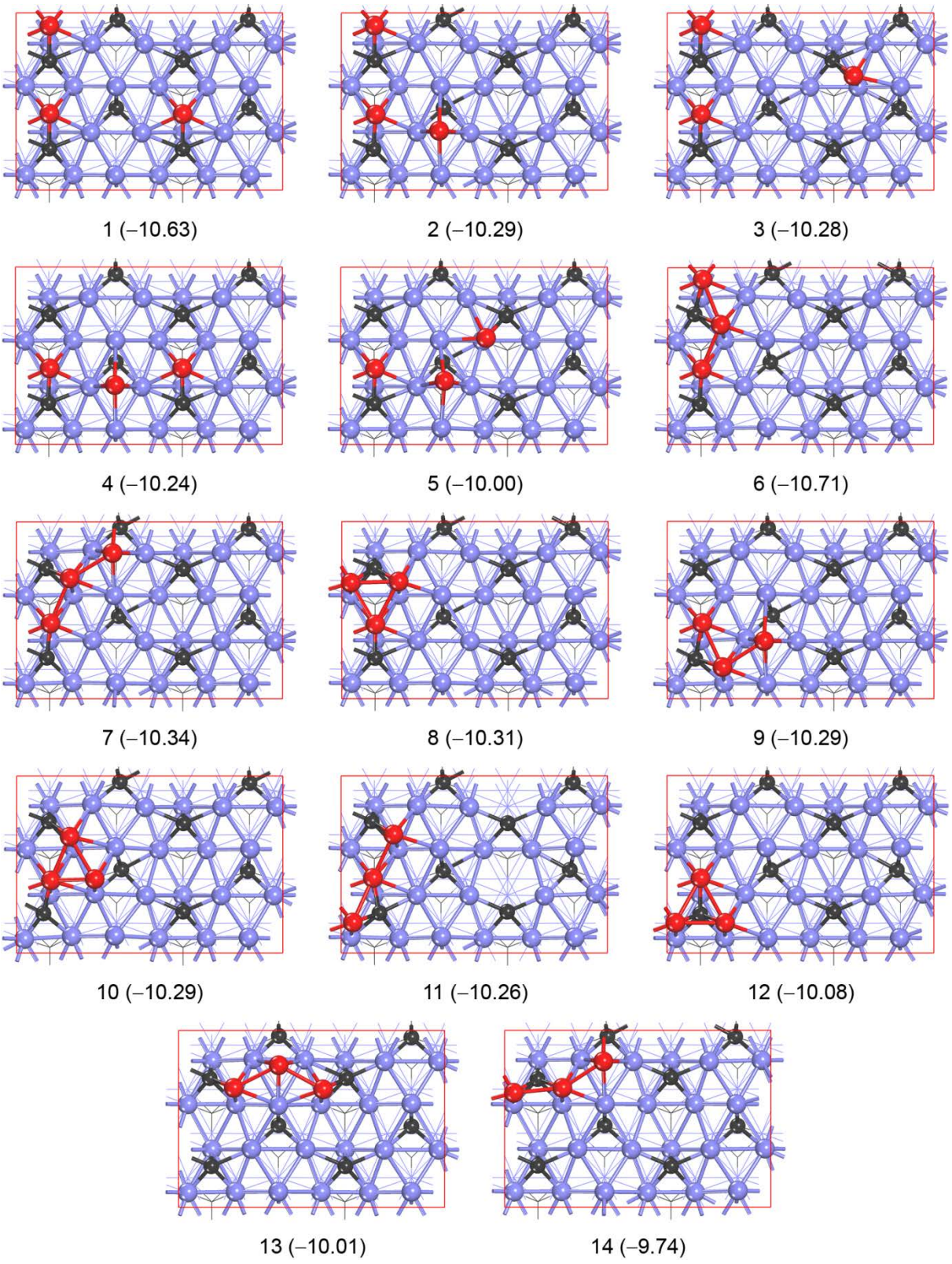


Fig. S20. Various optimized Cu_4 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

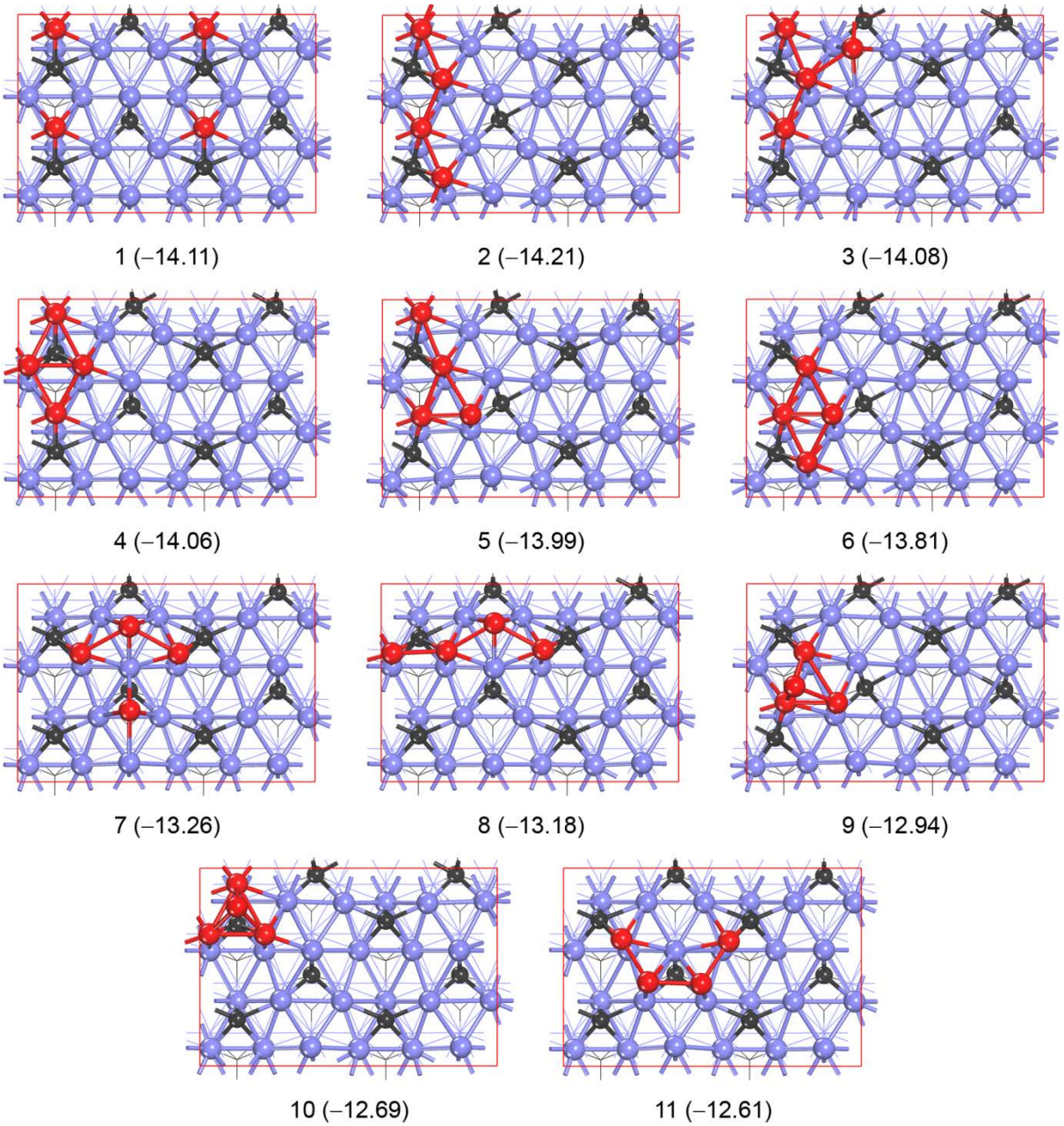


Fig. S21. Various optimized Cu_5 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

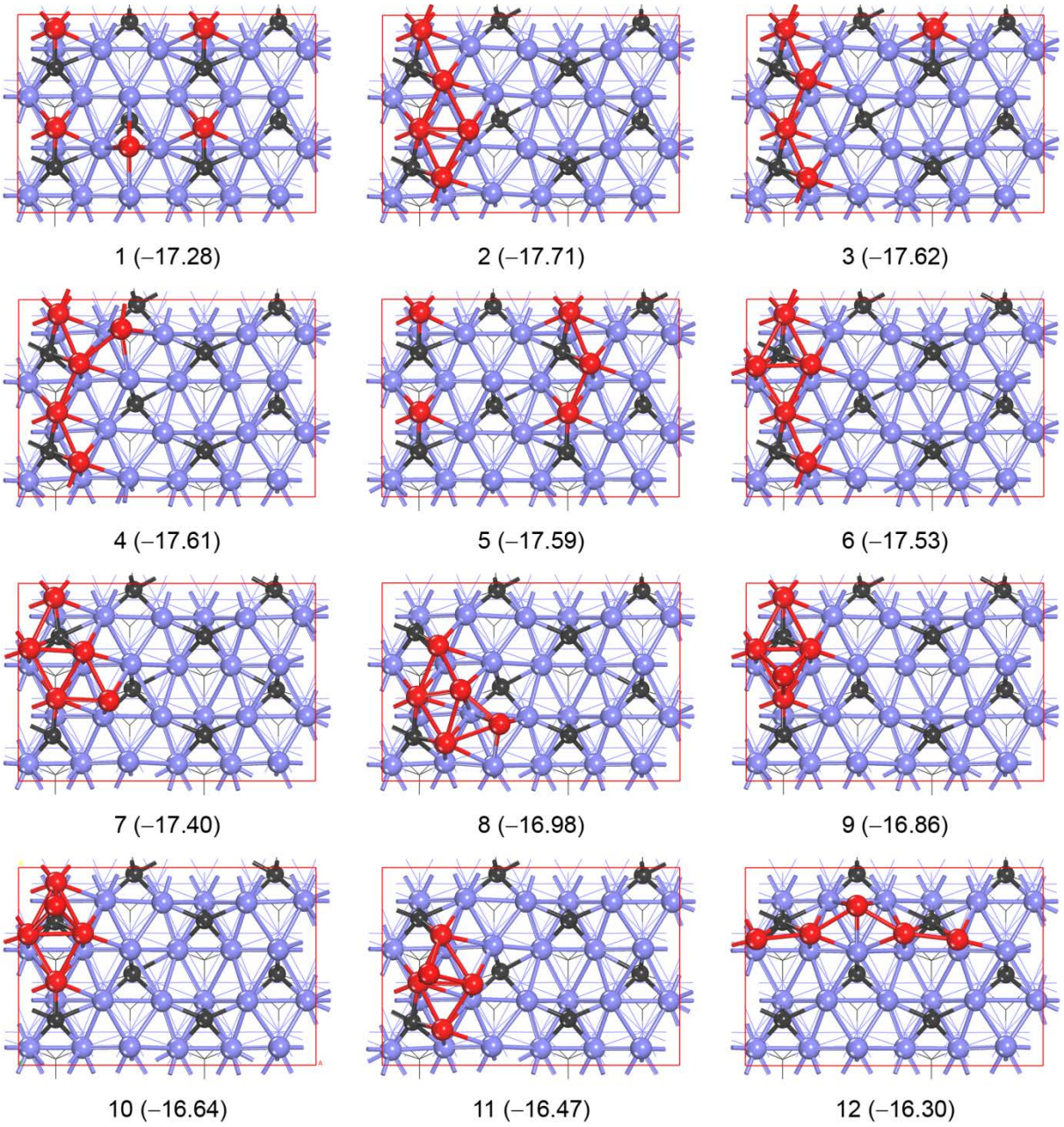


Fig. S22. Various optimized Cu_6 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

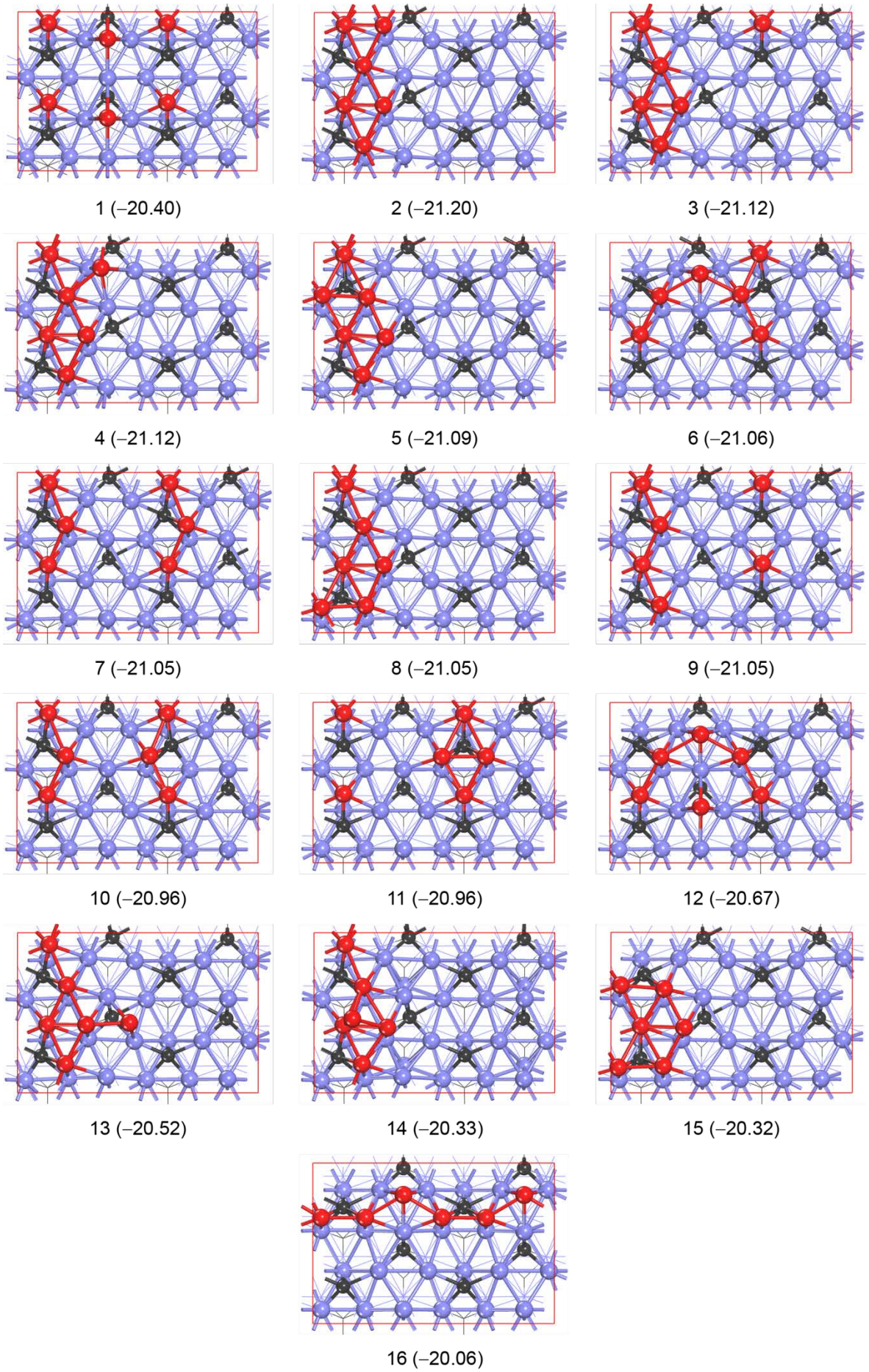


Fig. S23. Various optimized Cu_7 configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

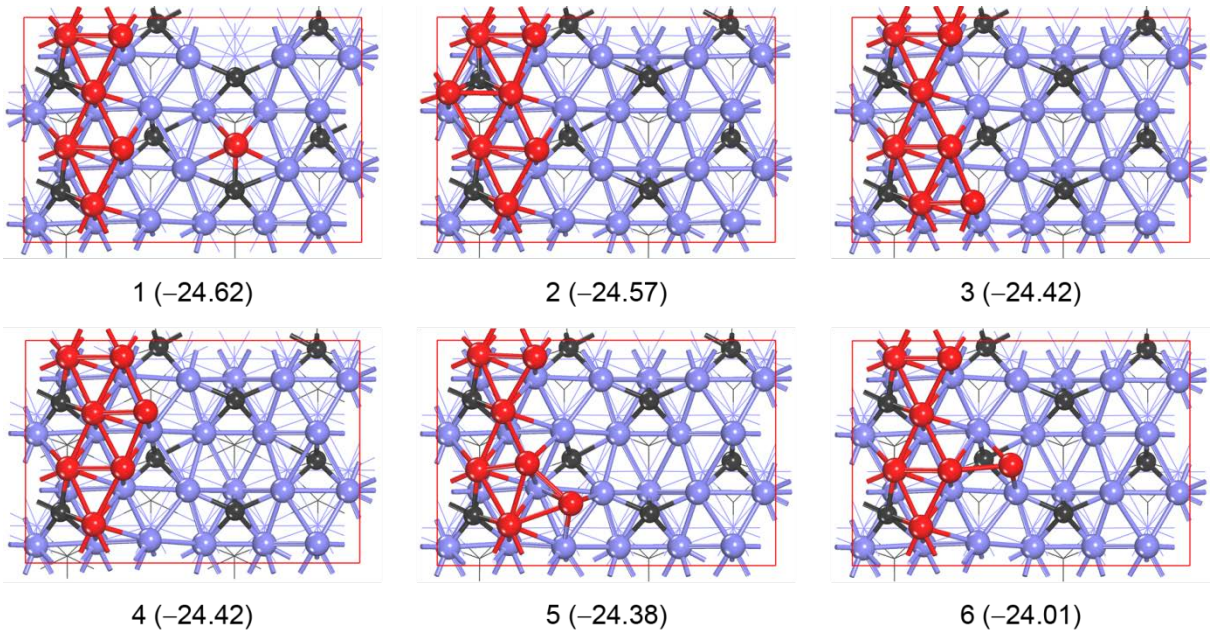


Fig. S24. Various optimized Cu_{13} configurations on the $Fe_3C(100)$ surface (adsorption energy in eV)

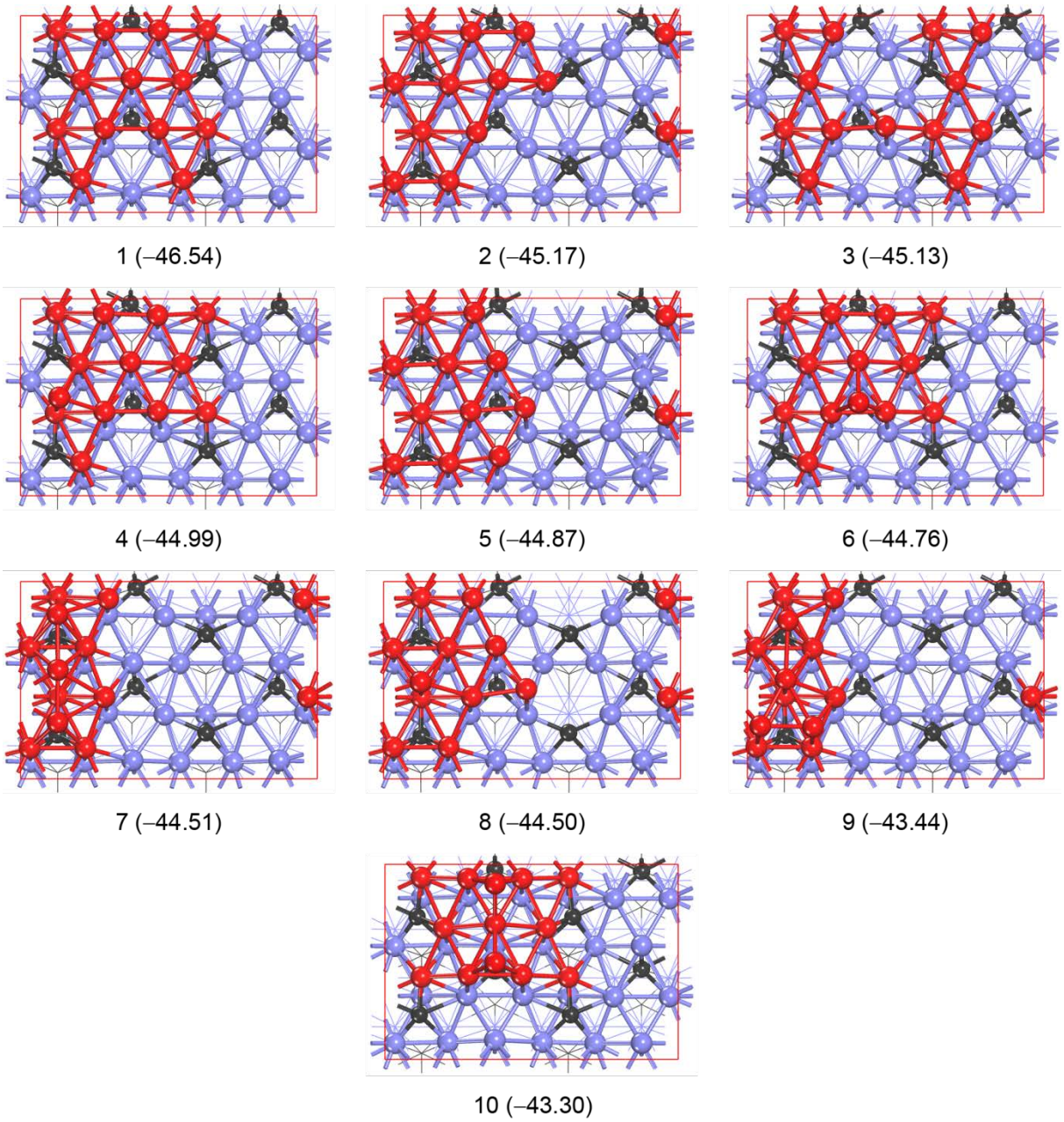


Fig. S25. Surface size effect test of Cu_4 and Cu_5 on the *p*(5×4) Fe(100) surface (adsorption energy in eV)

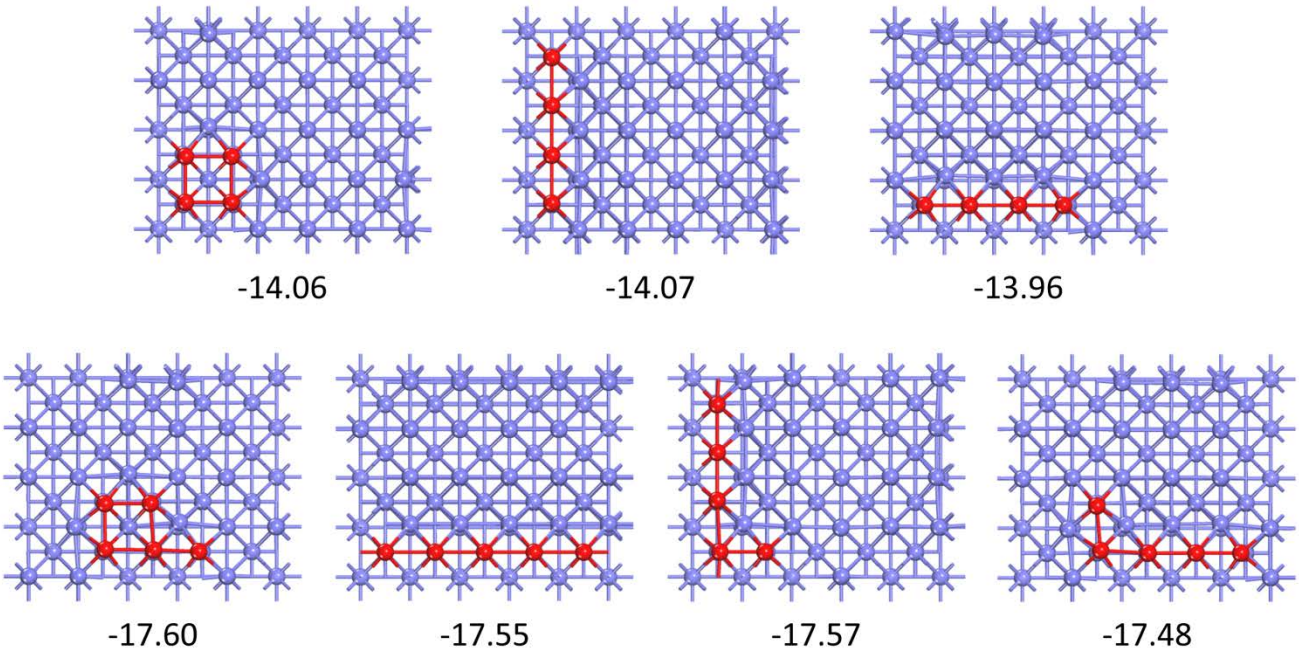
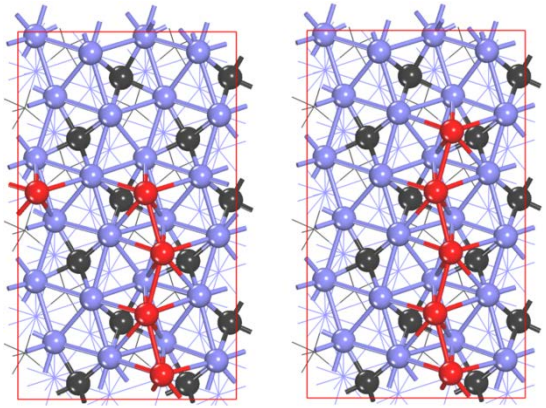


Fig. S26. Surface size effect test Cu_5 on the *p*(2×3) Fe_3C(010) surface (adsorption energy in eV)



-17.57 -17.78