Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Nitric oxide electrochemical reduction reaction on transition metal doped $MoSi_2N_4$ monolayers

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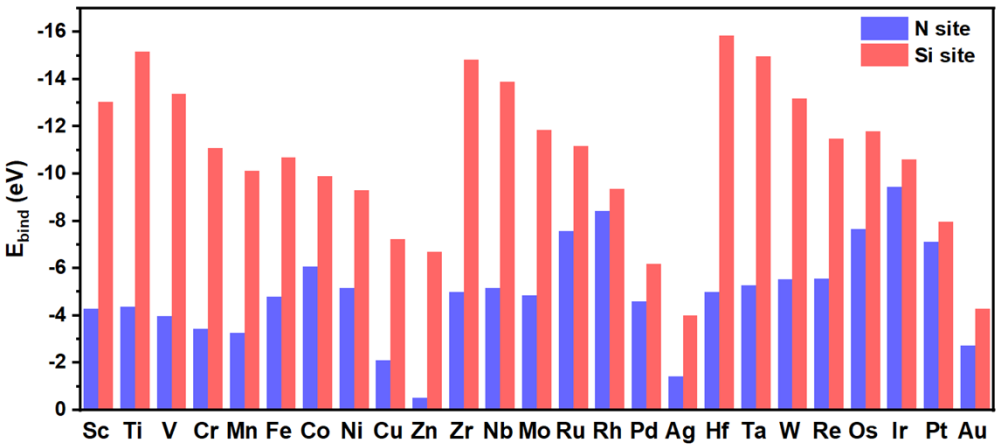

Figure S1 The calculated binding energy of transition metals at the N and Si sites of MSN monolayers.

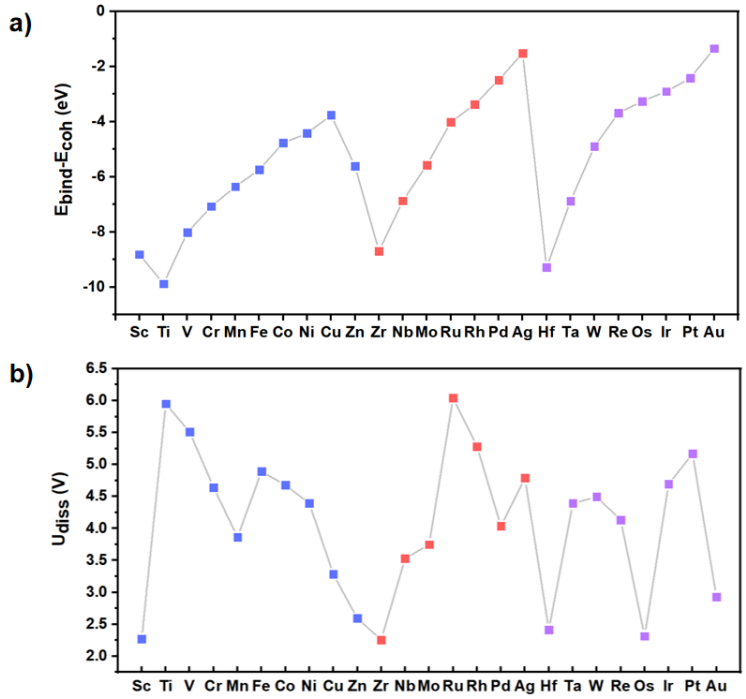

Figure S2 (a) The calculated energy difference between the binding energy and the cohesive energy (E_{bind} - E_{coh}) and (b) dissolution potential of TM-MSN.

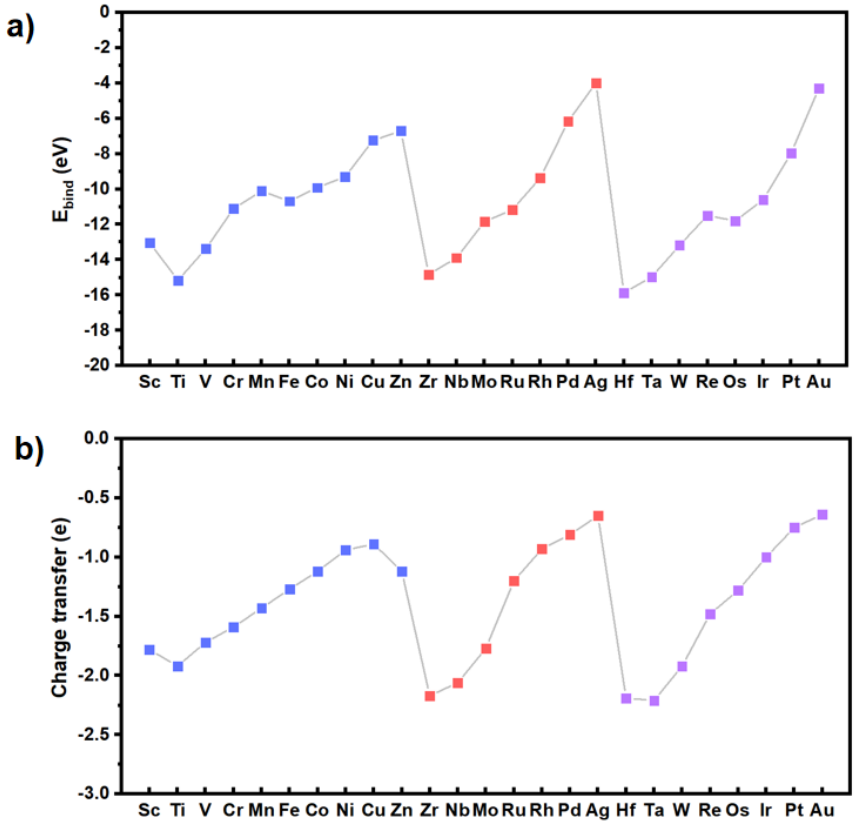

Figure S3 The (a) bind energy and (b) charge transfer between TM atoms and the substrates.

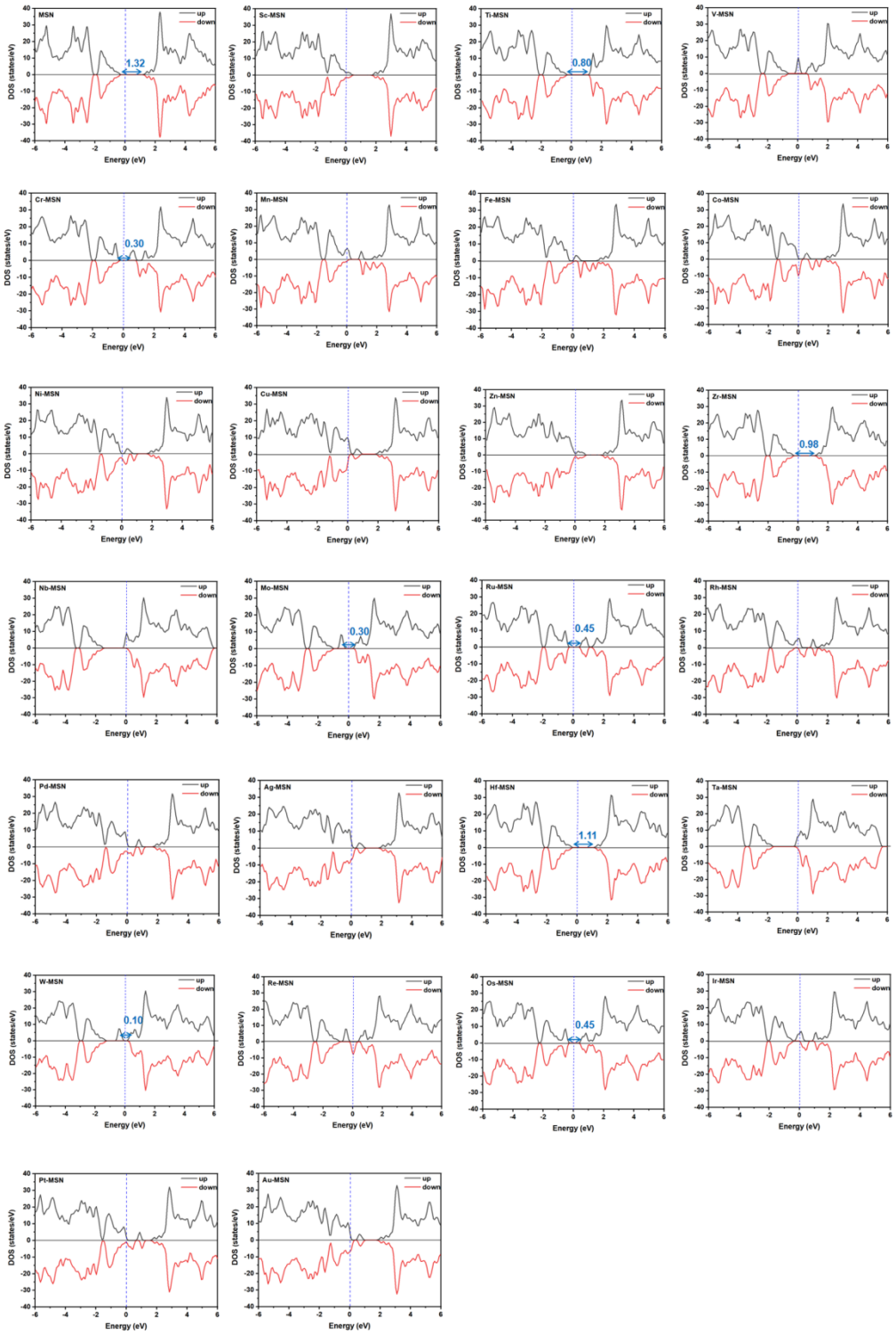

Figure S4 The DOS of pristine MSN and TM-MSN monolayers, the dotted blue lines represent Fermi energy, and the black and red lines represent spin up and spin down, respectively. The labelled numbers represent the exact band gap values.

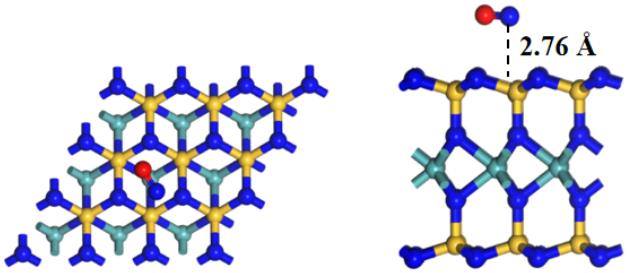

Figure S5 The top and side views of pristine MSN monolayer absorbed by NO molecule, the adsorption distance of NO molecule is about 2.76 Å.

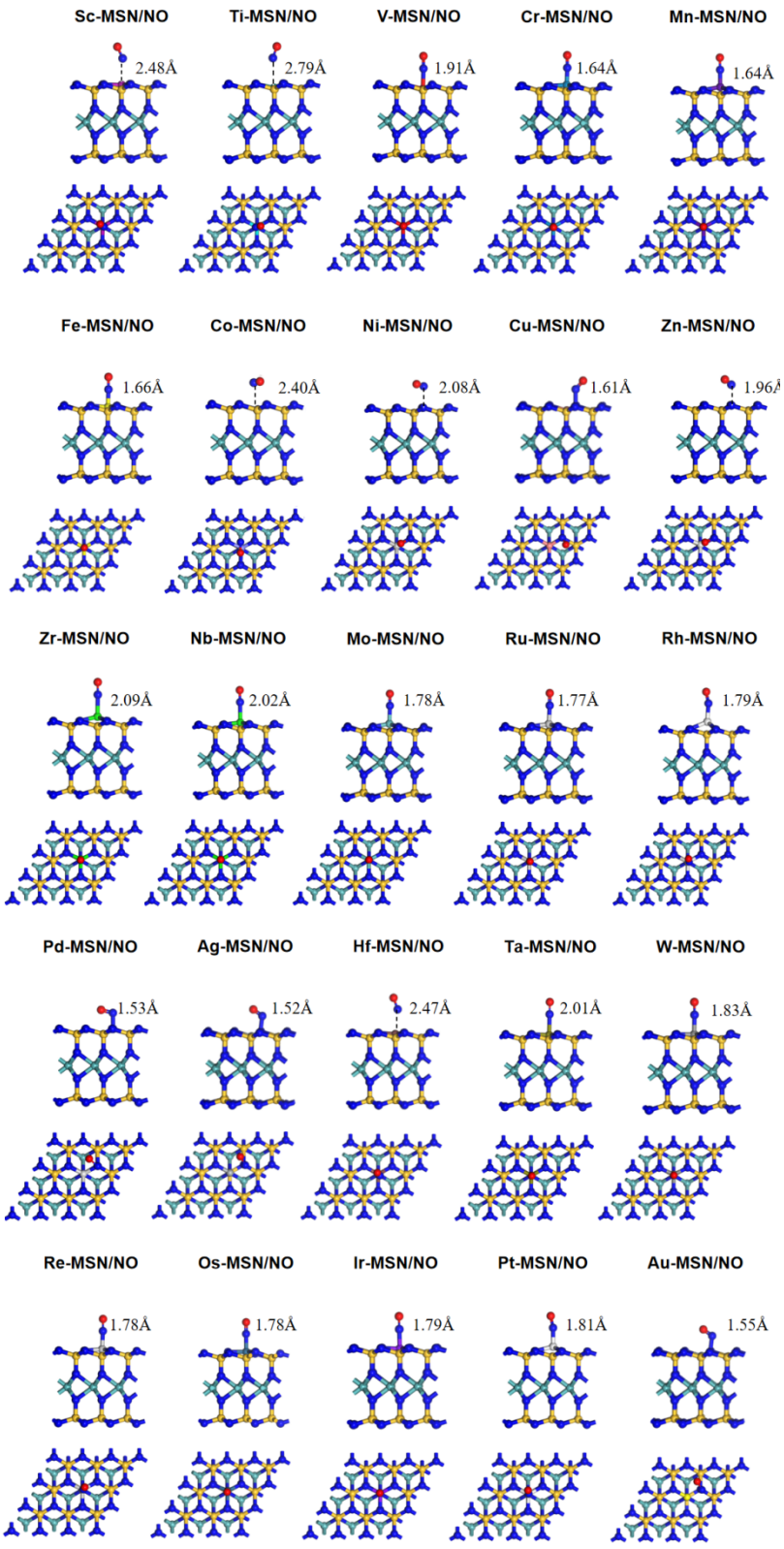

Figure S6 The top and side views of TM-MSN monolayers absorbed by NO molecule, and the adsorption heights of NO molecule are labelled in the figure.

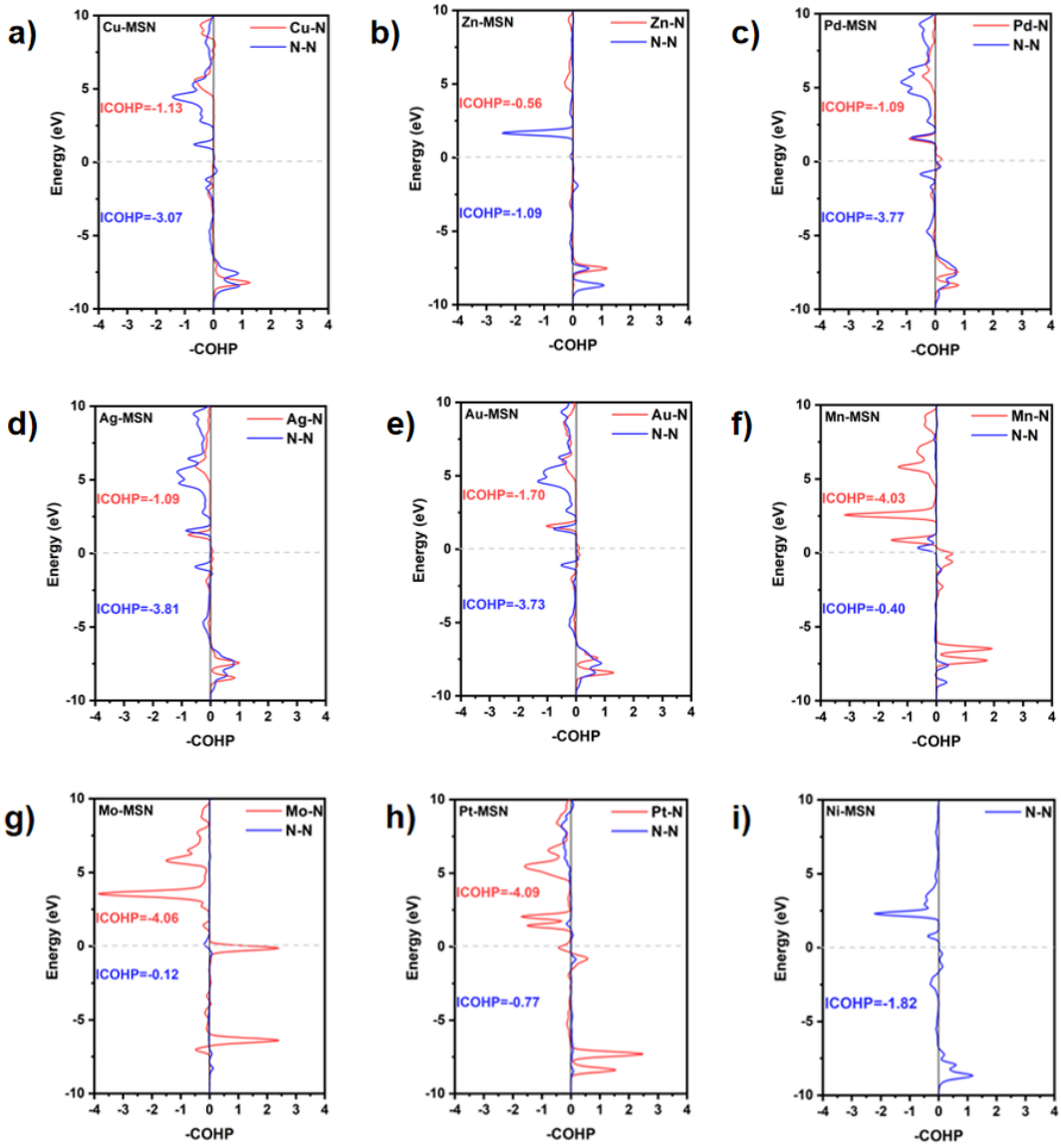

Figure S7 Negative COHP curves of TM-N bond and N-N bond of NO adsorption on the doped TM and the adjacent N sites of (a) Cu-, (b) Zn-, (c) Pd-, (d) Ag-, (e) Au-, (f) Mn-, (g) Mo-, (h) Pt- and (i) Ni-MSN, respectively. NO molecule on the Ni atom is unstable and spontaneously diffuses to the adjacent N atom, so the COHP curve of Ni-N bond for Ni-MSN monolayer was not considered.

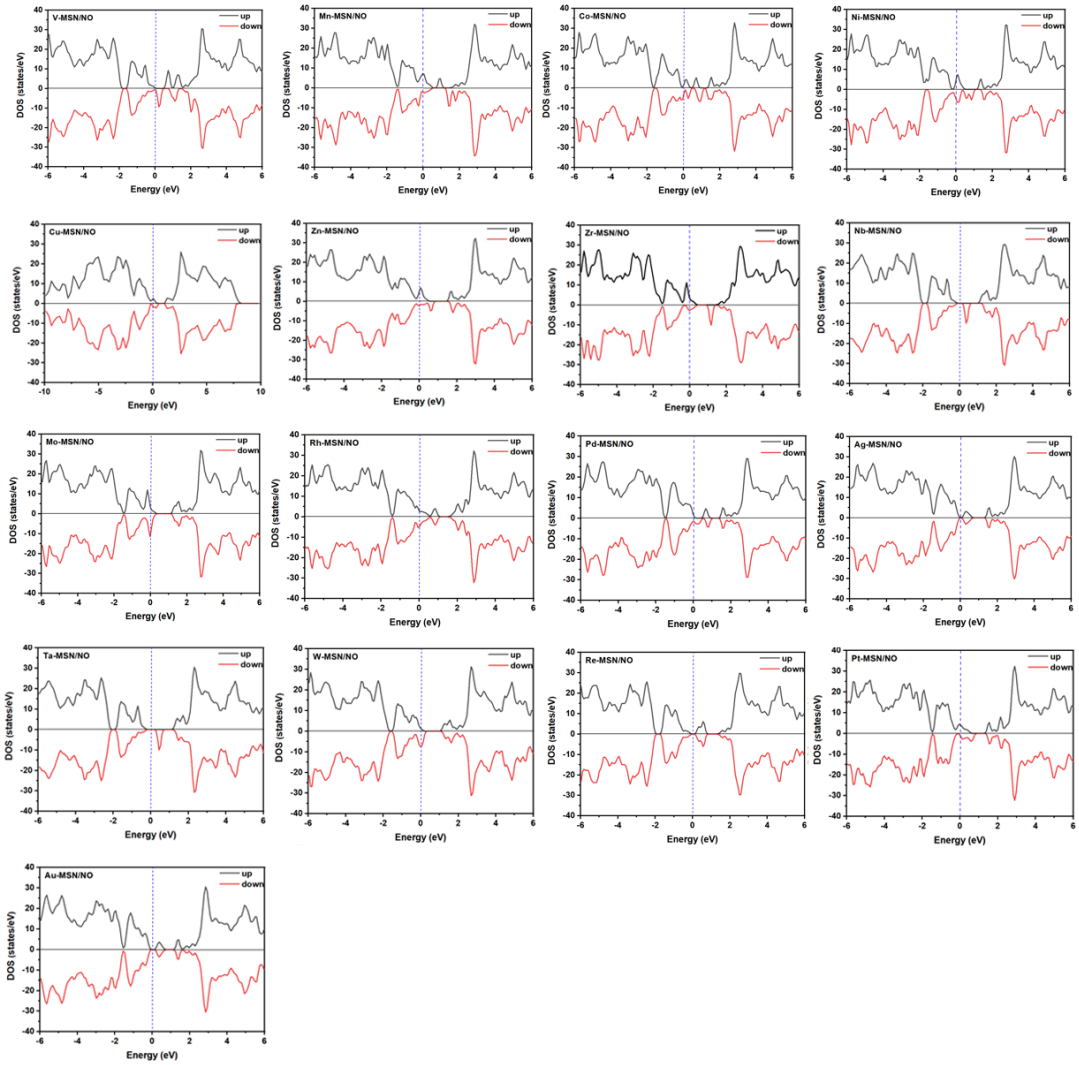

Figure S8 The DOS of NO adsorbed on TM-MSN (TM = V, Mn, Co, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Pd, Ag, Ta, W, Re, Pt and Au), the dotted lines are Fermi levels, and the black and red lines represent spin-up and spin-down, respectively.

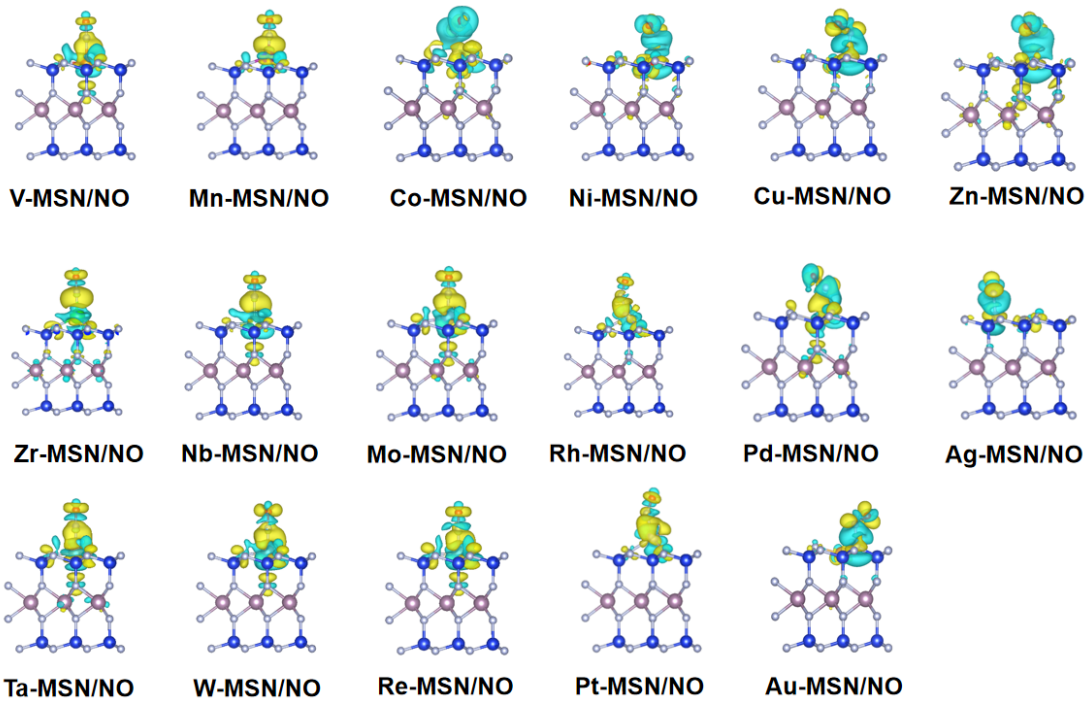

Figure S9 The charge density difference diagrams of TM-MSN (TM = V, Mn, Co, Ni, Cu, Zn, Zr, Nb, Mo, Rh, Pd, Ag, Ta, W, Re, Pt and Au) adsorbed by NO. The blue and the yellow areas represents the electron depletion and accumulation, respectively.

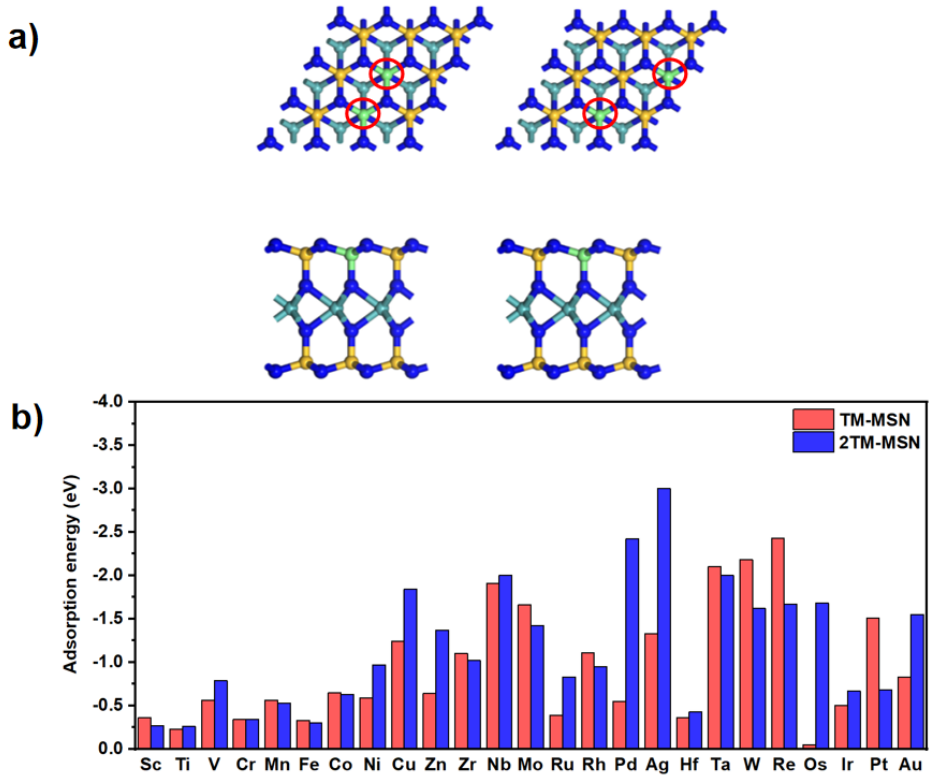

Figure S10 (a) The top and side views of possible configurations of 2TM-MSN, and (b) the comparison of NO adsorption energies of TM-MSN and 2TM-MSN in the most stable configuration. The doped TM atoms are circled in the figure a.

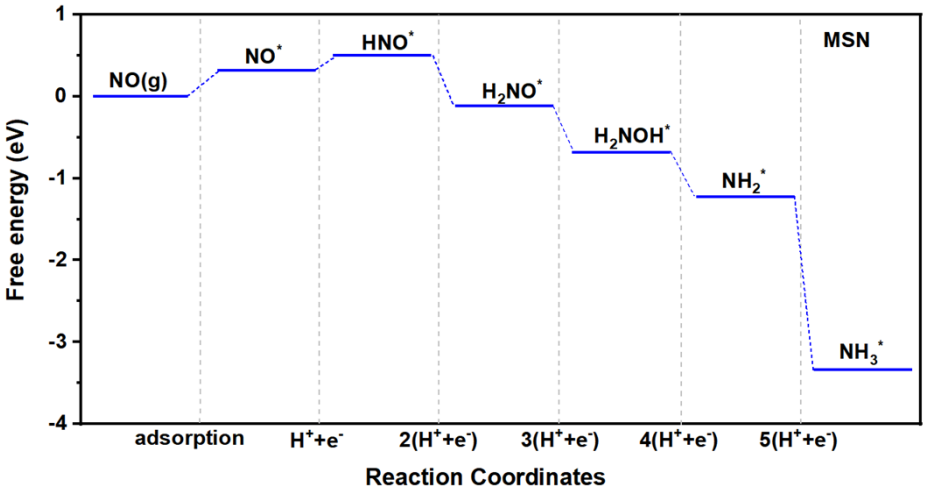

Figure S11 Free energy diagram of NOER over pristine MSN monolayer.

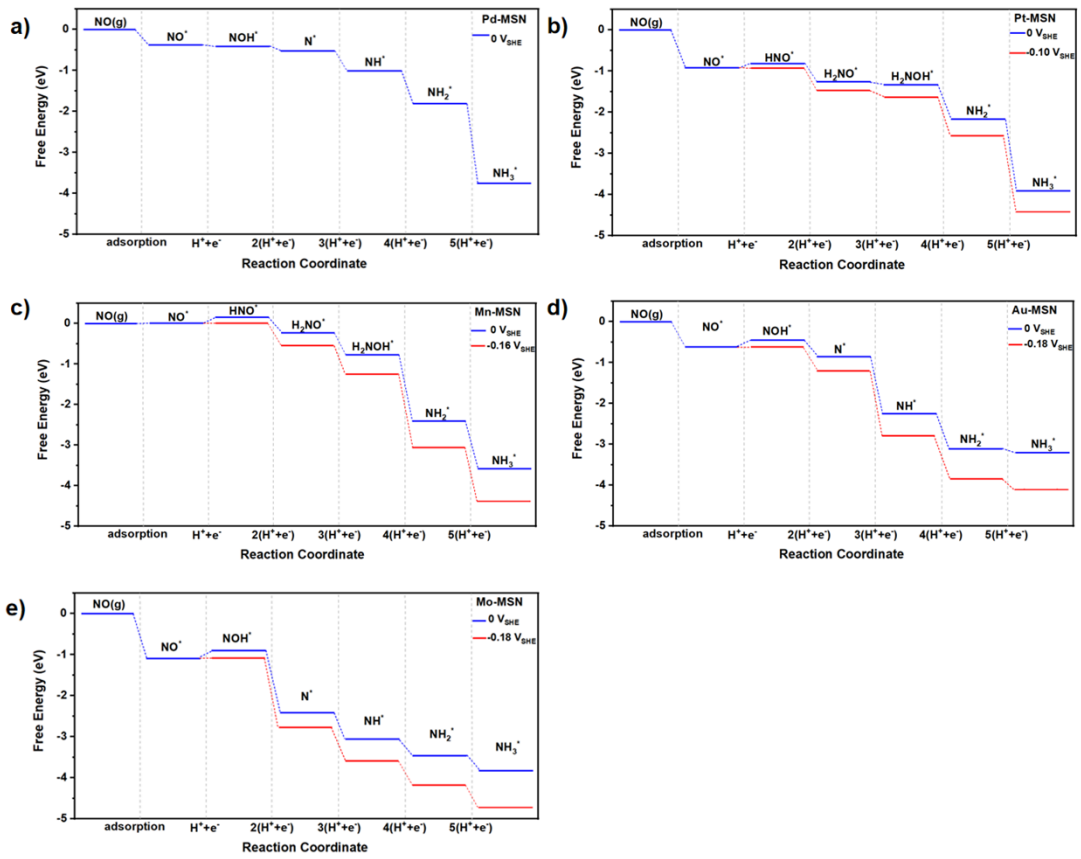

Figure S12 Free energy diagrams for (a) Pd-MSN, (b) Pt-MSN, (c) Mn-MSN, (d) Au-MSN, and (e) Mo-MSN at low NO coverage.

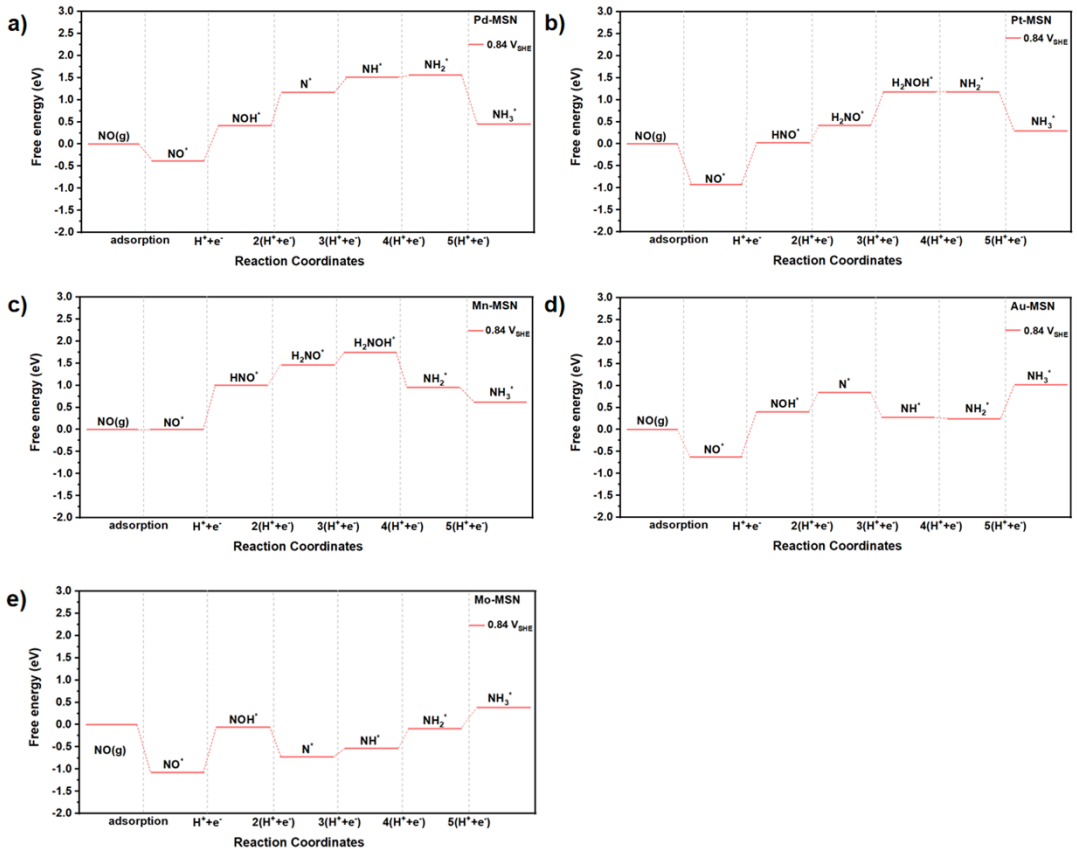

Figure S13 Free energy diagrams for (a) Pd-MSN, (b) Pt-MSN, (c) Mn-MSN, (d) Au-MSN, and (e) Mo-MSN at 0.84 V_{SHE}. 0.84 V_{SHE} is the equilibrium potential for NOER reaction.

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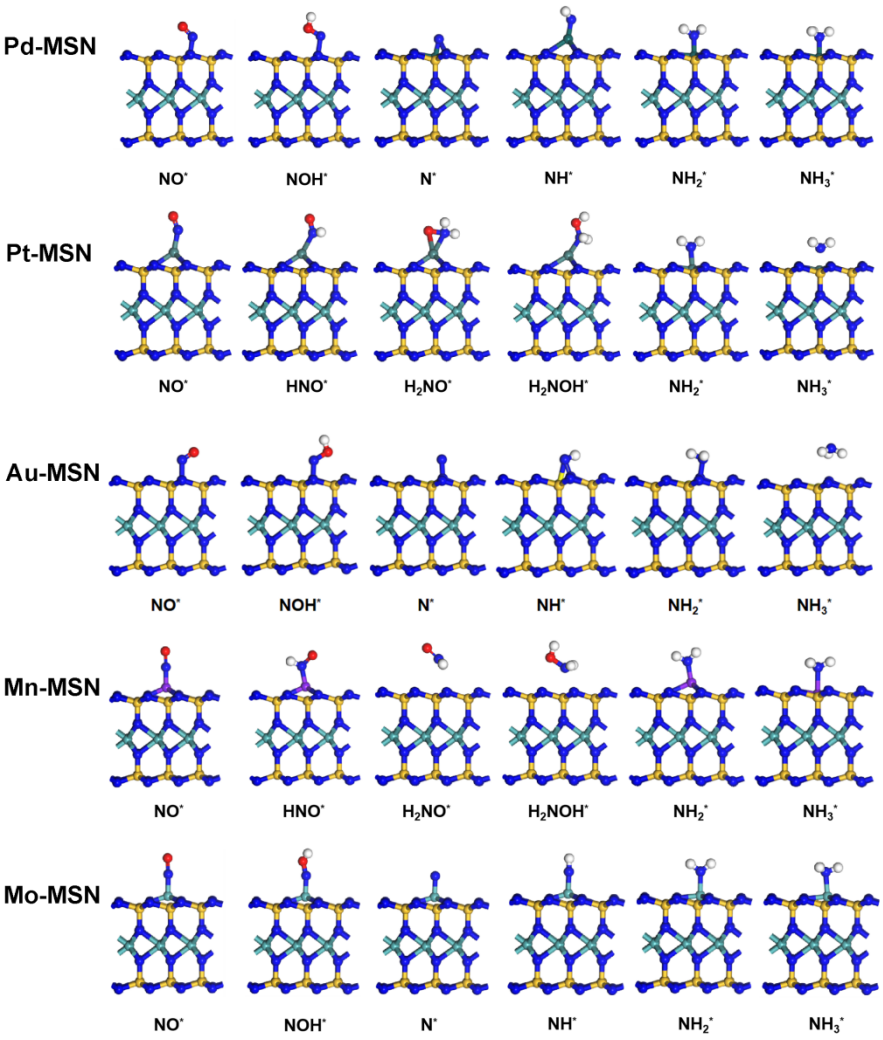

Figure S14 The optimized structures of various intermediates of TM-MSN (TM = Pd, Pt, Au, Mn, Mo) monolayers at low NO coverage.

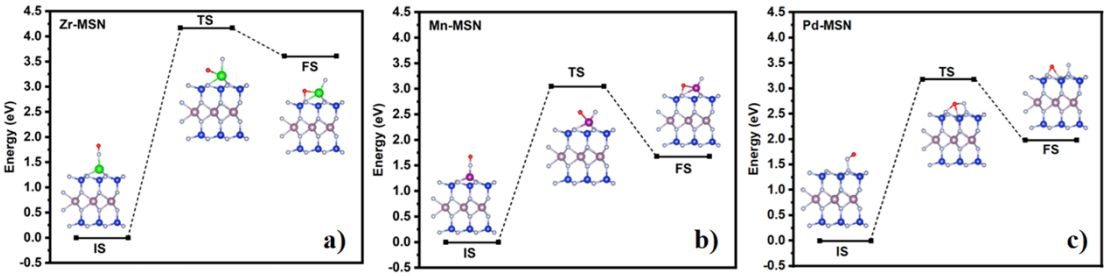

Figure S15 The energy barriers of NO dissociation on Zr-MSN, Mn-MSN and Pd-MSN monolayers.

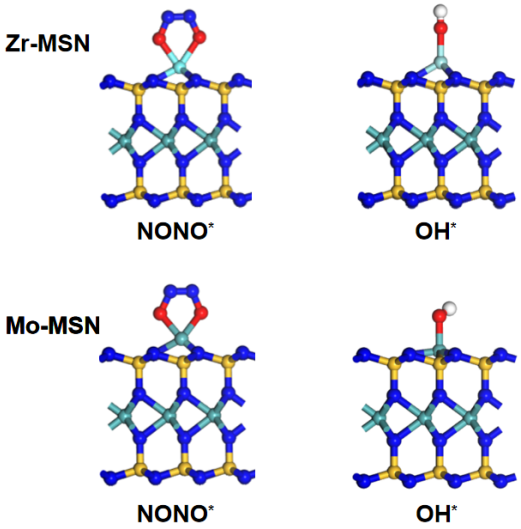

Figure S16 The optimized structures of various intermediates of Zr-MSN and Mo-MSN at high NO coverage.

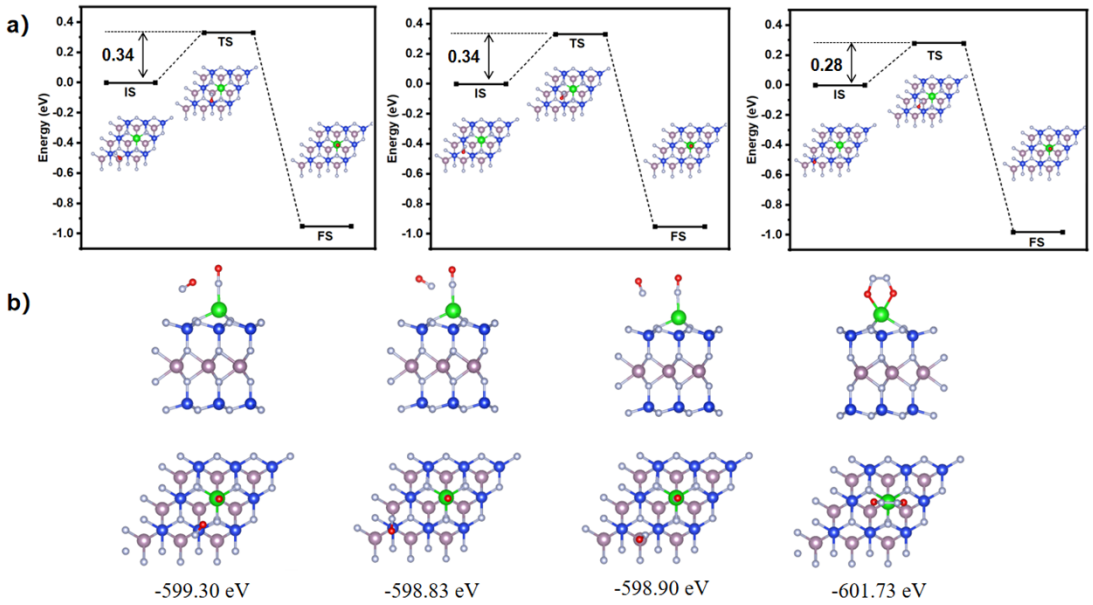

Figure S17 (a) The energy barriers of NO migration from distal Mo, N, Si to the Zr atom for Zr-MSN and (b) possible configurations of two NO molecule adsorbed on Zr-MSN. The labelled numbers mean the dissociation barriers of NO (a) and total energies of the configurations (b).

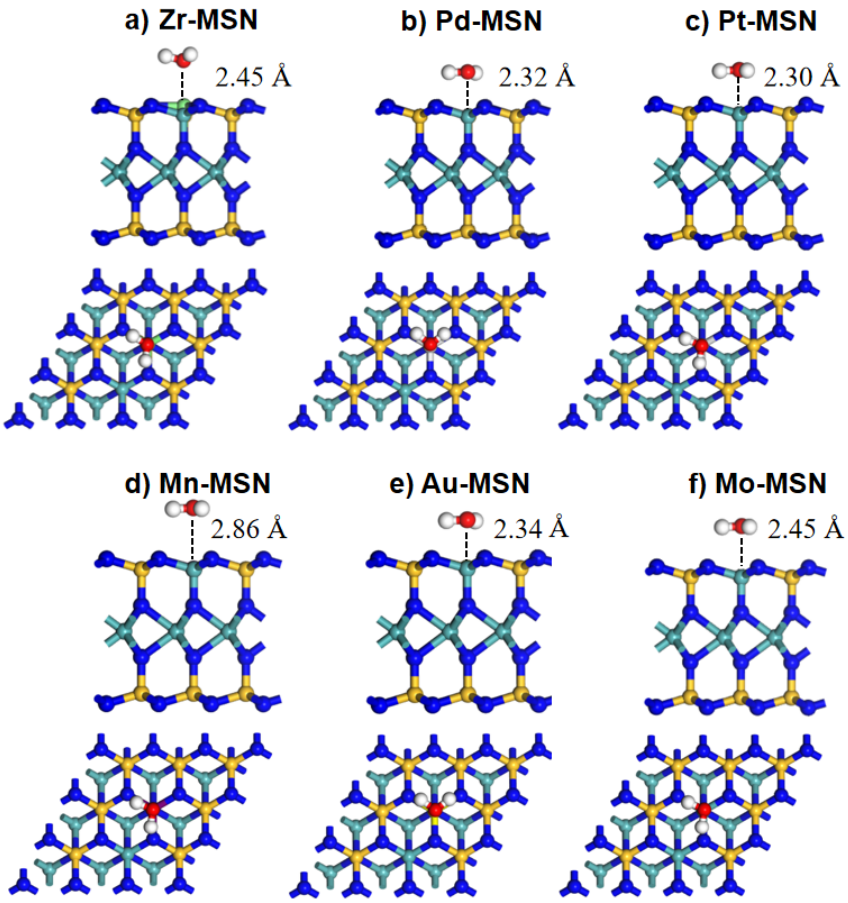

Figure S18 The adsorption configurations of H_2O molecule on Zr-, Pd-, Pt-, Mn-, Au- and Mo-MSN monolayers.

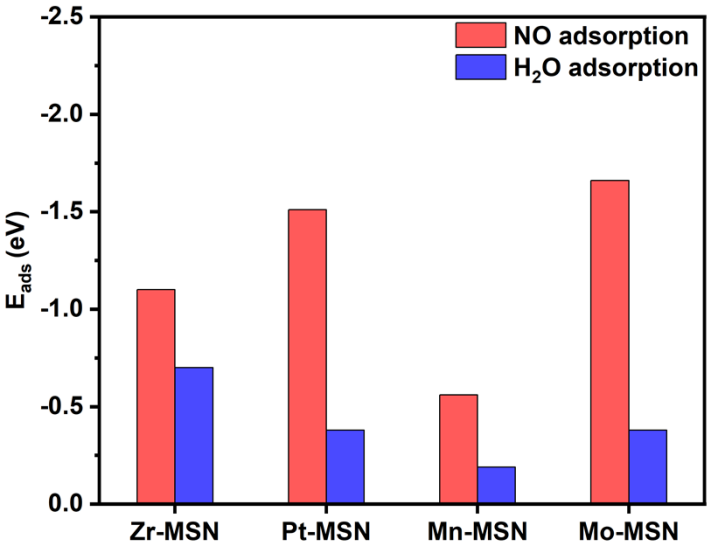

Figure S19 The adsorption energy comparison of NO and H_2O for Zr-, Pt-, Mn- and Mo-MSN monolayers.

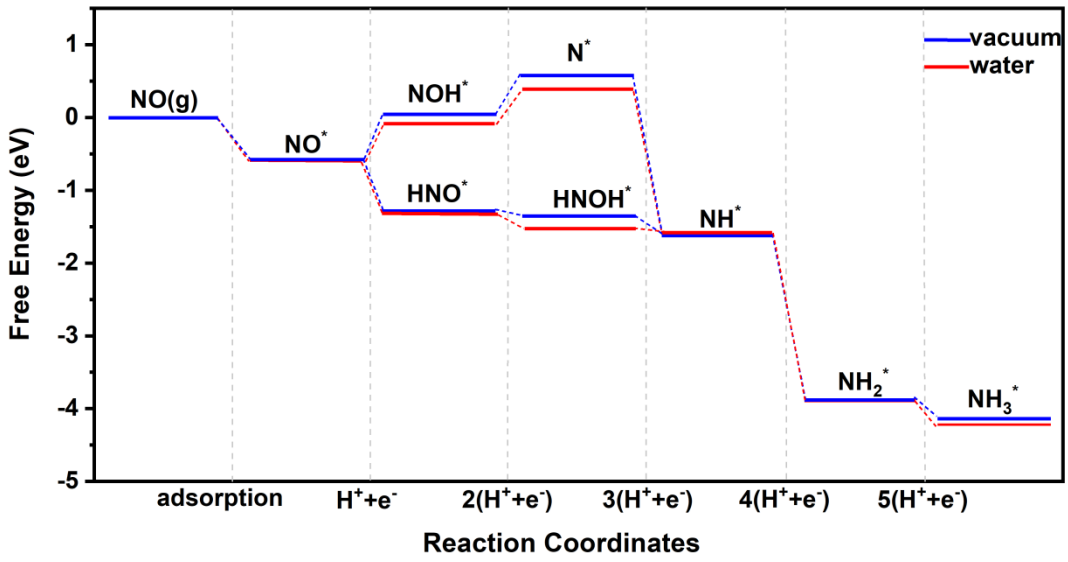

Figure S20 The calculated NOER free energy diagram of Zr-MSN under vacuum and water conditions, respectively.

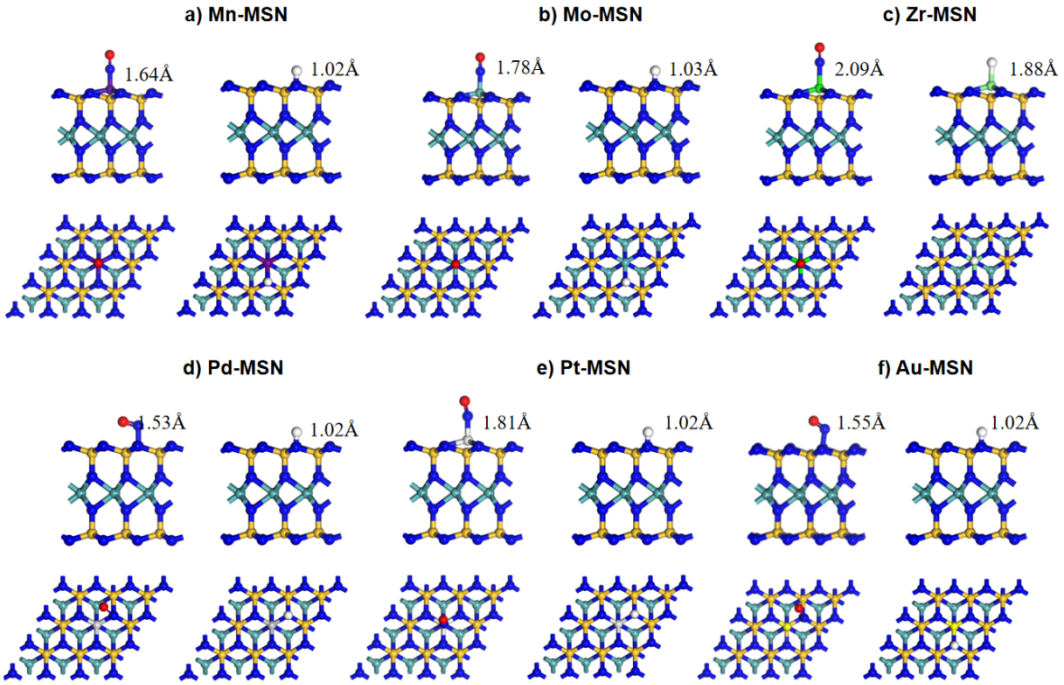

Figure S21 The adsorption configurations of H atom and NO molecule on Mn-, Mo-, Zr-, Pd-, Pt- and Au-MSN monolayers.

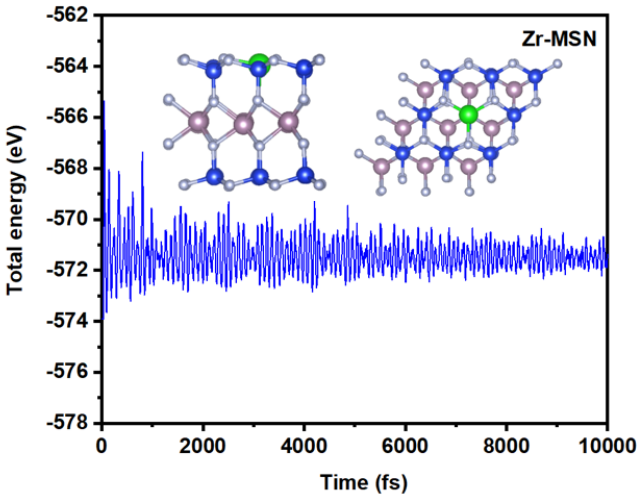

Figure S22 AIMD simulation of Zr-MSN at 300 K. The time step is 1 fs and the insets represent the final atomic configuration.

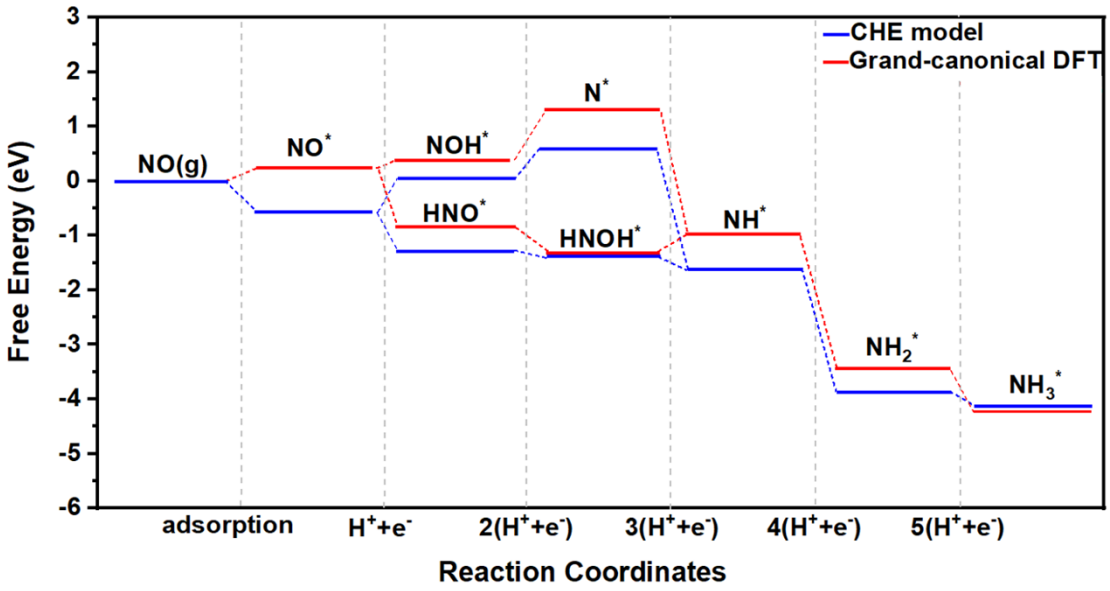

Figure S23 The free energy diagram of Zr-MSN under CHE model and Grand-canonical DFT.