Hydrogen Adsorption Structures and Energetics on Iron Surfaces at High Coverage

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Details of the method for desorption energy calculation.

Since desorption temperature of hydrogen reflects the strength of hydrogen adsorption, desorption energy can also be calculated from desorption temperatures. In the calculation of desorption energy, it is necessary to know the maximal initial coverage of hydrogen on the surface at the defined temperature.

Experimentally, the initial hydrogen coverage was determined by the exposure and pre-adsorption temperature as well as sweep temperature. Since we can well reproduce the position of hydrogen desorption peak, we suppose that our calculated initial coverage was approximately the same of the initial maximal coverage in experiment. In this respect, we can finally calculate the desorption free energy of hydrogen at the hydrogen desorption temperatures.

We took the (110) surface as an example to explain our calculation method. In our calculation, the coverage with 16H corresponds to the maximal coverage at the exposure temperature 140K; and the second coverage with 12 H corresponds to the maximal coverage at the desorption temperature (about 425K). The adsorption energy of those 16H under exposure conditions corresponds to the desorption energy. The calculated adsorption energy difference of 28.3 kcal/mole (1.22 eV) agrees with the experimentally detected desorption energy of 26±1 kcal/mol. The same procedure was also applied to other desorption peaks on different surfaces on the basis of experimental pre-adsorption temperature and exposures.

Table S1. Binding energies (E_b, kcal/mole), desorption energies (E_d, kcal/mole) and desorption temperature (T) from theory and experiments

Surface	$E_b{}^a$	E_d (T)^a	E_d (T)^b
(100)	63 [62.5]	17.4 [17.9] (310K)	18 (β_1, 300K)[12]
(110)	68 [67.5] (65)[12]	26.1 [23.7] (330K)	24 (β_1, 340K)[12]
		29.7 [28.3] (425K)	26 (β_2, 430~480K)
(111)	64 [63.8] (62)[12]	16.6 [15.3] (225K)	13 (β_1, 240K)[12]
		17.3 [17.1] (300K)	18 (β_2, 310K)
		18.9 [17.8] (350K)	21 (β_3, 375-400K)
(211)	66 [65.3]	21.3 [18.9] (250K)	9-12 (α_{1-3}, 210-270)[18]
		26.1 [22.1] (350K)	19.6-24.2 (β, 350K)[18]
(210)	67 [66.7]	19.8 [19.0] (400K)	
(310)	67 [66.6]	22.5 [21.7] (425K)	
(321)	67 [66.7]	20.7 [18.4] (400K)	

(a) Computed data in this work, and ZPE corrected values in square parenthesis. (b) Experimental data

Table S2 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(100)

Fe(100)	ΔE_{ads}	ΔE_{ads}+ZPV	ΔE
1H	-0.46	-0.44	+0.02
2H	-0.43	-0.48	-0.05
3H	-0.49	-0.51	-0.02
4H	-0.49	-0.47	+0.02
5H	-0.45	-0.47	-0.02
6H	-0.48	-0.43	+0.05
7H	-0.45	-0.46	-0.01
8H	-0.45	-0.43	+0.02
9H	-0.44	-0.46	-0.02
10H	-0.38	-0.45	-0.07
11H	-0.41	-0.45	-0.04
12H	-0.37	-0.43	-0.06
13H	-0.16	-0.05	+0.11
14H	-0.06	0.00	+0.06
ΔE-average			**0.04**

Table S3 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(110)

Fe(110)	ΔEads	ΔEads+ZPV	ΔE
1H	-0.70	-0.68	+0.02
2H	-0.71	-0.69	+0.02
3H	-0.72	-0.69	+0.03
4H	-0.71	-0.69	+0.02
5H	-0.72	-0.69	+0.03
6H	-0.72	-0.69	+0.03
7H	-0.70	-0.67	+0.03
8H	-0.71	-0.68	+0.03
9H	-0.57	-0.50	+0.07
10H	-0.60	-0.54	+0.06
11H	-0.55	-0.48	+0.07
12H	-0.55	-0.49	+0.06
13H	-0.51	-0.45	+0.06
14H	-0.56	-0.48	+0.08
15H	-0.53	-0.47	+0.06
16H	-0.54	-0.48	+0.06
ΔE-average			**0,05**

Table S4 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(111)

Fe(111)	ΔEads	ΔEads+ZPV	ΔE
1H	-0.51	-0.50	+0.01
2H	-0.52	-0.51	+0.01
3H	-0.53	-0.51	+0.02
4H	-0.51	-0.51	-0.00
5H	-0.52	-0.50	+0.02
6H	-0.51	-0.50	+0.01
7H	-0.50	-0.49	+0.01
8H	-0.51	-0.49	+0.02
9H	-0.51	-0.50	+0.01
10H	-0.48	-0.44	+0.04
11H	-0.44	-0.44	-0.00
12H	-0.42	-0.40	+0.02
13H	-0.47	-0.43	+0.04
14H	-0.51	-0.53	-0.02
15H	-0.42	-0.37	+0.05
16H	-0.38	-0.33	+0.05
17H	-0.33	-0.28	+0.05
18H	-0.25	-0.19	+0.06
19H	-0.19	-0.14	+0.05
20H	-0.28	-0.22	+0.06
21H	-0.14	-0.12	+0.02
22H	-0.05	-0.02	+0.03
23H	-0.07	-0.02	+0.05
ΔE-average			**0.03**

Table S5 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(210)

Fe(210)	ΔEads	ΔEads+ZPV	ΔE
1H	-0.66	-0.64	+0.02
2H	-0.66	-0.64	+0.02
3H	-0.60	-0.59	+0.01
4H	-0.67	-0.64	+0.03
5H	-0.60	-0.58	+0.02
6H	-0.61	-0.59	+0.02
7H	-0.60	-0.56	+0.04
8H	-0.59	-0.56	+0.03
9H	-0.55	-0.51	+0.04
10H	-0.53	-0.49	+0.04
11H	-0.53	-0.49	+0.04
12H	-0.51	-0.47	+0.04
13H	-0.28	-0.28	-0.001
14H	-0.29	-0.29	-0.00
15H	-0.29	-0.33	-0.04
16H	-0.30	-0.30	+0.00
17H	-0.29	-0.31	-0.02
18H	-0.32	-0.36	-0.04
ΔE-average			**0.03**

Table S6 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(211)

Fe(211)	ΔE_{ads}	ΔE_{ads}+ZPV	ΔE
1H	-0.60	-0.57	+0.03
2H	-0.60	-0.57	+0.03
3H	-0.55	-0.52	+0.03
4H	-0.64	-0.61	+0.03
5H	-0.50	-0.45	+0.05
6H	-0.57	-0.54	+0.03
7H	-0.58	-0.55	+0.03
8H	-0.61	-0.56	-0.05
9H	-0.33	-0.23	+0.1
10H	-0.39	-0.37	+0.02
11H	-0.72	-0.61	+0.11
12H	-0.63	-0.54	+0.09
13H	-0.06	-0.02	+0.04
14H	-0.20	-0.14	+0.06
15H	-0.35	-0.29	+0.06
16H	-0.35	-0.27	+0.08
ΔE-average			**0.05**

Table S7 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(310)

Fe(310)	ΔEads	ΔEads+ZPV	ΔE
1H	-0.65	-0.63	+0.02
2H	-0.67	-0.65	+0.02
3H	-0.67	-0.64	+0.03
4H	-0.69	-0.67	+0.02
5H	-0.65	-0.62	+0.03
6H	-0.67	-0.64	+0.03
7H	-0.49	-0.49	+0.00
8H	-0.48	-0.48	+0.00
9H	-0.46	-0.46	-0.00
10H	-0.41	-0.41	-0.00
11H	-0.40	-0.40	-0.00
12H	-0.39	-0.40	-0.01
ΔE-average			**0.01**

Table S8 Stepwise H adsorption energy before (ΔE_{ads}) and after ZPV (ΔE_{ads}+ZPV) correction on Fe(321)

Fe(321)	ΔE_{ads}	ΔE_{ads}+ZPV	ΔE
1H	-0.65	-0.64	+0.01
2H	-0.65	-0.64	+0.01
3H	-0.63	-0.61	+0.02
4H	-0.65	-0.63	+0.02
5H	-0.60	-0.56	+0.04
6H	-0.60	-0.56	+0.04
7H	-0.64	-0.58	+0.06
8H	-0.64	-0.58	+0.06
9H	-0.60	-0.54	+0.06
10H	-0.58	-0.52	+0.06
11H	-0.48	-0.42	+0.06
12H	-0.47	-0.41	+0.06
13H	-0.33	-0.28	+0.05
14H	-0.37	-0.33	+0.04
15H	-0.41	-0.36	+0.05
16H	-0.25	-0.20	+0.05
17H	-0.32	-0.27	+0.05
18H	-0.37	-0.32	+0.05
ΔE-average			**0.04**

Table S9 Surface energies (J/m^{-2}) of the clean iron surfaces as well as surfaces with hydrogen adsorption at atmosphere pressure and different temperatures

	clean	0K	425K	675K	1000K
Fe(100)	2.53	1.60	2.14	2.50	2.53
Fe(110)	2.47	0.70	1.39	1.93	2.47
Fe(111)	2.70	1.54	2.20	2.60	2.70
Fe(210)	2.57	1.25	1.91	2.29	2.57
Fe(211)	2.58	1.04	1.81	2.28	2.58
Fe(310)	2.55	1.21	1.81	2.25	2.55
Fe(321)	2.62	0.99	1.77	2.28	2.62

Table S10 The surface energy (J/m^{-2}) of the iron surfaces with hydrogen adsorption at 675K and different hydrogen pressures (atm).

p_{H2}	0.001	0.01	0.1	5	10	20
Fe(100)	2.53	2.53	2.53	2.43	2.39	2.35
Fe(110)	2.37	2.27	2.11	1.79	1.74	1.68
Fe(111)	2.70	2.70	2.69	2.51	2.47	2.43
Fe(210)	2.56	2.51	2.41	2.21	2.17	2.14
Fe(211)	2.58	2.56	2.45	2.17	2.12	2.07
Fe(310)	2.52	2.43	2.35	2.16	2.11	2.06
Fe(321)	2.62	2.53	2.41	2.18	2.13	2.08

Figure S1. Structures and stepwise adsorption energies of H on Fe (100) surface (Blue ball for Fe and yellow ball for H)
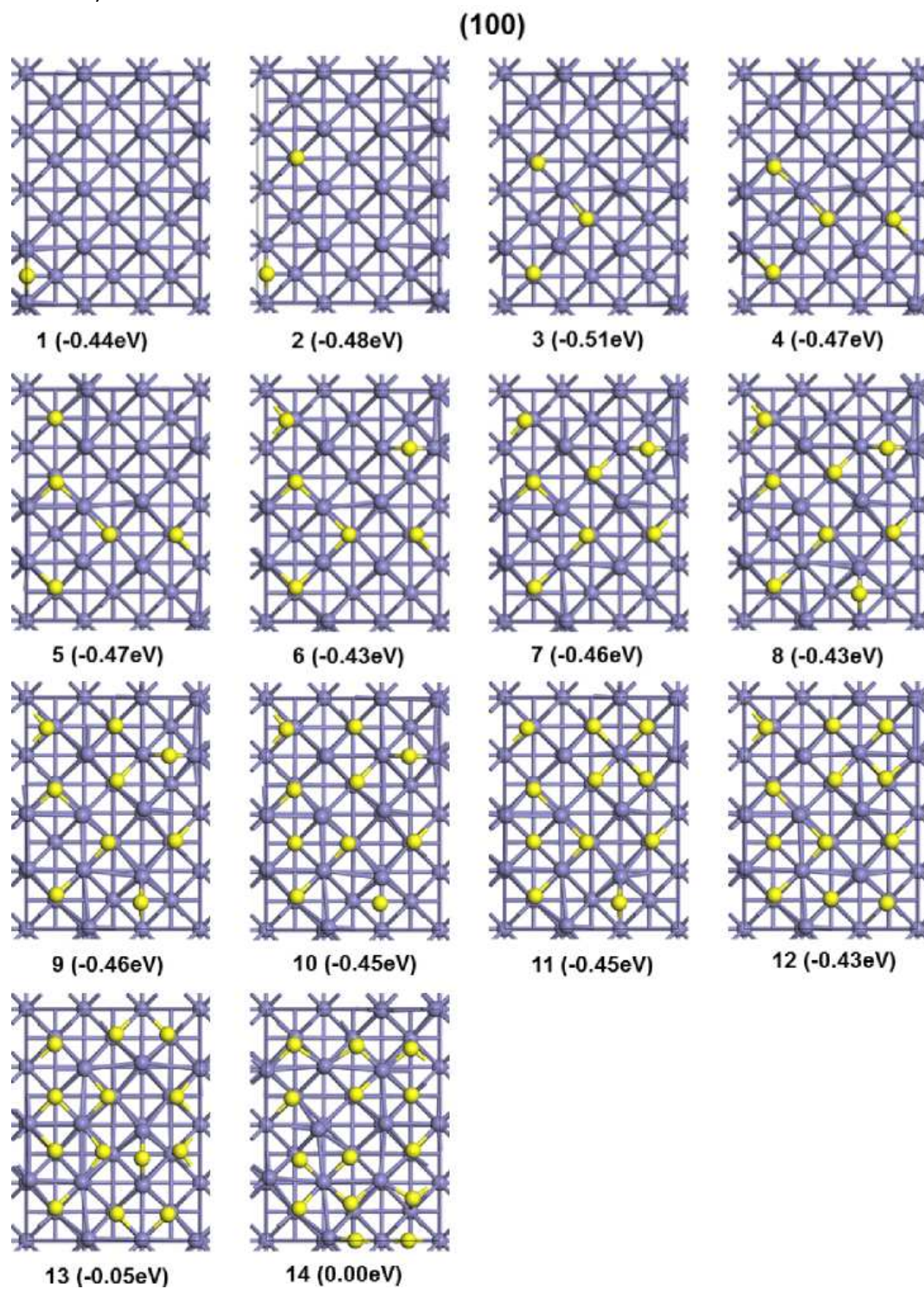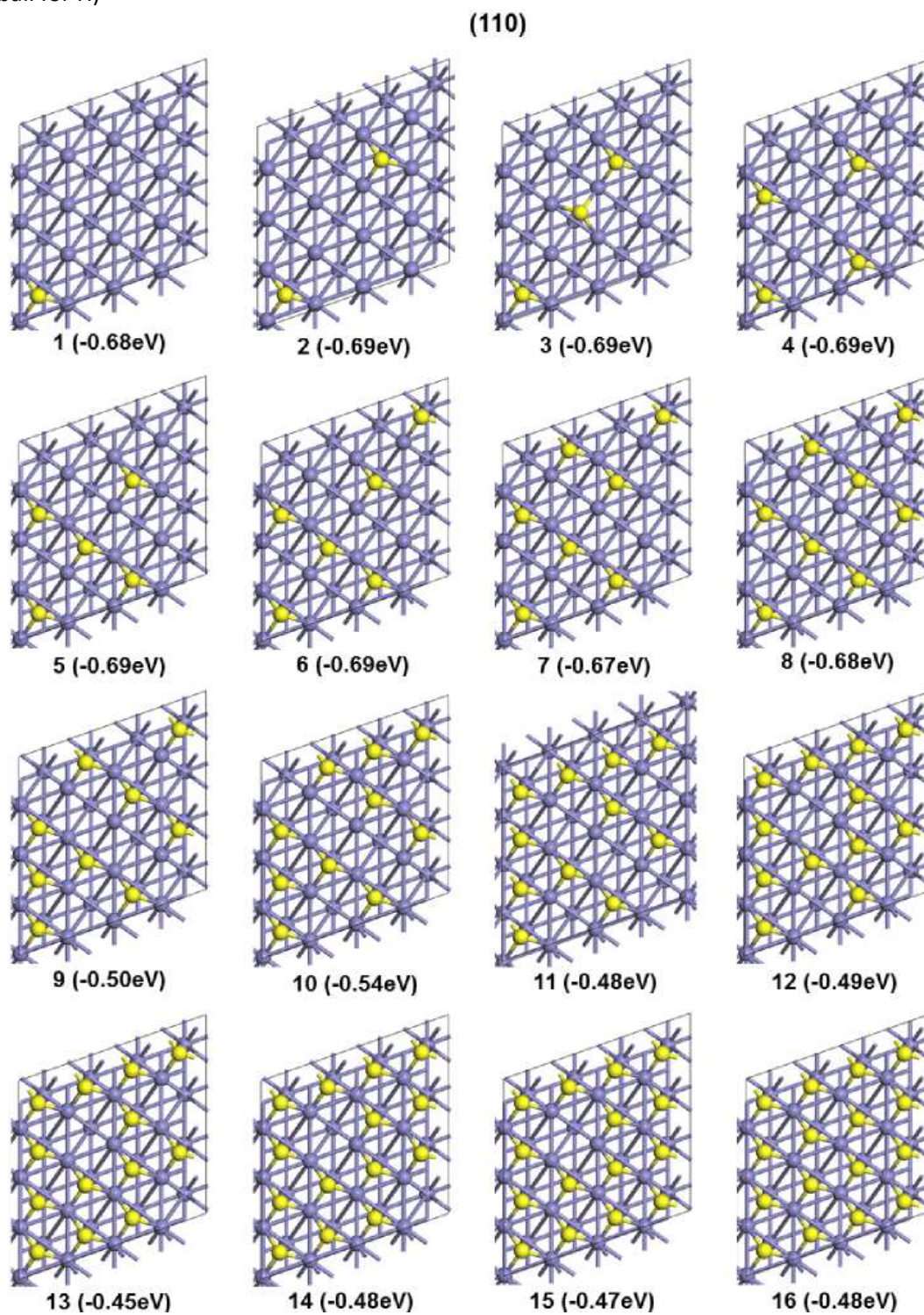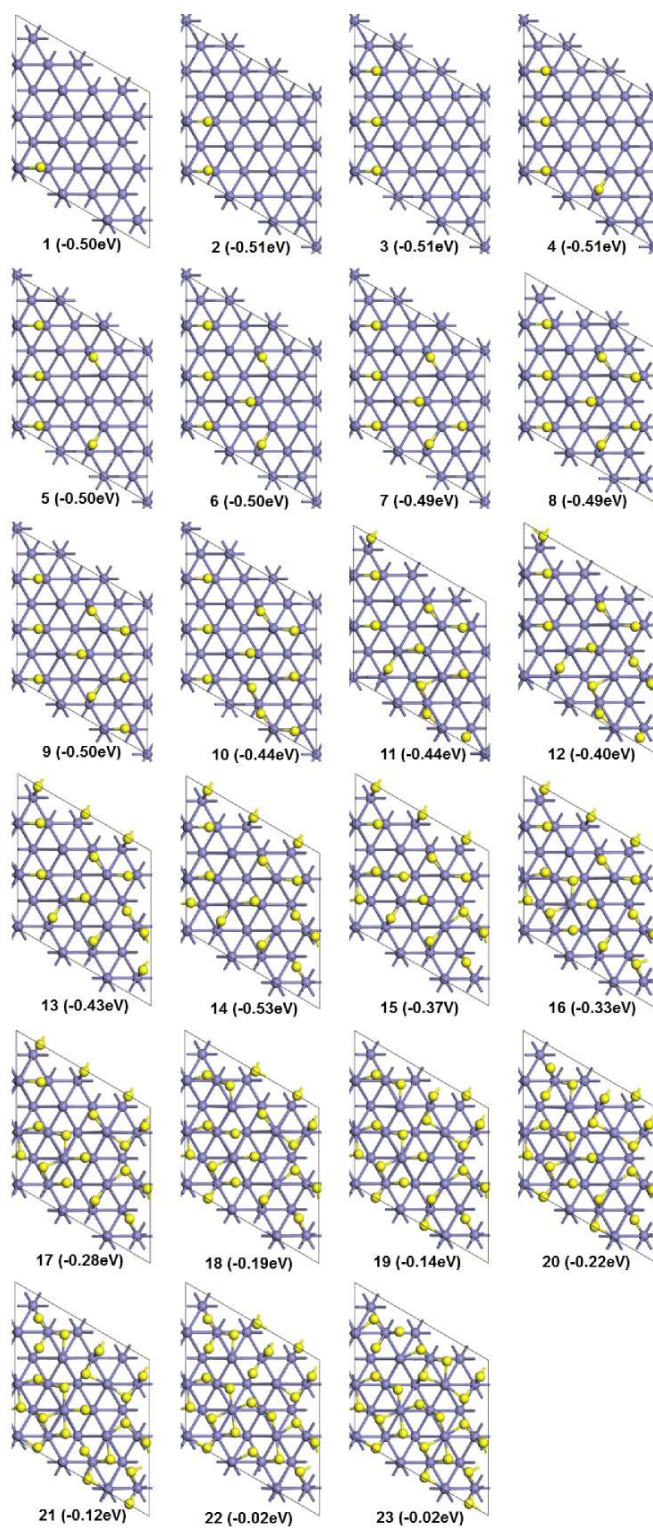

(100)

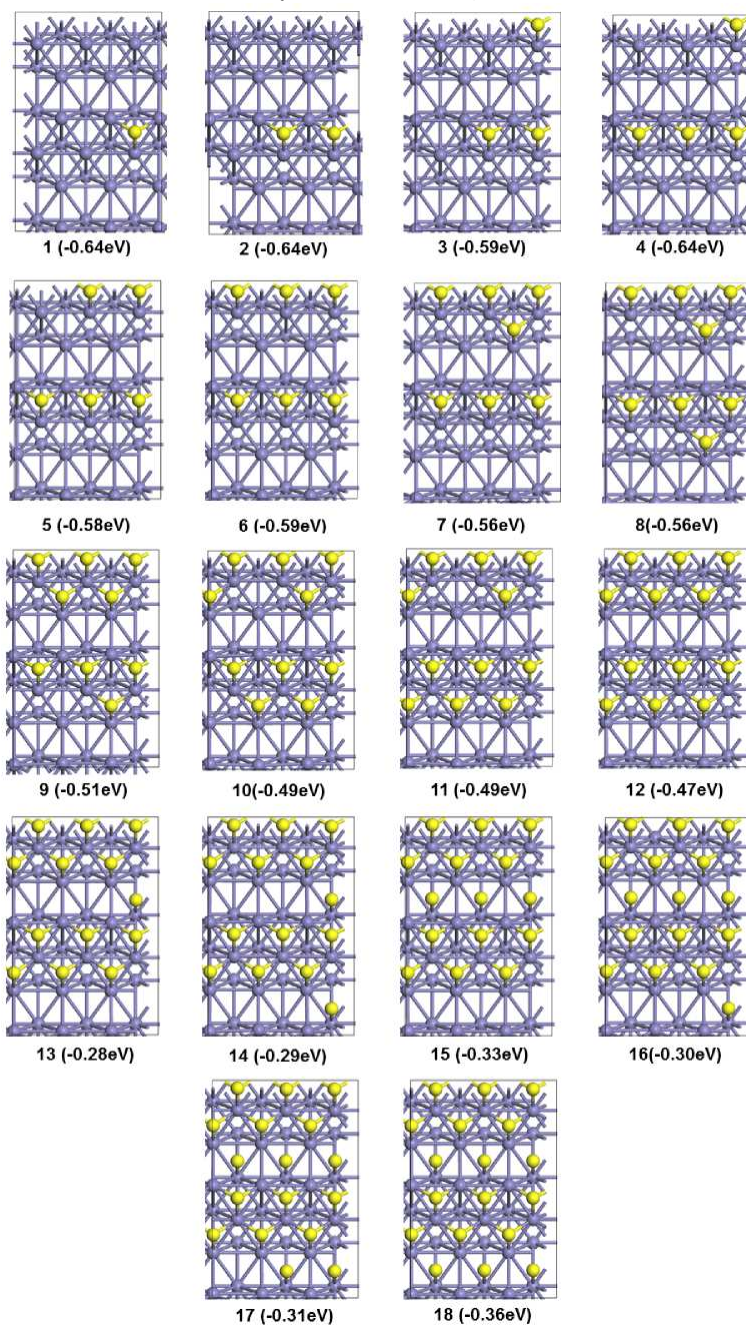1 (-0.44eV) 2 (-0.48eV) 3 (-0.51eV) 4 (-0.47eV)

5 (-0.47eV) 6 (-0.43eV) 7 (-0.46eV) 8 (-0.43eV)

9 (-0.46eV) 10 (-0.45eV) 11 (-0.45eV) 12 (-0.43eV)

13 (-0.05eV) 14 (0.00eV)

Figure S2. Structures and stepwise adsorption energies of H on Fe (110) surface (Blue ball for Fe and yellow ball for H)

(110)

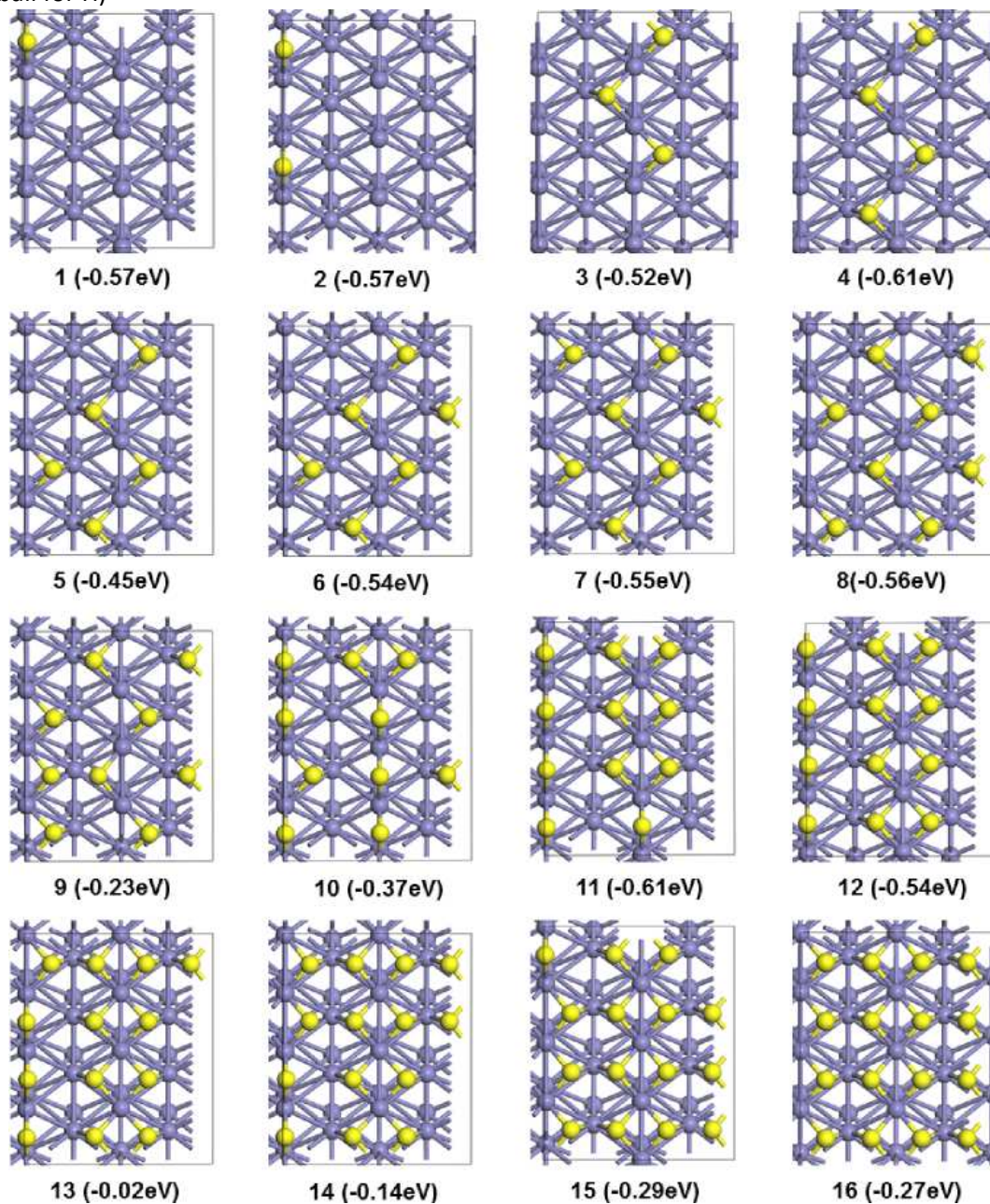1 (-0.68eV)   2 (-0.69eV)   3 (-0.69eV)   4 (-0.69eV)

5 (-0.69eV)   6 (-0.69eV)   7 (-0.67eV)   8 (-0.68eV)

9 (-0.50eV)   10 (-0.54eV)   11 (-0.48eV)   12 (-0.49eV)
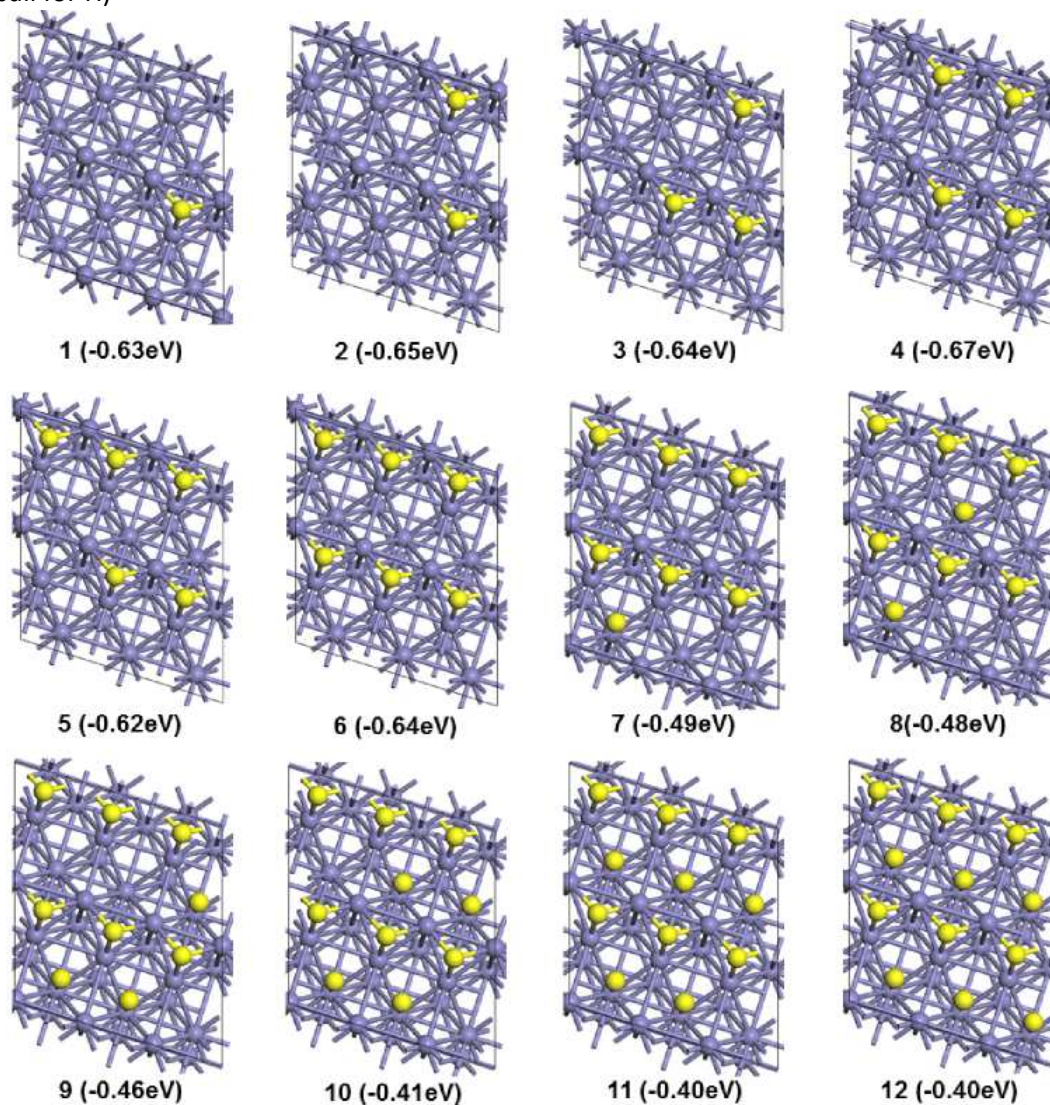
13 (-0.45eV)   14 (-0.48eV)   15 (-0.47eV)   16 (-0.48eV)

Figure S3. Structures and stepwise adsorption energies of H on Fe (111) surface (Blue ball for Fe and yellow ball for H)

1 (-0.50eV) 2 (-0.51eV) 3 (-0.51eV) 4 (-0.51eV)

5 (-0.50eV) 6 (-0.50eV) 7 (-0.49eV) 8 (-0.49eV)

9 (-0.50eV) 10 (-0.44eV) 11 (-0.44eV) 12 (-0.40eV)

13 (-0.43eV) 14 (-0.53eV) 15 (-0.37V) 16 (-0.33eV)

17 (-0.28eV) 18 (-0.19eV) 19 (-0.14eV) 20 (-0.22eV)

21 (-0.12eV) 22 (-0.02eV) 23 (-0.02eV)

Figure S4. Structures and stepwise adsorption energies of H on Fe (210) surface (Blue ball for Fe and yellow ball for H)

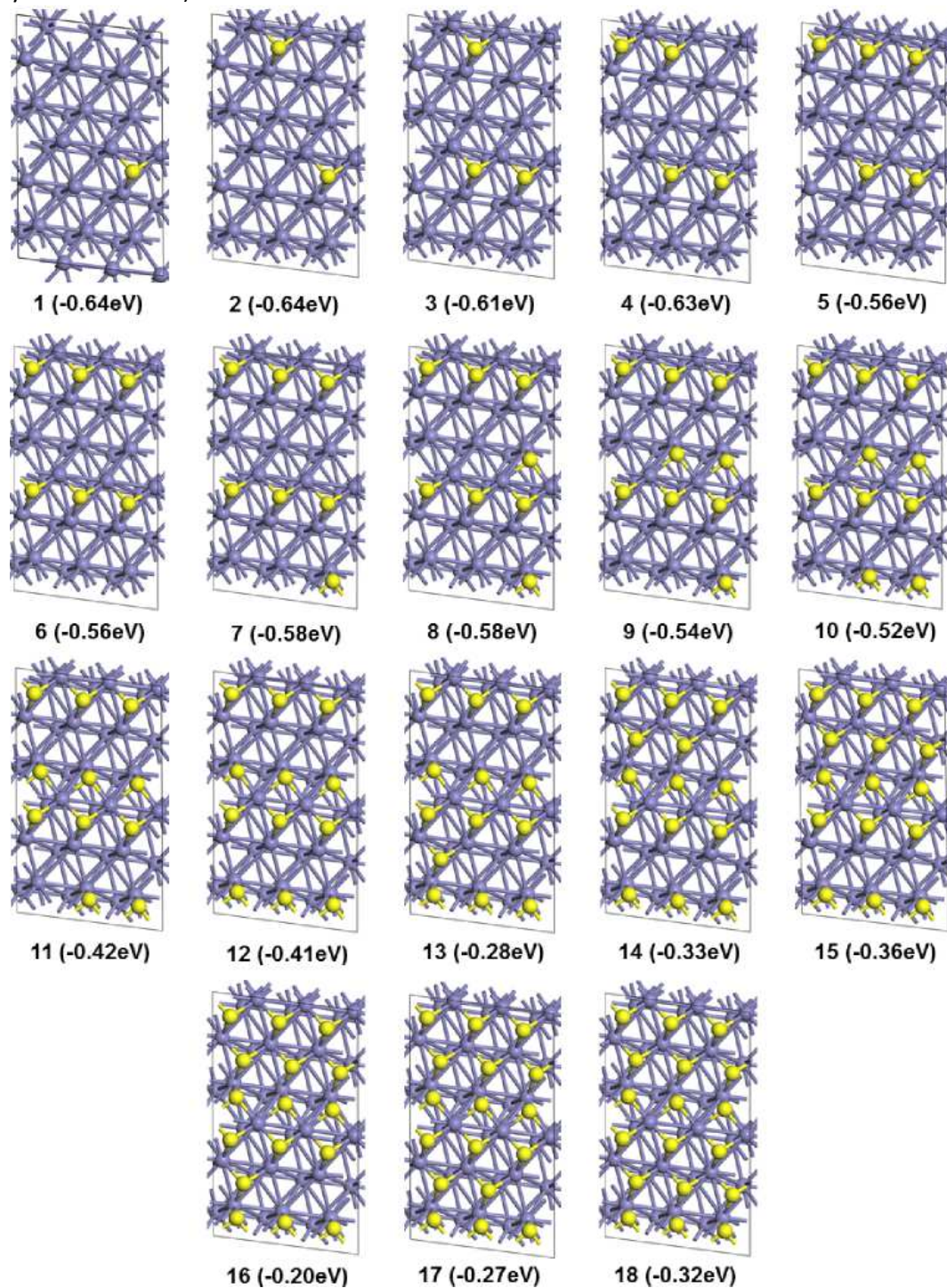1 (-0.64eV)   2 (-0.64eV)   3 (-0.59eV)   4 (-0.64eV)

5 (-0.58eV)   6 (-0.59eV)   7 (-0.56eV)   8(-0.56eV)

9 (-0.51eV)   10(-0.49eV)   11 (-0.49eV)   12 (-0.47eV)

13 (-0.28eV)   14 (-0.29eV)   15 (-0.33eV)   16(-0.30eV)

17 (-0.31eV)   18 (-0.36eV)

Figure S5. Structures and stepwise adsorption energies of H on Fe (211) surface (Blue ball for Fe and yellow ball for H)

1 (-0.57eV) 2 (-0.57eV) 3 (-0.52eV) 4 (-0.61eV)

5 (-0.45eV) 6 (-0.54eV) 7 (-0.55eV) 8(-0.56eV)

9 (-0.23eV) 10 (-0.37eV) 11 (-0.61eV) 12 (-0.54eV)

13 (-0.02eV) 14 (-0.14eV) 15 (-0.29eV) 16 (-0.27eV)

Figure S6. Structures and stepwise adsorption energies of H on Fe (310) surface (Blue ball for Fe and yellow ball for H)

1 (-0.63eV) 2 (-0.65eV) 3 (-0.64eV) 4 (-0.67eV)

5 (-0.62eV) 6 (-0.64eV) 7 (-0.49eV) 8(-0.48eV)

9 (-0.46eV) 10 (-0.41eV) 11 (-0.40eV) 12 (-0.40eV)

Figure S7. Structures and stepwise adsorption energies of H on Fe (321) surface (Blue ball for Fe and yellow ball for H)

1 (-0.64eV)   2 (-0.64eV)   3 (-0.61eV)   4 (-0.63eV)   5 (-0.56eV)

6 (-0.56eV)   7 (-0.58eV)   8 (-0.58eV)   9 (-0.54eV)   10 (-0.52eV)

11 (-0.42eV)   12 (-0.41eV)   13 (-0.28eV)   14 (-0.33eV)   15 (-0.36eV)

16 (-0.20eV)   17 (-0.27eV)   18 (-0.32eV)

Figure S8. Phase diagrams of H coverage on other six surfaces
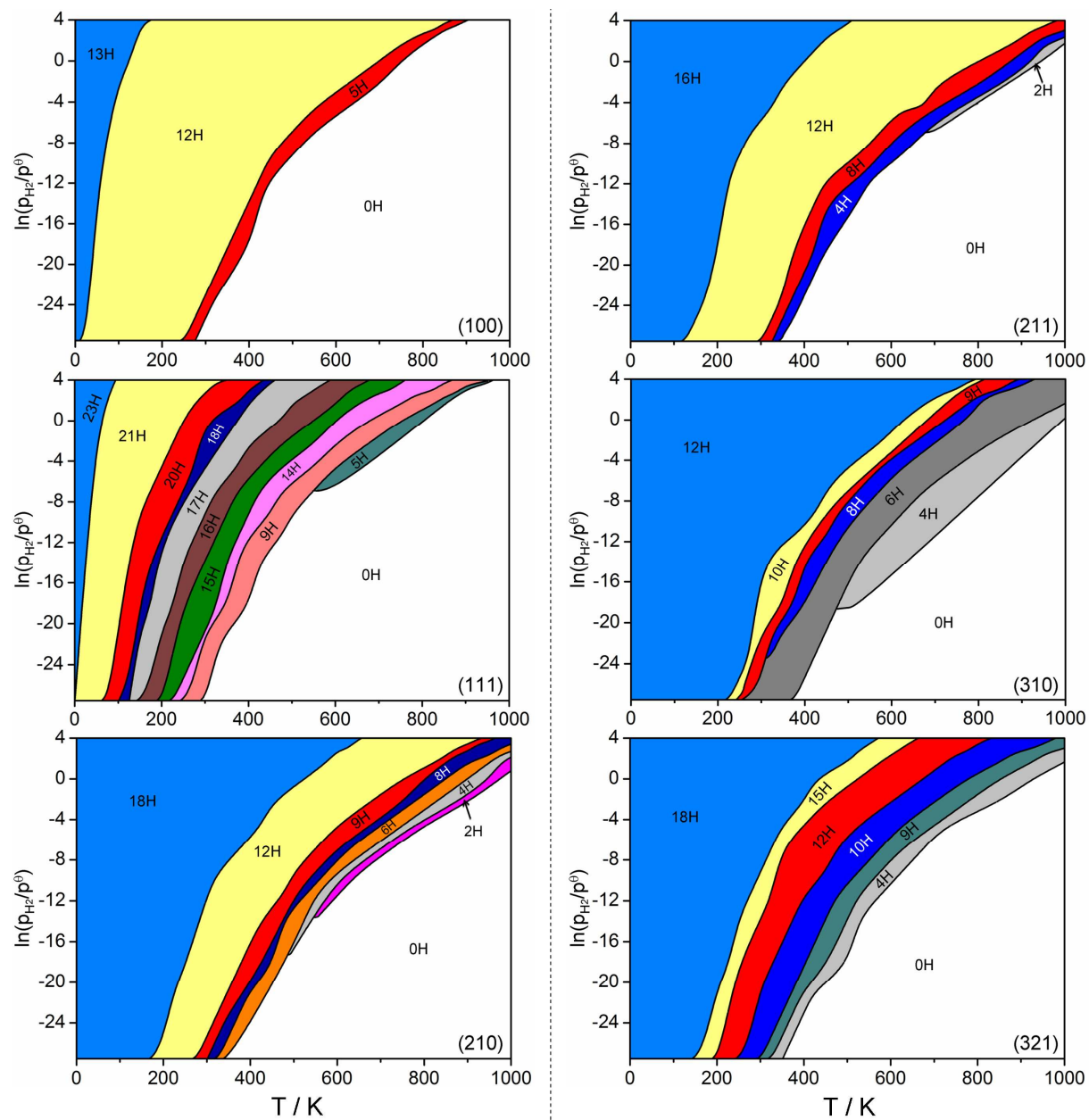
Figure S9. Wulff shapes of iron particles that reduced at 675K and different hydrogen presures (atm)
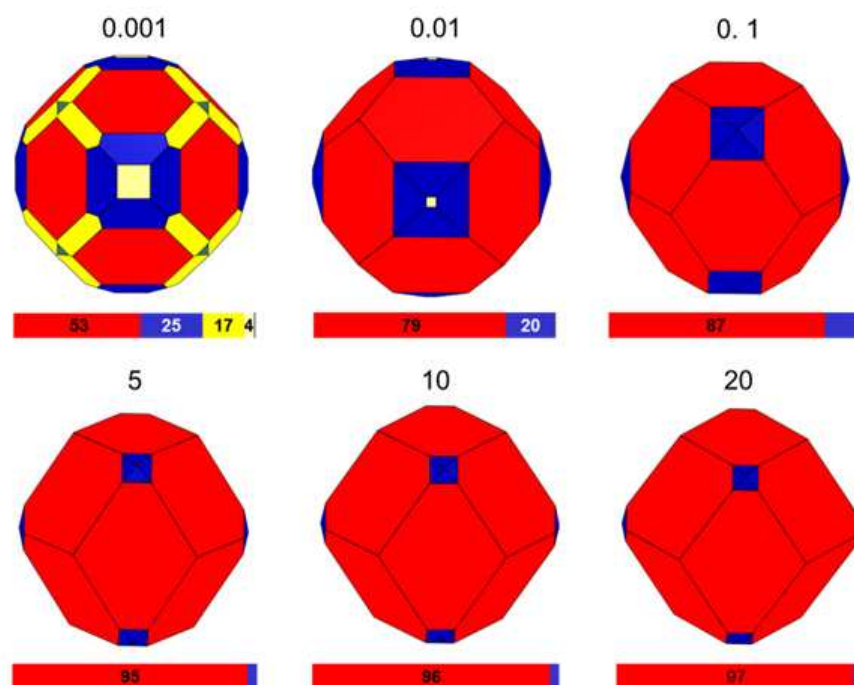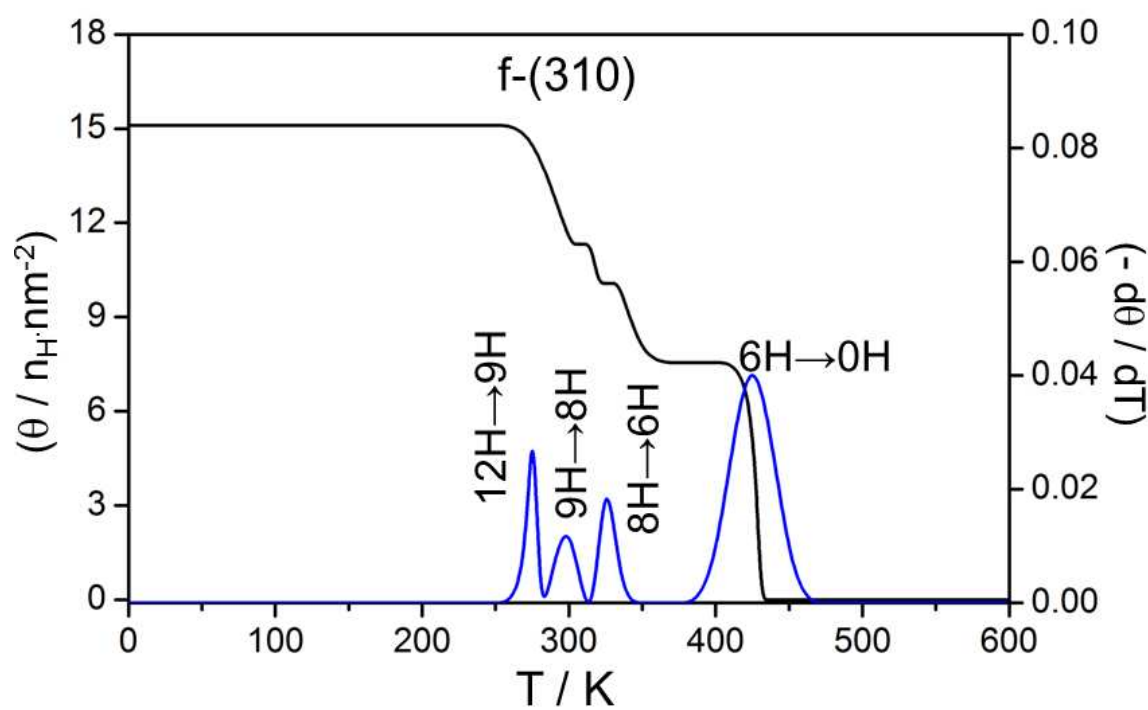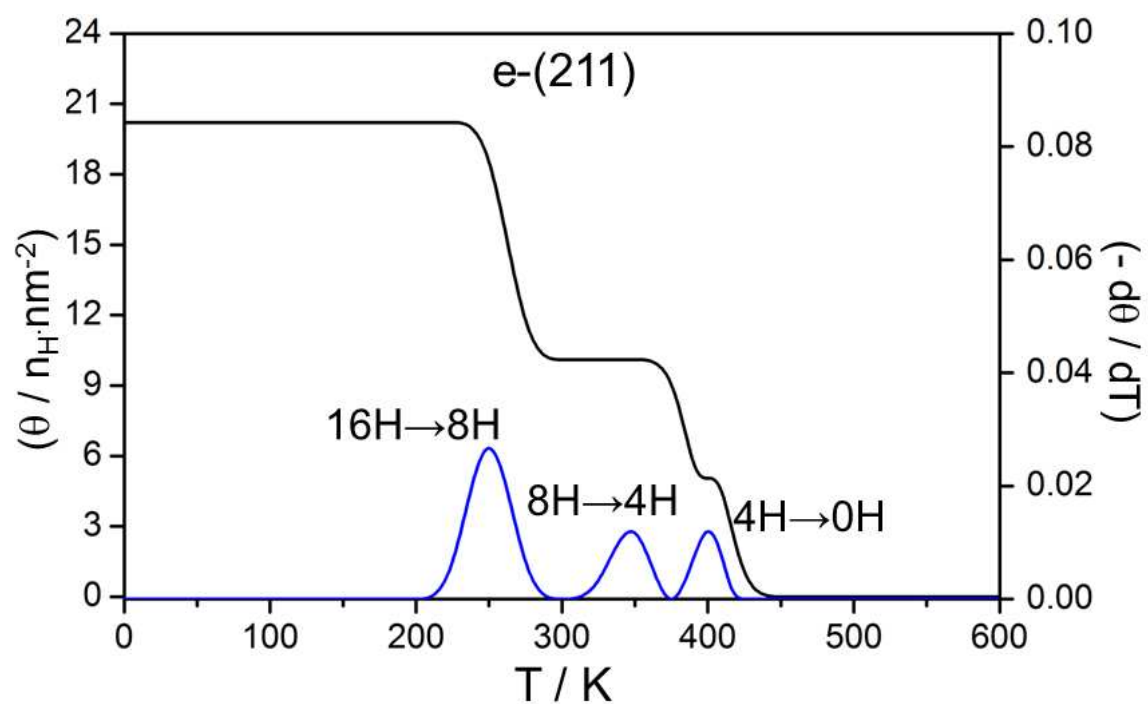
Figure S10. Hydrogen desorption peaks (red curve) on seven iron surfaces at 10^{-9} atmosphere
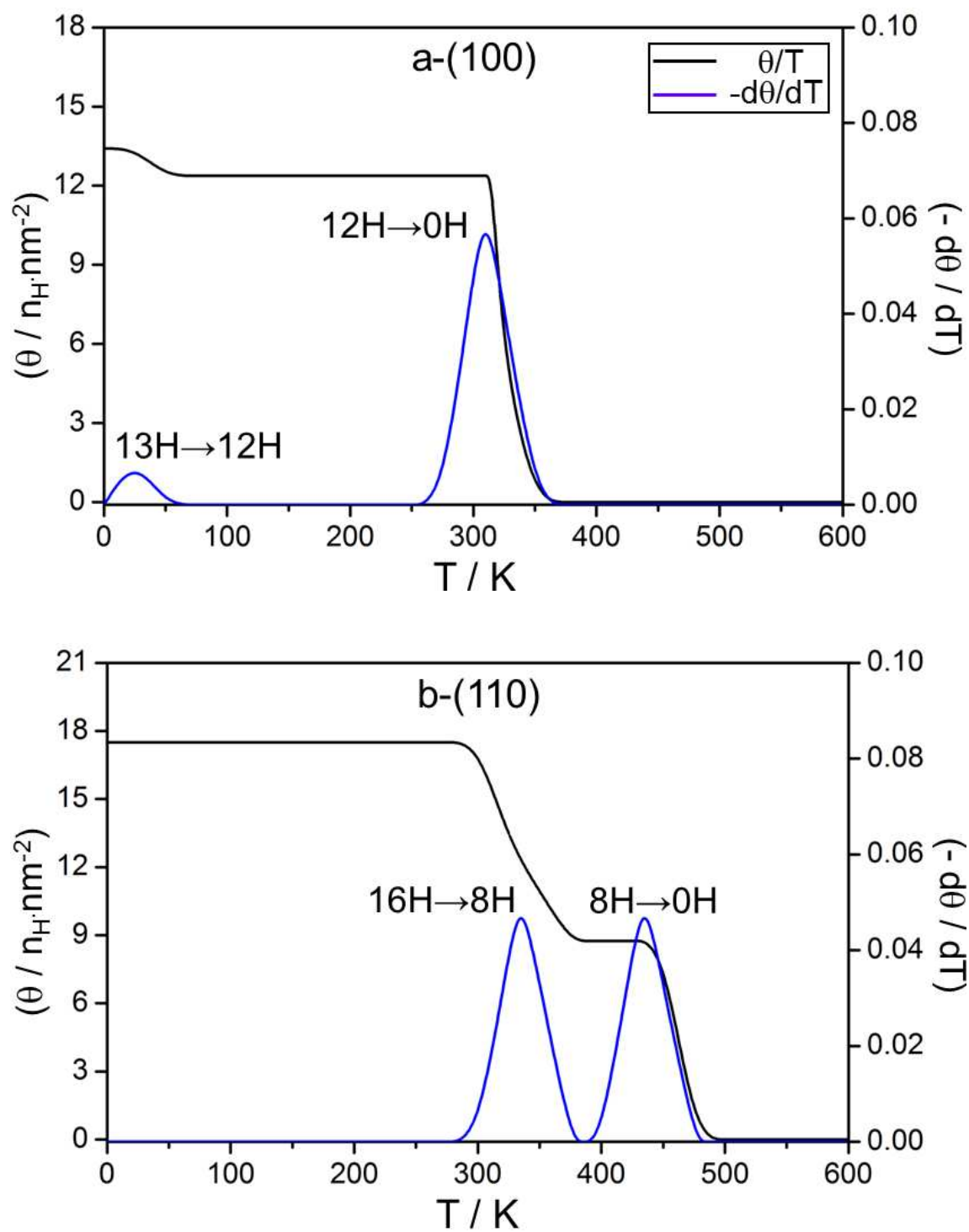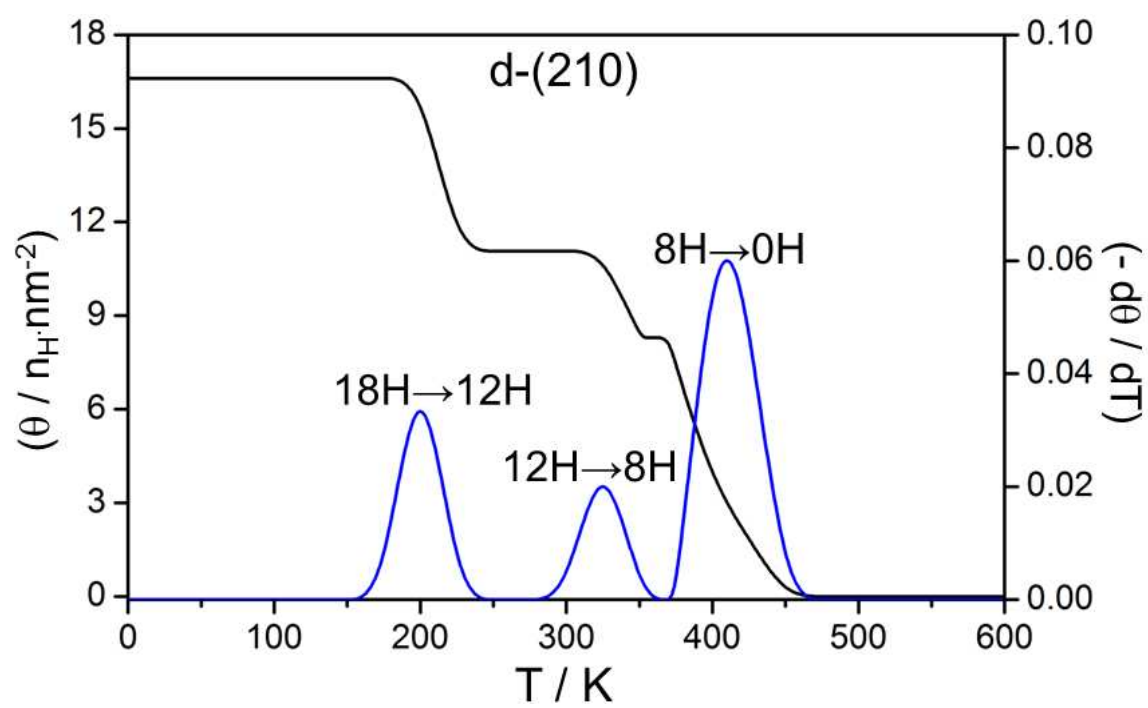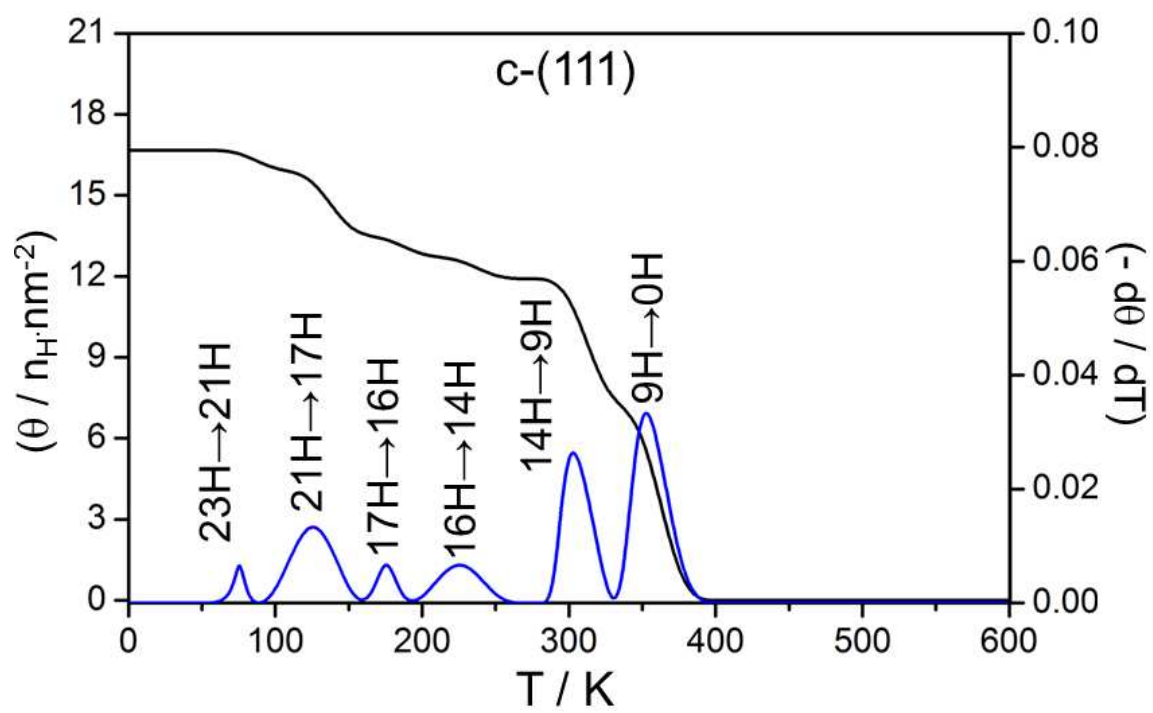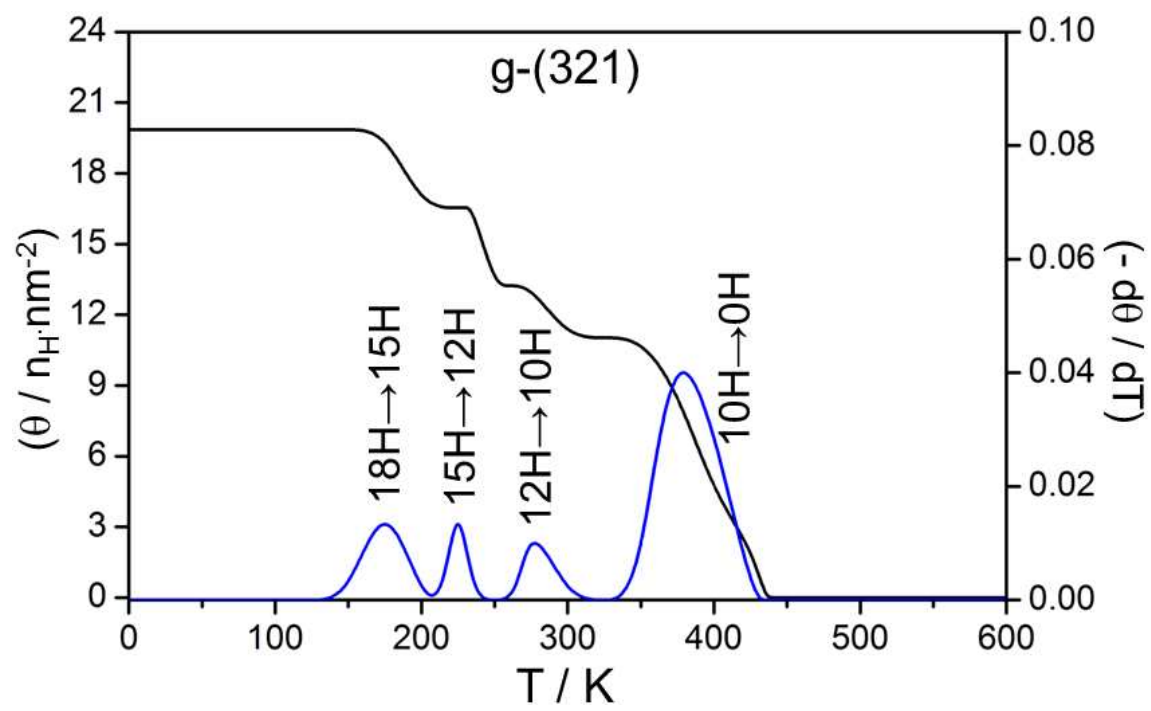
Figure S11. Structures of ordered hydrogen adsorption on Fe (110) and (211) surfaces (Blue ball for Fe and yellow ball for H)