## Supporting Information

# 2D Conductive Metal-Organic Frameworks for NO Electrochemical Reduction: A First-Principles Study

Xing Chen, <sup>a#</sup> Xiangyu Zhu, <sup>a#</sup> Zhiyuan Xia, <sup>a</sup> Shiting Qian,<sup>a</sup> Yanan Zhou <sup>b\*</sup> Qiquan Luo<sup>a\*</sup> and Jinlong Yang<sup>c\*</sup>

<sup>a</sup>Institutes of Physical Science and Information Technology, Anhui University, Hefei 230601, China. <sup>b</sup>School of Material Science and Chemical Engineering, Institute of Mass Spectrometry, Ningbo University, Fenghua Road 818, Ningbo 315211, China. <sup>c</sup>Key Laboratory of Precision and Intelligent Chemistry, Department of Chemical Physics, Hefei

National Research Center for Physical Sciences at the Microscale, University of Science and Technology of China, Hefei, Anhui 230026, China.

#X.C and X.Z contributed equally to this work\*Email: <u>qluo@ustc.edu.cn</u>; <u>zhouyanan@nbu.edu.cn</u>; jlyang@ustc.edu.cn.

# Table of content

Constant potential method	S1
The model details for Pt(100)	S3
Nitric oxide reduction five-electron mechanism	S4
Detailed descriptions and computational details of SISSO method	S5
One-dimensional descriptors of TMX <sub>4</sub> -HTPs	S6
Fig. S1 Top view of TMX <sub>4</sub> -HTP monolayer	S7
Fig. S2 Three possible adsorption patterns of NO on TMX <sub>4</sub> -HTPs	S8
Fig. S3 The energy profile of the protonation processes for Pt(100)	S9
<b>Fig. S4</b> Energy( $\Delta G_1$ ) required for the first protonation step	S10
Fig. S5 Schematic pathways of the NORR process toward NH <sub>3</sub> synthesis	S11
Fig. S6 Free energy diagrams of electrochemical NO-to-NH <sub>3</sub>	S12
Fig. S7 Energy profile for AIMD simulation	S13
Fig. S8 The molecular orbital diagram of NO	S14
Fig. S9 PDOS of (a)TMN <sub>4</sub> -HTPs, (b)TMO <sub>4</sub> -HTPs, (c) TMP <sub>4</sub> -HTPs, and (d)TMS <sub>4</sub> -HTP	Ps
Fig. S10 PDOS of NO-adsorbed (a)TMN <sub>4</sub> -HTPs, (b)TMO <sub>4</sub> -HTPs, (c) TMP <sub>4</sub> -HTPs, ar	nd (d)TMS <sub>4</sub> -
HTPs	S16
Fig. S11 Scaling relationship among free energies of NO, transfer charge of TM atoms	s, and the N-
O bond of adsorbed NO on TMX <sub>4</sub> -HTPs	S17
Fig. S12Adsorption free energies of HNO ( $\Delta G_{*\text{HNO}}$ ), NOH ( $\Delta G_{*\text{NHO}}$ )	S18
Fig. S13 PDOS of MnO <sub>4</sub> -HTP adsorbed with HNO and NOH	S19
Fig. S14 The PDOS of MnO-HTP by HSE06 hybrid functional	S20
Fig. S15 Free energy diagrams of electrochemical NO-to-NH3 conversion on Mr	O <sub>4</sub> -HTP by
PBE+SOL+U	S21
Fig. S16 Simulated polarization curve of MnO <sub>4</sub> -HTP and Pt (100)	S22
Fig. S17 Total energies of intermediates as a function of applied potential U	S23
Fig. S18 The free energy curves of $MnO_4$ -HTP under varying electrode potentials at (a	) pH=1, and
(b) pH=13.	S24
Fig. S19 pH-dependent and potential-dependent contour plot of the reaction energy fo	r the second
protonation step	S25
Fig. S20 The DFT-calculated $\Delta G_{*H}$ , $\Delta G_{*H2O}$ and $\Delta G_{*NH3}$ values of TMX <sub>4</sub> -HTP were con-	mpared with
the SISSO predicted values.	S26
Fig S21 Comparison of DFT-calculated $\Delta G_{*H}$ , $\Delta G_{*H2O}$ and $\Delta G_{*NH3}$ values with the SISS	O-predicted
values	S27
Fig. S21 The structure of Fe–N–C	S28
Fig. S23 Free energy diagrams of CoO <sub>4</sub> -HTP, CuO <sub>4</sub> -HTP, and Co <sub>0.5</sub> Cu <sub>0.5</sub> O <sub>4</sub> -HTP	S29
Tab. S1 Calculated energies of MnO <sub>4</sub> -HTP at different vacuum spaces	S30
Tab. S2 TMX <sub>4</sub> -HTP energy and lattice length a, b	S31
<b>Tab. S3</b> Computed the $\mu_{TM}$ , $E_f$ , $U^{\circ}_{diss}$ , $N_e$ , $U_{diss}$	S32
Tab. S4 Free energies of NO on TMX4-HTPs with N-end, O-end, and side-on patterns	S33
Tab. S5 Free energies of NO, H, H <sub>2</sub> O, and NH <sub>3</sub> on TMX <sub>4</sub> -HTPs	S34
<b>Tab. S6</b> Energy( $\Delta G_1$ ) required for the first protonation step	S35
Tab. S7 The energy of all the possible intermediates	S36

Tab. S8 Transfer charge of TM atoms, and the N-O bond of adsorbed NO on TMX <sub>4</sub> -HTPs	S40
<b>Tab. S9</b> Adsorption free energies of $\Delta^*G_{HNO}$ , $\Delta G_{*NOH}$ , $\Delta G_{HNO} - \Delta G_{NOH}$	. <b>S</b> 41
Tab. S10 $Q_X$ , N, AR, IR, IE, EA, $\rho_{TM}$ , M, $\chi$ of each investigated TMX <sub>4</sub> -HTPs.	.S42

#### **Constant potential method**

This method implements VASPsol to model the electrochemical electrode/solution interface and establish the relationship between charge and electrode potential. For each structure, thirteen different systems were performed at charges of  $-2e^-$  to  $+2e^-$  at a step of 0.5e<sup>-</sup> and the corresponding electrode potential referenced to the SHE scale could be calculated by

$$U_{q}(V/SHE) = (\phi_{q}(f) - 4.6)/e$$

where  $\phi_q(f)$  is the work function of the charging system and 4.6 V is the work function of the H<sub>2</sub>/H<sup>+</sup> couple under standard conditions.

Under the condition of fixed potential, the electrode potential referenced to the SHE scale is changed by pH values. The relationship is given by  $U_{\text{RHE}} = U_{\text{SHE}} + k_{\text{B}} \text{Tln} (10) \text{pH/e}$ 

Therefore, by adjusting the charge numbers of the system, the energies under specific potentials could be calculated. However, the DFT-calculated value also includes the interaction between the electrons in the slab and the background charge. It is given by  $E_{\text{DFT}}(\mathbf{n}_{e},\mathbf{n}_{\text{bg}}) = E_{\text{slab}}(\mathbf{n}_{e}) + E_{\text{slab}-\text{bg}}(\mathbf{n}_{e},\mathbf{n}_{\text{bg}}) + E_{\text{bg}}(\mathbf{n}_{\text{bg}})$ 

where  $E_{\text{slab}}$  is the energy of the slab without the background,  $E_{\text{bg}}$  is the energy of the background without the slab and  $E_{\text{slab-bg}}$  is the interaction energy between the slab and the background. According to Neurock's methods,<sup>1</sup> decoupling of the slab-background interaction involves subtracting the  $E_{\text{slab-bg}}$  and  $E_{\text{bg}}$  terms, which sum to equal –

$$\int_{0}^{0} \langle \bar{V}_{tot}(Q) \rangle dQ$$
where  $\langle \bar{V}_{tot}(Q) \rangle$  is the average potential in the unit cell. The  $\langle \bar{V}_{tot}(Q) \rangle$  is obtained from the LOCPOT file generated by VASP with LVHAR set as true. The average electrostatic potential in the x, y, and z directions provided by the LOCPOT

file is summed 
$$(\iiint V_{tot} dx dy dz)$$
.  $\frac{1}{\Sigma} \iiint V_{tot} dx dy dz$  (i.e., the potential shift to reference the system to vacuum as a function of q), and  $\Sigma$  is the volume of the unit cell. The correction results in the total electron energy,  $E_{elec}$ , defined as:

$$E_{elec} = E_{DFT} + \int_{0}^{6} \langle \bar{V}_{tot}(Q) \rangle dQ$$
  
where  $E_{elec}$  is equal to  $E_{slab}(n_e)$ ,  $E_{DFT}$  is equal to  $E_{DFT}(n_e, n_{bg})$ , and  
 $E_{slab - bg}(n_e, n_{bg}) + E_{bg}(n_{bg})$  is equal to  $-0$ . However, the total free  
energy of the system ( $E_{Free}$ ) also includes contributions for the excess electrons (q) at  
the Fermi potential ( $\phi_q(f)$ ) and is equivalent to  
 $E_{free}(U) = E_{DFT} + \int_{0}^{6} \langle \bar{V}_{tot}(Q) \rangle dQ - q\phi_q(f)$ 

 $E_{\text{free}}$  and U could be fitted to a quadratic function form, consistent with a capacitor created by the charged-slab/background-charge system, written as

$$E(U) = -\frac{1}{2}C(U - U_0)^2 + E_0$$

where  $U_0$  is the potential of zero charge (PZC),  $E_0$  is the energy at the PZC, and C is the capacitance of the surface. From the quadratic functions, the potential-dependent energy could be provided.

### The model details for Pt(100)

The Pt(100) surface is represented by a  $3 \times 3$  unit cell with five Pt layers (total of 45 atoms per unit cell). Surface relaxation is allowed in the top three layers of the (100) slab.

#### Nitric oxide reduction five-electron mechanism

The overall NORR process includes a five-electron mechanism, which consists of five elementary steps following the equations as reported in the previous literature:

the first protonation step	$^{*}$ + NO + H + $e^{-} \rightarrow ^{*}$ HNO( $^{*}$ NOH)		
the second metamotion stan	$^{*}\text{HNO} + \text{H} + \text{e}^{-} \rightarrow ^{*}\text{HNOH}(^{*}\text{H}_{2}\text{NO})$		
the second protonation step	*NOH + H + $e^- \rightarrow$ *HNOH(*N + H <sub>2</sub> O)		
	*HNOH + H + $e^{-} \rightarrow H_2$ NOH(*NH + H <sub>2</sub> O)		
the thrid protonation step	$^{*}\text{H}_{2}\text{NO} + \text{H} + \text{e}^{-} \rightarrow ^{*}\text{H}_{2}\text{NOH}(^{*}\text{O} + \text{NH}_{3})$		
	$^{*}N + H + e^{-} \rightarrow ^{*}NH$		
	$^*NH + H + e^- \rightarrow ^*NH_2$		
the fourth protonation step	$^{*}H_{2}NOH + H + e^{-} \rightarrow ^{*}NH_{2} + H_{2}O$		
	$^{*}\text{H}_{2}\text{NOH} + \text{H} + \text{e}^{-} \rightarrow ^{*}\text{OH} + \text{NH}_{3}$		
the fifth protonation stop	$^*\mathrm{NH}_2 + \mathrm{H} + \mathrm{e}^- \! \rightarrow ^*\!\mathrm{NH}_3$		
the fifth protonation step	$^{*}OH + H + e^{-} \rightarrow ^{*}H_{2}O$		

where \* represents the active site on the catalyst, and \*HNO, \*NOH, \*HNOH, \*H<sub>2</sub>NO, \*N, \*H<sub>2</sub>NOH, \*O, \*NH, \*NH<sub>2</sub>, \*OH, \*NH<sub>3</sub>, and \*H<sub>2</sub>O are the correspond adsorbed intermediates, respectively.

#### Detailed descriptions and computational details of SISSO method

SISSO is a data-driven method combining symbolic regression and compressed sensing to produce explicit mathematical expressions.<sup>2, 3</sup> The main steps of this method are: (1) uniformly sample a sufficient number of reliable data points; (2) identify key features based on domain knowledge or intuition; (3) construct a large feature space through feature transformations to better describe target properties; (4) assume that target properties can be linearly expanded in the feature space and solve for the sparse solution of the linear model. In this work, the initial feature space comprises 13 primary features  $\Phi_0 = [Q_x, Q_{TM}, Ne, N, AR, IR, IE, EA, \rho_{TM}, M, \chi, U^o_{diss}, \mu_{TM}]$ , and the mathematical operations for feature construction are  $(+, -, \times, /, ^{-1}, ^2, ^3, |-|, \sqrt{, \sqrt[3]{}})$ . With these primary features and mathematical operations, a large number of expressions are generated. The SISSO code is available at <u>http://github.com/rouyang2017/SISSO</u>.

### **One-dimensional descriptors of TMX4-HTPs**

The  $\Delta G_{*NO}$  is depicted as:

$$\Delta G_{*NO}(\text{SISSO}) = -38.97 \times \frac{\text{IE} \times (\frac{\mu_{\text{TM}}}{M})^2}{Q_{\text{X}} \times N \times N_{\text{e}}} + 1.17$$

The  $\Delta G_{*H}$  is depicted as:

$$\Delta G_{*\rm H} (\rm SISSO) = -0.38 \times (\frac{(Q_{\rm X} - N) \times N_{\rm e} + (N - N_{\rm e}) \times N}{(\mu_{\rm TM}}) - 2.35$$

The  $\Delta G_{*H2O}$  is depicted as:

$$\Delta G_{*\text{H2O}} \text{ (SISSO)} = -0.26 \times \left( \frac{e^{N_e} \times N \times \rho_{\text{TM}} \times \ln Q_X}{N + N_e} \right) \times 10^{-1} - 3.36$$

The  $\Delta G_{*_{\text{NH3}}}$  is depicted as:

$$\Delta G_{*_{\rm NH3}}({\rm SISSO}) = -1132.82 \times \frac{\mu_{\rm TM}^2}{{\rm N} \times \rho_{\rm TM} \times \sqrt{{\rm Q}_{\rm X}} \times {\rm N}_{\rm e} \times {\rm AR}} + 1.17$$



Fig. S1 Top view of TMX<sub>4</sub>-HTP monolayer.



Fig. S2 Three possible adsorption patterns of NO on  $TMX_4$ -HTPs.



Fig. S3 (a) The side and top views of the Pt(100), (b) The energy profile of the protonation processes for Pt(100)



Fig. S4 Energy( $\Delta G_1$ ) required for the first protonation step of NO + H<sup>+</sup> + e<sup>-</sup>  $\rightarrow$  HNO(NOH).



Fig. S5 Schematic pathways of the NORR process toward NH<sub>3</sub> synthesis.



**Fig. S6** Free energy diagrams of electrochemical NO-to-NH<sub>3</sub> conversion on (a) FeO<sub>4</sub>-HTP, (b) CoO<sub>4</sub>-HTP, (c)FeS<sub>4</sub>-HTP, (d) CoS<sub>4</sub>-HTP, (e) TiS<sub>4</sub>-HTP, (f) VS<sub>4</sub>-HTP, and (g) FeN<sub>4</sub>-HTP.



**Fig. S7** Energy profile for *ab initio* molecular dynamics (AIMD) simulation on (a)  $FeN_4$ -HTP, (b)  $FeO_4$ -HTP, (c)  $MnO_4$ -HTP, (d)  $CoO_4$ -HTP, (e)  $FeS_4$ -HTP, (f)  $CoO_4$ -HTP, (g) TiS\_4-HTP, and (h) VS\_4-HTP after 10 ps at 350 K, where the energy fluctuation is caused by thermal disturbance of temperature.



Fig. S8 The molecular orbital diagram of NO.



**Fig. S9** Partial density of states (PDOS) of (a)TMN<sub>4</sub>-HTPs, (b)TMO<sub>4</sub>-HTPs, (c) TMP<sub>4</sub>-HTPs, and (d)TMS<sub>4</sub>-HTPs. The Fermi level is set to 0 eV.



**Fig. S10** PDOS of NO-adsorbed (a)TMN<sub>4</sub>-HTPs, (b)TMO<sub>4</sub>-HTPs, (c) TMP<sub>4</sub>-HTPs, and (d)TMS<sub>4</sub>-HTPs. The Fermi level is set to 0 eV.



**Fig. S11** Scaling relationship among free energies of NO ( $\Delta G_{*NO}$ ), transfer charge of TM atoms ( $Q_{TM}$ ), and the N-O bond of adsorbed NO ( $d_{N-O}$ ) on TMX<sub>4</sub>-HTPs.



**Fig. S12** Adsorption free energies of HNO ( $\Delta G_{*HNO}$ ), NOH ( $\Delta G_{*NHO}$ ).



**Fig. S13** PDOS of MnO<sub>4</sub>-HTP adsorbed with HNO and NOH. The Fermi level is set to 0 eV.



**Fig. S14** The PBE functional and Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional are adopted to calculate the PDOS of MnO<sub>4</sub>-HTP.



## **Reaction Coordinate**

Fig. S15 Free energy diagrams of electrochemical NO-to- $NH_3$  conversion on  $MnO_4$ -HTP by PBE+SOL+U.



Fig. S16 Simulated polarization curve of  $MnO_4$ -HTP and Pt (100).



**Fig. S17** Total energies of \*HNO, \*HNOH, \*NH, \*NH<sub>2</sub> and \*NH<sub>3</sub> as a function of applied potential U. The calculated total energy is represented by triangles, and the fitting data is represented by solid lines.



Fig. S18 The free energy curves of  $MnO_4$ -HTP under varying electrode potentials at (a) pH=1, and (b) pH=13.



Fig. S19 pH-dependent and potential-dependent contour plot of the reaction energy for the second protonation step.



**Fig. S20** The DFT-calculated  $\Delta G_{*H}$ ,  $\Delta G_{*H2O}$  and  $\Delta G_{*NH3}$  values of TMX<sub>4</sub>-HTP were compared with the SISSO predicted values.



**Fig S21** Comparison of DFT-calculated  $\Delta G_{*H}$ ,  $\Delta G_{*H2O}$  and  $\Delta G_{*NH3}$  values with the SISSO-predicted values.



**Fig. S22** The structure of Fe–N–C. The Fe–N–C SAC was modeled by a FeN<sub>4</sub> site embedded into a monolayer graphene in an orthorhombic cell with the lattice parameter of a = 15.16 Å and b = 20 Å.



## **Reaction Coordinate**

Fig. S23 Free energy diagrams of electrochemical NO-to-NH<sub>3</sub> conversion on CoO<sub>4</sub>-HTP, CuO<sub>4</sub>-HTP and Cu<sub>0.5</sub>Co<sub>0.5</sub>O<sub>4</sub>-HTP.

Vacuum space (Å)	$\Delta E_{*\mathrm{NO}} (\mathrm{eV})$	$\Delta E_{\rm *HNO}~({\rm eV})$
12	0.00	0.00
15	0.00	0.02
20	0.00	0.02
30	-0.01	0.00

**Tab. S1**: Calculated energies of  $MnO_4$ -HTP at different vacuum spaces, using the energy of  $MnO_4$ -HTP at a 12 Å vacuum space as the reference.

TMN <sub>4</sub> -HTP	Energy (eV)	a = b (Å)	TMO <sub>4</sub> -HTP	Energy (eV)	a = b (Å)
Sc	-540.60	22.88	Sc	-480.37	22.37
Ti	-542.85	22.47	Ti	-482.29	22.02
V	-543.24	22.39	V	-481.94	21.91
Cr	-544.50	22.23	Cr	-480.77	21.84
Mn	-543.62	22.16	Mn	-479.86	21.71
Fe	-539.41	22.02	Fe	-474.16	21.63
Co	-535.84	21.86	Co	-469.20	21.45
Ni	-530.91	21.85	Ni	-464.51	21.44
TMP <sub>4</sub> -HTP	Energy (eV)	a = b (Å)	TMS <sub>4</sub> -HTP	Energy (eV)	a = b (Å)
TMP <sub>4</sub> -HTP Sc	Energy (eV) 489.84	a = b (Å) 25.43	TMS <sub>4</sub> -HTP Sc	Energy (eV) 444.02	a = b (Å) 24.25
TMP <sub>4</sub> -HTP Sc Ti	Energy (eV) -489.84 -493.00	a = b (Å) 25.43 24.96	TMS <sub>4</sub> -HTP Sc Ti	Energy (eV) -444.02 -446.77	a = b (Å) 24.25 23.89
TMP <sub>4</sub> -HTP Sc Ti V	Energy (eV) -489.84 -493.00 -494.91	a = b (Å) 25.43 24.96 24.52	TMS <sub>4</sub> -HTP Sc Ti V	Energy (eV) -444.02 -446.77 -447.32	a = b (Å)     24.25     23.89     23.75
TMP <sub>4</sub> -HTP Sc Ti V Cr	Energy (eV) -489.84 -493.00 -494.91 -496.60	a = b (Å) 25.43 24.96 24.52 24.32	TMS <sub>4</sub> -HTP Sc Ti V Cr	Energy (eV) -444.02 -446.77 -447.32 -448.77	a = b (Å) 24.25 23.89 23.75 23.57
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn	Energy (eV) -489.84 -493.00 -494.91 -496.60 -496.98	a = b (Å) 25.43 24.96 24.52 24.32 24.14	TMS <sub>4</sub> -HTP Sc Ti V Cr Mn	Energy (eV) -444.02 -446.77 -447.32 -448.77 -448.36	a = b (Å) 24.25 23.89 23.75 23.57 23.49
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe	Energy (eV) -489.84 -493.00 -494.91 -496.60 -496.98 -494.79	a = b (Å) 25.43 24.96 24.52 24.32 24.14 23.99	TMS <sub>4</sub> -HTP Sc Ti V Cr Mn Fe	Energy (eV) -444.02 -446.77 -447.32 -448.77 -448.36 -445.06	a = b (Å) 24.25 23.89 23.75 23.57 23.49 23.34
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co	Energy (eV) -489.84 -493.00 -494.91 -496.60 -496.98 -494.79 -490.79	a = b (Å) 25.43 24.96 24.52 24.32 24.14 23.99 23.87	TMS <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co	Energy (eV) -444.02 -446.77 -447.32 -448.77 -448.36 -445.06 -441.46	a = b (Å) 24.25 23.89 23.75 23.57 23.49 23.34 23.19

Tab. S2 TMX<sub>4</sub>-HTP energy and lattice length a, b

TMN <sub>4</sub> -HTP	$\mu_{\mathrm{TM}}(\mathrm{eV})$	$E_{\rm f}({\rm eV})$	$U^{\circ}_{diss}(V)$	Ne	$U_{ m diss}({ m V})$
Sc	-6.34	-7.75	-2.08	3	0.50
Ti	-7.9	-6.94	-1.63	2	1.84
V	-9.09	-5.88	-1.18	2	1.76
Cr	-9.64	-5.75	-0.91	2	1.97
Mn	-9.16	-5.94	-1.19	2	1.78
Fe	-8.46	-5.24	-0.45	2	2.17
Co	-7.11	-5.23	-0.28	2	2.33
Ni	-5.78	-5.08	-0.26	2	2.28
TMO <sub>4</sub> -HTP	$\mu_{\mathrm{TM}}(\mathrm{eV})$	$E_{\rm f}({\rm eV})$	$U^{\circ}_{diss}(V)$	Ne	$U_{ m diss}({ m V})$
Sc	-6.34	-9.09	-2.08	3	0.95
Ti	-7.9	-8.17	-1.63	2	2.45
V	-9.09	-6.86	-1.18	2	2.25
Cr	-9.64	-5.92	-0.91	2	2.05
Mn	-9.16	-6.10	-1.19	2	1.86
Fe	-8.46	-4.90	-0.45	2	2.00
Co	-7.11	-4.59	-0.28	2	2.02
Ni	-5.78	-4.36	-0.26	2	1.92
TMP <sub>4</sub> -HTP	$\mu_{\mathrm{TM}}(\mathrm{eV})$	$E_{\rm f}({\rm eV})$	$U^{\circ}_{diss}(V)$	Ne	$U_{\rm diss}({ m V})$
TMP <sub>4</sub> -HTP Sc	$\mu_{\rm TM} ({\rm eV})$ -6.34	$\frac{E_{\rm f}({\rm eV})}{-3.68}$	U° <sub>diss</sub> (V) -2.08	N <sub>e</sub> 3	U <sub>diss</sub> (V) -0.85
TMP <sub>4</sub> -HTP Sc Ti	$\mu_{\rm TM} ({\rm eV})$ -6.34 -7.9	$E_{\rm f}({\rm eV})$ -3.68 -3.17	$U^{\circ}_{\rm diss}({ m V})$ -2.08 -1.63	N <sub>e</sub> 3 2	U <sub>diss</sub> (V) -0.85 -0.04
TMP <sub>4</sub> -HTP Sc Ti V	$\mu_{\rm TM} (eV)$ -6.34 -7.9 -9.09		$     \begin{array}{r} U^{\circ}_{\rm diss}({\rm V}) \\         -2.08 \\         -1.63 \\         -1.18 \\     \end{array} $	N <sub>e</sub> 3 2 2	$     U_{diss}(V) \\     -0.85 \\     -0.04 \\     0.13   $
TMP <sub>4</sub> -HTP Sc Ti V Cr	$\frac{\mu_{\rm TM} ({\rm eV})}{-6.34}$ -7.9 -9.09 -9.64	$E_{\rm f}({\rm eV}) \\ -3.68 \\ -3.17 \\ -2.62 \\ -2.63 \\ -2.63$	$     \begin{array}{r} U^{\circ}_{\rm diss}({\rm V}) \\         -2.08 \\         -1.63 \\         -1.18 \\         -0.91 \end{array} $	N <sub>e</sub> 3 2 2 2	$\begin{array}{c} U_{\rm diss}({\rm V}) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \end{array}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn	$\frac{\mu_{\rm TM} ({\rm eV})}{-6.34}$ -7.9 -9.09 -9.64 -9.16	$E_{\rm f}({\rm eV}) \\ -3.68 \\ -3.17 \\ -2.62 \\ -2.63 \\ -3.24$	$U^{\circ}_{diss}(V) \\ -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19$	N <sub>e</sub> 3 2 2 2 2 2	$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43$
TMP₄-HTP Sc Ti V Cr Mn Fe	$\mu_{TM} (eV)$ -6.34 -7.9 -9.09 -9.64 -9.16 -8.46	$E_{\rm f}({\rm eV})$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21	$U^{\circ}_{diss}(V) = -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 = -0.45$	N <sub>e</sub> 3 2 2 2 2 2 2 2	$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co	$\frac{\mu_{\rm TM} ({\rm eV})}{-6.34}$ -7.9 -9.09 -9.64 -9.16 -8.46 -7.11	$E_{\rm f}({\rm eV})$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23	$U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18 -0.91 -1.19 -0.45 -0.28	N <sub>e</sub> 3 2 2 2 2 2 2 2 2 2	$\begin{array}{c} U_{\rm diss}({\rm V}) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \end{array}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni	$\begin{array}{r} \mu_{\rm TM} \ ({\rm eV}) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34	$U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18 -0.91 -1.19 -0.45 -0.28 -0.26	N <sub>e</sub> 3 2 2 2 2 2 2 2 2 2 2	$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ 0.41 \\ 0.43 \\ 0.41 \\ 0.43 \\ 0.43 \\ 0.41 \\ 0.44 \\ 0.14 \\ 0.43 \\ 0.41 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.44 \\ 0.14 \\ 0.4$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP	$\mu_{TM} (eV)$ -6.34 -7.9 -9.09 -9.64 -9.16 -8.46 -7.11 -5.78 $\mu_{TM} (eV)$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$	$U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18 -0.91 -1.19 -0.45 -0.28 -0.26 $U^{\circ}_{diss}(V)$	Ne           3           2           2           2           2           2           2           2           2           2           2           2           2           2           2           2           2           2           Ne	$U_{\rm diss}({\rm V}) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ U_{\rm diss}({\rm V}) \\ \end{bmatrix}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP Sc	$\begin{array}{r} \mu_{\rm TM}  ({\rm eV}) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \\ \hline \mu_{\rm TM}  ({\rm eV}) \\ \hline -6.34 \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80	$U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18 -0.91 -1.19 -0.45 -0.28 -0.26 $U^{\circ}_{diss}(V)$ -2.08		$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ U_{\rm diss}(V) \\ 0.19 \\ \end{bmatrix}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP Sc Ti	$\frac{\mu_{\text{TM}} (\text{eV})}{-6.34}$ -7.9 -9.09 -9.64 -9.16 -8.46 -7.11 -5.78 $\frac{\mu_{\text{TM}} (\text{eV})}{-6.34}$ -7.9	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80 -6.16	$U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18 -0.91 -1.19 -0.45 -0.28 -0.26 $U^{\circ}_{diss}(V)$ -2.08 -1.63		$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ U_{\rm diss}(V) \\ 0.19 \\ 1.45 \\ \end{bmatrix}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP Sc Ti V	$\begin{array}{r} \mu_{\rm TM}  ({\rm eV}) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \\ \hline \mu_{\rm TM}  ({\rm eV}) \\ \hline -6.34 \\ -7.9 \\ -9.09 \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80 -6.16 -5.15	$U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18 -0.91 -1.19 -0.45 -0.28 -0.26 $U^{\circ}_{diss}(V)$ -2.08 -1.63 -1.18		$\begin{array}{c} U_{\rm diss}({\rm V}) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ \hline U_{\rm diss}({\rm V}) \\ 0.19 \\ 1.45 \\ 1.39 \\ \end{array}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP Sc Ti V Cr	$\begin{array}{r} \mu_{TM} (eV) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \\ \hline \mu_{TM} (eV) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80 -6.16 -5.15 -5.08	$\begin{array}{r} U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 \\ -0.28 \\ -0.26 \\ \hline U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ \end{array}$		$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ U_{\rm diss}(V) \\ 0.19 \\ 1.45 \\ 1.39 \\ 1.63 \\ 0 \\ 1.63 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ $
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP Sc Ti V Cr Mn	$\begin{array}{r} \mu_{\rm TM}  ({\rm eV}) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \\ \hline \mu_{\rm TM}  ({\rm eV}) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80 -6.16 -5.15 -5.08 -5.43	$\begin{array}{c} U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 \\ -0.28 \\ -0.26 \\ \hline U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ \end{array}$	$     \begin{array}{r}             N_e \\             3 \\             2 \\           $	$U_{\rm diss}(V) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ U_{\rm diss}(V) \\ 0.19 \\ 1.45 \\ 1.39 \\ 1.63 \\ 1.52 \\ \end{bmatrix}$
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP Sc Ti V Cr Mn Fe	$\begin{array}{r} \mu_{TM} (eV) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \\ \hline \mu_{TM} (eV) \\ -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80 -6.16 -5.15 -5.08 -5.43 -5.03	$\begin{array}{r} U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 \\ -0.28 \\ -0.26 \\ \hline U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 \\ \end{array}$	$     \begin{array}{r}             N_e \\             3 \\             2 \\           $	$\begin{array}{c} U_{\rm diss}({\rm V}) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ \hline U_{\rm diss}({\rm V}) \\ 0.19 \\ 1.45 \\ 1.39 \\ 1.63 \\ 1.52 \\ 2.06 \\ \end{array}$
$\frac{TMP_4-HTP}{Sc}$ $\frac{V}{Cr}$ $Mn$ $Fe$ $Co$ $Ni$ $\frac{TMS_4-HTP}{Sc}$ $Ti$ $V$ $Cr$ $Mn$ $Fe$ $Co$	$\begin{array}{r} \mu_{\rm TM}  ({\rm eV}) \\ \hline -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ -5.78 \\ \hline \mu_{\rm TM}  ({\rm eV}) \\ \hline -6.34 \\ -7.9 \\ -9.09 \\ -9.64 \\ -9.16 \\ -8.46 \\ -7.11 \\ \end{array}$	$E_{f}(eV)$ -3.68 -3.17 -2.62 -2.63 -3.24 -3.21 -3.23 -3.34 $E_{f}(eV)$ -6.80 -6.16 -5.15 -5.08 -5.43 -5.03 -5.17	$\begin{array}{r} U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 \\ -0.28 \\ -0.26 \\ \hline U^{\circ}_{\rm diss}({\rm V}) \\ \hline -2.08 \\ -1.63 \\ -1.18 \\ -0.91 \\ -1.19 \\ -0.45 \\ -0.28 \\ \end{array}$	$     \begin{array}{r}             N_e \\             3 \\             2 \\           $	$\begin{array}{c} U_{\rm diss}({\rm V}) \\ -0.85 \\ -0.04 \\ 0.13 \\ 0.41 \\ 0.43 \\ 1.16 \\ 1.34 \\ 1.41 \\ \hline U_{\rm diss}({\rm V}) \\ 0.19 \\ 1.45 \\ 1.39 \\ 1.63 \\ 1.52 \\ 2.06 \\ 2.31 \\ \end{array}$

**Tab. S3** Computed the total energy of a metal atom in its most stable bulk structure  $(\mu_{\text{TM}})$ , formation energy  $(E_f)$ , standard dissolution potential  $(U^{\circ}_{\text{diss}})$  of metal atoms, the number of transferred electrons (*N*e) during the dissolution, and dissolution potential  $(U_{\text{diss}})$  of metals.

TMN <sub>4</sub> -	N-end	O-end	side-on	TMO <sub>4</sub> -	N-end	O-end	side-on
HTP	(eV)	(eV)	(eV)	HTP	(eV)	(eV)	(eV)
Sc	-1.47	-0.63	NAN	Sc	-1.01	-0.67	NAN
Ti	-2.38	-0.96	-1.28	Ti	-1.70	-1.29	-1.41
V	-2.09	-0.84	-1.58	V	-1.52	-0.31	-0.96
Cr	-1.69	-0.10	-0.76	Cr	-1.49	0.01	-0.65
Mn	-1.20	0.35	-0.30	Mn	-0.78	NAN	NAN
Fe	-1.23	0.28	NAN	Fe	-0.97	0.23	NAN
Co	-0.73	0.43	NAN	Co	-0.96	0.12	NAN
Ni	0.07	0.65	NAN	Ni	-0.21	NAN	NAN
TMP <sub>4</sub> -	N-end	O-end	side-on	TMS <sub>4</sub> -	N-end	O-end	side-on
TMP <sub>4</sub> - HTP	N-end (eV)	O-end (eV)	side-on (eV)	TMS <sub>4</sub> - HTP	N-end (eV)	O-end (eV)	side-on (eV)
TMP <sub>4</sub> - HTP Sc	N-end (eV) NAN	O-end (eV) NAN	side-on (eV) NAN	TMS <sub>4</sub> - HTP Sc	N-end (eV) -0.86	O-end (eV) -0.17	side-on (eV) NAN
TMP <sub>4</sub> - HTP Sc Ti	N-end (eV) NAN NAN	O-end (eV) NAN NAN	side-on (eV) NAN NAN	TMS <sub>4</sub> - HTP Sc Ti	N-end (eV) -0.86 -2.29	O-end (eV) -0.17 -1.42	side-on (eV) NAN NAN
TMP <sub>4</sub> - HTP Sc Ti V	N-end (eV) NAN NAN -3.59	O-end (eV) NAN NAN -1.26	side-on (eV) NAN NAN -2.67	TMS <sub>4</sub> - HTP Sc Ti V	N-end (eV) -0.86 -2.29 -2.35	O-end (eV) -0.17 -1.42 -1.24	side-on (eV) NAN NAN -1.51
TMP <sub>4</sub> - HTP Sc Ti V Cr	N-end (eV) NAN NAN -3.59 -2.75	O-end (eV) NAN NAN -1.26 -0.73	side-on (eV) NAN NAN -2.67 -1.61	TMS <sub>4</sub> - HTP Sc Ti V Cr	N-end (eV) -0.86 -2.29 -2.35 -1.71	O-end (eV) -0.17 -1.42 -1.24 -0.05	side-on (eV) NAN NAN –1.51 NAN
TMP <sub>4</sub> - HTP Sc Ti V Cr Mn	N-end (eV) NAN NAN -3.59 -2.75 -2.15	O-end (eV) NAN NAN -1.26 -0.73 -0.17	side-on (eV) NAN NAN -2.67 -1.61 -0.79	TMS <sub>4</sub> - HTP Sc Ti V Cr Mn	N-end (eV) -0.86 -2.29 -2.35 -1.71 -1.44	O-end (eV) -0.17 -1.42 -1.24 -0.05 0.42	side-on (eV) NAN NAN -1.51 NAN -0.69
TMP <sub>4</sub> - HTP Sc Ti V Cr Mn Fe	N-end (eV) NAN NAN -3.59 -2.75 -2.15 -2.00	O-end (eV) NAN NAN -1.26 -0.73 -0.17 -0.09	side-on (eV) NAN NAN -2.67 -1.61 -0.79 NAN	TMS <sub>4</sub> - HTP Sc Ti V Cr Mn Fe	N-end (eV) -0.86 -2.29 -2.35 -1.71 -1.44 -1.39	O-end (eV) -0.17 -1.42 -1.24 -0.05 0.42 0.44	side-on (eV) NAN NAN -1.51 NAN -0.69 -0.19
TMP <sub>4</sub> - HTP Sc Ti V Cr Mn Fe Co	N-end (eV) NAN NAN -3.59 -2.75 -2.15 -2.00 -2.22	O-end (eV) NAN NAN -1.26 -0.73 -0.17 -0.09 NAN	side-on (eV) NAN NAN -2.67 -1.61 -0.79 NAN NAN	TMS <sub>4</sub> - HTP Sc Ti V Cr Mn Fe Co	N-end (eV) -0.86 -2.29 -2.35 -1.71 -1.44 -1.39 -0.78	O-end (eV) -0.17 -1.42 -1.24 -0.05 0.42 0.44 0.30	side-on (eV) NAN NAN -1.51 NAN -0.69 -0.19 NAN

**Tab. S4** Free energies of NO on TMX<sub>4</sub>-HTPs with N-end, O-end, and side-on patterns, the lowest energies are highlighted in red.

TMN <sub>4</sub> -HTP	$\Delta G_{ m *NO}$	$\Delta G_{ m *H}$	$\Delta G_{ m *H2O}$	$\Delta G_{ m *NH3}$
Sc	-1.47	2.24	-0.74	-0.71
Ti	-2.38	-0.09	-1.16	-1.11
V	-2.09	0.04	-0.51	-1.03
Cr	-1.69	0.23	0.23	-0.35
Mn	-1.20	0.46	0.22	0.00
Fe	-1.23	0.22	0.23	-0.06
Co	-0.73	0.43	0.22	0.42
Ni	NAN	NAN	NAN	NAN
TMO <sub>4</sub> -HTP	$\Delta G_{*_{ m NO}}$	$\Delta G_{ m *H}$	$\Delta G_{ m *H2O}$	$\Delta G_{ m *_{NH3}}$
Sc	-1.01	2.24	-1.09	-1.32
Ti	-1.70	0.00	-1.66	-1.99
V	-1.52	0.09	-0.23	-0.76
Cr	-1.49	0.37	-0.11	-0.82
Mn	-0.78	1.35	0.07	-0.31
Fe	-0.97	0.65	0.14	-0.29
Co	-0.96	0.49	0.34	-0.08
Ni	-0.21	1.18	0.29	0.26
	$\wedge C$			10
TMP <sub>4</sub> -HTP	$\Delta G_{NO}$	$\Delta G_{*H}$	$\Delta G_{*H2O}$	$\Delta G_{*\rm NH3}$
TMP <sub>4</sub> -HTP Sc	NAN	NAN	NAN	NAN
TMP <sub>4</sub> -HTP Sc Ti	NAN NAN	NAN NAN	NAN NAN	NAN NAN
TMP <sub>4</sub> -HTP       Sc       Ti       V	NAN NAN -3.59	ΔG <sub>*H</sub> NAN NAN -0.75	NAN NAN -1.16	ΔG <sub>*NH3</sub> NAN NAN -1.83
TMP <sub>4</sub> -HTP Sc Ti V Cr	NAN NAN -3.59 -2.75	NAN NAN -0.75 -0.15	NAN NAN -1.16 -0.71	NAN NAN -1.83 -1.34
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn	NAN NAN -3.59 -2.75 -2.15	NAN NAN -0.75 -0.15 -0.12	NAN NAN -1.16 -0.71 0.15	NAN NAN -1.83 -1.34 -0.28
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe	ΔG*NO           NAN           NAN           -3.59           -2.75           -2.15           -2.00	ΔG*H           NAN           NAN           -0.75           -0.15           -0.12           -0.25	NAN NAN -1.16 -0.71 0.15 0.03	NAN NAN -1.83 -1.34 -0.28 -0.23
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co	NAN NAN -3.59 -2.75 -2.15 -2.00 -2.22	ΔG*H           NAN           NAN           -0.75           -0.15           -0.12           -0.25           -0.76	NAN NAN -1.16 -0.71 0.15 0.03 -0.59	ΔG* <sub>NH3</sub> NAN           NAN           -1.83           -1.34           -0.28           -0.23           -0.76
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni	NAN NAN -3.59 -2.75 -2.15 -2.00 -2.22 -0.88	<u>А</u> G <sub>*H</sub> NAN NAN -0.75 -0.15 -0.12 -0.25 -0.76 -0.67	NAN NAN -1.16 -0.71 0.15 0.03 -0.59 0.05	NAN NAN -1.83 -1.34 -0.28 -0.23 -0.76 -0.35
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co Ni TMS <sub>4</sub> -HTP	$\begin{array}{r} \Delta G_{*NO} \\ \hline NAN \\ NAN \\ -3.59 \\ -2.75 \\ -2.15 \\ -2.00 \\ -2.22 \\ -0.88 \\ \hline \Delta G_{*NO} \end{array}$	$\begin{array}{c} \Delta G_{*\rm H} \\ \\ {\rm NAN} \\ -0.75 \\ -0.15 \\ -0.12 \\ -0.25 \\ -0.76 \\ -0.67 \\ \\ \Delta G_{*\rm H} \end{array}$	$\begin{array}{r} \Delta G_{*\rm H2O} \\ \hline {\rm NAN} \\ {\rm NAN} \\ -1.16 \\ -0.71 \\ 0.15 \\ 0.03 \\ -0.59 \\ 0.05 \\ \hline \Delta G_{*\rm H2O} \end{array}$	$\begin{array}{r} \Delta G_{*_{\rm NH3}} \\ \\ & {\rm NAN} \\ -1.83 \\ -1.34 \\ -0.28 \\ -0.23 \\ -0.76 \\ -0.35 \\ \\ \Delta G_{*_{\rm NH3}} \end{array}$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Sc}}{\text{Ti}}$ $\frac{\text{V}}{\text{Cr}}$ $\frac{\text{Mn}}{\text{Fe}}$ $\frac{\text{Co}}{\text{Ni}}$ $\frac{\text{TMS}_{4}\text{-}\text{HTP}}{\text{Sc}}$	$\begin{array}{r} \Delta G_{*NO} \\ \hline NAN \\ NAN \\ -3.59 \\ -2.75 \\ -2.15 \\ -2.00 \\ -2.22 \\ -0.88 \\ \hline \Delta G_{*NO} \\ -0.86 \end{array}$	$\begin{array}{c c} \Delta G_{*\rm H} \\ \hline {\rm NAN} \\ {\rm NAN} \\ -0.75 \\ -0.15 \\ -0.12 \\ -0.25 \\ -0.76 \\ -0.67 \\ \hline \Delta G_{*\rm H} \\ \hline {\rm 1.01} \end{array}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Ti}}{\text{V}}$ $\frac{\text{Cr}}{\text{Mn}}$ $\frac{\text{Fe}}{\text{Co}}$ $\frac{\text{Ni}}{\text{TMS}_{4}\text{-}\text{HTP}}$ $\frac{\text{Sc}}{\text{Ti}}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c} \Delta G_{*\rm H} \\ \hline {\rm NAN} \\ {\rm NAN} \\ -0.75 \\ -0.15 \\ -0.12 \\ -0.25 \\ -0.76 \\ -0.67 \\ \hline \Delta G_{*\rm H} \\ \hline 1.01 \\ 0.47 \\ \end{array}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r} \Delta G_{*\rm NH3} \\ \hline {\rm NAN} \\ {\rm NAN} \\ -1.83 \\ -1.34 \\ -0.28 \\ -0.23 \\ -0.76 \\ -0.35 \\ \hline \Delta G_{*\rm NH3} \\ -1.06 \\ -2.02 \\ \end{array}$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Ti}}{\text{V}}$ $\frac{\text{Cr}}{\text{Mn}}$ $\frac{\text{Fe}}{\text{Co}}$ $\frac{\text{Ni}}{\text{TMS}_{4}\text{-}\text{HTP}}$ $\frac{\text{Sc}}{\text{Ti}}$ $\frac{\text{V}}{\text{V}}$	$\begin{array}{r} \Delta G_{*NO} \\ \hline NAN \\ NAN \\ -3.59 \\ -2.75 \\ -2.15 \\ -2.00 \\ -2.22 \\ -0.88 \\ \hline \Delta G_{*NO} \\ \hline -0.86 \\ -2.29 \\ -2.35 \\ \end{array}$	$\begin{array}{c} \Delta G_{*\rm H} \\ \\ \rm NAN \\ -0.75 \\ -0.15 \\ -0.12 \\ -0.25 \\ -0.76 \\ -0.67 \\ \hline \Delta G_{*\rm H} \\ 1.01 \\ 0.47 \\ -0.05 \\ \end{array}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Ti}}{\text{V}}$ $\frac{\text{Cr}}{\text{Mn}}$ $\frac{\text{Fe}}{\text{Co}}$ $\frac{\text{Ni}}{\text{TMS}_{4}\text{-}\text{HTP}}$ $\frac{\text{Sc}}{\text{Ti}}$ $\frac{\text{V}}{\text{Cr}}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Ti}}{\text{V}}$ $\frac{\text{Cr}}{\text{Mn}}$ $\frac{\text{Fe}}{\text{Co}}$ $\frac{\text{Ni}}{\text{TMS}_{4}\text{-}\text{HTP}}$ $\frac{\text{Sc}}{\text{Ti}}$ $\frac{\text{V}}{\text{Cr}}$ $\frac{\text{Mn}}{\text{Mn}}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{c c} \Delta G_{*\rm H} \\ \hline {\rm NAN} \\ {\rm NAN} \\ -0.75 \\ -0.15 \\ -0.12 \\ -0.25 \\ -0.76 \\ -0.67 \\ \hline \Delta G_{*\rm H} \\ \hline 1.01 \\ 0.47 \\ -0.05 \\ 0.32 \\ 0.50 \\ \end{array}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Ti}}{\text{V}}$ $\frac{\text{Cr}}{\text{Mn}}$ $\frac{\text{Fe}}{\text{Co}}$ $\frac{\text{Ni}}{\text{TMS}_{4}\text{-}\text{HTP}}$ $\frac{\text{Sc}}{\text{Ti}}$ $\frac{\text{V}}{\text{Cr}}$ $\frac{\text{Mn}}{\text{Fe}}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$
$\frac{\text{TMP}_{4}\text{-}\text{HTP}}{\text{Sc}}$ $\frac{\text{Ti}}{\text{V}}$ $\frac{\text{Cr}}{\text{Mn}}$ $\frac{\text{Fe}}{\text{Co}}$ $\frac{\text{Ni}}{\text{TMS}_{4}\text{-}\text{HTP}}$ $\frac{\text{Sc}}{\text{Ti}}$ $\frac{\text{V}}{\text{Cr}}$ $\frac{\text{Mn}}{\text{Fe}}$ $\frac{\text{Co}}{\text{Co}}$	$\begin{array}{r} \Delta G_{*NO} \\ \hline NAN \\ NAN \\ -3.59 \\ -2.75 \\ -2.15 \\ -2.00 \\ -2.22 \\ -0.88 \\ \hline \Delta G_{*NO} \\ \hline -0.86 \\ -2.29 \\ -2.35 \\ -1.71 \\ -1.44 \\ -1.39 \\ -0.78 \\ \end{array}$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$	$\begin{array}{r c c c c c c c c c c c c c c c c c c c$

**Tab. S5** Free energies of NO ( $\Delta G_{*NO}$ ), H ( $\Delta G_{*H}$ ), H2O molecules ( $\Delta G_{*H2O}$ ), and NH3 molecules ( $\Delta G_{*NH3}$ ) on TMX<sub>4</sub>-HTPs, the lowest energies are highlighted in red.

TMN <sub>4</sub> -HTP	$\Delta G_1$	TMO <sub>4</sub> -HTP	$\Delta G_1$
Sc	-0.24	Sc	NAN
Ti	0.16	Ti	NAN
V	0.53	V	0.27
Cr	0.86	Cr	1.86
Mn	0.54	Mn	0.21
Fe	0.30	Fe	0.32
Со	0.55	Со	0.43
Ni	NAN	Ni	0.55
TMP <sub>4</sub> -HTP	$\Delta G_1$	TMS <sub>4</sub> -HTP	$\Delta G_1$
Sc	NAN	Sc	NAN
Ti	NAN	Ti	0.43
V	1.00	V	0.34
Cr	1.01	Cr	0.63
Mn	1.17	Mn	0.80
Fe	0.92	Fe	0.40
Co	0.78	Со	0.42

**Tab. S6** Energy( $\Delta G_1$ ) required for the first protonation step of NO + H + e<sup>-</sup>  $\rightarrow$  HNO(NOH), those with  $\Delta G_1 < 0.5$  eV are highlighted in red.

SoN HTD	adsorbate	Energy (eV)	Eros sparau (aV)
Scin4-IIIF	slab	-540.60	Free energy (ev)
step0	*N_0	-554.80	-1.47
aton 1	*HN_O	-558.79	-0.24
step1	*N_OH	-557.41	1.00
	*2HN_0	-563.43	-0.83
step2	*HN_OH	-562.54	0.01
	*2HN_OH	-566.04	1.07
step3	*0	-546.43	0.57
step4	*ОН	-552.52	-2.43
step5	*H <sub>2</sub> O	-556.10	0.15
step6	H <sub>2</sub> O	-540.60	0.74
	adsorbate	Energy (eV)	
I 1N <sub>4</sub> -H I P	slab	-542.85	Free energy (eV)
step0	*N_0	-558.02	-2.38
. 1	*HN_O	-561.53	0.16
step1	*N_OH	-561.18	0.55
	*2HN_0	-566.39	-0.95
step2	*HN_OH	-565.50	-0.18
	*2HN_OH	-568.71	1.27
step3	*0	-549.94	-0.06
step4	*ОН	-555.69	-2.09
step5	*H <sub>2</sub> O	-558.85	0.66
step6	H <sub>2</sub> O	-542.85	1.16
	adsorbate	Energy (eV)	
FeN <sub>4</sub> -HTP	slab	-539.41	Free energy (eV)
step0	*N_0	-553.50	-1.23
. 1	*HN_O	-556.93	0.30
step1	*N_OH	-556.28	0.94
	*2HN_0	-560.25	0.39
step2	*HN_OH	-560.31	0.36
	*2HN_OH	-564.07	0.09
step3	*NH	-550.00	-1.19
step4	*NH <sub>2</sub>	-555.07	-1.06
step5	*NH <sub>3</sub>	-559.55	-0.75
step6	NH <sub>3</sub>	-539.41	0.06
	adsorbate	Energy (eV)	
VO <sub>4</sub> -HTP	slab	-481.94	Free energy (eV)
step0	*N_0	-496.29	-1.52
step1	*HN_O	-499.71	0.27

**Tab. S7** The energy of all the possible intermediates, and the free energy of the five hydrogenation steps.

	*N_OH	-499.52	0.46
	*2HN_O	-504.72	-1.13
step2	*HN_OH	-504.10	-0.60
	*2HN_OH	-507.55	0.81
step3	*0	-489.86	-1.60
step4	*OH	-493.87	-0.27
step5	*H <sub>2</sub> O	-497.03	0.52
step6	H <sub>2</sub> O	-481.94	0.23
	adsorbate	Energy (eV)	
MnO <sub>4</sub> -HTP	slab	-479.86	Free energy (eV)
step0	*N_0	-493.48	-0.78
	*HN_O	-496.98	0.21
stepl	*N_OH	-496.44	0.75
	*2HN_O	-499.66	1.06
step2	*HN_OH	-500.57	0.15
	*2HN_OH	-504.90	-0.58
step3	*NH	-490.26	-0.90
step4	*NH <sub>2</sub>	-495.43	-1.41
step5	*NH3	-500.27	-1.08
step6	NH <sub>3</sub>	-479.86	0.31
	adsorbate	Energy (eV)	
FeO <sub>4</sub> -HTP	slab	-474.16	Free energy (eV)
step0	*N_0	-487.99	-0.97
	*HN_O	-491.38	0.32
step1	*N_OH	-490.79	0.90
	*2HN_0	-494.83	0.23
step2	*HN_OH	-494.64	0.45
stop?	*2HN_OH	-499.16	-0.80
step5	*O	-479.45	-0.94
step4	*ОН	-484.37	-1.15
step5	*H <sub>2</sub> O	-488.82	-0.85
step6	H <sub>2</sub> O	-474.16	-0.14
	adsorbate	Energy (eV)	- Eraa anargy (aV)
004-1117	slab	-469.20	Thee energy (ev)
step0	*N_0	-482.99	-0.96
stop 1	*HN_O	-486.29	0.43
Sicht	*N_OH	-485.51	1.21
sten?	*2HN_0	-489.92	0.12
500p2	*HN_OH	-489.86	0.15
sten3	*2HN_OH	-494.06	-0.42
sups	*0	-473.97	-0.45
step4	*OH	-479.13	-1.36
step5	*H <sub>2</sub> O	-483.67	-0.95

step6	H <sub>2</sub> O	-469.20	-0.34
N'D LITD	adsorbate	Energy (eV)	Encourse (aV)
NIP <sub>4</sub> -HIP	slab	-487.44	Free energy (ev)
step0	*N_0	-501.16	-0.88
	*HN_O	-503.72	1.14
step1	*N_OH	-504.56	0.28
atan	*2HN_0	-508.10	0.25
step2	*HN_OH	-508.35	0.04
atom?	*2HN_OH	-512.79	-0.91
steps	*NH	-499.73	-2.74
step4	*NH <sub>2</sub>	-502.79	0.59
step5	*NH <sub>3</sub>	-507.90	-1.35
step6	NH <sub>3</sub>	-487.44	0.35
T:C LITD	adsorbate	Energy (eV)	
П54-ПТР	slab	-446.77	Free energy (ev)
step0	*N_0	-461.79	-2.29
aton 1	*HN_O	-465.16	0.43
step1	*N_OH	-464.89	0.73
aton 2	*2HN_O	-470.14	-1.23
step2	*HN_OH	-469.39	-0.45
aton?	*2HN_OH	-473.57	0.35
steps	*0	-454.79	-1.00
step4	*OH	-459.41	-0.99
step5	*H <sub>2</sub> O	-463.24	-0.05
step6	H <sub>2</sub> O	-446.77	1.64
VC HTD	adsorbate	Energy (eV)	
v 34-111F	slab	-447.32	Thee energy (ev)
step0	*N_0	-462.51	-2.35
ste <b>n</b> 1	*HN_O	-465.84	0.35
step1	*N_OH	-465.72	0.48
sten?	*2HN_0	-470.85	-1.13
step2	*HN_OH	-470.07	-0.44
sten3	*2HN_OH	-474.00	0.52
steps	*0	-455.77	-1.38
step4	*ОН	-459.67	-0.24
step5	*H <sub>2</sub> O	-463.48	-0.05
step6	H <sub>2</sub> O	-447.32	1.30
FeSteHTP	adsorbate	Energy (eV)	Free energy (eV)
	slab	-445.06	
step0	*N_0	-459.32	-1.39
sten1	*HN_O	-462.54	0.47
Step1	*N_OH	-461.93	1.09
step2	*2HN_0	-465.81	0.46

	*HN_OH	-465.90	0.39	
sten3	*2HN_OH	-470.10	-0.51	
steps	*NH	-455.61	-0.93	
step4	*NH <sub>2</sub>	-460.71	-1.30	
step5	*NH <sub>3</sub>	-465.44	-1.03	
step6	NH <sub>3</sub>	-445.06	0.30	
	adsorbate	Energy (eV)		
С054-ПТР	slab	-441.46	Free energy (ev)	
step0	*N_0	-455.03	-0.78	
step1	*HN_O	-458.37	0.42	
	*N_OH	-457.71	1.08	
step2	*2HN_0	-461.94	0.15	
	*HN_OH	-461.74	0.37	
step3	*2HN_OH	-466.17	-0.43	
	*0	*O -446.20		
step4	*ОН	-451.10	-1.17	
step5	*H <sub>2</sub> O	-455.76	-1.02	
step6	H <sub>2</sub> O	-441.46	-0.48	

TMN <sub>4</sub> -HTP	Translate	N-O bond	TMO LITE	Translate	N-O bond
	charge (e <sup>-</sup> )	(Å)	TMO <sub>4</sub> -HTP	charge (e <sup>-</sup> )	(Å)
Sc	0.40348	1.19808	Sc	0.26167	1.18518
Ti	0.50708	1.20156	Ti	0.41017	1.19433
V	0.44967	1.20008	V	0.30807	1.19106
Cr	0.43873	1.1995	Cr	0.29874	1.18734
Mn	0.34409	1.1906	Mn	0.15188	1.1784
Fe	0.38448	1.19437	Fe	0.23941	1.18434
Co	0.18459	1.18634	Co	0.17147	1.18179
Ni	NAN	NAN	Ni	0.08413	1.17775
TMD UTD	Translate	N-O bond	TMC LITD	Translate	N-O bond
TMP <sub>4</sub> -HTP	Translate charge (e <sup>-</sup> )	N-O bond (Å)	TMS <sub>4</sub> -HTP	Translate charge (e <sup>-</sup> )	N-O bond (Å)
TMP <sub>4</sub> -HTP Sc	Translate charge (e⁻ ) NAN	N-O bond (Å) NAN	TMS <sub>4</sub> -HTP Sc	Translate charge (e <sup>-</sup> ) 0.22112	N-O bond (Å) 1.17567
TMP <sub>4</sub> -HTP Sc Ti	Translate charge (e <sup>-</sup> ) NAN NAN	N-O bond (Å) NAN NAN	TMS <sub>4</sub> -HTP Sc Ti	Translate charge (e <sup>-</sup> ) 0.22112 0.32804	N-O bond (Å) 1.17567 1.1829
TMP <sub>4</sub> -HTP Sc Ti V	Translate charge (e <sup>-</sup> ) NAN NAN 0.48947	N-O bond (Å) NAN NAN 1.19306	TMS <sub>4</sub> -HTP Sc Ti V	Translate charge (e <sup>-</sup> ) 0.22112 0.32804 0.35708	N-O bond (Å) 1.17567 1.1829 1.18548
TMP <sub>4</sub> -HTP Sc Ti V Cr	Translate charge (e <sup>-</sup> ) NAN NAN 0.48947 0.42713	N-O bond (Å) NAN NAN 1.19306 1.18901	TMS <sub>4</sub> -HTP Sc Ti V Cr	Translate charge (e <sup>-</sup> ) 0.22112 0.32804 0.35708 0.3021	N-O bond (Å) 1.17567 1.1829 1.18548 1.18283
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn	Translate charge (e <sup>-</sup> ) NAN NAN 0.48947 0.42713 0.26618	N-O bond (Å) NAN NAN 1.19306 1.18901 1.17993	TMS4-HTP Sc Ti V Cr Mn	Translate charge (e <sup>-</sup> ) 0.22112 0.32804 0.35708 0.3021 0.28027	N-O bond (Å) 1.17567 1.1829 1.18548 1.18283 1.18199
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe	Translate charge (e <sup>-</sup> ) NAN NAN 0.48947 0.42713 0.26618 0.18829	N-O bond (Å) NAN NAN 1.19306 1.18901 1.17993 1.17966	TMS <sub>4</sub> -HTP Sc Ti V Cr Mn Fe	Translate charge (e <sup>-</sup> ) 0.22112 0.32804 0.35708 0.3021 0.28027 0.22167	N-O bond (Å) 1.17567 1.1829 1.18548 1.18283 1.18199 1.18116
TMP <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co	Translate charge (e <sup>-</sup> ) NAN NAN 0.48947 0.42713 0.26618 0.18829 0.36646	N-O bond (Å) NAN NAN 1.19306 1.18901 1.17993 1.17966 1.18601	TMS <sub>4</sub> -HTP Sc Ti V Cr Mn Fe Co	Translate charge (e <sup>-</sup> ) 0.22112 0.32804 0.35708 0.3021 0.28027 0.22167 0.1449	N-O bond (Å) 1.17567 1.1829 1.18548 1.18283 1.18199 1.18116 1.17477

**Tab. S8** Transfer charge of TM atoms, and the N-O bond of adsorbed NO on  $TMX_4$ -HTPs.

TMN <sub>4</sub> - HTP	$\Delta G_{*_{ m HNO}}$ (eV)	$\Delta G_{\rm *NOH}$ (eV)	$\Delta G_{ m *HNO} - \Delta G_{ m *NOH}$ (eV)	TMO <sub>4</sub> - HTP	$\Delta G_{*_{ m HNO}}$ (eV)	$\Delta G_{ m NOH}$ (eV)	$\Delta G_{*_{ m HNO}} - \Delta G_{*_{ m NOH}}$ (eV)
Sc	-1.72	-0.34	-1.38	Sc	NAN	NAN	NAN
Ti	-2.22	-1.87	-0.35	Ti	NAN	NAN	NAN
V	-1.56	-1.47	-0.09	V	-1.25	-1.06	-0.19
Cr	-0.18	-0.82	0.64	Cr	0.37	0.68	-0.31
Mn	-0.66	-0.09	-0.57	Mn	-0.57	-0.02	-0.54
Fe	-0.93	-0.28	-0.65	Fe	-0.65	-0.05	-0.59
Co	-0.18	0.63	-0.81	Co	-0.52	0.26	-0.78
Ni	NAN	NAN	NAN	Ni	0.34	1.12	-0.77
			1C				10
TMP <sub>4</sub> - HTP	$\Delta G_{\rm HNO}$ (eV)	$\Delta G_{ m NOH}$ (eV)	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV)	TMS <sub>4</sub> - HTP	$\Delta G_{ m HNO}$ (eV)	$\Delta G_{ m NOH}$ (eV)	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV)
TMP <sub>4</sub> - HTP	$\Delta G_{\rm HNO}$ (eV) NAN	$\frac{\Delta G_{\rm NOH}}{\rm (eV)}$ NAN	$\frac{\Delta G_{\rm HNO} - }{\Delta G_{\rm NOH}}$ (eV) NAN	TMS <sub>4</sub> - HTP Sc	$\Delta G_{\rm HNO}$ (eV)	$\Delta G_{\rm NOH}$ (eV)	$\frac{\Delta G_{\rm HNO} - \Delta G_{\rm NOH}}{(eV)}$
TMP <sub>4</sub> - HTP Sc Ti	$\Delta G_{\rm HNO}$ (eV) NAN NAN	$\Delta G_{\rm NOH}$ (eV) NAN NAN	$\Delta G_{\rm NNO} - \Delta G_{\rm NOH}$ (eV) NAN NAN	TMS <sub>4</sub> - HTP Sc Ti	$\Delta G_{\rm HNO}$ (eV) NAN -1.86	$\Delta G_{\rm NOH}$ (eV) NAN $-1.60$	$\frac{\Delta G_{\rm HNO} -}{\Delta G_{\rm NOH}}$ (eV) NAN -0.27
TMP <sub>4</sub> - HTP Sc Ti V	$\Delta G_{\rm HNO}$ (eV) NAN NAN -2.27	$\frac{\Delta G_{\rm NOH}}{\rm (eV)}$ NAN NAN -2.58	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV) NAN NAN 0.31	TMS <sub>4</sub> - HTP Sc Ti V	ΔG <sub>HNO</sub> (eV) NAN -1.86 -2.01	ΔG <sub>NOH</sub> (eV) NAN -1.60 -1.88	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV) NAN -0.27 -0.13
TMP <sub>4</sub> - HTP Sc Ti V Cr	ΔG <sub>HNO</sub> (eV) NAN NAN -2.27 -1.59	$\Delta G_{\rm NOH}$ (eV) NAN NAN -2.58 -1.74	$\Delta G_{\rm NNO} - \Delta G_{\rm NOH}$ (eV) NAN NAN 0.31 0.15	TMS <sub>4</sub> - HTP Sc Ti V Cr	ΔG <sub>HNO</sub> (eV) NAN -1.86 -2.01 -1.08	ΔG <sub>NOH</sub> (eV) NAN -1.60 -1.88 -1.07	$\frac{\Delta G_{\rm HNO} - \Delta G_{\rm NOH}}{(eV)}$ (eV) NAN -0.27 -0.13 -0.01
TMP <sub>4</sub> - HTP Sc Ti V Cr Mn	ΔG <sub>HNO</sub> (eV) NAN NAN -2.27 -1.59 -0.97	$\Delta G_{\rm NOH}$ (eV) NAN NAN -2.58 -1.74 -0.80	$\Delta G_{\rm NNO} - \Delta G_{\rm NOH}$ (eV) NAN NAN 0.31 0.15 -0.17	TMS <sub>4</sub> - HTP Sc Ti V Cr Mn	$\Delta G_{\rm HNO}$ (eV) NAN -1.86 -2.01 -1.08 -0.64	$\Delta G_{\rm NOH}$ (eV) NAN -1.60 -1.88 -1.07 -0.32	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH} \\ (eV) \\ NAN \\ -0.27 \\ -0.13 \\ -0.01 \\ -0.31 \\ \label{eq:deltaG_NOH}$
TMP <sub>4</sub> - HTP Sc Ti V Cr Mn Fe	ΔG <sub>HNO</sub> (eV) NAN NAN -2.27 -1.59 -0.97 -1.08	$\Delta G_{\rm NOH}$ (eV) NAN NAN -2.58 -1.74 -0.80 -0.46	$\begin{array}{r} \Delta G_{\rm HNO} - \\ \Delta G_{\rm NOH} \\ (eV) \\ \hline \\ NAN \\ NAN \\ 0.31 \\ 0.15 \\ -0.17 \\ -0.62 \\ \end{array}$	TMS <sub>4</sub> - HTP Sc Ti V Cr Mn Fe	$\Delta G_{\rm HNO}$ (eV) NAN -1.86 -2.01 -1.08 -0.64 -0.99	$\begin{array}{c} \Delta G_{\rm NOH} \\ (eV) \\ \hline \\ NAN \\ -1.60 \\ -1.88 \\ -1.07 \\ -0.32 \\ -0.38 \\ \end{array}$	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV) NAN -0.27 -0.13 -0.01 -0.31 -0.61
TMP <sub>4</sub> - HTP Sc Ti V Cr Mn Fe Co	$\Delta G_{\rm HNO}$ (eV) NAN NAN -2.27 -1.59 -0.97 -1.08 -1.43	$\Delta G_{\rm NOH}$ (eV) NAN NAN -2.58 -1.74 -0.80 -0.46 -0.84	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV) NAN NAN 0.31 0.15 -0.17 -0.62 -0.60	TMS <sub>4</sub> - HTP Sc Ti V Cr Mn Fe Co	$\begin{array}{c} \Delta G_{\rm HNO} \\ ({\rm eV}) \end{array}$ NAN -1.86 -2.01 -1.08 -0.64 -0.99 -0.36	$\begin{array}{c} \Delta G_{\rm NOH} \\ (eV) \\ \hline \\ NAN \\ -1.60 \\ -1.88 \\ -1.07 \\ -0.32 \\ -0.38 \\ 0.30 \\ \end{array}$	$\Delta G_{\rm HNO} - \Delta G_{\rm NOH}$ (eV) NAN -0.27 -0.13 -0.01 -0.31 -0.61 -0.66

**Tab. S9** Adsorption free energies of HNO ( $\Delta^*G_{HNO}$ ), NOH ( $\Delta G_{*NOH}$ ),  $\Delta G_{HNO} - \Delta G_{NOH}$ , the lowest energies are highlighted in red.

**Tab. S10** Charge transfer of X atoms ( $Q_X$ ) before reaction, number of valence electrons (N), atomic radius (AR), ion radius (IR), first ionization energy (IE), electron affinity of the metal atom (EA), density of TM ( $\rho_{TM}$ ), relative atomic mass (M), pauling electronegativity ( $\chi$ ) of each investigated TMX<sub>4</sub>-HTPs.

Materials	$Q_{\rm X}$	N	AR	IR	IE	EA	$ ho_{ m TM}$	М	χ
ScN	25.33405	3	144	74.5	633	-18	2.99	44.95591	1.36
TiN	25.21795	4	136	86	659	-8	4.51	47.867	1.54
VN	25.0772	5	125	79	651	-51	6.11	50.9415	1.63
CrN	24.82608	6	127	80	653	-64	7.14	51.9961	1.66
MnN	24.69297	7	139	67	717	0	7.47	54.93805	1.55
FeN	24.64825	6	125	78	763	-16	7.87	55.845	1.83
CoN	24.6003	4	126	74.5	760	-64	8.9	58.9332	1.88
NiN	24.59735	4	121	69	737	-112	8.91	58.6934	1.91
VP	17.53348	5	125	79	651	-51	6.11	50.9415	1.63
CrP	17.2083	6	127	80	653	-64	7.14	51.9961	1.66
MnP	16.91967	7	139	67	717	0	7.47	54.93805	1.55
FeP	16.62054	6	125	78	763	-16	7.87	55.845	1.83
CoP	16.54063	4	126	74.5	760	-64	8.9	58.9332	1.88
NiP	16.48769	4	121	69	737	-112	8.91	58.6934	1.91
ScO	28.57744	3	144	74.5	633	-18	2.99	44.95591	1.36
TiO	28.34883	4	136	86	659	-8	4.51	47.867	1.54
VO	28.20933	5	125	79	651	-51	6.11	50.9415	1.63
CrO	28.19818	6	127	80	653	-64	7.14	51.9961	1.66
MnO	28.12737	7	139	67	717	0	7.47	54.93805	1.55
FeO	27.93121	6	125	78	763	-16	7.87	55.845	1.83
CoO	27.83559	4	126	74.5	760	-64	8.9	58.9332	1.88
NiO	27.80528	4	121	69	737	-112	8.91	58.6934	1.91
ScS	25.53636	3	144	74.5	633	-18	2.99	44.95591	1.36
TiS	25.47583	4	136	86	659	-8	4.51	47.867	1.54
VS	25.20713	5	125	79	651	-51	6.11	50.9415	1.63
CrS	25.00778	6	127	80	653	-64	7.14	51.9961	1.66
MnS	24.90353	7	139	67	717	0	7.47	54.93805	1.55
FeS	24.51769	6	125	78	763	-16	7.87	55.845	1.83
CoS	24.21995	4	126	74.5	760	-64	8.9	58.9332	1.88
NiS	24.1118	4	121	69	737	-112	8.91	58.6934	1.91

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