

Modelling the effect of surface charging on plasma synthesis of ammonia using DFT

Aditya Dilip Lele, Yijie Xu, Yiguang Ju

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey

S1. Accuracy of the calculations

As the differences in adsorption energies due to the surface charge are in the range of $O(10^{-1} \text{ eV})$, we tested the numerical accuracy of our calculations along with the choice of level of theory. To test the numerical accuracy of the calculations, we changed the cutoff energy value to assess the impact of the energy calculations. Table S2 shows the relative change in energy value as a function of cutoff value. The relative change in energy is less than $O(10^{-3} \text{ eV})$, which is 2 orders of magnitude less than the changes in adsorption energy due to surface charge.

Table S1 Change in structure energy value as a function of cutoff energy.

Cutoff Energy	Rel. change (eV)
700	0.002837556
800	0.000459078
900	0.000793348
1000	0.000550511

Another source of error for DFT calculations is the level of theory used for the calculations. We use PBE functionals in our work which are routinely used for catalysis calculations.¹ As a comparison, we

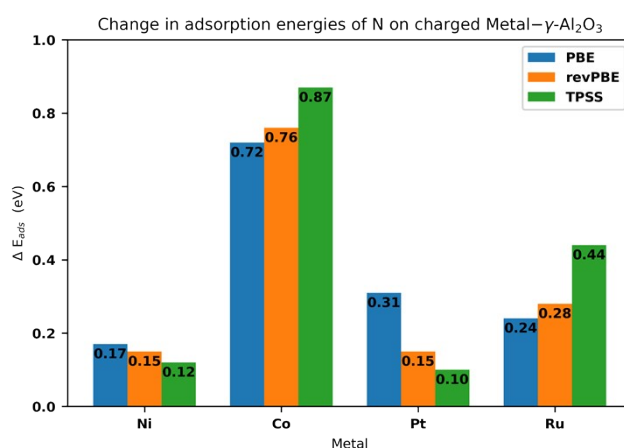


Figure S1 Change in adsorption energy of N-atom on a M-Al₂O₃ system due to surface charge calculated using different functionals.

also use revPBE, which is supposed to perform better than the PBE functional, and TPSS, which is one rung higher on the Jacob's ladder² to calculate the effect of surface charge. Figure S2 shows the effect of surface charge on adsorption energy of N-atom on a M-Al₂O₃ system calculated using PBE, revPBE, and TPSS functionals. These results validate the trends presented in the main manuscript using the PBE functional. However, the calculations with higher level of theory also indicate that the magnitude of change in adsorption energy predicted by the PBE functional could change by up to 0.2 eV. However, considering the number of calculations performed in this work, we perform our calculations using PBE functional as described in S1 to limit the computational expense.

S2. Gibbs free energy calculations

We also calculated Gibbs free energies for all the adsorbate systems following the work of Martinez and Carter.³ The Gibbs free energy for the adsorbate systems is determined using the following expression:

$$G_{slab+ads}(T) = E_{slab+ads}^{DFT} + A_{slab+ads}^{vib}(T)$$

Where, $A_{slab+ads}^{vib}(T)$ is determined by

$$A_{slab+ads}^{vib}(T) = \sum_{3N}^j \left[\frac{h\nu_j}{2} + k_B T \ln \left(1 - e^{-h\nu_j/k_B T} \right) \right]$$

Here, ν_j represents different vibrational modes calculated using the DFT calculations. h is Planck's constant and k_B is Boltzmann's constant. The values for the free energy of gas-phase species are retrieved from NIST database (<https://janaf.nist.gov>).

Following tables list the adsorption free energies of different species at different temperatures.

Table S2 Adsorption free energy of N on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-3.36	-3.53	-3.51	-4.23	-6.04	-6.28	-3.91	-4.07	-3.81	-4.45
300	-2.87	-3.04	-2.99	-3.79	-5.54	-5.78	-3.40	-3.57	-3.25	-3.92
400	-2.76	-2.92	-2.87	-3.70	-5.44	-5.67	-3.29	-3.47	-3.10	-3.78
500	-2.66	-2.81	-2.75	-3.61	-5.34	-5.56	-3.18	-3.37	-2.95	-3.64
600	-2.55	-2.69	-2.62	-3.52	-5.24	-5.45	-3.07	-3.26	-2.80	-3.50
700	-2.44	-2.56	-2.49	-3.44	-5.13	-5.34	-2.97	-3.16	-2.64	-3.35
800	-2.33	-2.44	-2.36	-3.35	-5.03	-5.23	-2.86	-3.05	-2.48	-3.20

Table S3 Adsorption free energy of H on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-3.71	-4.37	-3.93	-4.25	-4.17	-4.29	-4.18	-4.69	-4.09	-4.28
300	-3.23	-3.86	-3.37	-3.71	-4.08	-3.72	-3.60	-4.11	-3.58	-3.74
400	-3.14	-3.77	-3.26	-3.61	-3.90	-3.60	-3.51	-4.02	-3.49	-3.65
500	-3.05	-3.67	-3.14	-3.50	-3.69	-3.48	-3.41	-3.92	-3.39	-3.55
600	-2.95	-3.56	-3.02	-3.39	-3.45	-3.36	-3.32	-3.83	-3.30	-3.45
700	-2.85	-3.46	-2.90	-3.27	-3.19	-3.24	-3.22	-3.73	-3.20	-3.35

800	-2.75	-3.35	-2.77	-3.15	-2.91	-3.12	-3.12	-3.64	-3.11	-3.25
-----	-------	-------	-------	-------	-------	-------	-------	-------	-------	-------

Table S4 Adsorption free energy of N₂ on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-0.84	-2.07	-0.83	-2.13	-1.93	-2.18	-2.60	-2.07	-0.12	-1.35
300	0.04	-1.21	-0.02	-1.28	-1.14	-1.43	-1.72	-1.18	0.69	-0.54
400	0.15	-1.10	0.09	-1.17	-1.06	-1.33	-1.62	-1.07	0.82	-0.43
500	0.26	-0.99	0.21	-1.06	-0.97	-1.23	-1.52	-0.96	0.96	-0.32
600	0.38	-0.87	0.33	-0.94	-0.89	-1.13	-1.41	-0.85	1.11	-0.20
700	0.50	-0.75	0.46	-0.83	-0.80	-1.03	-1.30	-0.74	1.25	-0.08
800	0.61	-0.64	0.59	-0.72	-0.72	-0.92	-1.20	-0.63	1.41	0.04

Table S5 Adsorption free energy of H₂ on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-0.84	-2.07	-0.83	-2.13	-1.93	-2.18	-2.60	-2.07	-0.12	-1.35
300	-0.52	-1.76	-0.58	-1.83	-1.70	-1.98	-2.28	-1.73	0.14	-1.10
400	-0.51	-1.76	-0.57	-1.83	-1.72	-1.99	-2.28	-1.73	0.16	-1.09
500	-0.52	-1.76	-0.57	-1.84	-1.75	-2.01	-2.29	-1.74	0.18	-1.10
600	-0.52	-1.77	-0.57	-1.85	-1.79	-2.03	-2.31	-1.75	0.20	-1.10
700	-0.53	-1.78	-0.57	-1.86	-1.83	-2.06	-2.33	-1.77	0.22	-1.11
800	-0.55	-1.80	-0.58	-1.88	-1.88	-2.08	-2.36	-1.79	0.24	-1.13

Table S6 Adsorption free energy of NH on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-4.06	-4.86	-4.06	-5.13	-4.83	-5.38	-3.58	-3.59	-3.53	-4.29
300	-3.34	-4.11	-3.36	-4.38	-4.12	-4.61	-2.80	-2.82	-2.82	-4.33
400	-3.27	-4.02	-3.29	-4.29	-4.04	-4.53	-2.71	-2.74	-2.74	-4.09
500	-3.19	-3.94	-3.22	-4.20	-3.96	-4.44	-2.61	-2.66	-2.66	-3.81
600	-3.12	-3.86	-3.16	-4.10	-3.88	-4.36	-2.51	-2.57	-2.57	-3.50
700	-3.05	-3.78	-3.09	-4.01	-3.80	-4.28	-2.41	-2.49	-2.49	-3.15
800	-2.98	-3.70	-3.03	-3.92	-3.71	-4.19	-2.30	-2.41	-2.40	-2.77

Table S7 Adsorption free energy of NH₂ on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-4.02	-4.40	-0.48	-1.15	-3.84	-3.90	-3.39	-0.96	-3.70	-1.29
300	-2.90	-3.31	0.29	-0.35	-2.81	-2.85	-2.58	-0.15	-2.96	-1.32
400	-2.82	-3.24	0.34	-0.29	-2.74	-2.77	-2.53	-0.09	-2.91	-1.09
500	-2.73	-3.16	0.38	-0.23	-2.67	-2.69	-2.49	-0.04	-2.86	-0.81
600	-2.65	-3.09	0.42	-0.18	-2.60	-2.61	-2.45	0.01	-2.82	-0.50
700	-2.57	-3.02	0.46	-0.13	-2.53	-2.54	-2.42	0.06	-2.78	-0.15
800	-2.50	-2.95	0.49	-0.08	-2.46	-2.46	-2.39	0.10	-2.74	0.23

Table S8 Adsorption free energy of NH₃ on M-Al₂O₃ system (M stands for different transition metal atoms).

Temperature (K)	Ni		Co		Ru		Pt		Fe	
	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged	Neutral	Charged
0	-1.70	-1.34	-1.83	-1.39	-1.98	-1.53	-2.74	-2.36	-1.85	-1.40
300	-0.29	0.05	-0.42	0.00	-0.55	-0.11	-1.30	-0.93	-0.49	-0.06
400	-0.22	0.11	-0.34	0.07	-0.46	-0.04	-1.23	-0.86	-0.44	-0.01
500	-0.14	0.17	-0.26	0.14	-0.37	0.03	-1.16	-0.79	-0.39	0.04
600	-0.07	0.22	-0.19	0.21	-0.28	0.10	-1.10	-0.73	-0.35	0.08
700	0.00	0.27	-0.12	0.27	-0.19	0.16	-1.04	-0.67	-0.31	0.12
800	0.06	0.32	-0.05	0.34	-0.10	0.22	-0.99	-0.61	-0.27	0.15

S3. Effect of countercharge location on calculations

The location of countercharge could potentially affect the surface charging. Bal et. al.⁴ reported the effect of Z-position of the countercharge on surface charging. If the countercharge is placed very close to the catalyst surface, the electric field generated due to charge-countercharge system would start strongly affecting the energetics of the surface reactions. Bal et. al.⁴ indicated that a Z-distance of more than 30 Angstrom is enough to isolate this effect. That is, the charge-countercharge interactions become negligible if the countercharge is placed at a Z-height of more than 30 Angstrom. As we are using an equivalent system, we did not repeat those calculations. Additionally, we put countercharge at Z-location of 40 Angstrom to further minimize this effect. Bal et al.⁴ did not consider the effect of changing the countercharge positions in the XY plane. Considering the symmetry of the slab, the XY position of the charge could also affect the reaction energetics upon the introduction of the countercharge. We calculated the energy of the Ru- γ -Al₂O₃ surface with 3 different countercharge XY locations as shown in Table 1. The calculations clearly show that the effect of XY location of the countercharge is negligible.

Table S9 Effect of XY location of the countercharge on system energy.

Position	1	2	3
x-coordinate of countercharge	5.25	10.25	7.25
y-coordinate of countercharge	10.60	5.60	7.60
z-coordinate of countercharge	40	40	40
System energy (a.u.)	-2615.778	-2615.778	-2615.773

S4. Geometry parameters

○ Geometry parameters for metal atom adsorption

Table S10 Distances and angles for metal atoms on neutral surface

Metal	Ni	Co	Ru	Pt	Fe
M-O1 (Angstrom)	1.81	1.80	1.98	2.04	1.81
M-O2 (Angstrom)	1.82	1.83	2.13	2.03	1.85
O1-M-O2 (°)	125.44	135.19	94.66	155.43	128.89

Table S11 Distances and angles for metal atoms on charged surface

Metal	Ni	Co	Ru	Pt	Fe
M-O1 (Angstrom)	1.81	1.79	1.99	2.04	1.80
M-O2 (Angstrom)	1.82	1.82	2.16	2.03	1.83
O1-M-O2 (°)	143.63	141.90	94.73	154.56	137.70

○ Geometry parameters for N* adsorption

Table S12 Distance between N* and metal atom on a neutral surface

Metal	Ni	Co	Ru	Pt	Fe
M-N*	1.70	1.56	1.60	1.75	1.51

(Angstrom)					
------------	--	--	--	--	--

Table S13 Distance between N* and metal atom on a charged surface

Metal	Ni	Co	Ru	Pt	Fe
M-N* (Angstrom)	1.64	1.59	1.63	1.75	1.55

○ **Geometry parameters for N₂* adsorption**

Table S14 Distance between N₂* and metal atom on a neutral surface

Metal	Ni	Co	Ru	Pt	Fe
M-N ₂ (Angstrom)	1.90	1.74	1.86	1.86	1.76
N-N (Angstrom)	1.17	1.15	1.15	1.14	1.15
M-N-N (degrees)	72.58	178.92	178.67	179.54	178.10

Table S15 Distance between N₂* and metal atom on a charged surface

Metal	Ni	Co	Ru	Pt	Fe
M-N ₂ (Angstrom)	1.69	1.70	1.83	1.84	1.76
N-N (Angstrom)	1.16	1.16	1.16	1.14	1.17
M-N-N (degrees)	173.29	175.37	173.61	177.55	175.86

○ **Geometry parameters for H* adsorption**

Table S16 Distances and angles for H* and metal atoms on neutral surface

Metal	Ni	Co	Ru	Pt	Fe
M-O1 (Angstrom)	1.98	1.94	1.96	2.24	1.90
M-O2 (Angstrom)	1.91	1.91	2.12	2.09	1.90
O1-M-O2 (°)	98.05	98.98	90.40	88.42	101.23
M-H* (Angstrom)	1.56	1.60	1.64	1.58	1.66

Table S17 Distances and angles for H* and metal atoms on charged surface

Metal	Ni	Co	Ru	Pt	Fe
M-O1 (Angstrom)	2.02	1.99	1.98	3.05	1.94
M-O2 (Angstrom)	1.91	1.91	2.14	2.21	1.91
O1-M-O2 (°)	98.04	99.16	90.72	66.90	100.47
M-H* (Angstrom)	1.56	1.59	1.65	1.55	1.65

○ **Geometry parameters for NH* adsorption**

Table S18 Distance between NH and metal atom on a neutral surface*

Metal	Ni	Co	Ru	Pt	Fe
M-N (Angstrom)	1.78	1.75	1.70	1.82	1.62
N-H (Angstrom)	1.02	1.02	1.03	1.05	1.03
M-N-H (degrees)	127.39	127.55	143.41	105.62	159.92

Table S19 Distance between NH and metal atom on a charged surface*

Metal	Ni	Co	Ru	Pt	Fe
M-N (Angstrom)	1.78	1.80	1.71	1.83	1.69
N-H (Angstrom)	1.02	1.02	1.03	1.05	1.03
M-N-H (degrees)	125.99	127.55	148.33	103.76	129.52

○ **Geometry parameters for NH₂* adsorption**

Table S20 Distance between NH₂ and metal atom on a neutral surface*

Metal	Ni	Co	Ru	Pt	Fe
M-N (Angstrom)	1.91	1.80	1.88	1.89	1.95
N- H1(Angstrom)	1.02	1.02	1.02	1.02	1.03
N- H2(Angstrom)	1.02	1.02	1.02	1.03	1.02
M-N-H1 (degrees)	121.81	124.60	124.06	118.51	126.37
M-N-H2 (degrees)	108.35	125.34	125.14	125.53	111.56
H-N-H (degrees)	108.13	109.89	110.30	115.54	108.02

Table S21 Distance between NH₂ and metal atom on a charged surface*

Metal	Ni	Co	Ru	Pt	Fe
M-N (Angstrom)	1.91	1.58	1.90	1.92	1.87
N-H1 (Angstrom)	1.02	2.89	1.02	1.02	1.02
N-H2 (Angstrom)	1.02	3.05	1.02	1.02	1.02

M-N-H1 (degrees)	123.67	81.60	123.25	118.55	112.98
M-N-H2 (degrees)	109.82	87.34	122.99	121.56	115.76
H-N-H (degrees)	109.15	14.25	109.94	111.09	105.74

○ **Geometry parameters for NH₃* adsorption**

Table S22 Distance between NH₃ and metal atom on a neutral surface*

Metal	Ni	Co	Ru	Pt	Fe
M-N (Angstrom)	1.98	1.99	2.13	2.04	2.04
N- H1(Angstrom)	1.02	1.05	1.02	1.05	1.05
N- H2(Angstrom)	1.02	1.03	1.03	1.02	1.03
N- H3(Angstrom)	1.04	1.03	1.05	1.03	1.03
M-N-H1 (degrees)	116.72	111.47	117.35	103.22	108.48
M-N-H2 (degrees)	113.93	113.28	113.12	113.39	115.66
M-N-H3 (degrees)	104.74	113.01	104.82	114.84	113.00
H1-N-H3 (degrees)	106.26	106.86	106.55	109.94	107.11
H2-N-H3 (degrees)	107.63	105.04	107.92	106.59	105.29
H3-N-H1 (degrees)	107.04	106.61	106.50	108.48	106.66

Table S23 Distance between NH₃ and metal atom on a charged surface*

Metal	Ni	Co	Ru	Pt	Fe
M-N (Angstrom)	1.99	1.99	2.14	2.04	2.04
N-H1 (Angstrom)	1.02	1.06	1.02	1.06	1.06
N-H2 (Angstrom)	1.02	1.02	1.02	1.02	1.03
N-H3 (Angstrom)	1.06	1.02	1.06	1.03	1.02
M-N- H1(degrees)	115.46	111.80	116.61	102.40	109.04
M-N- H2(degrees)	115.66	113.91	114.29	115.17	116.73
M-N-	104.81	112.95	104.52	114.23	112.37

H3(degrees)					
M-N-H1 (degrees)	106.76	106.09	107.14	110.05	106.32
M-N-H2 (degrees)	106.81	103.82	107.52	104.39	103.85
M-N-H3 (degrees)	106.66	107.54	106.03	109.75	107.60

S5. Partial atomic charges

○ Partial atomic charges for metal atom adsorption

Table S24 Change in metal atom partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
Partial Charge(charged) - Partial Charge(neutral)	-0.26	-0.19	-0.32	-0.06	-0.11

○ Partial atomic charges for N* adsorption

Table S25 Change in partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
M	-0.24	-0.04	-0.20	-0.02	-0.05
N	0.02	0.01	-0.16	-0.11	-0.23

○ Partial atomic charges for N₂* adsorption

Table S26 Change in partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
M	-0.12	-0.12	-0.25	-0.03	0.01
N1	-0.01	-0.01	-0.01	-0.03	-0.08
N2	-0.18	-0.12	-0.12	-0.06	-0.13

○ Partial atomic charges for H* adsorption

Table S27 Change in partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
M	-0.18	-0.21	-0.31	-0.36	-0.18
H	0.34	-0.05	0.10	0.68	-0.25

○ Partial atomic charges for NH* adsorption

Table S28 Change in partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
M	-0.03	-0.04	-0.22	-0.01	0.02

N	-0.06	-0.15	-0.06	-0.09	-0.18
H	-0.02	-0.03	-0.04	-0.04	-0.03

○ **Partial atomic charges for NH₂* adsorption**

Table S29 Change in partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
M	-0.05	-0.05	-0.22	-0.02	-0.14
N	-0.03	-0.22	-0.06	-0.11	-0.14
H1	-0.01	-0.01	-0.03	-0.01	-0.02
H2	-0.02	-0.01	-0.04	-0.01	0.01

○ **Partial atomic charges for NH₃* adsorption**

Table S30 Change in partial charge as per Mulliken charge calculation scheme

Metal	Ni	Co	Ru	Pt	Fe
M	-0.04	-0.07	-0.23	-0.06	-0.06
N	-0.03	-0.02	-0.02	-0.03	-0.02
H1	-0.02	0.00	-0.02	0.00	0.00
H2	-0.02	-0.02	-0.03	-0.02	-0.02
H3	0.00	-0.01	0.00	-0.01	-0.01

S6. Adsorption sites on γ -Al₂O₃ (110)

The adsorption energy of an adsorbate is strongly dependent on the adsorption site. The fig. S3 shows 7 different adsorption sites explored on the γ -Al₂O₃ (110). These adsorption sites include 2 or 3 coordinated O atoms and 3 or 4 coordinated Al atoms. N and N₂ atom adsorption energies were calculated for all these adsorption sites (see table S3). The optimal metal atom adsorption sites were taken from the literature⁴ to avoid additional computations. The adsorption energies from the most stable adsorption site are listed in table S3.

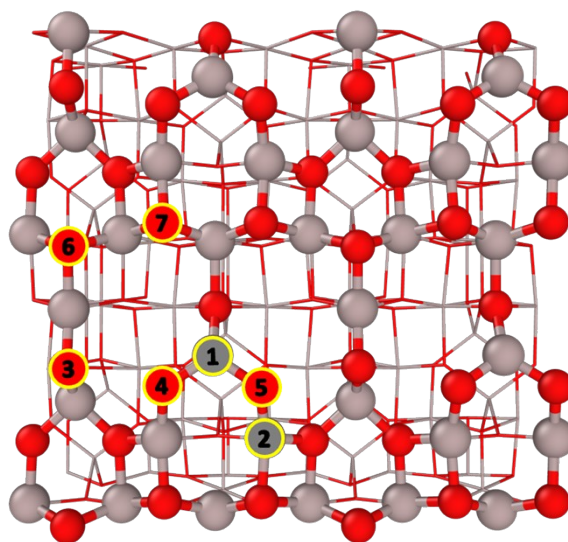


Figure S2 Different adsorption sites explored on a $\gamma\text{-Al}_2\text{O}_3$ 110 surface.

Table S31 Adsorption energies of N and N_2 at different adsorption sites on $\gamma\text{-Al}_2\text{O}_3$ with highest adsorption energies for all cases highlighted in bold.

Adsorption site	1	2	3	4	5	6	7
N-Al_2O_3 neutral	-1.48	-0.81	-1.69	-0.85	-0.58	-0.75	-1.76
N-Al_2O_3 charged	-1.26	-0.94	-1.34	-1.19	-0.15	-0.94	-1.34
N_2-Al_2O_3 neutral	-0.63	-0.31	-0.08	-0.27	-0.27	-0.35	-0.26
N_2-Al_2O_3 charged	-0.48	-0.22	-0.03	-0.25	-0.25	-0.28	-0.22

S7. PDOS for metal atom and surface oxygen

As pointed out in Bal et al. ⁴, metal adsorption on $\gamma\text{-Al}_2\text{O}_3$ support is a redox reaction. Hence, an additional surface electron prevents further reduction of the support through adsorption. Therefore, the metal atom adsorption energy reduces on surface charging. One of the indicators for this hypothesis is that metal-support bonding is mostly ionic in nature. Bal et al. used lack of overlap between the PDOS of metal atoms and the support oxygen to support this hypothesis. Our calculations show (see Fig. S6) that it might not be the case for all the metal atoms. For example, Fe PDOS shows a relatively larger overlap with surface O-atom PDOS. This could result in a metal-surface binding that is not completely ionic in nature. Although all the metal adsorption energies reduce upon surface charging, the metal-surface atom interaction is dependent on the metal atom involved. The difference in this interaction perhaps extends to different adsorbates showing different changes to the adsorption energy on these metal atoms.

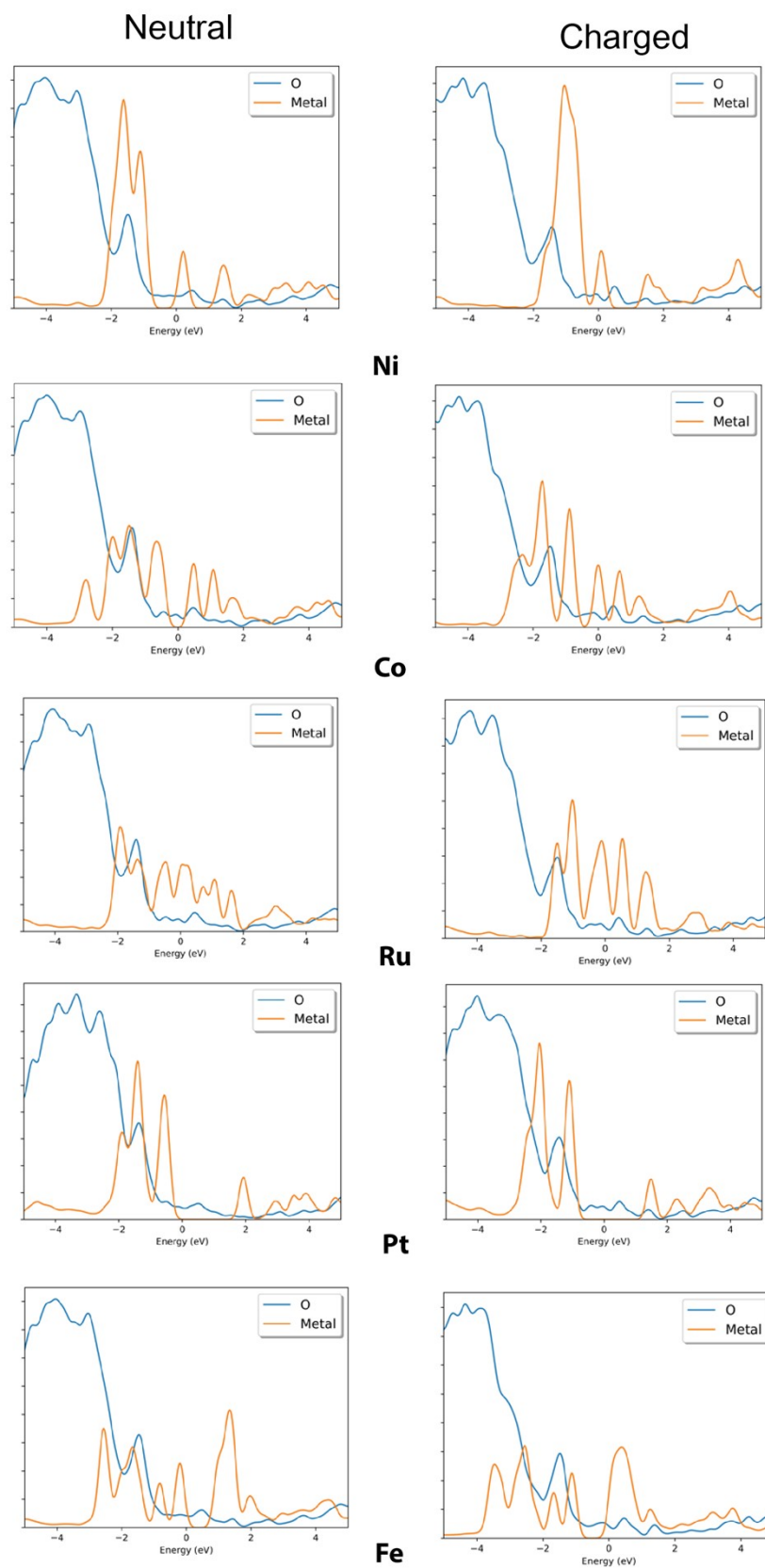


Figure S3 PDOS of adsorbed metal atom and O-atom on the surface.

S8. H, H₂, NH, NH₂ adsorption

H, H₂, NH, NH₂ shows similar adsorption energy trends as compared to N and N₂. Their adsorption energy increases with the addition of surface charge with the exception of H₂ on charged Pt. Similar to N and N₂, the effect of surface charge on adsorption energy varies depending on the metal atom without any clear trend.

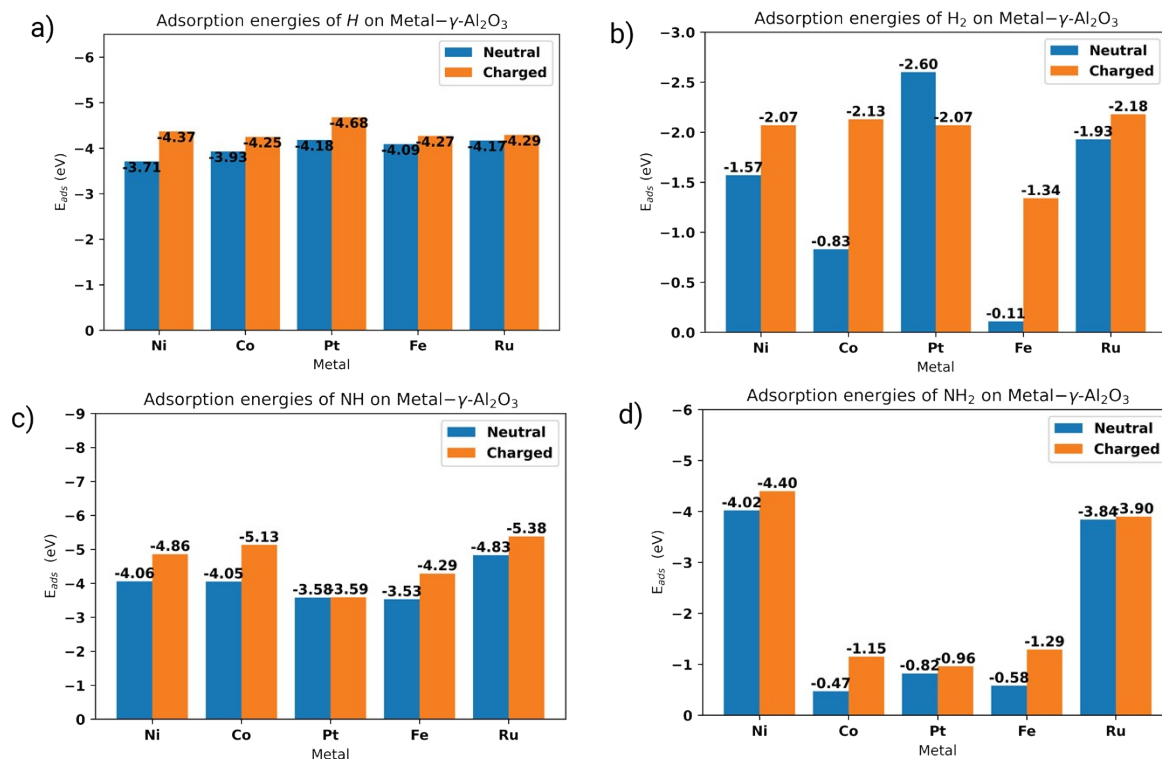


Figure S4 a) H, b) H₂, c) NH, and d) NH₂ adsorption energies on neutral (blue bars) and charged (orange bars) M-Al₂O₃. Metal indicates different single metal atoms as specified on the x-axis.

S9. Adsorption sites explored on Ru cluster

Figure S8 shows different adsorption sites explored on the Ru 18-atom cluster. In the case of N-atom adsorption, site 1 was preferred for neutral case, whereas site 4 was optimal in the case of surface charging.

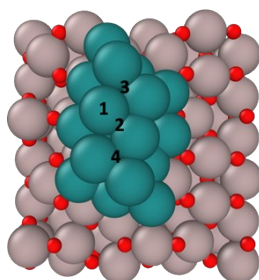


Figure S5 Different adsorption sites explored on the Ru-18 cluster.

S10. Scaling relations changes

Figure S9 shows NH, NH₂ and NH₃ adsorption energies as a function of E_{ads-N} for charged and neutral surfaces. As mentioned in the main text, we do not observe a linear relationship between different adsorption energies and E_{ads-N} for the neutral surfaces as these calculations are performed on a single metal atom catalyst. However, the overall trend changes upon surface charging.

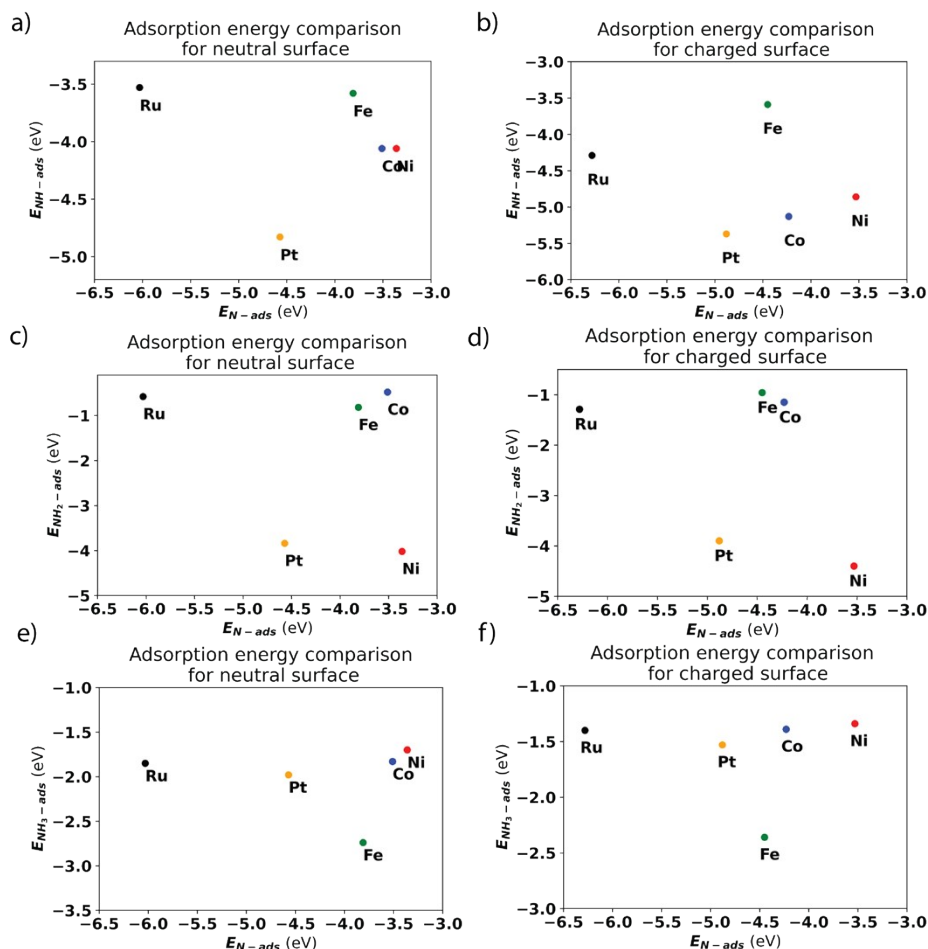


Figure S6 Relationship between different adsorption energies and N-adsorption energy with and without surface charging.

S11. Effect of adsorbates on metal cluster adsorption

The substrate could play an important role in the adsorption of these species. We performed a comparative analysis to calculate adsorption energies of N, N₂, and NH₃ on pure Ru cluster. The table below shows the results of our comparison. The differences in adsorption energies range from ~0.1-0.7 eV.

Table S32 Comparison of adsorption energies of N, N₂ and NH₃ on pure Ru_{cluster} and Ru_{cluster}- γ -Al₂O₃.

System	E _{ads,N}	E _{ads,N2}	E _{ads,NH3}
Ru _{cluster} - γ -Al ₂ O ₃ (Neutral)	-6.16	-0.87	-1.08
Ru _{cluster} - γ -Al ₂ O ₃ (Charged)	-6.56	-1.20	-0.54
Ru _{cluster} (Neutral)	-5.74	-1.06	-0.82

Ru_{cluster} (Charged)	-5.98	-1.82	-0.75
---------------------------------	-------	-------	-------

References

- (1) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys Rev Lett* **1996**, *77* (18), 3865–3868. <https://doi.org/10.1103/PhysRevLett.77.3865>.
- (2) Perdew; Schmidt, K. Jacob ' s Ladder of Density Functional Approximations for the Exchange-Correlation Energy Jacob ' s Ladder of Density Functional Approximations for the Exchange-Correlation Energy. *AIP Conf. Proc.* **2011**, *1* (May), 577.
- (3) Martirez, J. M. P.; Carter, E. A. First-Principles Insights into the Thermocatalytic Cracking of Ammonia-Hydrogen Blends on Fe(110): 1. Thermodynamics. *Journal of Physical Chemistry C* **2022**, *126* (46), 19733–19744. <https://doi.org/10.1021/acs.jpcc.2c06003>.
- (4) Bal, K. M.; Huygh, S.; Bogaerts, A.; Neyts, E. C. Effect of Plasma-Induced Surface Charging on Catalytic Processes: Application to CO₂ Activation. *Plasma Sources Sci Technol* **2018**, *27* (2). <https://doi.org/10.1088/1361-6595/aaa868>.