Analysis of Photocatalytic Nitrogen Fixation on Rutile TiO_2(110) Supporting Information

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Adsorption energies for all compounds are provided in Table S1 with zero-point vibrational energy (ZPE) added. The hydrogen, oxygen, and nitrogen reference states are H_2, H_2O, and N_2 respectively. No gas-phase corrections have been applied because the BEEF-vdW uncertainty is expected to account for DFT error. The vibrational frequencies for all species are available in Table S2, and images of the most stable structures are shown in Table S3. Vibrational frequencies are calculated for the pristine surface and are used to compute thermodynamic corrections at both the pristine surface and defect sites.

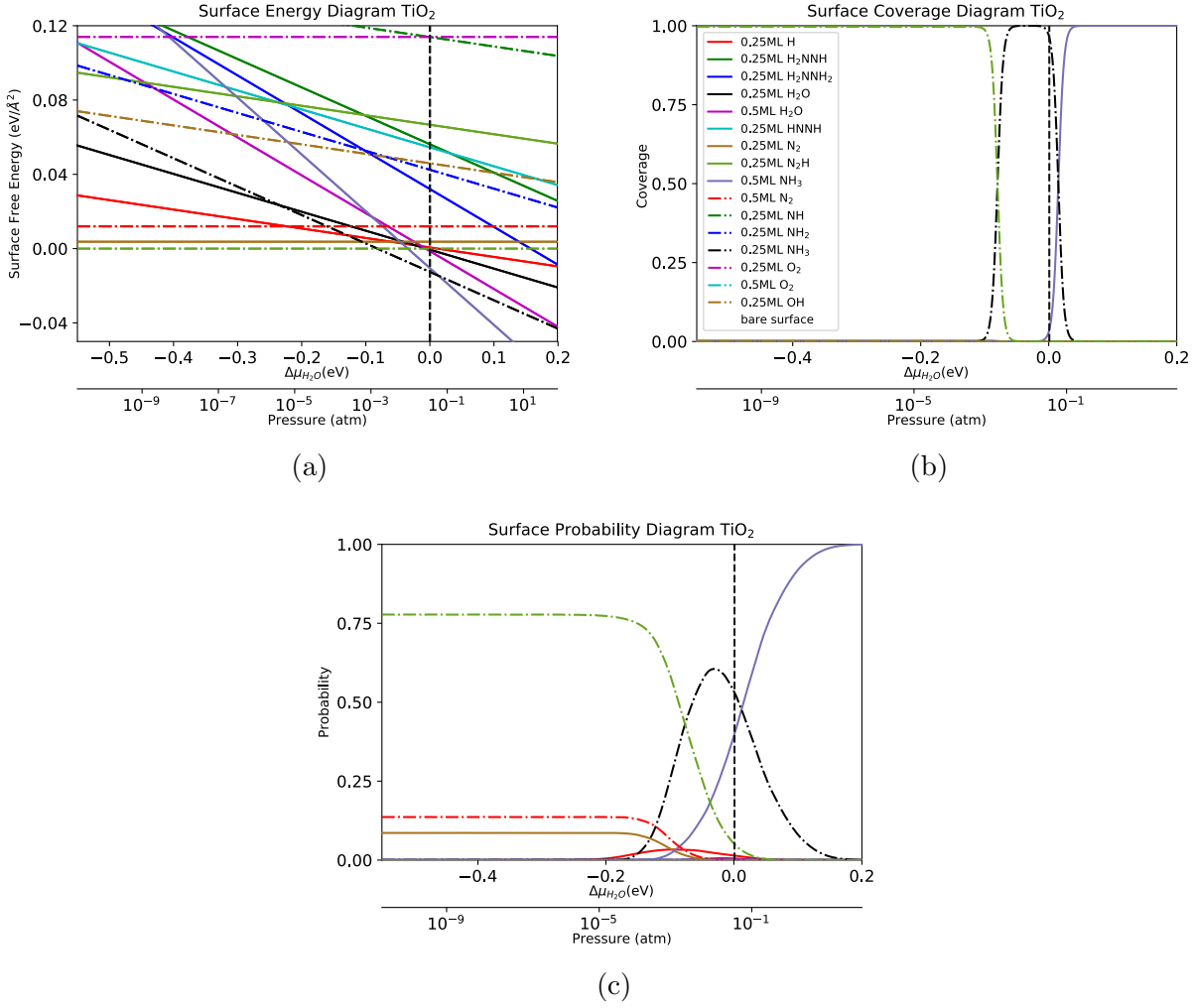


Figure S1: The surface energy (a), coverage (b), and probability (c) diagram of pristine rutile TiO_2 (110) at the reductive band edge including N_xH_y species. These were generated by the process outlined in the methods section.

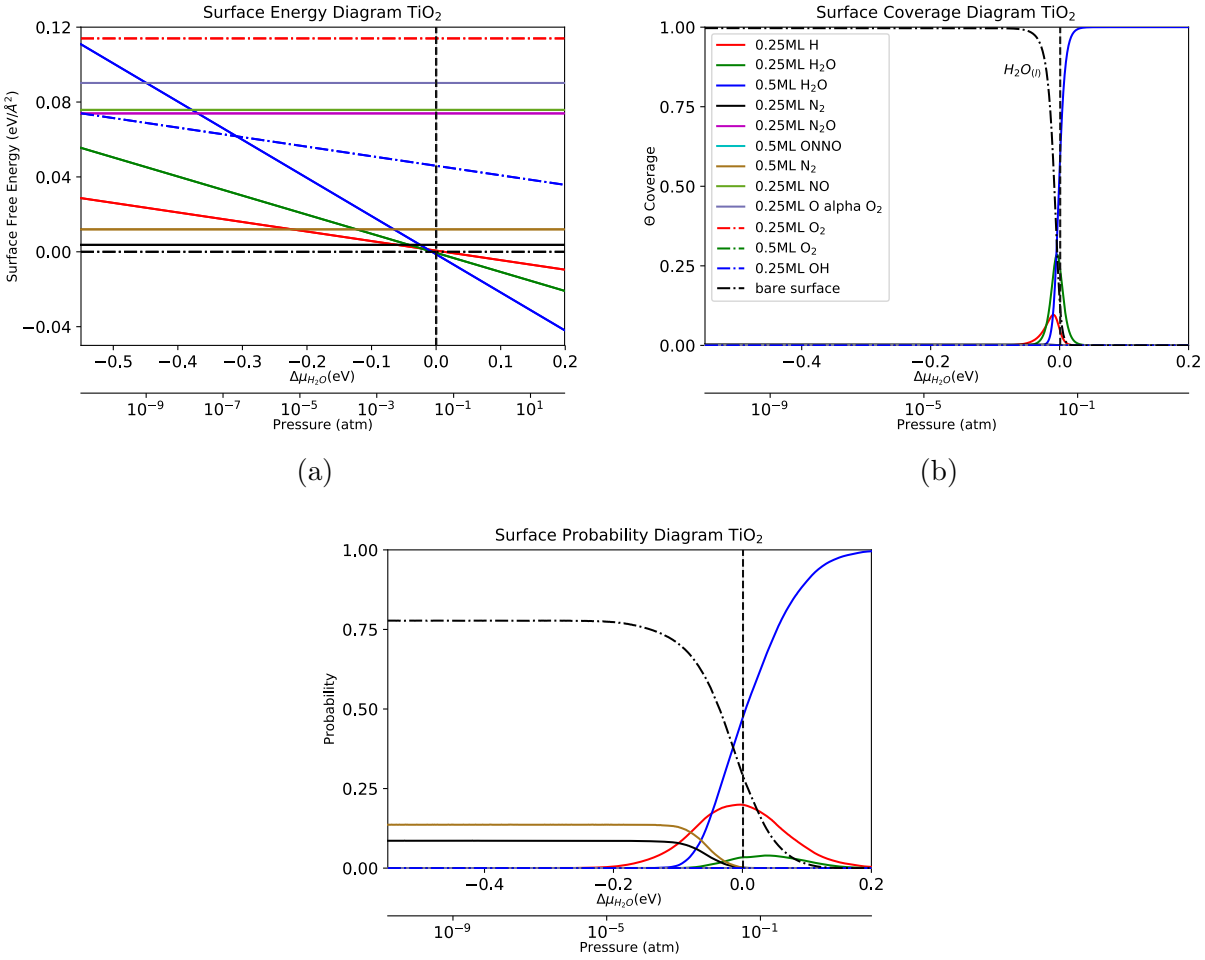
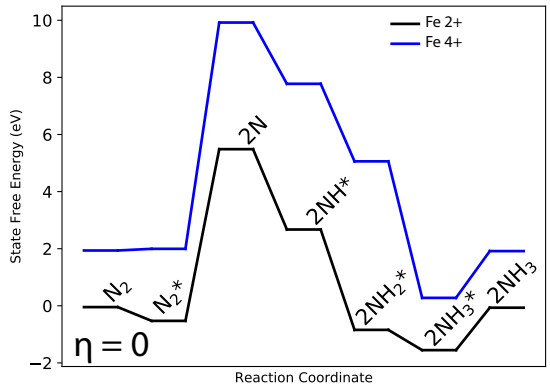
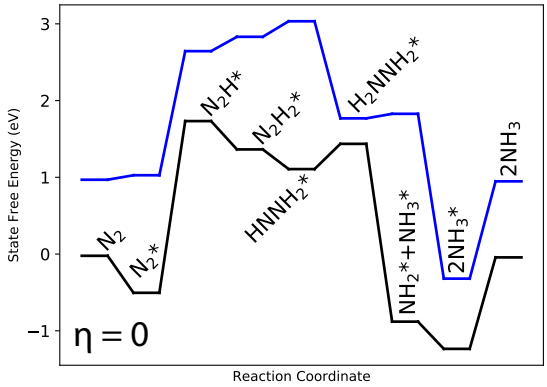


Figure S2: The surface energy (a), coverage (b), and probability (c) diagram of pristine rutile TiO_2 (110) at the oxidative band edge including N_xO_y species. These were generated by the process outlined in the methods section.



(a)



(b)

Figure S3: A comparison dissociative (a) and associative (b) nitrogen reduction pathway on Fe^{4+} (blue) and Fe $^{2+}$ (black) iron defect sites. Zero is set to the energy of the Fe^{2+} site.

In each reaction * represents a surface site and a molecule with a star (i.e. N_2^*) represents that molecule adsorbed to a surface site. The reactions in figures 4 and 8b:

$$N_2(g)+^* \rightarrow N_2^* \tag{S1}$$

$$N_2^*+^* \rightarrow 2N^* \tag{S2}$$

$$2N^* + 2(H^+ + e^-) \rightarrow 2NH^* \tag{S3}$$

$$2NH^* + 2(H^+ + e^-) \rightarrow 2NH_2^* \tag{S4}$$

$$2NH_2^* + 2(H^+ + e^-) \rightarrow 2NH_3^* \tag{S5}$$

$$2NH_3^* \rightarrow 2NH_3(g) + 2^* \tag{S6}$$

$$\tag{S7}$$

The reactions in figures 5,6, and 8a:

$$N_2(g)+^* \rightarrow N_2^* \tag{S8}$$

$$N_2^* + H^+ + e^- \rightarrow NNH^* \tag{S9}$$

$$NNH^* + H^+ + e^- \rightarrow HNNH^* \tag{S10}$$

$$HNNH^* + H^+ + e^- \rightarrow HNNH_2^* \tag{S11}$$

$$HNNH_2^* + H^+ + e^- \rightarrow H_2NNH_2^* \tag{S12}$$

$$H_2NNH_2^* +^* + H^+ + e^- \rightarrow NH_2^* + NH_3^* \tag{S13}$$

$$NH_2^* + NH_3^* + H^+ + e^- \rightarrow 2NH_3^* \tag{S14}$$

$$2NH_3^* \rightarrow 2NH_3(g) + 2^* \tag{S15}$$

The reactions in figure 7 are identical to figures 5, 6, and 8a except that reactions S16-S17 are replaced by:

$$NNH^* + H^+ + e^- \rightarrow NNH_2^* \tag{S16}$$

$$NNH_2^* + H^+ + e^- \rightarrow HNNH_2^* \tag{S17}$$

$$\tag{S18}$$

The reactions in Figure 9:

$$N_2(g) + ^* \rightarrow N_2^* \tag{S19}$$

$$H_2O(l) + ^* \rightarrow OH^* + (H^+ + e^-) \tag{S20}$$

$$OH^* \rightarrow O^* + (H^+ + e^-) \tag{S21}$$

$$N_2^* + O^* \rightarrow N_2O^* \tag{S22}$$

$$N_2O^* + O^* \rightarrow N_2O_2^* \tag{S23}$$

$$N_2O_2^* \rightarrow 2NO^* \tag{S24}$$

$$2NO^* \rightarrow NO(g) + 2^* \tag{S25}$$

The reactions in Figure 10:

$$NO(g)+^* \rightarrow NO^* \tag{S26}$$

$$NO^* + (H^+ + e^-) \rightarrow HNO^* \tag{S27}$$

$$HNO^* + (H^+ + e^-) \rightarrow HNOH^* \tag{S28}$$

$$HNOH^* + (H^+ + e^-) \rightarrow H_2NOH^* \tag{S29}$$

$$H_2NOH^* + (H^+ + e^-) \rightarrow NH_2^* + H_2O(l) \tag{S30}$$

$$NH_2^* + (H^+ + e^-) \rightarrow NH_3^* \tag{S31}$$

$$NH_3^* \rightarrow NH_3(g)+^* \tag{S32}$$

The reactions to form surface defects are as follows:

oxygen defect formation:

$$Ti_{16}O_{32} + 2(H^+ + e^-) \rightarrow Ti_{16}O_{31} + H_2O \tag{S33}$$

Iron defect formation:

$$Ti_{16}O_{32} + Fe_{BCC} + 2H_2O \rightarrow Ti_{15}FeO_{32} + TiO_2 + 4(H^+ + e^-) \tag{S34}$$

Table S1: Energies of all species used relative to a bare slab, H_2, N_2, and H_2O at 0K (ZPE included)

compound	BEEF energy	ensemble mean	ensemble standard deviation
defect ads NH_2	0.26	0.26	0.25
0.5ML NH_3	-1.71	-1.69	0.64
Iron ads NH	1.82	1.82	0.72
defect ads NH	1.5	1.5	0.14
0.25ML O ads Ti	4.04	4.04	0.31
0.5ML ONNO	5.21	5.22	0.51
defect ads N_2H	2.39	2.39	0.22
0.25ML ONH	2.68	2.68	0.24
defect ads NH_3	0.58	0.57	0.35
0.5ML N_2	-0.24	-0.23	0.48
Iron ads HNNH	1.45	1.44	0.75
0.25ML O alpha O_2	3.29	3.3	0.15
0.25ML N_2	-0.2	-0.2	0.19
Iron ads N2	-0.02	-0.04	0.66
defect ads H_2NNH	1.56	1.56	0.32
Iron ads N	3.34	3.34	0.64
Iron ads H_2NNH_2	1.22	1.21	0.98
0.25ML NH_2O	2.72	2.73	0.29
0.5ML H_2O	-1.03	-1.02	0.49
0.25ML NO	2.67	2.68	0.21
bridging oxygen defect slab	1.78	1.77	0.35
0.25ML NH	4.12	4.13	0.3
0.25ML HNNH	1.43	1.43	0.29
0.5ML O_2	8.87	8.88	0.64

Iron ads N_2H	1.98	1.97	0.69
0.25ML H_2O	-0.49	-0.48	0.21
Iron ads NH_3	-0.57	-0.58	0.93
0.25ML H_2N-OH	1.07	1.08	0.34
0.25ML H ads Ti	2.66	2.67	0.17
Iron 2+ Slab	0.84	0.82	0.79
0.25ML N_2H	2.09	2.09	0.25
0.25ML H_2NNH_2	0.23	0.24	0.45
0.25ML H	-0.08	-0.08	0.17
0.25ML N ads O	4.34	4.34	0.11
bare surface	0.0	0.0	0.0
0.25ML N_2O	2.36	2.36	0.2
0.25ML H_2NNH	1.33	1.34	0.37
Iron ads NH_2	-0.12	-0.13	0.78
Original Iron Slab	1.56	1.55	0.75
0.25ML OH	1.43	1.44	0.29
defect ads HNNH	2.7	2.7	0.28
0.25ML O_2	4.19	4.19	0.24
defect ads N	3.27	3.27	0.17
0.25ML NH_2	1.19	1.2	0.33
0.25ML NH_3	-1.12	-1.11	0.3
0.25ML NO_2	3.89	3.9	0.29
Iron ads H_2NNH	1.04	1.03	0.82
defect ads N_2	1.53	1.53	0.29
0.25ML N ads Ti	4.73	4.73	0.2

Table S2: Vibrational frequencies of all species

compound	Vibrational Frequencies (cm^{-1})
0.5ML O_2	30, 30, 30, 46.5, 56.6, 61.7, 66.9, 104.1, 122.9, 147.0, 1485.6, 1530.3,
0.25ML N_2O	30, 30, 56.4, 82.6, 103.5, 570.5, 574.2, 1332.2, 2378.8,
0.25ML NH_3	30, 124.0, 150.5, 278.5, 549.5, 578.2, 1160.9, 1618.2, 1623.3, 3402.9, 3528.6, 3536.4,
0.25ML NO_2	30, 30, 30, 35.9, 66.5, 164.3, 702.5, 1296.0, 1639.3,
Iron ads H_2NNH_2	30, 113.0, 152.9, 183.7, 304.1, 432.2, 676.0, 898.4, 1028.2, 1170.8, 1240.2, 1373.9, 1614.5, 1627.4, 3316.8, 3383.4, 3418.8, 3496.7,
0.25ML N ads Ti	119.6, 131.1, 132.4,
0.25ML O alpha O_2	295.8, 352.3, 731.8,

defect ads NH_3	30, 124.0, 150.5, 278.5, 549.5, 578.2, 1160.9, 1618.2, 1623.3, 3402.9, 3528.6, 3536.4,
0.25ML N_2	30, 33.2, 64.6, 142.0, 153.7, 2448.7,
0.25ML NH	67.5, 102.6, 340.5, 346.1, 549.6, 3498.0,
0.25ML HNNH	53.0, 81.0, 103.3, 168.0, 316.2, 386.7, 1197.0, 1325.7, 1517.4, 1650.6, 3128.9, 3199.7,
0.25ML O ads Ti	79.0, 165.1, 474.3,
defect ads N_2H	30, 161.0, 287.6, 317.7, 362.9, 610.0, 1370.0, 1631.6, 3009.0,
0.25ML NO	30, 30, 71.0, 80.9, 126.6, 1915.3,
0.25ML NH_2O	73.3, 93.1, 149.0, 173.4, 304.3, 534.4, 962.4, 1288.2, 1303.6, 1618.7, 3112.1, 3319.8,
0.25ML N_2H	48.0, 58.5, 71.4, 103.7, 228.8, 416.0, 1085.3, 1916.0, 2821.7,

defect ads NH	214.0, 377.9, 508.1, 565.8, 567.9, 3487.3,
0.25ML H ads Ti	206.5, 222.8, 1012.3,
0.25ML ONH	30, 43.2, 74.3, 159.0, 325.6, 582.4, 1505.8, 1619.5, 2942.0,
0.25ML OH	139.9, 172.0, 217.8, 529.9, 614.0, 3716.0,
defect ads H_2NNH	30, 30, 152.8, 250.1, 319.2, 377.8, 497.3, 539.7, 880.0, 966.6, 1129.4, 1245.1, 1443.4, 1620.4, 2585.2, 3372.4, 3476.0, 3492.4,
0.5ML NH_3	30, 112.2, 119.8, 166.1, 189.5, 211.2, 263.0, 289.6, 300.0, 434.4, 486.3, 506.0, 972.8, 1109.7, 1554.0, 1628.5, 1640.1, 1665.3, 3413.6, 3419.7, 3541.8, 3544.8, 3551.2, 3554.8,
Iron ads N_2H	30, 159.1, 290.6, 327.1, 593.7, 685.9, 1252.3, 1717.6, 3066.5,

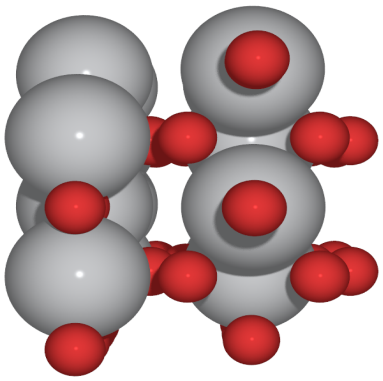
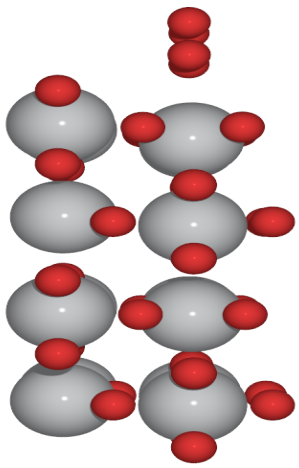
0.25ML H_2N-OH	57.2, 108.8, 150.8, 174.9, 322.8, 335.6, 559.2, 950.1, 1209.5, 1284.3, 1442.7, 1618.7, 3352.6, 3441.3, 3604.2,
0.25ML H_2NNH_2	30, 98.8, 112.0, 224.1, 384.1, 416.2, 477.0, 906.5, 1039.4, 1102.2, 1176.4, 1420.7, 1592.2, 1627.3, 3366.9, 3382.2, 3469.5, 3492.3,
Iron ads N	240.1, 345.7, 769.1,
defect ads H_2NNH	116.3, 149.0, 188.1, 270.2, 385.6, 394.5, 645.4, 853.5, 1086.6, 1267.9, 1383.0, 1636.0, 3378.9, 3420.4, 3481.7,
defect ads NH_2	30, 94.2, 166.3, 395.6, 434.5, 575.7, 1521.6, 3435.4, 3544.8,
0.25ML H	30, 611.1, 3676.9,
Iron ads NH_2	150.4, 210.4, 315.1, 492.3, 593.2, 730.2, 1471.2, 3403.3, 3541.0,

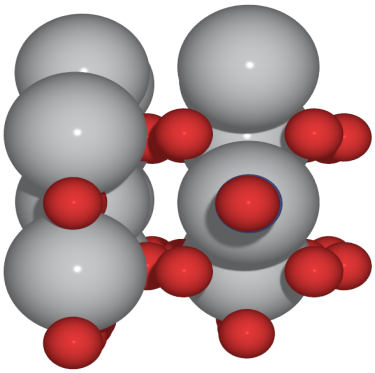
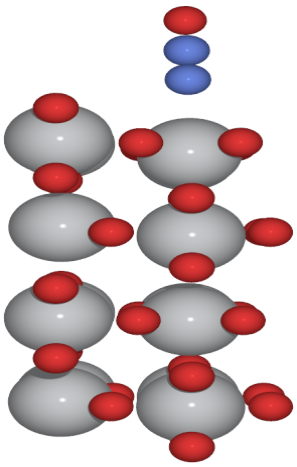
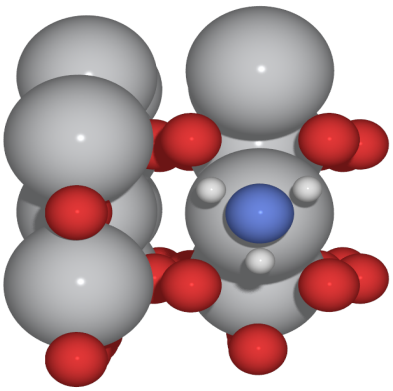
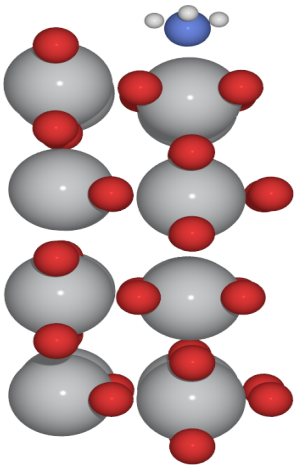
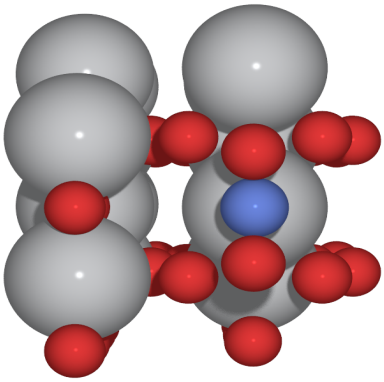
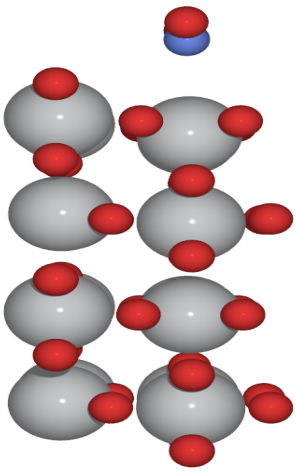
Iron ads HNNH	30, 131.8, 323.5, 365.2, 537.0, 579.4, 689.5, 1272.3, 1434.1, 1580.9, 3278.0, 3422.3,
0.25ML H_2O	30, 122.8, 150.7, 192.4, 508.0, 543.1, 1634.4, 3665.7, 3746.9,
0.25ML H_2NNH	30, 108.0, 174.3, 198.3, 288.9, 351.6, 496.6, 745.5, 1161.3, 1335.1, 1459.9, 1625.2, 3399.1, 3409.2, 3547.9,
defect ads N_2	30.1, 51.2, 54.2, 132.2, 158.8, 2425.7,
0.25ML NH_2	30, 94.2, 166.3, 395.6, 434.5, 575.7, 1521.6, 3435.4, 3544.8,
Iron ads H_2NNH	30, 129.6, 226.6, 269.3, 396.4, 465.5, 589.7, 951.3, 1190.9, 1407.7, 1428.5, 1618.0, 3087.3, 3324.6, 3496.4,
Iron ads NH_3	30, 125.8, 134.1, 214.1, 539.4, 613.7, 1200.9, 1620.3, 1625.3, 3334.7, 3472.7, 3526.7,

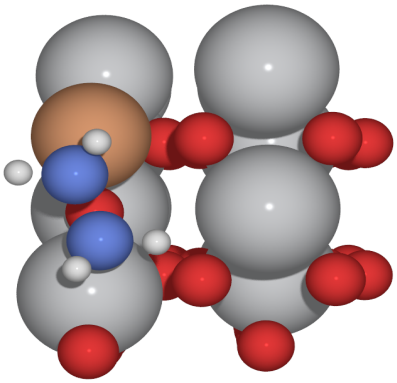
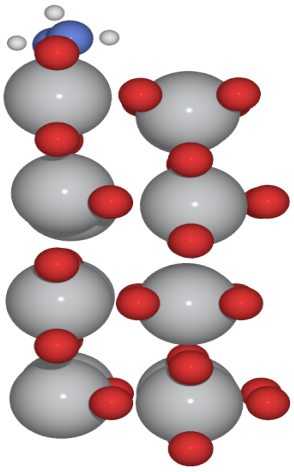
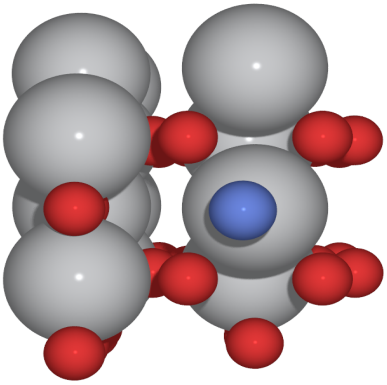
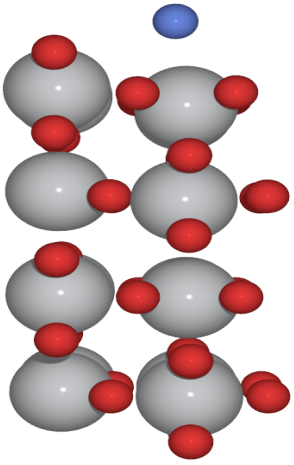
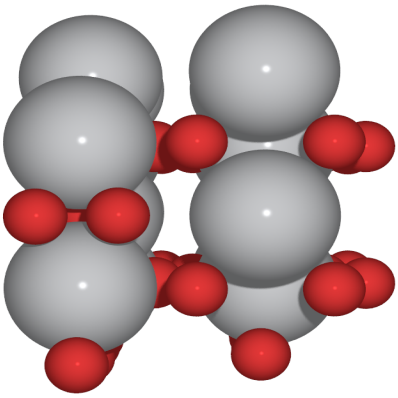
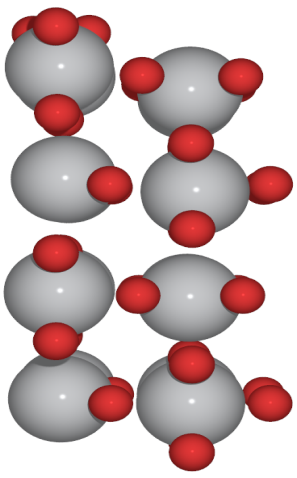
Iron ads NH	30, 317.1, 415.3, 442.6, 807.3, 3416.9,
Iron ads N2	30, 54.6, 95.6, 148.4, 206.6, 2434.3,
0.25ML NO_2	50.4, 77.8, 103.4, 109.5, 191.7, 256.6, 727.3, 1263.9, 1553.0,
0.25ML N_2O	30, 30, 47.0, 51.6, 64.8, 567.0, 568.3, 1315.6, 2357.5,
defect ads HNNH	89.4, 112.7, 198.9, 251.5, 362.1, 377.5, 931.1, 1277.3, 1354.0, 1494.1, 3254.1, 3307.0,
0.5ML N_2	30, 30, 30, 32.2, 77.8, 130.9, 142.4, 191.7, 199.2, 245.9, 2448.7, 2452.0,
0.5ML ONNO	30, 30.2, 56.2, 77.9, 130.7, 197.6, 203.1, 332.3, 456.4, 642.4, 1737.1, 1889.0,

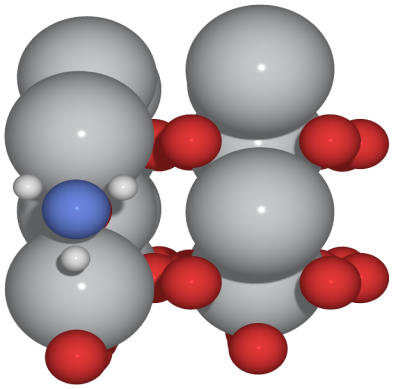
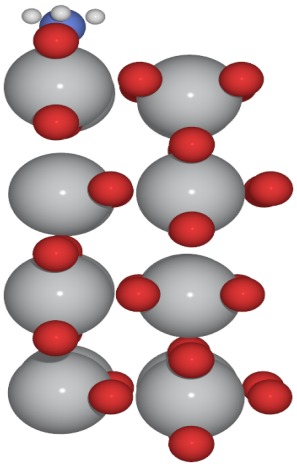
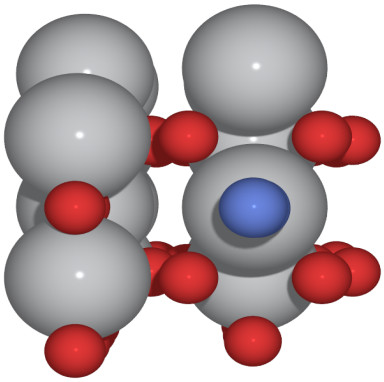
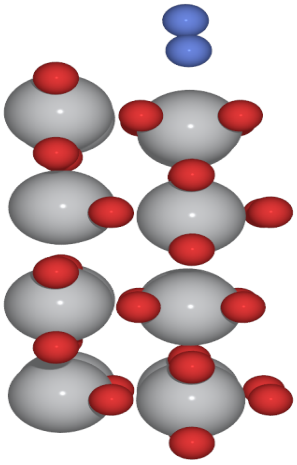
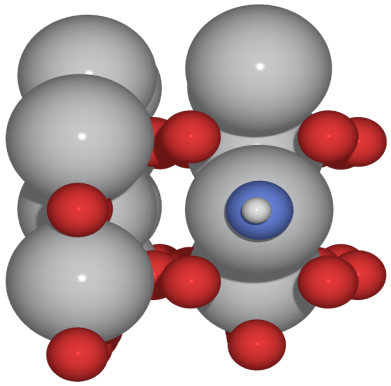
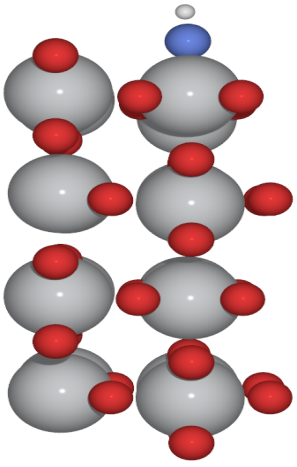
0.5ML H_2O	30, 107.0, 122.3, 147.8, 164.2, 179.9, 188.1, 415.1, 437.1, 519.6, 547.1, 652.8, 1622.1, 1677.2, 3646.3, 3652.7, 3717.2, 3718.9,
0.25ML O_2	30, 30, 30, 55.8, 58.0, 1531.7,
0.25ML N ads O	65.7, 145.4, 1115.7,
defect ads N	195.2, 524.9, 559.4,

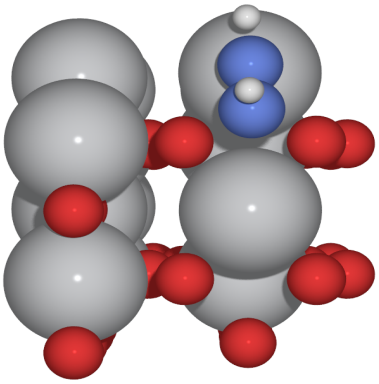
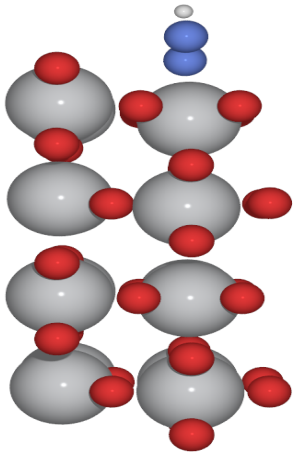
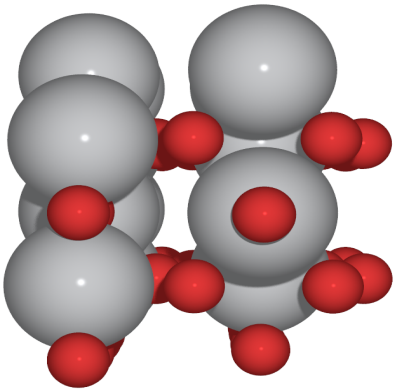
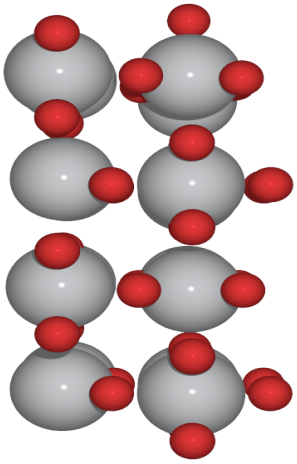
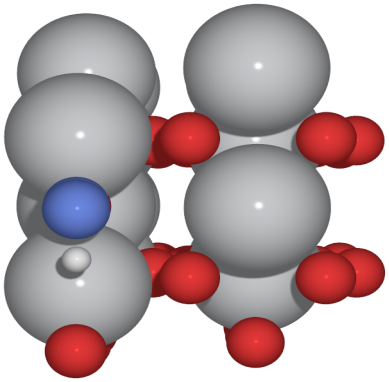
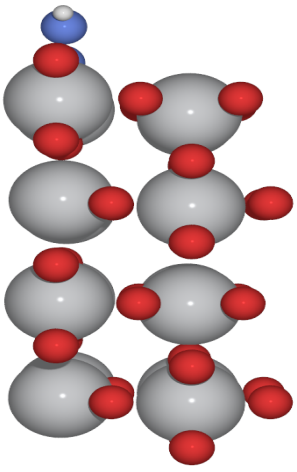
Table S3: Equilibrium geometries

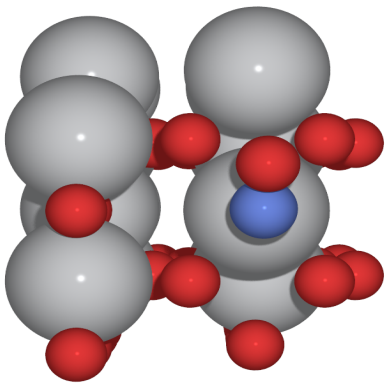
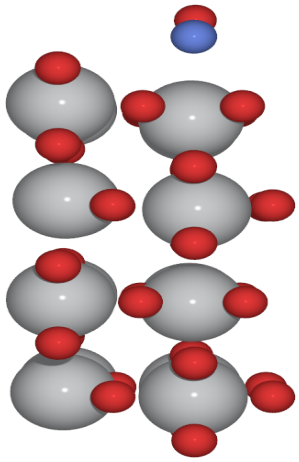
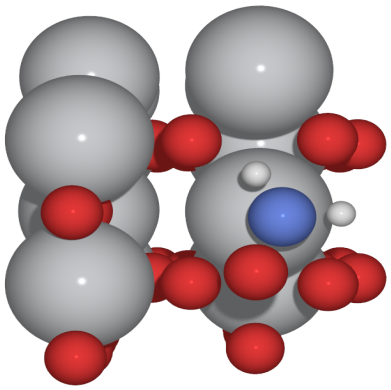
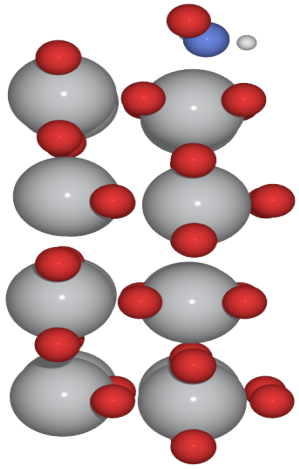
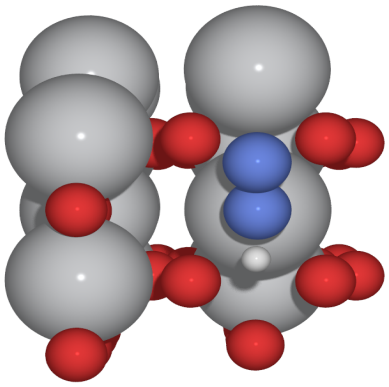
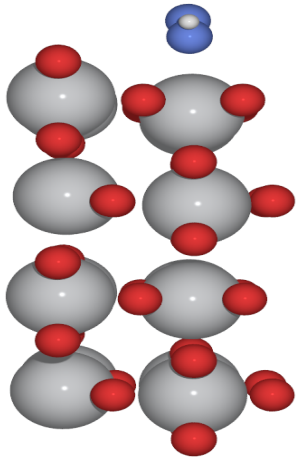
compound	Top View	Side View
0.5ML O_2		

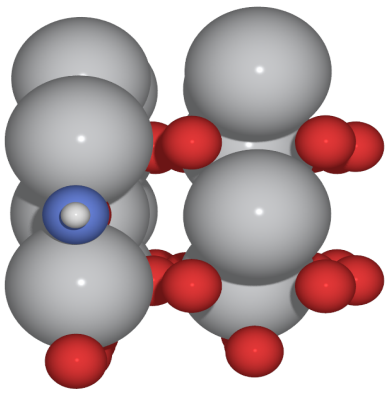
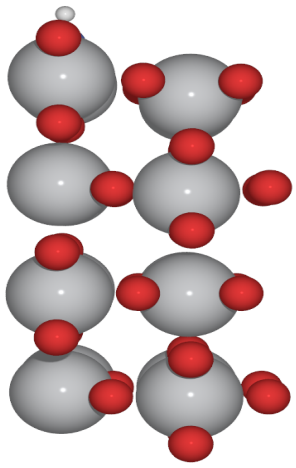
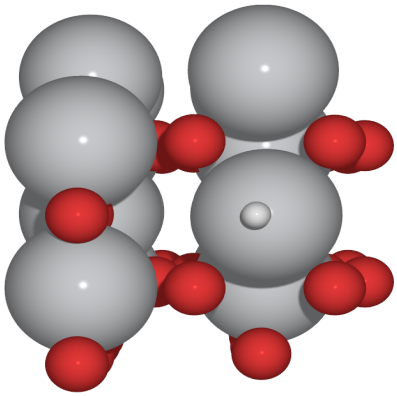
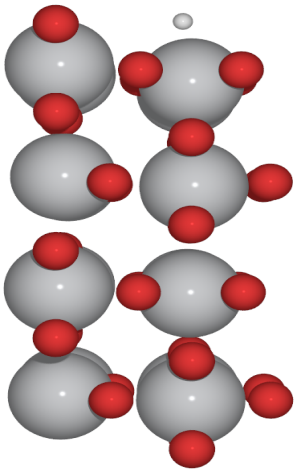
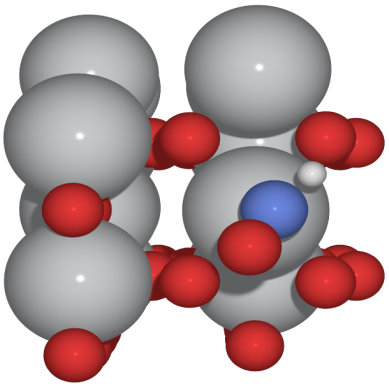
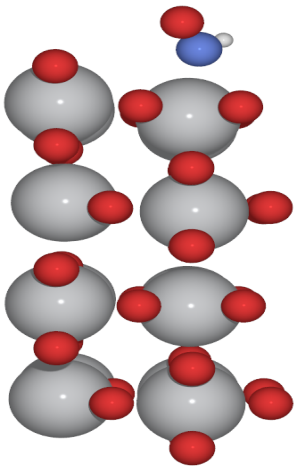
0.25ML N_2O		
0.25ML NH_3		
0.25ML NO_2		

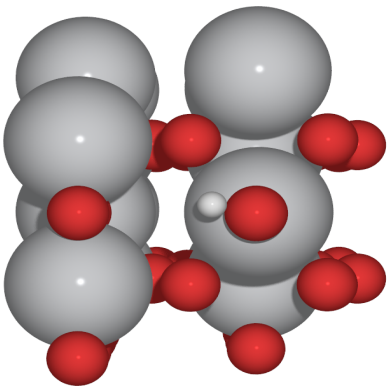
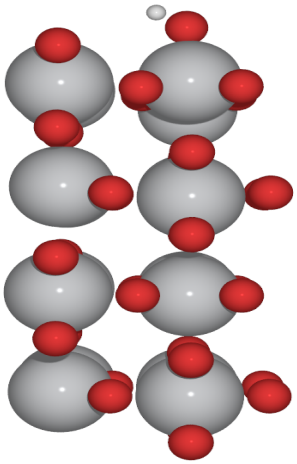
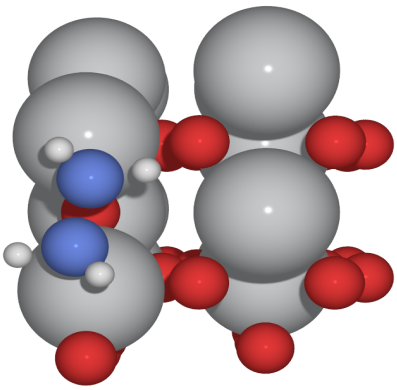
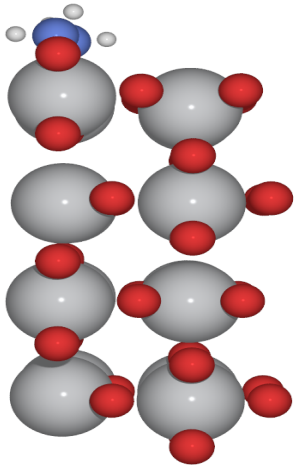
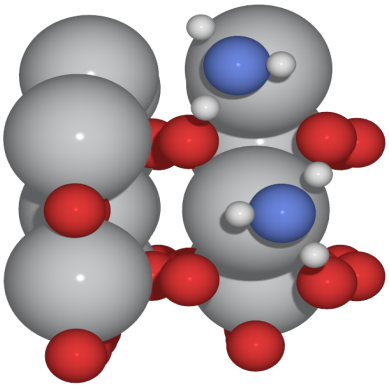
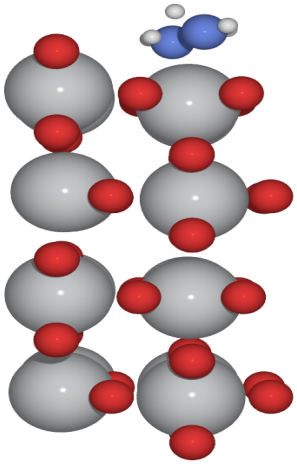
Iron ads H_2NNH_2		
0.25ML N ads Ti		
0.25ML O alpha O_2		

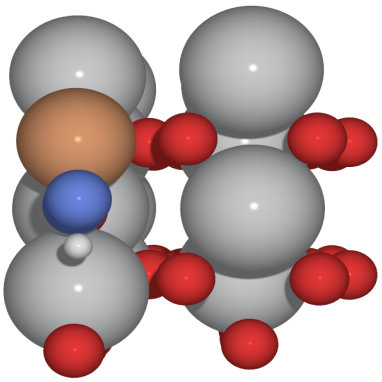
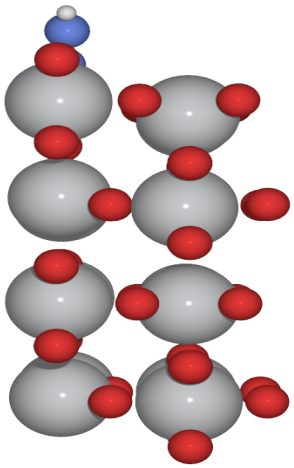
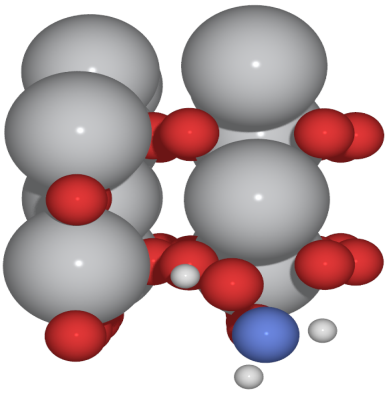
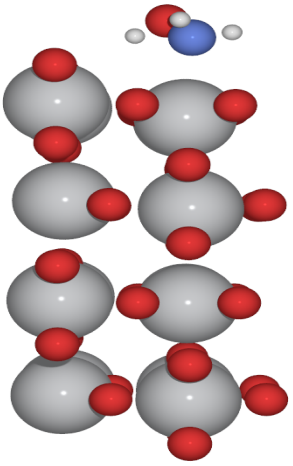
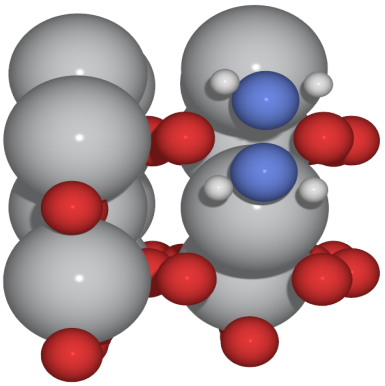
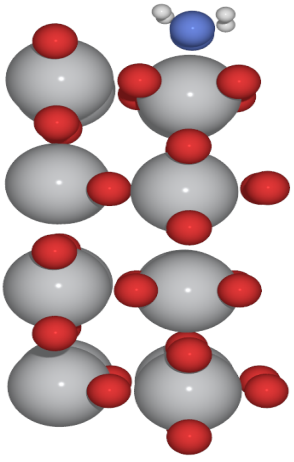
defect ads NH_3		
0.25ML N_2		
0.25ML NH		

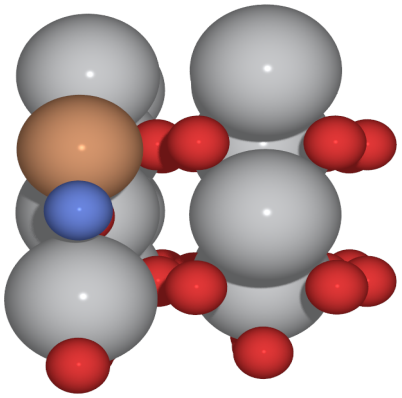
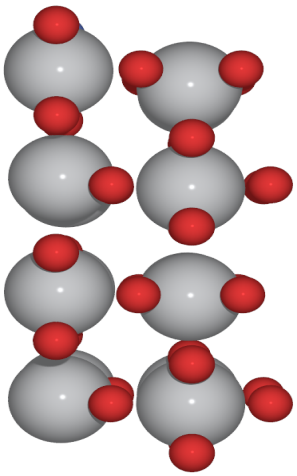
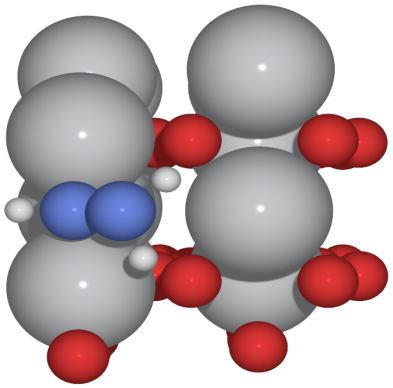
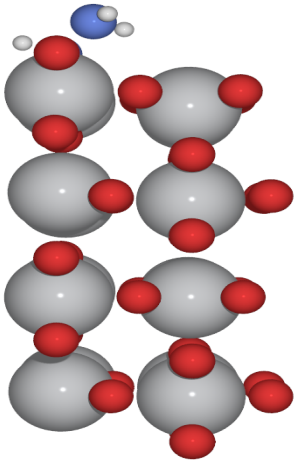
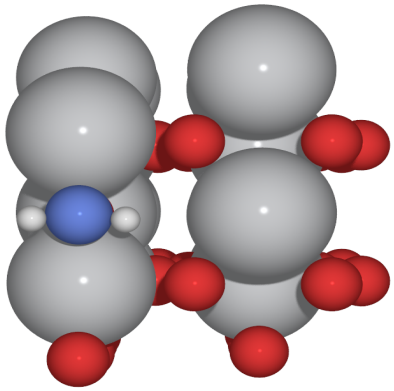
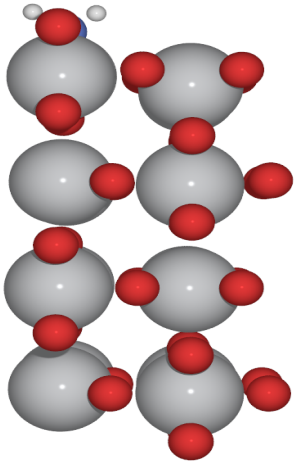
0.25ML HNNH		
0.25ML O ads Ti		
defect ads N_2H		

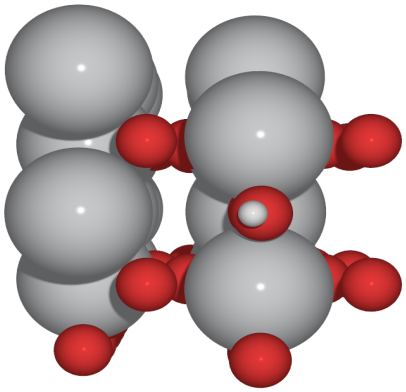
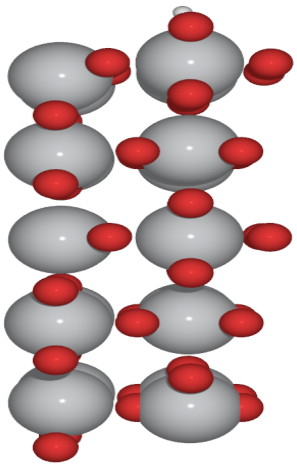
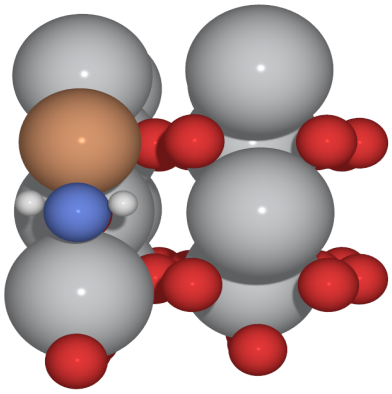
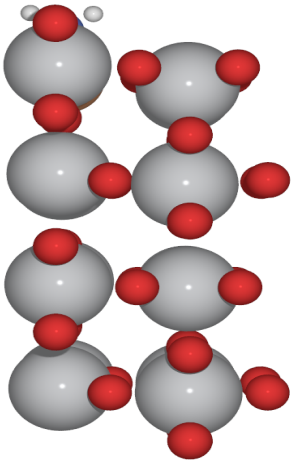
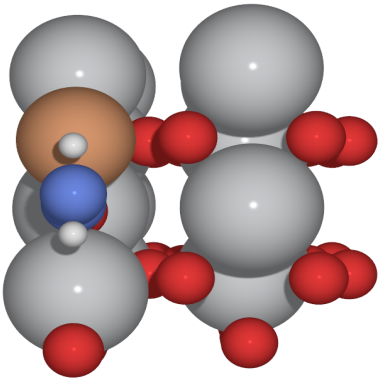
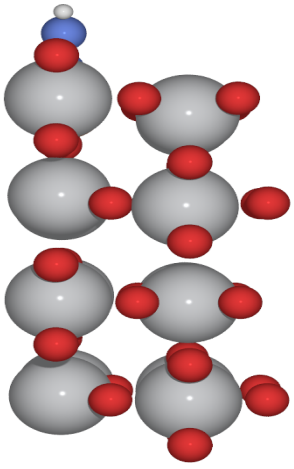
0.25ML NO		
0.25ML NH_2O		
0.25ML N_2H		

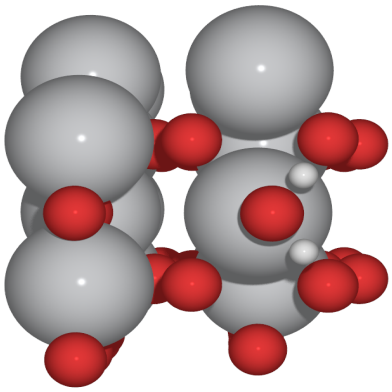
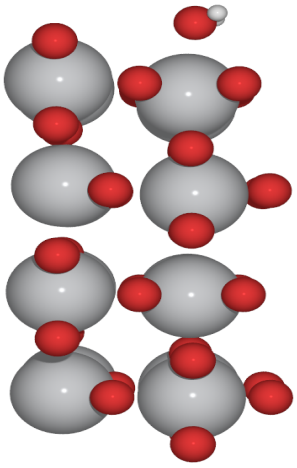
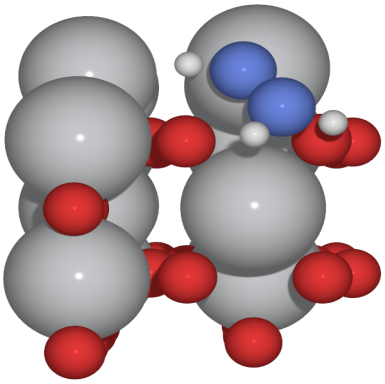
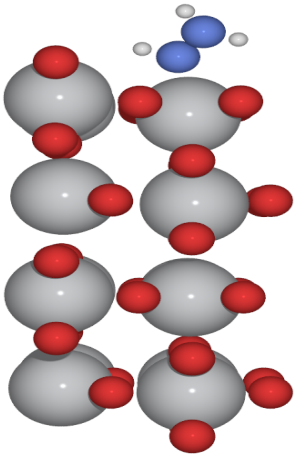
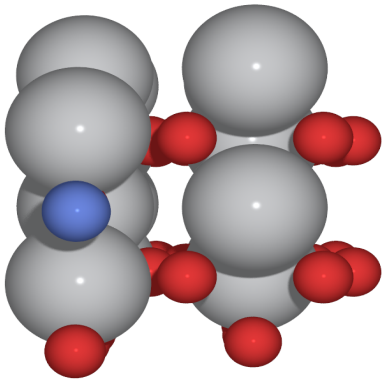
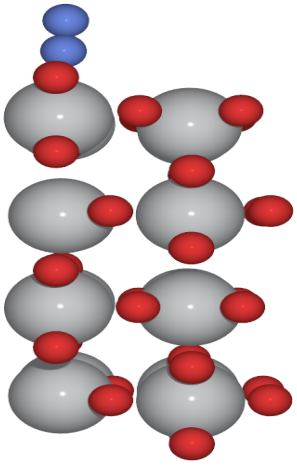
defect ads NH		
0.25ML H ads Ti		
0.25ML ONH		

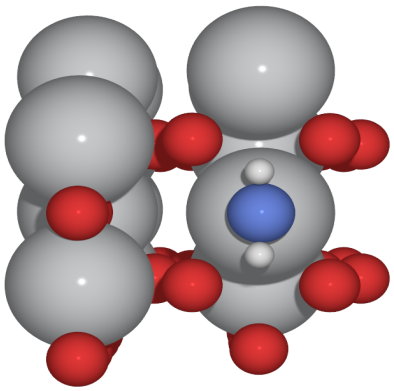
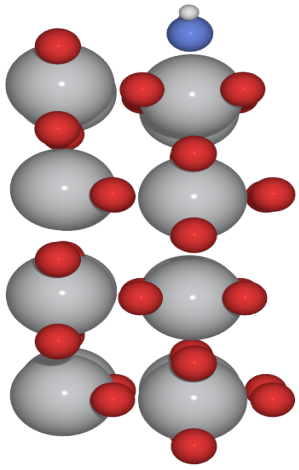
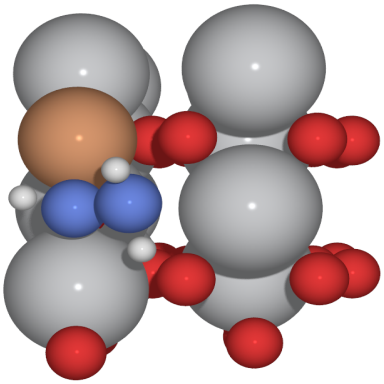
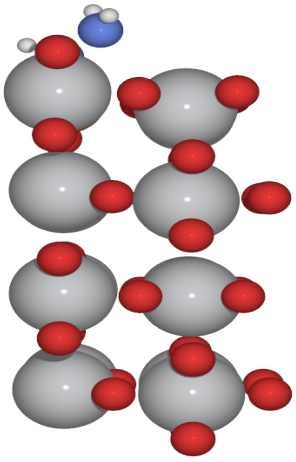
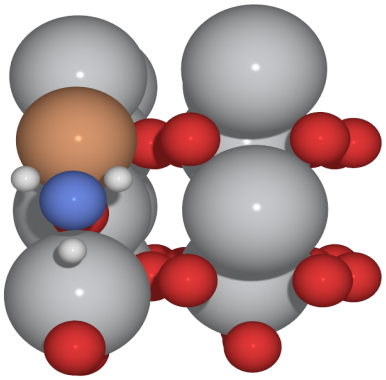
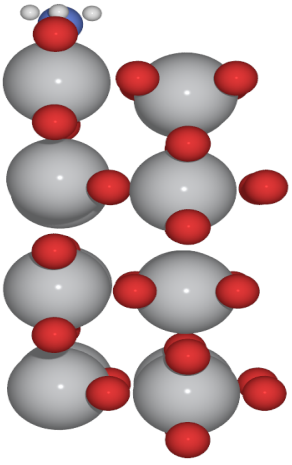
0.25ML OH		
defect ads H_2NNH		
0.5ML NH_3		

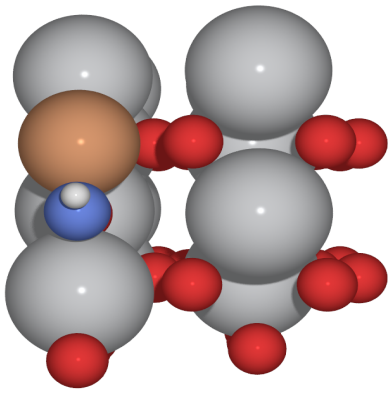
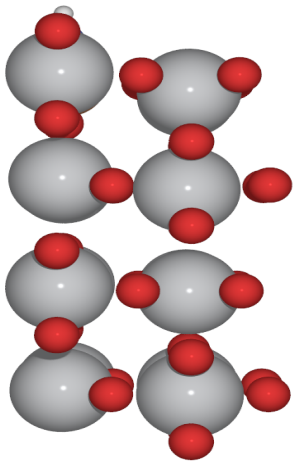
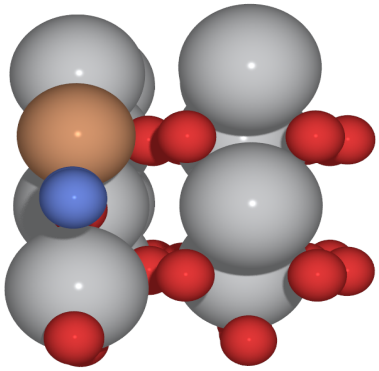
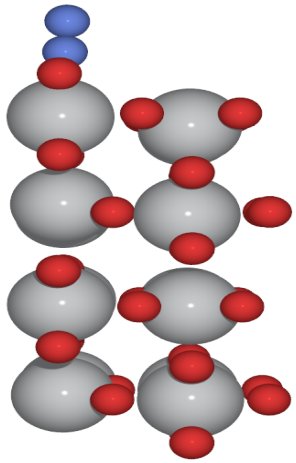
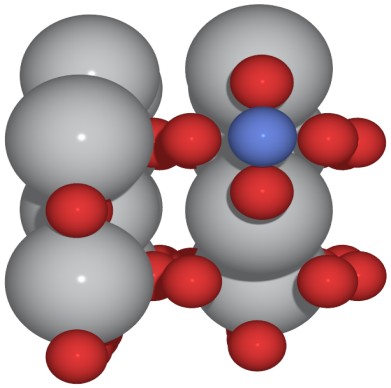
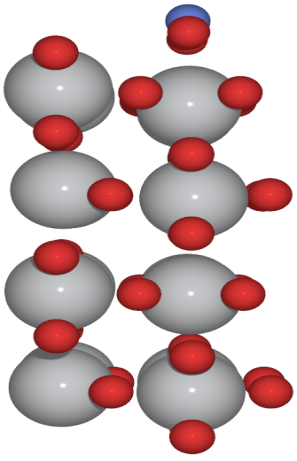
Iron ads N_2H		
0.25ML H_2N-OH		
0.25ML H_2NNH_2		

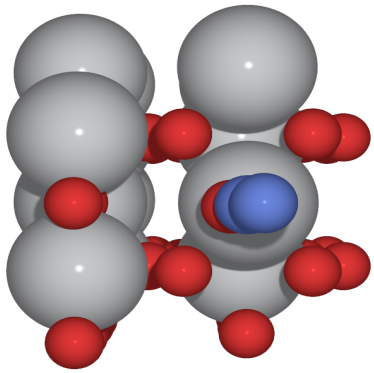
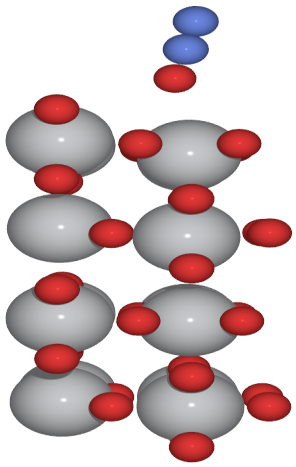
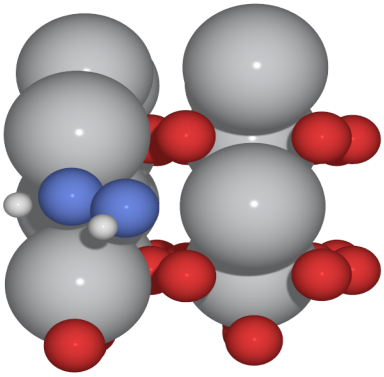
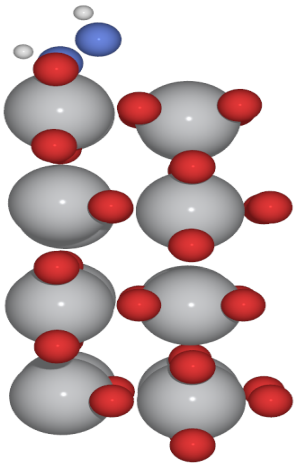
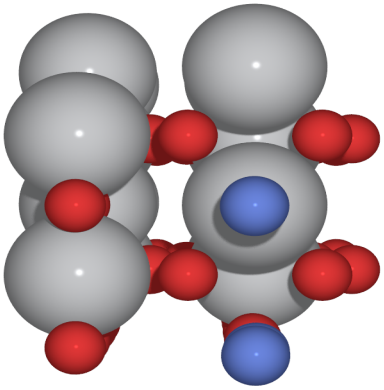
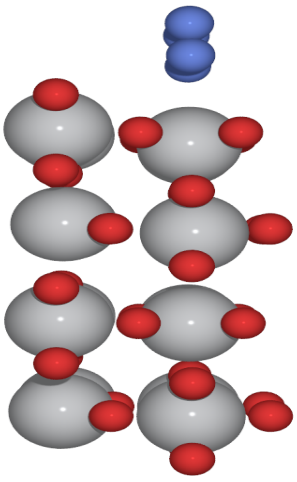
Iron ads N		
defect ads H_2NNH		
defect ads NH_2		

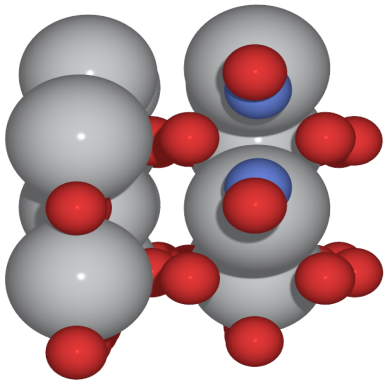
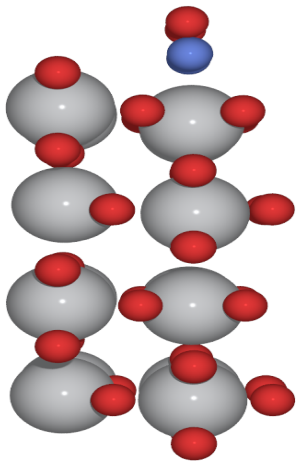
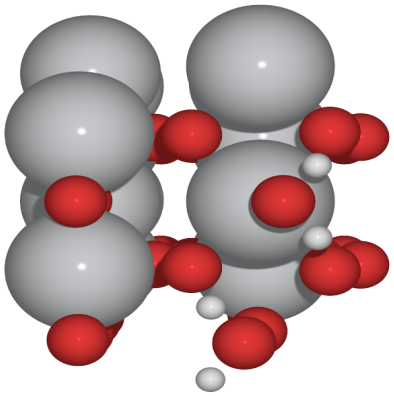
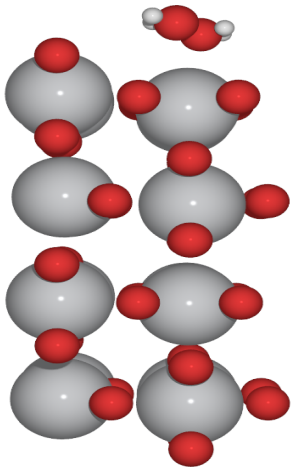
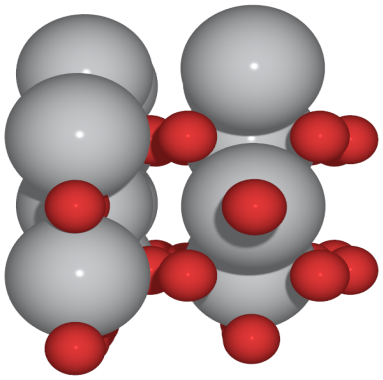
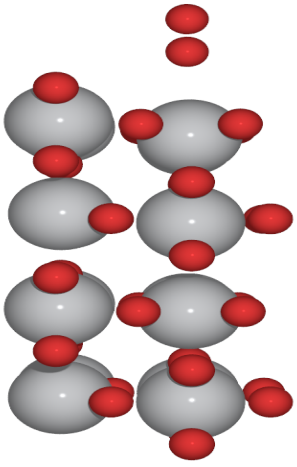
0.25ML H		
Iron ads NH_2		
Iron ads HNNH		

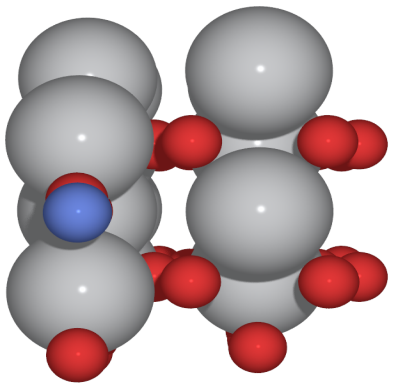
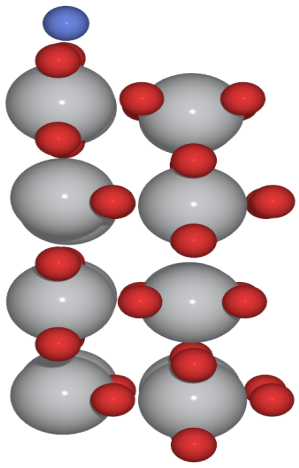
0.25ML H_2O		
0.25ML H_2NNH		
defect ads N_2		

0.25ML NH_2		
Iron ads H_2NNH		
Iron ads NH_3		

Iron ads NH		
Iron ads N2		
0.25ML NO_2		

0.25ML N_2O		
defect ads HNNH		
0.5ML N_2		

0.5ML ONNO		
0.5ML H_2O		
0.25ML O_2		

0.25ML N ads O		
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