Supporting Information

**CO₂ Conversion on N-doped Carbon Catalysts via Thermal- and Electro catalysis: the Role of C-NOₓ Moieties**

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Figure S1. TEM images of PPy-C, PoPD-C, PANI(30)-PoPD(70)-C, PANI(70)-PoPD(30)-C, PoPD-C-NH$_3$ and PoPD-C-KOH.
Figure S2. N$_2$ adsorption / desorption isotherms of the catalysts.
Figure S3. Pore-size distribution curves of PANI-C (A), PPy-C (B), PANI(30)-PoPD(70)-C (C), PANI(70)-PoPD(30)-C (D) PoPD-C-NH$_3$ (E) and PoPD-C-KOH (F) in the mesopore range, calculated by the BJH-method.
Figure S4. Electrochemical impedance spectra of the PoPD-C and PoPD-C-NH$_3$ electrodes in an Ar-purged 1 M Na$_2$SO$_4$ solution.

Figure S5. Raman spectra of the studied catalysts.
Figure S6. Survey XPS spectra of the studied catalysts.

Figure S7. Fitting of the N1s region of the XPS spectra of the studied catalysts.
Figure S8: Partial current densities of CO and H\textsubscript{2} recorded on PPy-C (A) and PoPD-C (B) electrodes, measured with Pt and glassy carbon (CG) counterelectrodes. Measurements were performed in a CO\textsubscript{2}-saturated 0.1 M KHCO\textsubscript{3} solution.
Figure S9. (A,B): LSV curves of the studied catalysts, recorded in a CO₂-saturated 0.5 M KHCO₃ solution with 5 mV s⁻¹ sweep rate. (C,D): Total current densities measured in the 40th minute of the potentiostatic electrolysis in a CO₂-saturated 0.1 M KHCO₃ solution. Lines serve only as a guide for the eye.

Figure S10. First derivatives of the LSV curves in Fig.S9, to determine the onset potentials of the reduction reaction.
**Figure S11.** CO partial current densities on the studied N-C catalysts, normalized by the roughness factor of the electrodes (1.00 mg cm$^{-2}$ loadings). Measurements were performed in a CO$_2$-saturated KHCO$_3$ solution. Lines serve as a guide for the eye.

**Figure S12.** Faradaic efficiencies and partial current densities of methane on the studied N-C catalysts. A: PoPD-C; B: PPy-C; C: PANI-C; D: PANI(30)-PoPD(70)-C; E: PANI(70)-PoPD(30)-C; F: PoPD-C-NH$_3$; G: PoPD-C-KOH.
**Figure S13.** Stability of the TC CO\(_2\) conversion process on the studied catalysts. (A): CO formation rate, (B): CH\(_4\) formation rate.

**Figure S14.** Correlation between the amount of different N-species and the EC CO\(_2\) reduction activity (CO partial current densities normalized by the double layer capacitance value) of the studied catalysts.
**Figure S15.** Correlation between the amount of different N-species and the TC CO formation rate.

**Figure S16.** Potentiostatic electrolysis on a PoPD-C-NH$_3$ electrode in a CO$_2$-saturated 0.1 M KHCO$_3$-electrolyte at -0.6 V (vs. RHE). XPS analysis of the electrode was performed before and after electrolysis. (A): Chronoamperometric curve and the molar ratio of the formed CO and H$_2$. (B): Partial current densities of H$_2$ and CO during electrolysis.
Figure S17. Hydrogen adsorption over defects containing graphitic N, pyrrolic (N5), pyridinic (N6) and oxo-pyridinic (NO) Nitrogen atoms. Relaxed structures corresponding to hydrogen physisorption (1), as well as activated H adsorption (2-7) are shown in the bottom panel. The energy plots are derived from the electronic energy of the empty defects and isolated H$_2$ molecules, versus configurations shown in the bottom inset.
Figure S18. Electronic adsorption energy of CO$_2$ at the defect edges. CO$_2$ adsorption was computed over all nonsymetrically identical bridge sites of the corresponding defects (top inset). CO$_2$ adsorption was found to happen in two modes (i) vdW adsorption with adsorption energies of around 0.2 eV and (ii) Configurations in which 4-member rings are formed leading to typically highly endothermic adsorption energies in the 0.5 - 3.5 eV range depending on the defect.
Figure S19. Electronic adsorption energies of CO$_2$ (left) and “one step” CO$_2$+1/2H$_2$ adsorption (right) over all symmetrically non-equivalent sites of the examined defects (top inset). No local minima were found corresponding to chemisorbed CO$_2$ molecules bound via a direct C(CO$_2$)-N(defect) bond (left), resulting in vdW adsorbed configurations. However, stable COOH motifs were found for several defect motifs (motifs), most notably on the pyrrolic N atoms (as in the NO+N6+2N5 defect).
Figure S20. Deactivation pathways (electronic energy, referenced to isolated $\frac{1}{2} H_2$ and $CO_2$) of the oxo-pyridinic N containing defects, that indicate the possible deactivation via $^*NO$ reduction (red), and bicarbonate formation (blue).

| Catalyst                  | Roughness factor (CV) | BET surface area / m$^2$ g$^{-1}$ |
|---------------------------|------------------------|----------------------------------|
| PoPD-C                    | 2293                   | 930                              |
| PPy-C                     | 1642                   | 403                              |
| PANI-C                    | 1794                   | 563                              |
| PANI(30)-PoPD(70)-C       | 1825                   | 727                              |
| PANI(70)-PoPD(30)-C       | 1791                   | 621                              |
| PoPD-C- NH$_3$            | 1982                   | 1233                             |
| PoPD-C-KOH                | 4060                   | 2182                             |

Table S1. Roughness factors determined from the double layer capacitance values (cyclic voltammetry) and BET surface areas calculated from the N2 adsorption / desorption isotherms of the studies N-C samples.

| Catalyst                          | $E_{onset}$ / V (vs. RHE) | Activation energy / kcal mol$^{-1}$ |
|-----------------------------------|---------------------------|------------------------------------|
| PoPD-C                            | -0.318                    | 8.77                               |
| PPy-C                             | -0.356                    | 10.48                              |
| PANI-C                            | -0.352                    | 11.05                              |
| PANI(30)-PoPD(70)                 | -0.337                    | 7.07                               |
| PANI(70)-PoPD(30)                 | -0.344                    | 11.18                              |
| PoPD-C-NH3                        | -0.297                    | 10.63                              |
| PoPD-C-KOH                        | -0.616                    | N/A                                |

Table S2. Onset potentials of the EC reduction reaction for the different samples, determined from the derivatives of the LSV curves. Activation energy of the TC CO-formation.
| Catalyst                      | Rel. % |   |   |   |
|------------------------------|--------|---|---|---|
|                              | C      | N | O |
| PoPD-C                       | 82.86  | 9.57| 6.46 |
| PPy-C                        | 80.24  | 5.75| 13.52 |
| PANI-C                       | 83.90  | 6.65| 8.98 |
| PANI(30)-PoPD(70)-C          | 87.13  | 8.46| 4.41 |
| PANI(70)-PoPD(30)-C          | 84.25  | 8.36| 7.39 |
| PoPD-C-NH₃                   | 89.13  | 6.45| 4.42 |
| PoPD-C-KOH                   | 91.70  | 1.53| 6.78 |

**Table S3.** Elemental composition of the studied catalysts, determined from XPS measurements.

| Catalyst                      | Pyridinic N | Amine N | In plane N-H | N⁺ | Edge N-H | N-Oₓ |
|------------------------------|-------------|---------|--------------|----|----------|------|
| PoPD-C                       | 28.16       | 18.94   | 18.94        | 12.93| 6.81     | 7.16 |
| PPy-C                        | 34.35       | 14.32   | 14.32        | 8.64 | 6.13     | 4.32 |
| PANI-C                       | 31.17       | 16.18   | 16.18        | 9.68 | 6.68     | 5.54 |
| PANI(30)-PoPD(70)-C          | 28.65       | 21.67   | 21.67        | 14.18| 7.70     | 9.08 |
| PANI(70)-PoPD(30)-C          | 27.86       | 18.41   | 18.41        | 8.14 | 7.75     | 8.13 |
| PoPD-C-NH₃                   | 27.04       | 18.58   | 18.58        | 13.41| 5.35     | 12.38 |
| PoPD-C-KOH                   | 18.12       | 29.91   | 29.91        | 6.84 | 8.24     | 11.16 |

**Table S4.** Relative amounts of the different N-species in the studied catalysts determined from XPS measurements.

| Catalyst                      | I₀ / I₉ |
|------------------------------|---------|
| PoPD-C                       | 0.88 ± 0.03 |
| PPy-C                        | 0.92 ± 0.01 |
| PANI-C                       | 0.95 ± 0.01 |
| PANI(30)-PoPD(70)-C          | 0.91 ± 0.03 |
| PANI(70)-PoPD(30)-C          | 0.97 ± 0.01 |
| PoPD-C-NH₃                   | 0.87 ± 0.02 |
| PoPD-C-KOH                   | 0.87 ± 0.00 |

**Table S5.** Intensity ratios of the D and G bands in the Raman spectra of the studied catalysts.
Theoretical and computational details

For the calculation of the Gibbs energies for the thermal path, we have used

\[ \Delta G = \Delta H + \Delta ZPE - T \Delta S + 10 k_b T \ln(Q) \]

While the pH is not present in the thermal path, the term \( 10 k_b T \ln(Q) \) has been estimated for each reaction with

\[ Q = [C_{\text{product}}]/([C_{\text{reactant}}][*H]) \]

Except in the first step, there are not extra C atoms playing in the reaction, and we have assumed \( [C_{\text{product}}] \approx [C_{\text{reactant}}] \approx [CO_2] \).

Assuming to loss of hydrogen \([*H] = 2[H_2(g)]\), therefore

\[ Q = [CO_2]/([CO_2] 2[H_2(g)]) \]

Since the ratio of CO_2:H_2 is 1:4 we have \([H_2]=4[CO_2]\) thus

\[ Q = 1/(2*4) \approx 1/8 \]

The translational and rotational contribution to the enthalpy was approximated as \( 3/2 k_b T \)

The vibrational contribution of the entropy was approximated as

\[ S_{\text{vib}} = R \sum_i \left[ \frac{\hbar \nu_i}{e^{\hbar \nu_i/k_b T} - 1} - \ln\left(1 - e^{-\hbar \nu_i/k_b T}\right) \right] \]

Where \( R \) is the ideal gas constant, \( h \) is the Planck constant, \( \nu_i \) is the frequency, \( k_b \) is the Boltzmann constant. For all tables we named the surfaces with the convention clean is the basic 4N and a O cavity, hrol is the cavity with a pyrrolic H, hdim is the cavity with a H pyridinic and hh with both pyrrolic and pyridinic. All applied voltage are vs RHE. All numbers in the following tables are given in eV.

The following CO path without allowing *H transfer was investigated:

1. \(* + CO_2(g) + H^+ + e^- \rightarrow *COOH\)
2. \(*COOH \rightarrow COO^- + *H\)
3. \(*COO^- + H^+ + e^- \rightarrow *CO + H_2O (g)\)
4. \(*CO \rightarrow CO (g)\)
Table S6. Gibbs energies for the electrochemical CO path without permitting H transfer from the cavity at 298.15K, $V_{ext}=0.9$ V, pH=5.

| Surface | $\Delta G(*\text{COOH})$ (eV) | $\Delta G(*\text{CO})$ (eV) | $\Delta G(\text{CO})(g)$ (eV) | Overpotential (eV) |
|---------|-------------------------------|-----------------------------|-------------------------------|-------------------|
| clean   | -1.809                        | -2.139                      | 1.804                         | 1.804             |
| hrol    | -1.219                        | 0.330                       | -1.255                        | 0.330             |
| hdin    | -1.771                        | -1.256                      | 0.883                         | 0.883             |
| hh      | -0.611                        | 0.273                       | -1.806                        | 0.273             |

Table S7. Gibbs energies for the thermal CO path without permitting H transfer from the cavity at 298.15K, $V_{ext}=0$, $Q=1/8$.

| Surface | $\Delta G(*\text{COOH})$ (eV) | $\Delta G(*\text{CO})$ (eV) | $\Delta G(\text{CO})(g)$ (eV) | Overpotential (eV) |
|---------|-------------------------------|-----------------------------|-------------------------------|-------------------|
| clean   | -0.962                        | -0.761                      | 2.791                         | 2.791             |
| hrol    | -0.372                        | 1.709                       | -0.268                        | 1.709             |
| hdin    | -0.923                        | 0.122                       | 1.869                         | 1.869             |
| hh      | 0.236                         | 1.651                       | -0.819                        | 1.651             |

Table S8. Gibbs energies for the thermal CO path without permitting H transfer from the cavity at 900K, $V_{ext}=0$, $Q=1/8$.

| Surface | $\Delta G(*\text{COOH})$ (eV) | $\Delta G(*\text{CO})$ (eV) | $\Delta G(\text{CO})(g)$ (eV) | Overpotential (eV) |
|---------|-------------------------------|-----------------------------|-------------------------------|-------------------|
| clean   | -1.812                        | -0.616                      | 3.028                         | 3.028             |
| hrol    | -1.242                        | 1.777                       | 0.064                         | 1.777             |
| hdin    | -1.769                        | 0.243                       | 2.126                         | 2.126             |
| hh      | -0.657                        | 1.716                       | -0.460                        | 1.716             |

Table S9. Gibbs energies for the thermal CO path without permitting H transfer from the cavity at 1000K, $V_{ext}=0$, $Q=1/8$.

The path without allowing H transfer from the cavities all have an overpotential $>0$ and are therefore not thermodynamically meaningful. The optimal path presented in the paper follow the reaction presented in Table 1 of the manuscript. For the electrochemical path:
Electrochemical path

| Electrochemical path | Thermal path |
|----------------------|--------------|
| 1                    | * + CO\(_2\)(g) + H\(^+\) + e\(^-\) → *COOH |
|                      | * + CO\(_2\)(g) + \(\frac{1}{2}\) H\(_2\)(g) → *COOH |
| 2                    | *COOH + H\(^+\) + e\(^-\) → *CO + H\(_2\)O (g) |
|                      | *COOH + \(\frac{1}{2}\) H\(_2\)(g) → *CO + H\(_2\)O (g) |
| 3                    | *CO + 2H\(^+\) + 2 e\(^-\) → *CO + *H\(_{\text{dip}}\) + *H\(_{\text{roll}}\) |
|                      | *CO + H\(_2\)(g) → *CO + *H\(_{\text{dip}}\) + *H\(_{\text{roll}}\) |
| 4                    | *CO → CO(g) + * |
|                      | *CO → CO(g) + * |

Table S10. Optimal CO path.

|               | ΔG(1) (eV) | ΔG(2) (eV) | ΔG(3)(g) (eV) | ΔG(4)(g) (eV) |
|---------------|------------|------------|---------------|---------------|
| 298K, pH=5, V=0.9 | -1.809     | -2.139     | -0.934        | -1.806        |
| 298K, Q=1/8   | -0.962     | -0.761     | -0.106        | -0.819        |
| 900K, Q=1/8   | -1.812     | -0.616     | -0.222        | -0.460        |
| 1000K, Q=1/8  | -2.001     | -0.583     | -0.254        | -0.387        |

Table S11. Gibbs energy for the optimal CO path.

Electrochemical CH\(_4\) paths without *H transfer from the cavity has been investigated.

1. * + CO\(_2\)(g) + H\(^+\) + e\(^-\) → *HCOO
2. *HCOO + H\(^+\) + e\(^-\) → *CO + H\(_2\)O (g)
3. *CO + H\(^+\) + e\(^-\) → *CHO
4. *CHO + H\(^+\) + e\(^-\) → *CHOH
5. *CHOH + H\(^+\) + e\(^-\) → *CH + H\(_2\)O(g)
6. *CH + H\(^+\) + e\(^-\) → *CH\(_2\)
7. *CH\(_2\) + H\(^+\) + e\(^-\) → *CH\(_3\)
8. *CH\(_3\) + H\(^+\) + e\(^-\) → CH\(_4\)(g) + *

It turns out however that step 4 cannot produce *CHOH but always converge to a *CHO with a *H\(_{\text{roll}}\) on the clean surface.
Table S12. Gibbs energy for the CH₄ electrochemical path at 298.15K, V_{ext}=0.9 V, pH=5. All numbers are in eV. Column 4 produce in reality *CHO + *H_{rol} for the clean surface.

Table S13. Gibbs energy for the CH₄ electrochemical path at 298.15K, V_{ext}=0 V, pH=5. All numbers are in eV. Column 4 produce in reality *CHO + *H_{rol} for the clean surface.

Thermal path was also investigated.

1. * + CO₂(g) + ½ H₂(g) → *HCOO
2. *HCOO + ½ H₂(g) → *CO + H₂O (g)
3. *CO + ½ H₂(g) → *CHO
4. *CHO + ½ H₂(g) → *CHOH
5. *CHOH + ½ H₂(g) → *CH + H₂O(g)
6. *CH + ½ H₂(g) → *CH₂
7. *CH₂ + ½ H₂(g) → *CH₃
8. *CH₃ + ½ H₂(g) → CH₄(g) + *
|        | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|--------|------|------|------|------|------|------|------|------|
| *Surface | ΔG(HCOO) | ΔG(CO) | ΔG(CHO) | ΔG(CHOH) | ΔG(CH) | ΔG(CH₂) | ΔG(CH₃) | ΔG(CH₄) | Overpot. |
| clean   | -0.962 | -0.761 | 0.559  | -1.765 | 1.283 | -1.140 | 0.657  | 0.431  | 1.283    |
| hrol    | -0.372 | 1.709  | -1.782 | -0.686 | 2.863 | -1.626 | -1.581 | -0.170 | 2.863    |
| hdin    | -0.923 | 0.122  | -0.380 | -0.802 | 1.779 | -1.258 | -0.361 | 0.233  | 1.779    |
| hh      | 0.236  | 1.651  | -1.774 | 0.677  | 0.464 | -0.554 | -1.560 | -0.527 | 1.651    |

**Table S14.** Gibbs energy for the CH₄ thermal path at 298.15K, Q=1/8, all energies in eV.

|        | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|--------|------|------|------|------|------|------|------|------|
| *Surface | ΔG(HCOO) | ΔG(CO) | ΔG(CHO) | ΔG(CHOH) | ΔG(CH) | ΔG(CH₂) | ΔG(CH₃) | ΔG(CH₄) | Overpot. |
| clean   | -1.812 | -0.616 | 0.488  | -1.808 | 1.402 | -1.152 | 0.525  | 0.245  | 1.402    |
| hrol    | -1.242 | 1.777  | -1.790 | -0.725 | 2.913 | -1.720 | -1.568 | -0.187 | 2.913    |
| hdin    | -1.769 | 0.243  | -0.431 | -0.877 | 3.479 | -1.248 | -0.347 | -0.216 | 3.479    |
| hh      | -0.657 | 1.716  | -1.782 | 0.629  | 0.646 | -0.777 | -1.544 | -0.513 | 1.716    |

**Table S15.** Gibbs energy for the CH₄ thermal path at 900K, Q=1/8, all energies in eV.

|        | 1   | 2   | 3   | 4   | 5   | 6   | 7   | 8   |
|--------|------|------|------|------|------|------|------|------|
| *Surface | ΔG(HCOO) | ΔG(CO) | ΔG(CHO) | ΔG(CHOH) | ΔG(CH) | ΔG(CH₂) | ΔG(CH₃) | ΔG(CH₄) | Overpot. |
| clean   | -2.001 | -0.583 | 0.470  | -1.822 | 1.431 | -1.161 | 0.497  | 0.213  | 1.431    |
| hrol    | -1.434 | 1.799  | -1.798 | -0.739 | 2.931 | -1.742 | -1.573 | -0.186 | 2.931    |
| hdin    | -1.957 | 0.273  | -0.447 | -0.896 | 3.880 | -1.253 | -0.346 | -0.300 | 3.880    |
| hh      | -0.851 | 1.737  | -1.790 | 0.614  | 0.686 | -0.819 | -1.548 | -0.507 | 1.737    |

**Table S16.** Gibbs energy for the CH₄ thermal path at 1000K, Q=1/8, all energies in eV.

The optimal thermal path has been written in 8 steps in the manuscript to allow easy comparison with the electrochemical path. The adsorptions of H₂(g) can however be taken as separated steps.

1. * + CO₂(g) + ½ H₂(g) → *COOH
2. *COOH + ½ H₂(g) → *CO + H₂O (g)
3. 2* + H₂(g) → + *H₅d₁ + *H₅rol

The optimal thermal path has been written in 8 steps in the manuscript to allow easy comparison with the electrochemical path. The adsorptions of H₂(g) can however be taken as separated steps.

1. * + CO₂(g) + ½ H₂(g) → *COOH
2. *COOH + ½ H₂(g) → *CO + H₂O (g)
3. 2* + H₂(g) → + *H₅d₁ + *H₅rol
4. \( \text{CO} + \text{H}_{\text{din/rol}} \rightarrow \text{CHO} \)
5. \( \text{CHO} + \text{H}_{\text{rol/din}} \rightarrow \text{CHOH} \)
6. \( 2\text{H}_2(g) \rightarrow \text{H}_{\text{din}} + \text{H}_{\text{rol}} \)
7. \( \text{CHOH} + \frac{1}{2} \text{H}_2(g) \rightarrow \text{CH}_2\text{OH} \)
8. \( \text{CH}_2\text{OH} + \frac{1}{2} \text{H}_2(g) \rightarrow \text{CH}_3\text{OH} \)
9. \( \text{CH}_3\text{OH} + \frac{1}{2} \text{H}_2(g) \rightarrow \text{CH}_3 + \text{H}_2\text{O}(g) \)
10. \( \text{CH}_3 + \frac{1}{2} \text{H}_2(g) \rightarrow \text{CH}_4(g) + * \)

|                | \(\Delta G(1)\) | \(\Delta G(2)\) | \(\Delta G(3)\) | \(\Delta G(4)\) | \(\Delta G(5)\) | \(\Delta G(6)\) | \(\Delta G(7)\) | \(\Delta G(8)\) | \(\Delta G(9)\) | \(\Delta G(10)\) |
|----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| T=1000K        | -2.001          | -0.583          | -0.254          | -1.094          | -0.057          | -0.077          | -0.921          | -0.225          | -0.536          | -0.507          |
| T=900K         | -1.812          | -0.616          | -0.222          | -1.094          | -0.051          | -0.055          | -0.906          | -0.262          | -0.507          | -0.513          |
| T=298.15K      | -0.962          | -0.761          | -0.106          | -1.097          | -0.019          | 0.004           | -0.857          | -0.442          | -0.352          | -0.527          |

Table S17. Gibbs energy for the CH\(_4\) optimal thermal path with \(Q = 1/8\), all energies in eV.

We see that the step 6 is blocking the reaction at 298.15 K.

|          | E0 (eV) | TS (298.15K) | ZPE (eV) | TS (900K) | TS (1000K) |
|----------|---------|--------------|----------|-----------|------------|
| clean    | ncoo    | -646.0407    | 0.2343   | 0.9566    | 2.1326     | 2.5553     |
| clean    | ncooh   | -650.501     | 0.2392   | 1.3359    | 2.313      | 2.7818     |
| clean    | nco     | -640.4451    | 0.1747   | 0.9072    | 1.8088     | 2.1801     |
| clean    | ncoh    | -644.7097    | 0.1756   | 1.2265    | 1.904      | 2.3027     |
| clean    | nch1o   | -643.4008    | 0.1954   | 1.2069    | 1.9691     | 2.3748     |
| clean    | nch1oh  | -648.726     | 0.2038   | 1.5406    | 2.0902     | 2.5257     |
| clean    | nch1    | -636.6128    | 0.1385   | 1.0969    | 1.6105     | 1.9528     |
| clean    | nch2oh  | -650.9816    | 0.2091   | 1.8468    | 2.2014     | 2.6666     |
| clean    | nch2    | -641.3224    | 0.1443   | 1.4372    | 1.6973     | 2.0646     |
| clean    | nch3oh  | -653.6392    | 0.2602   | 2.0187    | 2.439      | 2.9408     |
| clean    | nch3    | -644.14      | 0.1827   | 1.7152    | 1.9369     | 2.3481     |
| clean    | nch4    | -647.0059    | 0.2526   | 1.8466    | 2.2619     | 2.7208     |
| H pyrolic |         |              |          |           |            |            |
| hrol     | ncoo    | -652.0118    | 0.2333   | 1.2871    | 2.2128     | 2.6605     |
| hrol     | ncooh   | -655.9607    | 0.2423   | 1.6735    | 2.4144     | 2.9106     |
| hrol     | nco     | -643.3739    | 0.2034   | 1.2085    | 2.0114     | 2.4221     |
| hrol     | ncoh    | -648.5443    | 0.1954   | 1.4153    | 1.9385     | 2.3408     |
| hrol     | nch1o   | -648.7224    | 0.2036   | 1.54      | 2.0885     | 2.5238     |
| hrol     | nch1oh  | -652.9436    | 0.2107   | 1.8474    | 2.2044     | 2.6695     |
| hrol     | nch1    | -639.2102    | 0.1665   | 1.3852    | 1.8152     | 2.1977     |
| hrol     | nch2oh  | -656.2373    | 0.2167   | 2.1766    | 2.3248     | 2.8201     |
| hrol     | nch2    | -644.3555    | 0.1832   | 1.6856    | 1.9947     | 2.4147     |
| hrol     | nch3oh  | -659.4222    | 0.2306   | 2.3574    | 2.3485     | 2.8472     |
| hrol     | nch3    | -649.5255    | 0.1906   | 2.047     | 2.0581     | 2.4991     |
| Surface | Molecule | $E_0$ (eV) | ZPE (eV) | TS (eV) | $E_{total}$ (eV) |
|---------|----------|-----------|---------|---------|------------------|
| hrol    | nch4     | -653.0229 | 0.2242  | 2.1725  | 2.1774           |
| H pyridinic |          |           |         |         |                  |
| hdin    | ncoo     | -649.1347 | 0.2396  | 1.2642  | 2.2653           |
| hdin    | ncooh    | -655.6619 | 0.2353  | 1.6627  | 2.3816           |
| hdin    | nco      | -644.7092 | 0.1765  | 1.2258  | 2.3067           |
| hdin    | ncoh     | -646.36   | 0.2059  | 1.4819  | 2.1725           |
| hdin    | nch1o    | -648.6171 | 0.1933  | 1.5535  | 2.1028           |
| hdin    | nch1oh   | -652.9454 | 0.2109  | 1.8438  | 2.2057           |
| hdin    | nch1     | -640.4902 | 0.1478  | 1.4091  | 2.1130           |
| hdin    | nch2oh   | -655.9542 | 0.2138  | 2.1524  | 2.7791           |
| hdin    | nch2     | -645.324  | 0.146   | 1.748   | 2.1924           |
| hdin    | nch3oh   | -658.842  | 0.2303  | 2.3439  | 2.8423           |
| hdin    | nch3     | -649.1791 | 0.1575  | 2.018   | 2.2735           |
| hdin    | nch4     | -652.2192 | 0.2777  | 2.176   | 3.0115           |
| H both  |          |           |         |         |                  |
| hh      | ncoo     | -654.6493 | 0.2073  | 1.5929  | 2.1359           |
| hh      | ncooh    | -660.1386 | 0.2484  | 1.9792  | 3.0527           |
| hh      | nco      | -647.6086 | 0.2111  | 1.5151  | 2.5078           |
| hh      | ncoh     | -650.8293 | 0.2185  | 1.7973  | 2.7374           |
| hh      | nch1o    | -652.944  | 0.2113  | 1.8416  | 2.2072           |
| hh      | nch1oh   | -655.827  | 0.2236  | 2.1789  | 2.8333           |
| hh      | nch1     | -644.5931 | 0.1457  | 1.7831  | 2.1737           |
| hh      | nch2oh   | -660.2079 | 0.23    | 2.4742  | 2.9891           |
| hh      | nch2     | -648.5473 | 0.193   | 1.9949  | 2.5706           |
| hh      | nch3oh   | -664.0614 | 0.222   | 2.6422  | 2.8486           |
| hh      | nch3     | -653.6875 | 0.199   | 2.3457  | 2.6501           |
| hh      | nch4     | -657.5628 | 0.224   | 2.4836  | 2.7402           |

*Table S18.* Raw data for ground state energy ($E_0$), zero point energy (ZPE) and entropic contribution (TS) at different temperature. The first column specifies the surface, clean is the basic 4N and a O cavity, hrol is the cavity with a pyrrolic H, hdin is the cavity with a H pyridinic and hh with both pyrrolic and pyridinic. The second column specify which molecule was attached.

**Geometrical structures**

All geometrical structures are available on the ioChem-BD database through the following link:

https://iochem-bd.iciq.es/browse/review-collection//fcf24395bc7810b48bf95bea