

# Self-limiting Nitrogen/Hydrogen Plasma Radical Chemistry in Plasma-Enhanced Atomic Layer Deposition of Cobalt

Ji Liu<sup>a</sup>, Hongliang Lu<sup>b</sup>, David Wei Zhang<sup>b</sup>, and Michael Nolan<sup>a,\*</sup>

<sup>a</sup> Tyndall National Institute, University College Cork, Lee Maltings, Dyke Parade, Cork, T12 R5CP, Ireland

<sup>b</sup> State Key Laboratory of ASIC and System, Shanghai Institute of Intelligent Electronics & Systems, School of Microelectronics, Fudan University, Shanghai 200433, China

[Corresponding author:](#)

[\\*E-mail: Michael.nolan@tyndall.ie](mailto:Michael.nolan@tyndall.ie). Tel: +353 021 2346983

## Contents

A. Reactions of one plasma radical with low coverage of one CoCp fragment on NH <sub>x</sub> -terminated Co(001) surface.....	S2
1. Elimination of Cp ligand via CpH formation and desorption.....	S3
2. Elimination of Cp ligand via pyridine formation and desorption.....	S4
3. Elimination of surface NH <sub>x</sub> species with the presence of Cp ligand.....	S5
4. Elimination of surface NH <sub>x</sub> species with initial Cp ligand removal.....	S8
B. Reactions of plasma radicals with highest coverage of three CoCp fragments on NH <sub>x</sub> -terminated Co(001) surface.....	S11

A. *Reactions of one plasma radical with one CoCp fragment on NH<sub>x</sub>-terminated Co(001) surface*

As a starting point, to assess the chemistry of the possible radicals from the plasma, we have performed static DFT relaxations of a single plasma radical, that being  $\cdot\text{H}$ ,  $\cdot\text{N}$ ,  $\cdot\text{NH}$ , or  $\cdot\text{NH}_2$ , which reacts with the Co(001) surface terminated with one CoCp fragment.<sup>1</sup> These results are summarized in Table S1.

The reaction energies are calculated by

$$\Delta E = E_{total} - E_{sub} - E_{plasma} \quad (\text{S1})$$

where  $E_{total}$  is the energy of the CoCp-NH<sub>x</sub>-terminated Co surface after introducing the plasma radicals.  $E_{sub}$  represents the energy of the CoCp-NH<sub>x</sub>-terminated Co surface.  $E_{plasma}$  is the energy of the plasma generated radicals  $\cdot\text{H}$ ,  $\cdot\text{N}$ ,  $\cdot\text{NH}$ , and  $\cdot\text{NH}_2$ . In this study,  $\cdot\text{H}$  and  $\cdot\text{N}$  radicals are referenced to half of H<sub>2</sub> and N<sub>2</sub> while  $\cdot\text{NH}$  or  $\cdot\text{NH}_2$  radicals are referenced to  $\frac{1}{2}(\text{N}_2+\text{H}_2)$  or  $(\frac{1}{2}\text{N}_2 + \text{H}_2)$ , respectively, which is consistent with our previous thermodynamic study of NH<sub>x</sub>-terminations.<sup>2</sup>

Table S1. Summary of reactions of surface species, *i.e.* Cp ligand and NH<sub>x</sub> species, and a single plasma radical, that being  $\cdot\text{H}$ ,  $\cdot\text{N}$ ,  $\cdot\text{NH}$ , or  $\cdot\text{NH}_2$  on one CoCp fragment terminated Co(001) surface. The by-products are formed spontaneously after structure relaxing.

Surface species	Plasma radicals	by-product	Energy change upon by-product formation/eV	desorption energy/eV
Cp	$\cdot\text{H}$	CpH (C <sub>5</sub> H <sub>6</sub> )	1.93	2.77
	$\cdot\text{N}$	Pyridine (C <sub>5</sub> H <sub>5</sub> N)	-0.07	2.39
	$\cdot\text{NH}$	Pyridinium (C <sub>5</sub> H <sub>5</sub> NH)	0.23	2.77
NH	$\cdot\text{H}$	NH <sub>2</sub>	1.21	-
NH <sub>2</sub>	$\cdot\text{H}$	NH <sub>3</sub>	-0.51	0.80

## 1. Elimination of Cp ligand via CpH formation and desorption

To investigate the formation of CpH from a single bound CoCp on the Co(001) surface, one hydrogen radical is placed near Cp, with an initial C-H distance of 1.90Å. The initial structure and the relaxed stable structure are shown in Figure S1. After relaxing, CpH is formed spontaneously, with a computed positive reaction energy of 1.93eV using equation (S1) and C-H bond distance of 1.1Å. The computed energy cost of removing the CpH, resulting one Co atom deposited on the Co(001) surface, is 2.77eV. After this, the Co-N distance on the surface is 1.73Å, which is slightly shortened compared to surface-terminated CoCp with Co-N distance at 1.74Å. The removal of Cp ligand for one CoCp fragment on Co(001) surface via CpH formation and desorption is overall endothermic with an energy cost of 4.70eV, so this pathway is not a favourable pathway for eliminating Cp ligand at plasma cycle and we therefore do not expect release of CpH during the plasma half reaction.

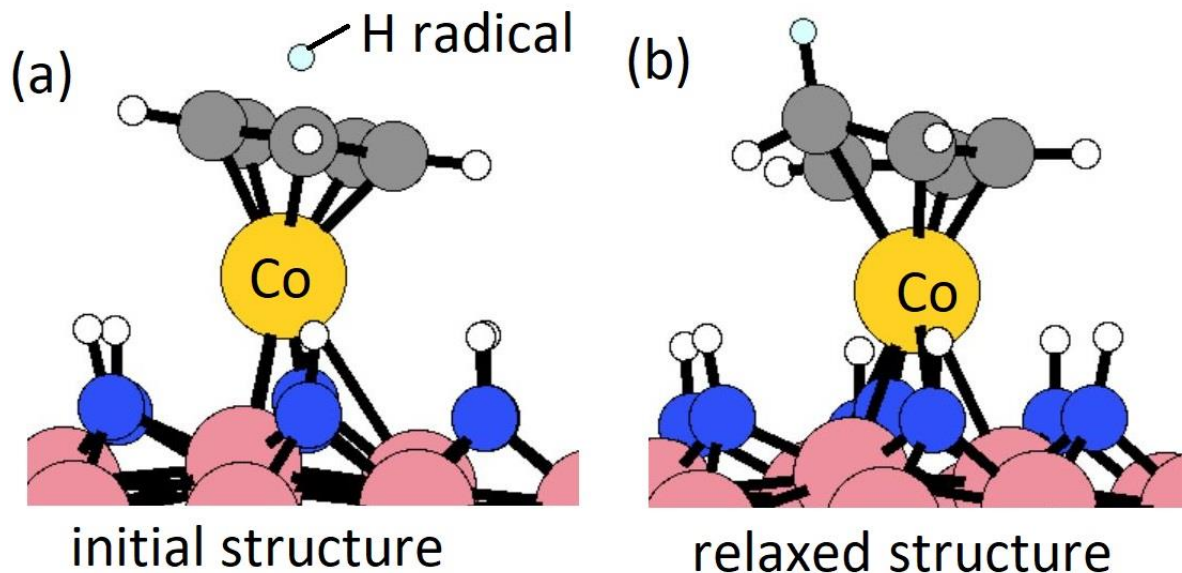


Figure S1. The configurations of one hydrogen radical interacting with CoCp on the Co(001) surface. (a) initial structure, and (b) stable structure after relaxing. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. H radical is represented by light blue sphere. Substrate Co and Co from CoCp<sub>2</sub> are represented by orange and yellow spheres, respectively.

## 2. Elimination of Cp ligand via pyridine formation and desorption

An alternative chemistry is that  $\cdot\text{N}$  or  $\cdot\text{NH}$  radicals can react with a Cp ligand and insert into a C=C bond to form pyridine ( $\text{C}_5\text{H}_4\text{N}$ ) or the pyridinium cation ( $\text{C}_5\text{H}_5\text{NH}$ ). The configurations of relaxed structures after inserting single  $\cdot\text{N}$  or  $\cdot\text{NH}$  radical into a C=C bond of the Cp ligand are shown in Figure S2; the computed reaction energies in these cases are  $-0.07\text{eV}$  for pyridine and  $0.23\text{eV}$  for pyridinium. The computed energy cost of removing pyridine or pyridinium, resulting one Co atom deposited on the surface, are  $2.39\text{eV}$  and  $2.77\text{eV}$ , respectively. Pyridine has overall less positive reaction energies and is less endothermic than pyridinium and CpH, so we could expect pyridine as the primary elimination product during the plasma cycle.

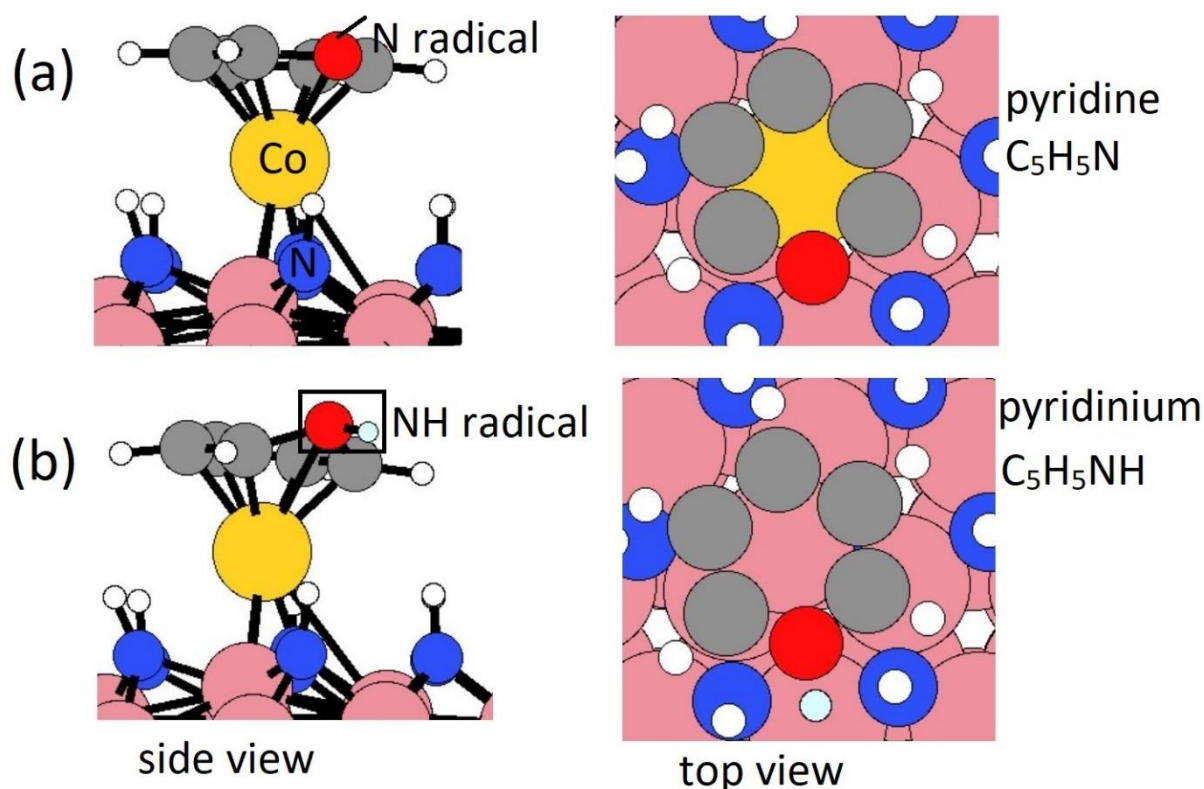


Figure S2. The top view and side view of pyridine formed from the interaction of CoCp with (a) N radical, and (b) NH radical. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. NH radicals are represented by light blue sphere for H radical and red sphere for N radical. Substrate Co and Co from CoCp<sub>2</sub> are represented by orange and yellow spheres, respectively.

### 3. Elimination of surface NH<sub>x</sub> species with the presence of Cp ligand

Turning now to the surface NH<sub>x</sub> species, these can be removed via successive hydrogenation NH → NH<sub>2</sub> → NH<sub>3</sub> with H radicals. We consider firstly that the Cp ligand is present throughout the process of elimination of surface NH species on the Co(001) surface terminated with a single CoCp fragment. The reaction energies along the elimination of NH<sub>x</sub> species are calculated by

$$\Delta E = E_{total} - E_{sub} - n * E_H + m * E_{NH3} \quad (2)$$

where  $E_{total}$  and  $E_{sub}$  are the energies of plasma H radical treated CoCp-NH<sub>x</sub>-terminated Co(001) surface and the single CoCp-NH<sub>x</sub>-terminated Co(001) surface, respectively.  $E_H$  is the energy of plasma generated H radical, which is referenced to half of H<sub>2</sub>.  $E_{NH3}$  is the energy of NH<sub>3</sub> that desorbs from metal surface. The number of H radicals and NH<sub>3</sub> are indicated by  $n$  and  $m$ , respectively.

One H radical is placed near one surface NH species with an initial N-H distance of 1.5Å, where the Cp ligand is present on the surface. The configurations of the initial and relaxed stable structures are shown in Figure S3. The intermediate NH<sub>2</sub> is formed spontaneously, with a positive reaction energy of 1.21eV and N-H bond distance of 1.0Å. We then add an additional H radical near this NH<sub>2</sub> species. After relaxing the structure, NH<sub>3</sub> is formed spontaneously, with an energy gain of -0.51eV and the computed energy cost of the NH<sub>3</sub> desorption is 0.80eV. The removal of first NH species on Co(001) surface with the presence of one CoCp fragment via NH<sub>3</sub> formation and desorption is overall endothermic with an energy cost of 1.50eV.

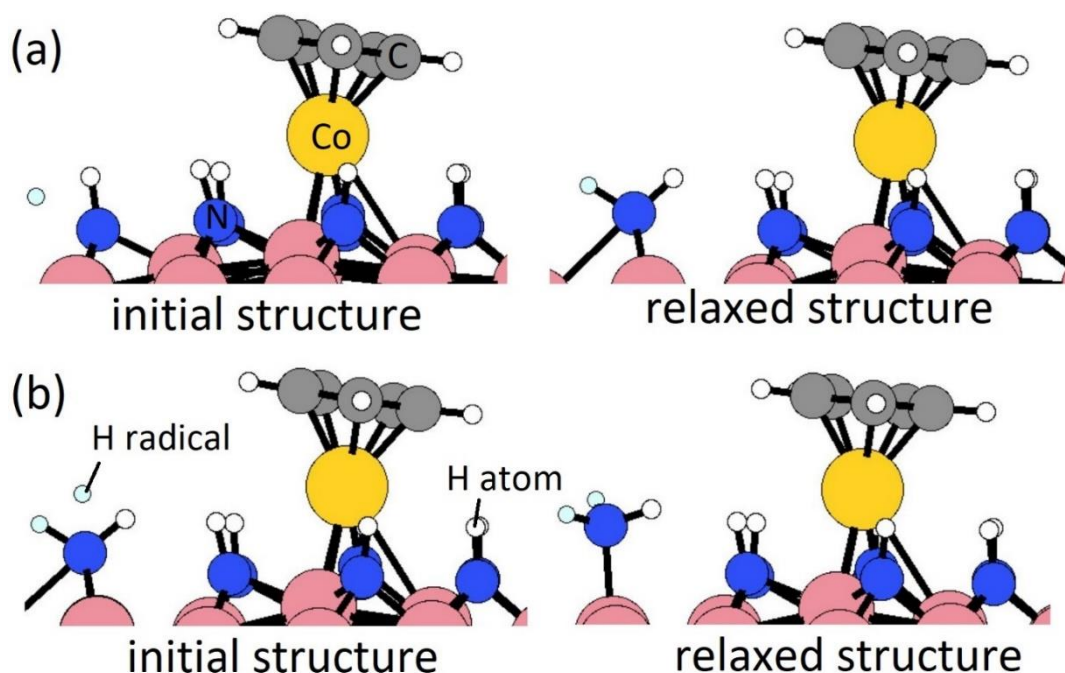


Figure S3. The configurations of initial structure and stable structure of H radical reacting with **(a)** surface NH species (to form  $\text{H}_2$ ), and **(b)** intermediate  $\text{NH}_2$  species (to form  $\text{NH}_3$ ). Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. H radical is represented by light blue sphere. Substrate Co and Co from  $\text{CoCp}_2$  are represented by orange and yellow spheres, respectively.

Figure S4 shows the reaction pathway for elimination of up to 4 NH surface species via  $\text{NH} \rightarrow \text{NH}_2 \rightarrow \text{NH}_3$  for the case in which the Cp ligand is present throughout. This pathway is overall endothermic. The computed reaction energies for intermediate  $\text{NH}_2$  formation, by-product  $\text{NH}_3$  formation and desorption are positive in the range of 0.06eV to 1.07eV, except for the 3<sup>rd</sup>  $\text{NH}_3$  formation, which has an exothermic energy at -0.19eV. The configurations of structures along the pathway are shown in Figure S5.

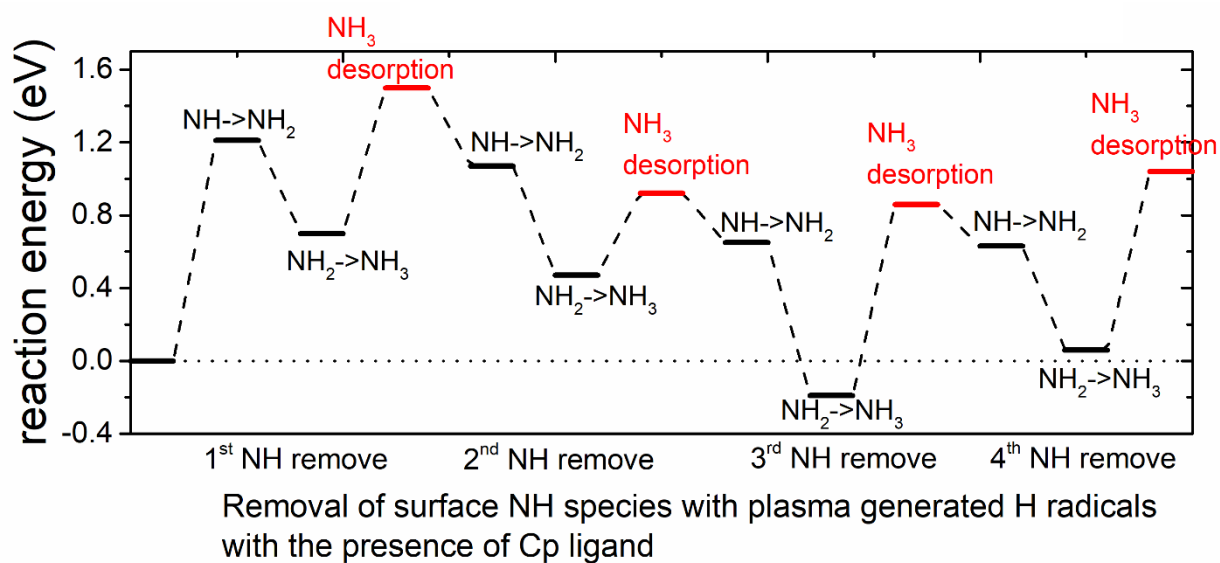


Figure S4. The plotted reaction pathway for removal of surface NH species with plasma generated H radicals with the presence of Cp ring on one CoCp-terminated Co(001) surface. The energy of Co(001) surface with  $\text{NH}_x$ -termination and one CoCp fragment is set to be the reference energy at 0eV.

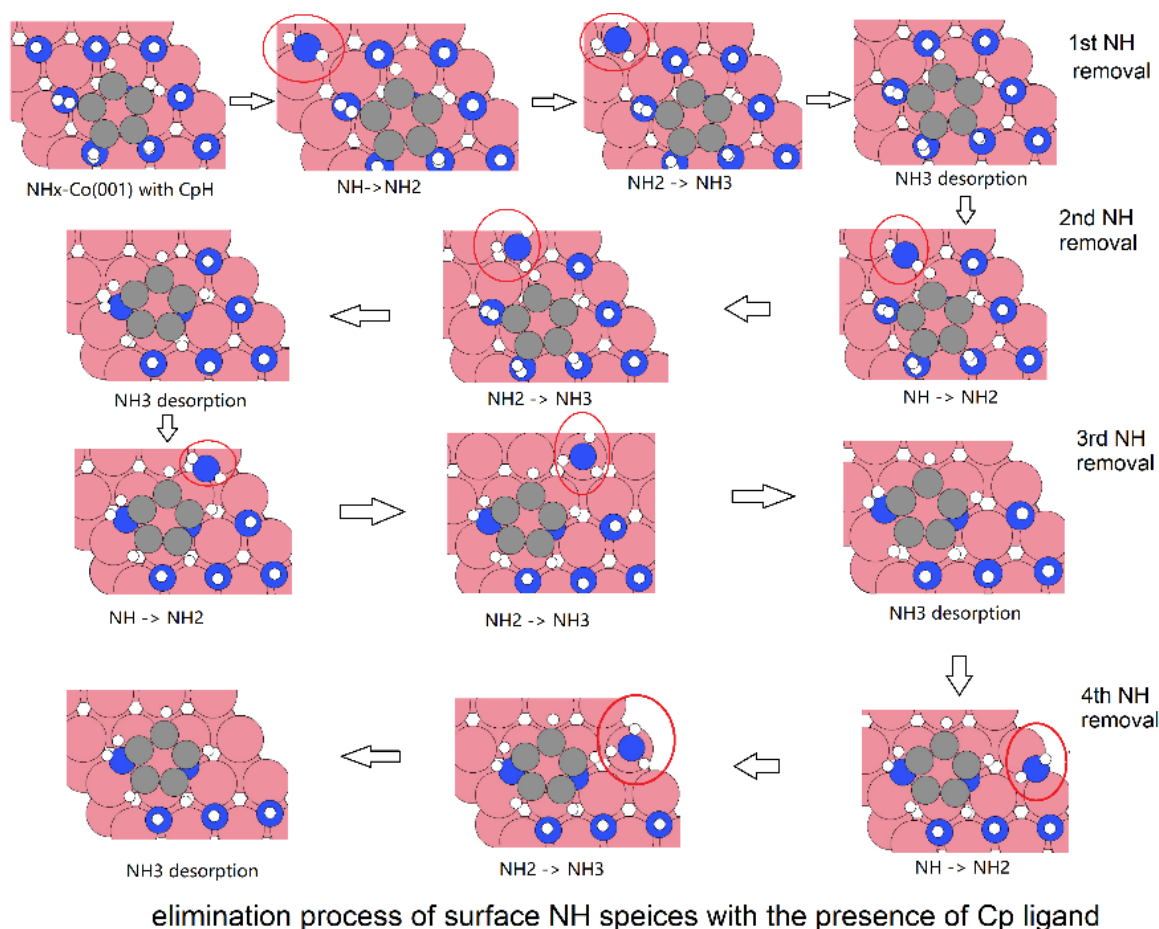


Figure S5. The configurations of structures along the pathway for elimination process of surface NH species with the presence of Cp ligand on Co(001) surface. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. Co atom is represented by orange sphere.

#### 4. Elimination of surface NH<sub>x</sub> species with initial Cp ligand removal

The alternative situation is that Cp is first eliminated as pyridine and in Figure S6, we show the reaction pathway for this case. Now the reactions of intermediate NH<sub>2</sub> formation and by-product NH<sub>3</sub> formation and desorption are overall exothermic, except for the initial removal of Cp ligand and NH<sub>3</sub> desorption. The computed energy cost of NH<sub>3</sub> desorption are in the range of -1.41eV to 1.86eV. The positive energy cost is still likely to be overcome by the energy available from plasma-generated excited ·H radicals at plasma operating condition. The configurations of structures along the pathway are shown in Figure S7.

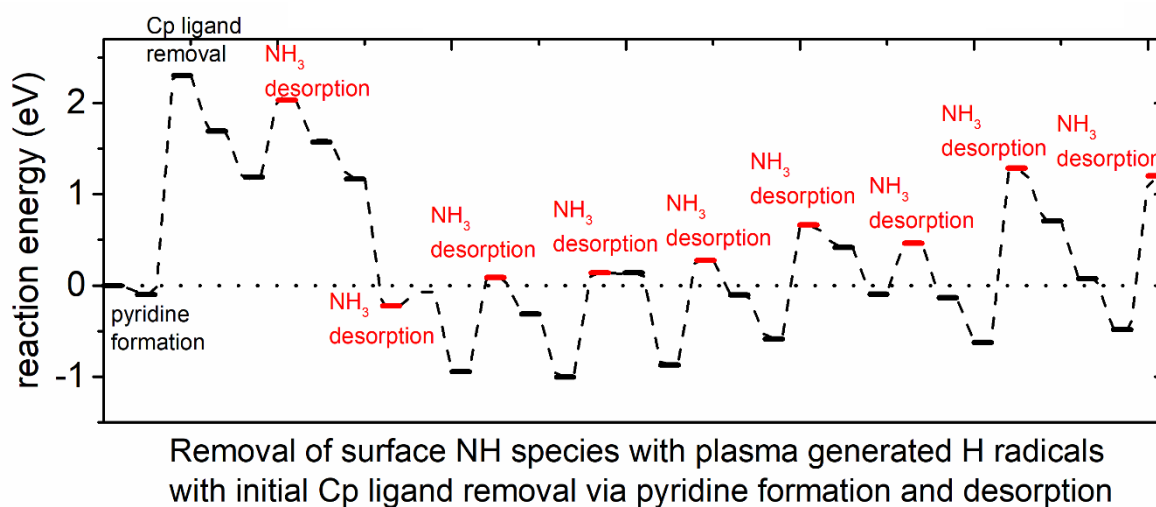
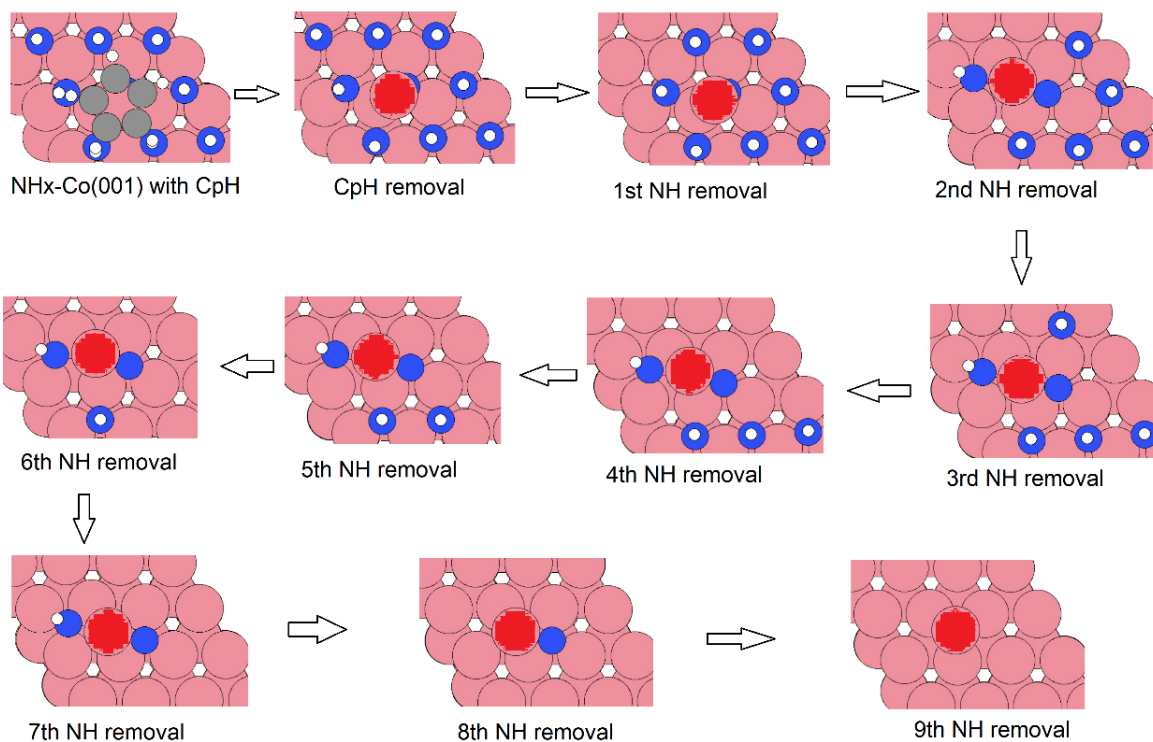


Figure S6. The plotted reaction pathway for removal of surface NH species with plasma generated H radicals with initial Cp ligand removed on one CoCp-terminated Co(001) surface. The energy of Co(001) surface with NH<sub>x</sub>-termination and one CoCp fragment is set to be the reference energy at 0eV. The steps of H radical addition are indicated by the black markers and the steps of NH<sub>3</sub> desorption are indicated by the red markers. CpH is first eliminated as pyridine.





elimination process of surface NH species with Cp ligand removed in the first step

Figure S7. The configurations of structures along the pathway for elimination process of surface NH species with Cp ligand removed prior to surface NH species on Co(001) surface. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. Substrate Co and Co from CoCp<sub>2</sub> are represented by orange and red spheres, respectively.

The plotted reaction energies for the case that Cp is first eliminated as CpH is shown in Figure S8. We see that the computed reaction energies of CpH and NH<sub>3</sub> formation and desorption are all positive and the reactions are endothermic, compared to overall exothermic reactions via Cp eliminated as pyridine. We would expect that pyridine is the primary product from eliminating Cp ligand during plasma cycle.

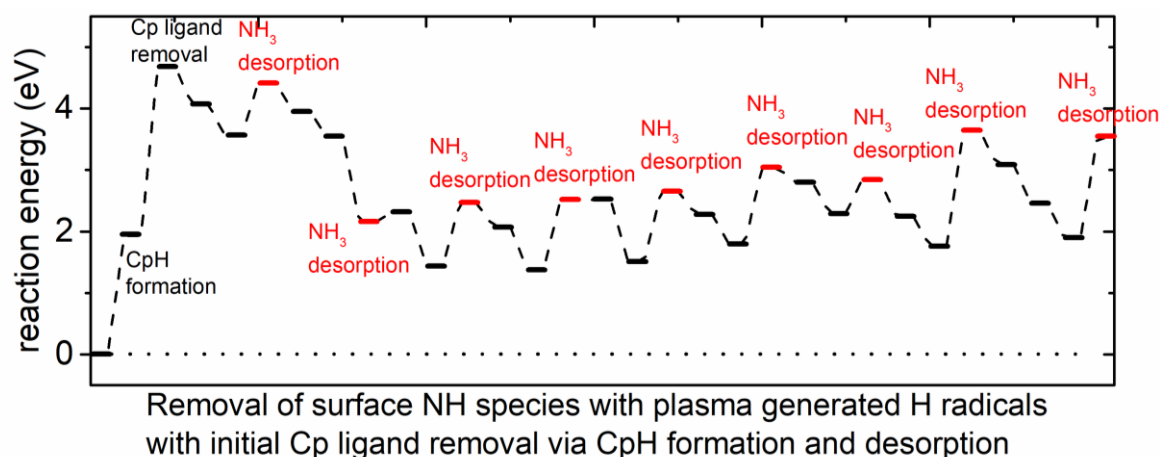


Figure S8. The plotted reaction pathway for removal of surface NH species with plasma generated H radicals with initial Cp ligand removed on one CoCp-terminated Co(001) surface. The energy of Co(001) surface with  $\text{NH}_x$ -termination and one CoCp fragment is set to be the reference energy at 0eV. The step of  $\text{NH}_3$  desorption is marked in red line. Cp ligand is first eliminated as CpH.

We applied Bader charge analysis to the structures formed for both the  $\text{NH}_2$  intermediate and the ammonia by-product for the cases in which the Cp ligand is present and the Cp ligand was removed prior to formation of surface  $\text{NH}_x$  species. The results are summarized in Table S2.

Table S2. The computed charge transfer with Bader charge analysis,  $q(\text{Bader}) - q(\text{valence})$ , for the elimination of surface NH species with the presence of Cp ligand and Cp ligand removed prior to surface  $\text{NH}_x$  species.

	1 <sup>st</sup> NH removal		2 <sup>nd</sup> NH removal		3 <sup>rd</sup> NH removal		4 <sup>th</sup> NH removal	
	$\text{NH}_2$	$\text{NH}_3$	$\text{NH}_2$	$\text{NH}_3$	$\text{NH}_2$	$\text{NH}_3$	$\text{NH}_2$	$\text{NH}_3$
Cp ligand present	$0.43e^-$	$-0.08e^-$	$0.36e^-$	$-0.07e^-$	$0.35e^-$	$-0.07e^-$	$0.38e^-$	$-0.11e^-$
Cp ligand removed	$0.42e^-$	$-0.08e^-$	$0.37e^-$	$-0.05e^-$	$0.32e^-$	$-0.05e^-$	$0.35e^-$	$-0.06e^-$

For both cases, the transferred charge to intermediate  $\text{NH}_2$  shows no differences and is in the range of  $0.35e^-$  to  $0.43e^-$  for each  $\text{NH}_2$  formation step. For the ammonia formation step, if the Cp ligand is present throughout the elimination of surface NH species, there is an increasing trend of charge transfer from  $\text{NH}_3$  to the substrate, which suggests an increasing interaction between surface Co atoms and  $\text{NH}_3$ . When the Cp ligand is removed prior to the NH species,

the transferred charge from  $\text{NH}_3$  to substrate shows a decreasing trend, which suggests a decreasing interaction between surface Co atoms and  $\text{NH}_3$ . We can infer that the computed positive reaction energies for the presence of Cp ligand in the elimination process is due to the stronger interaction (more charge transfer) between  $\text{NH}_3$  and substrate Co atoms. Thus, the removal of the Cp ligand prior to surface  $\text{NH}_x$  species is the preferred reaction mechanism and most of the surface  $\text{NH}_x$  species will be removed with plasma-generated H radicals for lower CoCp coverage case.

B. Reactions of plasma radicals with highest coverage of three CoCp fragment on  $\text{NH}_x$ -terminated Co(001) surface

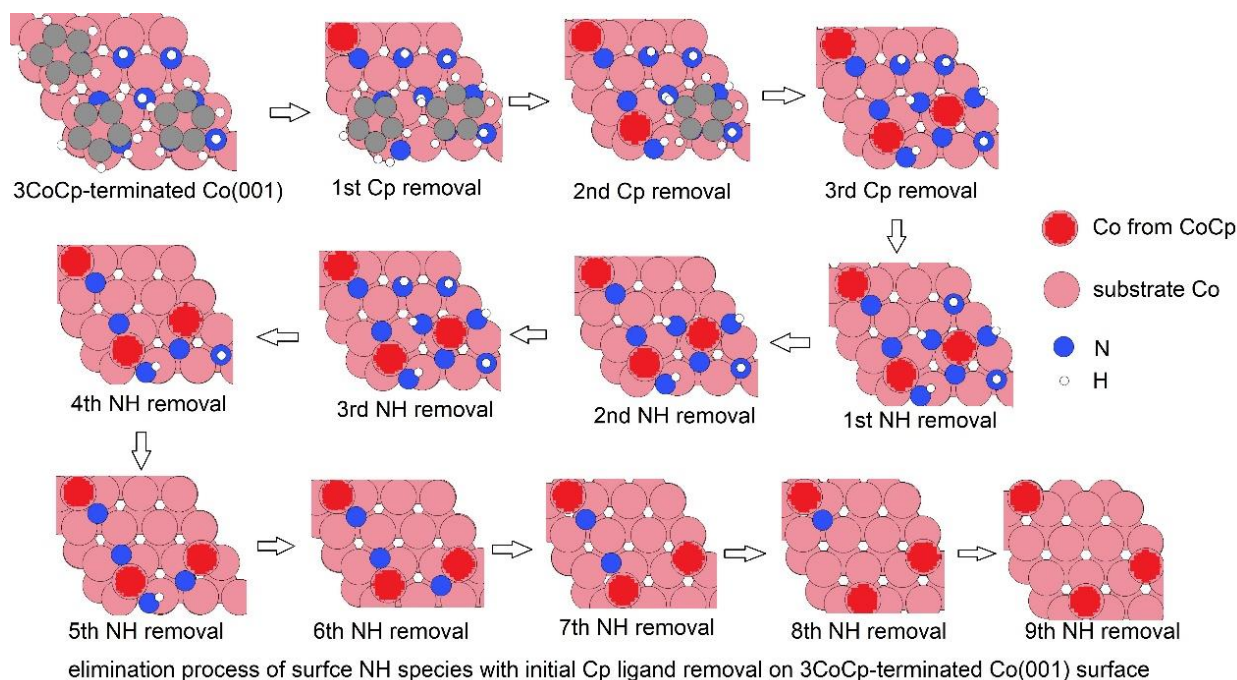
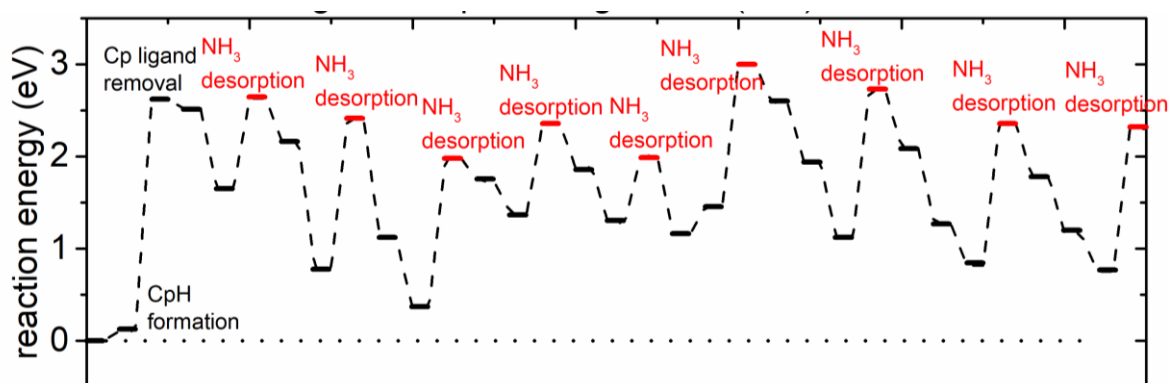


Figure S9. The configurations of structures along the reaction pathway for removal of surface NH species on  $(\text{CoCp})_3\text{NH}_x$ -terminated Co(001) surface with initial Cp ligand removal. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. Substrate Co and Co from  $\text{CoCp}_2$  are represented by orange and red spheres, respectively.



Removal of surface NH species with plasma generated H radicals with initial Cp ligand removal via CpH formation and desorption

Figure S10. The plotted reaction pathway for removal of surface NH species with plasma generated H radicals with initial Cp ligand removed on  $(\text{CoCp})_3\text{NH}_x$ -terminated  $\text{Co}(001)$  surface. The energy of  $\text{Co}(001)$  surface with  $\text{NH}_x$ -termination and one  $\text{CoCp}$  fragment is set to be the reference energy at 0eV. The step of  $\text{NH}_3$  desorption is marked in red line. Cp ligand is first eliminated as CpH.

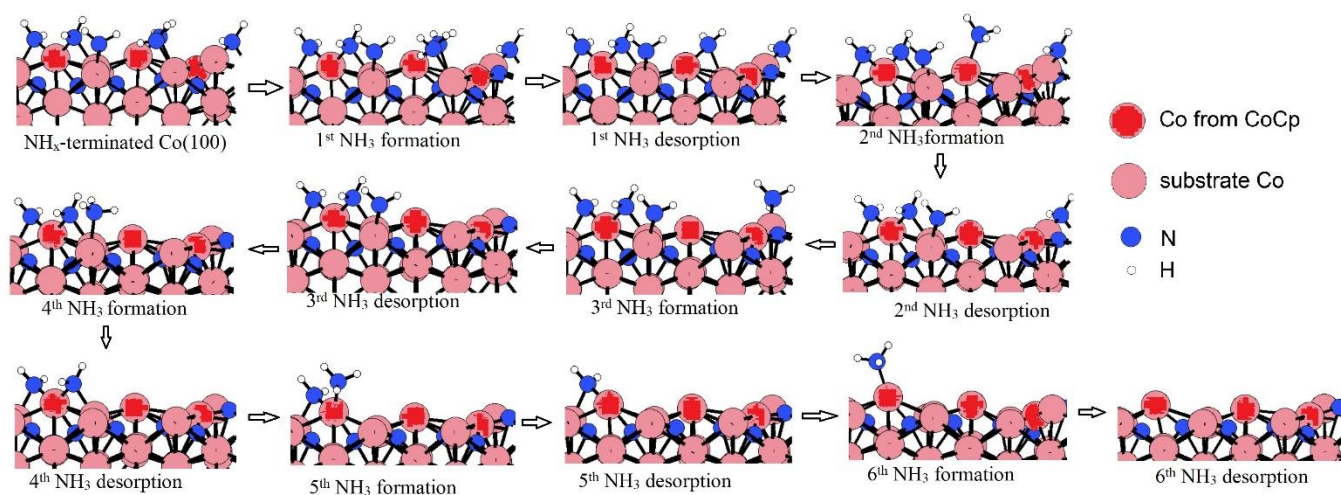


Figure S11. The configurations of structures along the reaction pathway for removal of surface  $\text{NH}_2$  species on  $\text{Co}(100)$  surface. Substrate Co and Co from  $\text{CoCp}_2$  are represented by orange and red spheres, respectively.

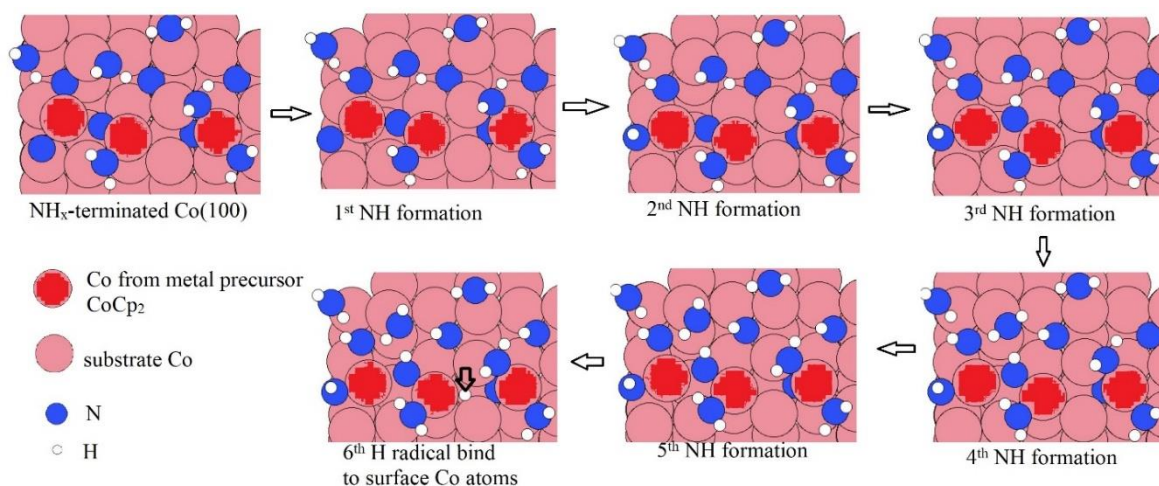


Figure S12. The configurations of structures along the reaction pathway for channel N species recover to channel NH on NH<sub>x</sub>-terminated Co(100) surface. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. Substrate Co and Co from CoCp<sub>2</sub> are represented by orange and red spheres, respectively.

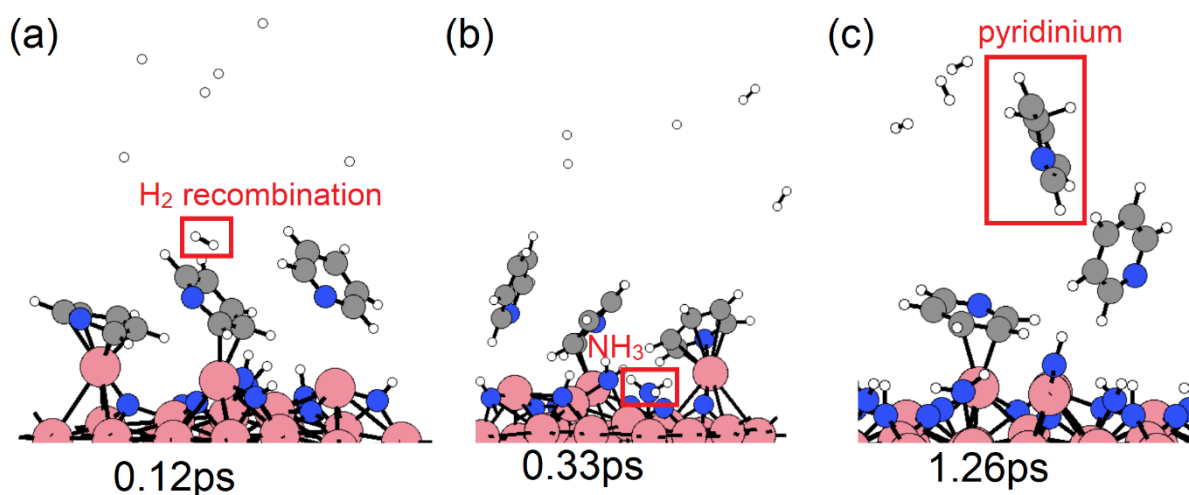


Figure S13. The configurations of snapshots of MD at (a) 0.12ps with H<sub>2</sub> recombination, (b) 0.33ps with NH<sub>3</sub> formation, and (c) 1.26ps with pyridinium formation. Carbon, nitrogen, and hydrogen atoms are presented by grey, blue, and white colour. Co is represented by orange sphere.

## References

1. Liu, J.; Lu, H.; Zhang, D. W.; Nolan, M., Reaction Mechanism of the Metal Precursor Pulse in Plasma-Enhanced Atomic Layer Deposition of Cobalt and the Role of Surface Facets. *J. Phys. Chem. C* **2020**, *124*, 11990-12000.
2. Liu, J.; Nolan, M., Coverage and Stability of NH<sub>x</sub>-Terminated Cobalt and Ruthenium Surfaces: A First-Principles Investigation. *J. Phys. Chem. C* **2019**, *123*, 25166-25175.