1 **Supporting Information**

2 # Design of Single-Atom Catalyst for NO Oxidation Using OH Radical

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14 Computation and Modeling Methods

15 In this work, we employed a microkinetic framework based on Sabatier analysis[1] to find the upper limit of the

16 overall reaction rate for NO oxidation. The *Sabatier* rate is the reaction rate assumed to be optimal for each

17 basic reaction, which can well reflect the catalytic reaction ability of the surface. This process is similar to the

18 previously reported oxidation reaction model.[2, 3] According to the discussion in the main text, the NO

19 oxidation reaction can be divided into the following three basic steps:

$$OH + * = {}^*OH \tag{R1}$$

$$NO + {}^*OH = {}^*HNO_2 \tag{R2}$$

$${}^*HNO_2 = HNO_2 + * \tag{R3}$$

20 It is assumed that R1 is in an equilibrium state. The forward rate constants of other steps are given by:

$$k_i = v_i \exp[\frac{-\Delta G_{ai}}{kT}] = v_i \exp[\frac{-(E_{ai} - T\Delta S_{ai})}{kT}] \tag{1}$$

21 where v_i is the prefactor, E_{ai} is the activation energy, and ΔS_{ai} is the entropy difference between the

22 transition state and the initial state, k is the Boltzmann constant, and T is the temperature. v_i is estimated

23 by KT/h, where h is the Planck's constant.

24 Assuming R1 is in equilibrium, this gives:

$$\theta_{H_2O_2} = \frac{1}{1 + K_1 p(H_2O_2)} \tag{2}$$

25 where K_i is the equilibrium constant of R1, $p(H_2O_2)$ is the partial pressure of H$_2$O$_2$. K_i was calculated by:

$$K_1 = Exp[\frac{-G_1}{kT}] \tag{3}$$

26 where G_1 is the free energy of R1. The *Sabatier* rate ($r_i^{S_{max}} = \theta_i k_i$) of the overall reaction (r_s) was

27 estimated by the minimum reaction rate among R2-R3 as a function of OH adsorption energy:

$$r_s = Min[r_2^{S_{max}}, r_3^{S_{max}}] \tag{4}$$

28 Finally, the volcano activity plot was plotted as:

$$A = kTLn[r_s h / kT] \tag{5}$$

29 The following equation can be used to calculate binding energy (E_{bind}).

$$E_{bind} = E_{sur} - E_{sub} - E_M \tag{6}$$

where E_{sur}, E_{sub}, and E_M are the electronic energies of the catalyst, graphene substrate, and single metal

atom, respectively.

Adsorption energies (E_{ads}) were computed based on the following equation to examine how strongly gas

molecules adhere to catalyst surfaces:

$$E_{ads} = E_{absorb} - E_{sur} - E_{gas} \tag{7}$$

30 where E_{absorb}, E_{sur}, and E_{gas} represent the total energies of adsorption systems, catalyst surface, and gases,

31 respectively.

32 The reaction energy barrier (E_b) and reaction heat (ΔE) in the reaction pathways were computed based on:

$$E_b = G_{TS} - G_{IS} \tag{8}$$

$$\Delta E = G_{FS} - G_{IS} \tag{9}$$

33   where G_{IS}, G_{TS}, and G_{FS} are the Gibbs free energy energies of the initial, transition, and final states,

34   respectively.

35   The Gibbs free energies were obtained using the following equation:

$$G(T,P) = E_{ele} + ZPE + \Delta H - TS(T,P) + K_B T \ln \frac{P}{P^0} \tag{10}$$

36   where E_{ele} is the system energy in the ground state; ZPE is the zero-correction energy; ΔH is the enthalpy

37   variation from 0 K to a given temperature; T is the temperature and $TS(T,P)$ is the entropy of the system

38   acquired from vibrational frequency analyses; KB is the Boltzmann constant, $8.6173303 \times 10\text{-}5$ eV·K^{-1}; P^0 is

39   the standing pressure.

40   The system electronegativity (X) gives a good description of the interaction of charged metal atoms in different

41   coordination environments. In this study, the value of X was calculated using the following equation:

$$X = (xX_C + yX_N - X_M)\frac{\theta_d}{n_d} \tag{11}$$

42   where x is the number of C atoms adjacent to the metal atom, X_C is the electronegativity of the C atom, y is

43   the number of N atoms adjacent to the metal atom, X_N is the electronegativity of the N atom, X_M is the

44   electronegativity of the metal atom, θ_d is the number of occupied electrons in the d orbital, and n_d is the

45   maximum number of electrons in the d orbital.

References

47   1.   T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen, C. H. Christensen and J. Sehested, *Journal of*

48   *Catalysis*, 2004, **224**, 206-217.

49 2. H. Li, A. Cao and J. K. Nørskov, *ACS Catalysis*, 2021, **11**, 12052-12057.

50 3. H. Falsig, B. Hvolbæk, I. S. Kristensen, T. Jiang, T. Bligaard, C. H. Christensen and J. K. Nørskov,

51   *Angewandte Chemie International Edition*, 2008, **47**, 4835-4839.

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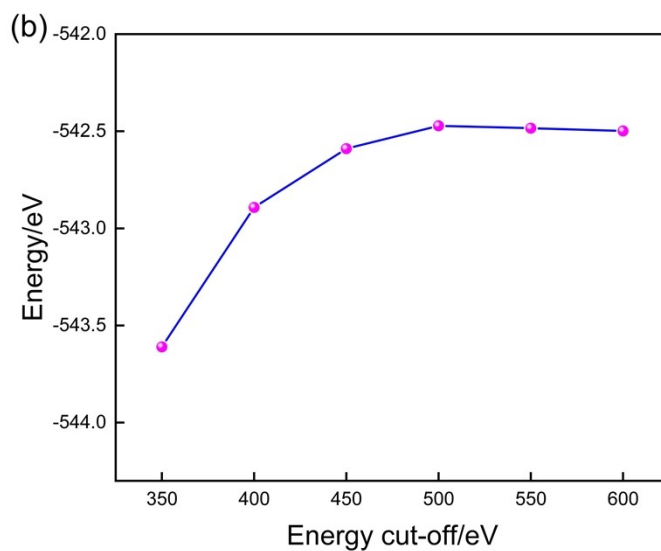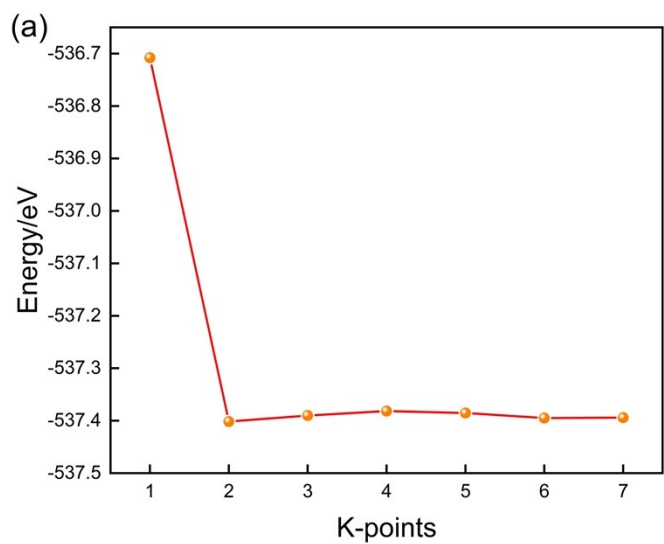
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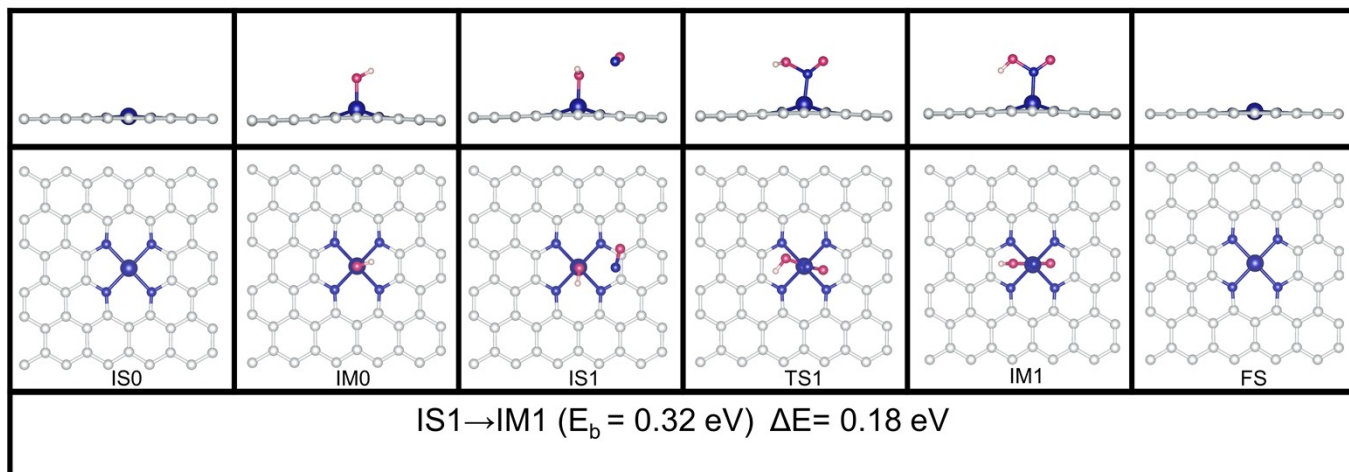54 **Fig. S1** Parameter tests on the settings of (a) *k*-points and (b) energy cutoff.

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IS1→IM1 (E_b = 0.02 eV) ΔE= 0.71 eV
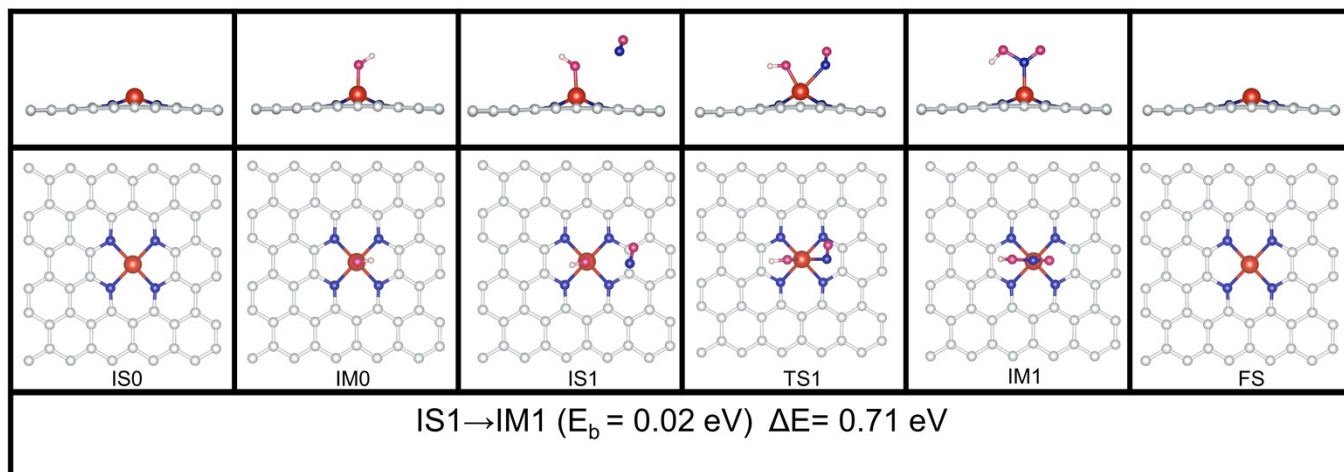
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57 **Fig. S2** Reaction pathway of catalytic oxidation of NO at V-N$_4$-C. C, N, and V are denoted by gray, blue, and

58 red, respectively.

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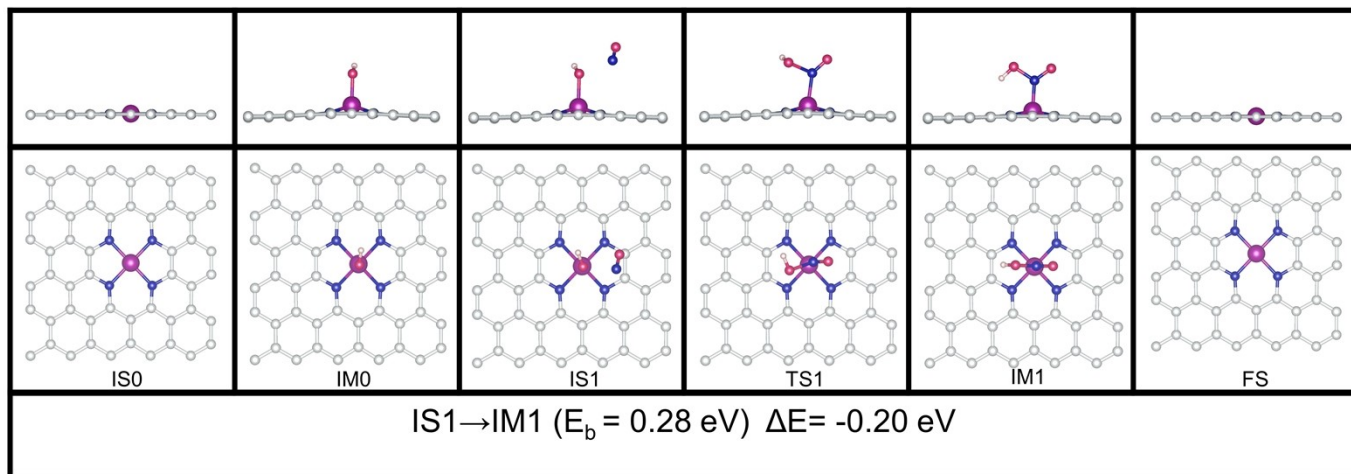IS1→IM1 (E_b = 0.32 eV) ΔE= 0.18 eV

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61 **Fig. S3** Reaction pathway of catalytic oxidation of NO at Cr-N_4-C. C, N, and Cr are denoted by gray, blue,

62 and dark blue, respectively.

63

IS0	IM0	IS1	TS1	IM1	FS

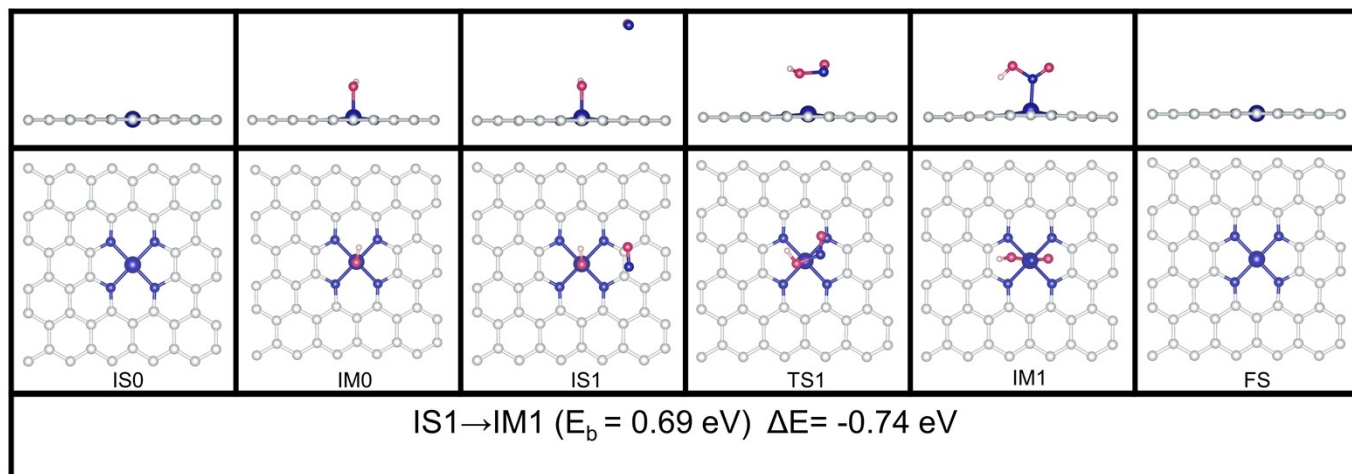IS1→IM1 (E_b = 0.28 eV) ΔE= -0.20 eV

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65　**Fig. S4** Reaction pathway of catalytic oxidation of NO at Mn-N$_4$-C. C, N, and Mn are denoted by gray, blue,

66　and purple, respectively.

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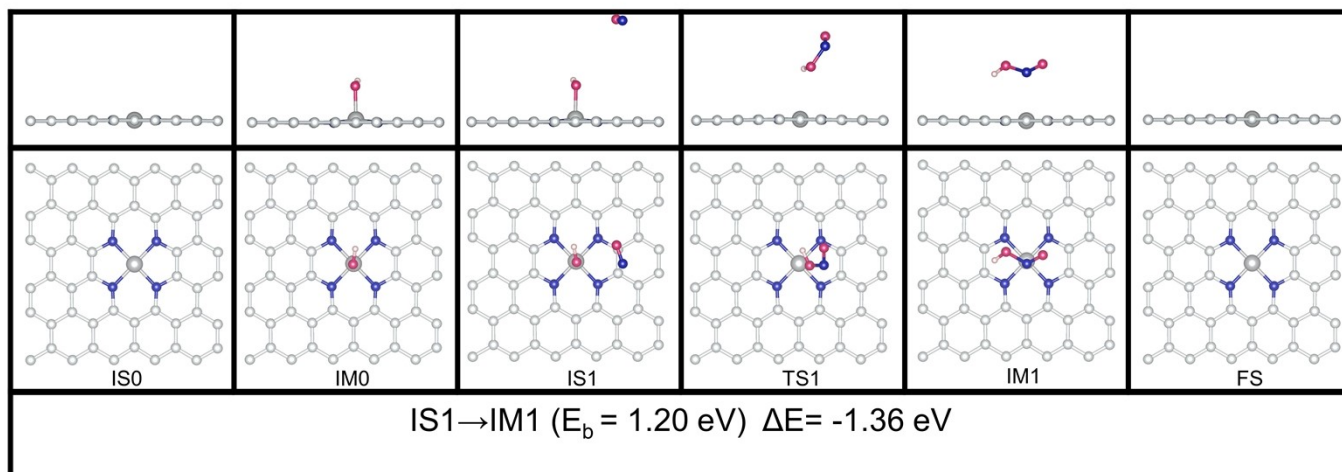|					
IS0	IM0	IS1	TS1	IM1	FS

IS1→IM1 (E$_b$ = 0.69 eV) ΔE= -0.74 eV

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69 **Fig. S5** Reaction pathway of catalytic oxidation of NO at Co-N$_4$-C. C, N, and Co are denoted by gray, blue,
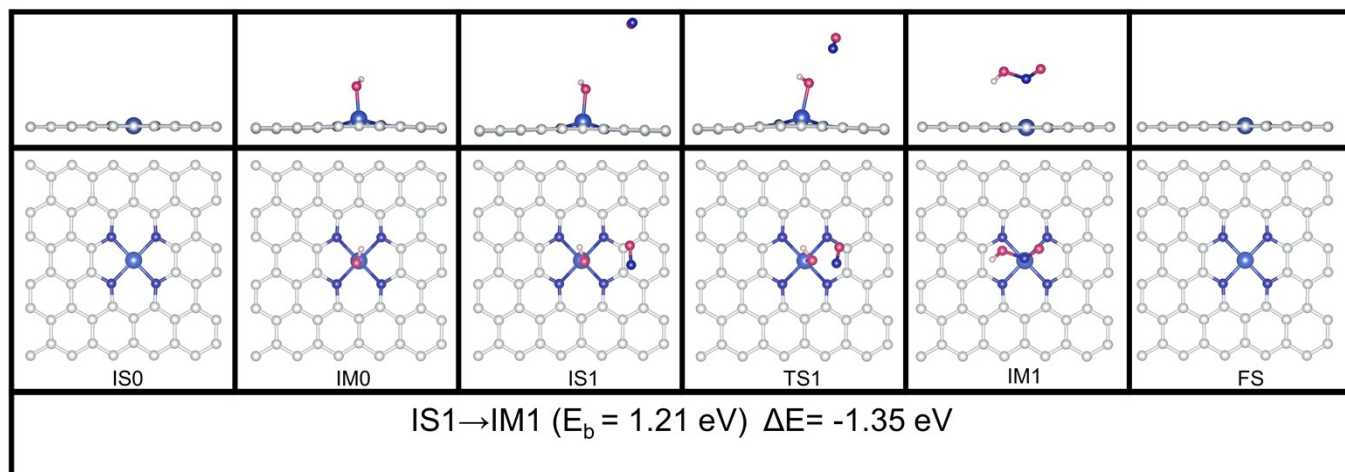
70 and light blue, respectively.

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| IS0 | IM0 | IS1 | TS1 | IM1 | FS |

IS1→IM1 (E$_b$ = 1.20 eV) ΔE= -1.36 eV

Fig. S6 Reaction pathway of catalytic oxidation of NO at Ni-N$_4$-C. C, N, and Ni are denoted by gray, blue, and light gray, respectively.

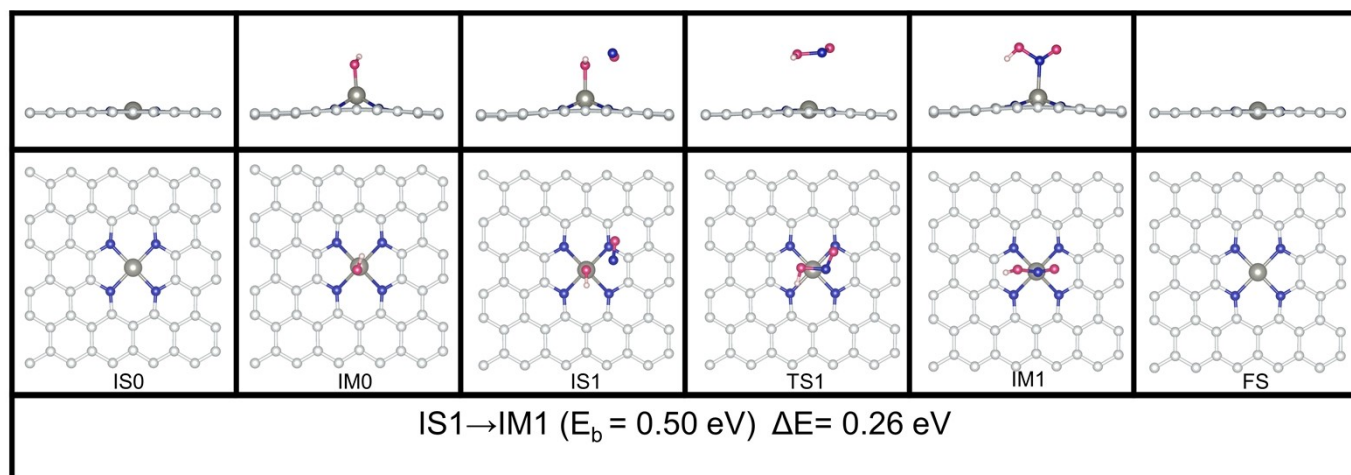|					
IS0	IM0	IS1	TS1	IM1	FS

IS1→IM1 (E_b = 1.21 eV) ΔE = -1.35 eV

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77 **Fig. S7** Reaction pathway of catalytic oxidation of NO at Cu-N$_4$-C. C, N, and Cu are denoted by gray, blue,
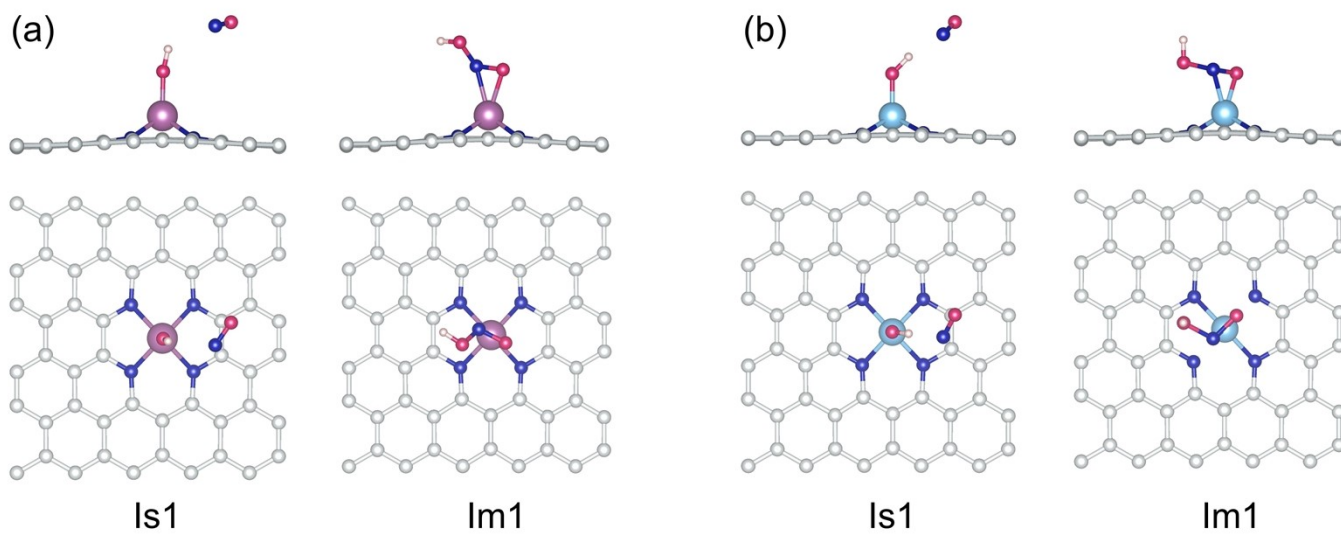
78 and light blue, respectively.

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IS1→IM1 (E_b = 0.50 eV) ΔE = 0.26 eV

Fig. S8 Reaction pathway of catalytic oxidation of NO at Zn-N$_4$-C. C, N, and Zn are denoted by gray, blue, and dark gray, respectively.

Is1   Im1   Is1   Im1

Fig. S9 The initial state IS1 and intermediate state IM1 of NO oxidation using OH radical. (a) Sc-N_4-C catalyst, (b) Ti-N_4-C catalyst.

88 **Table S1.** Imaginary frequency statistics of different transition state reaction processes in the catalytic of NO

89 oxidation using OH radical.

Oxidant	Reaction pathway	Imaginary frequency(cm^{-1})
V-N_4-C	TS1	524.66
Cr-N_4-C	TS1	202.98
Mn-N_4-C	TS1	368.72
Fe-N_4-C	TS1	151.46
Co-N_4-C	TS1	153.42
Ni-N_4-C	TS1	148.80
Cu-N_4-C	TS1	127.85
Zn-N_4-C	TS1	193.81

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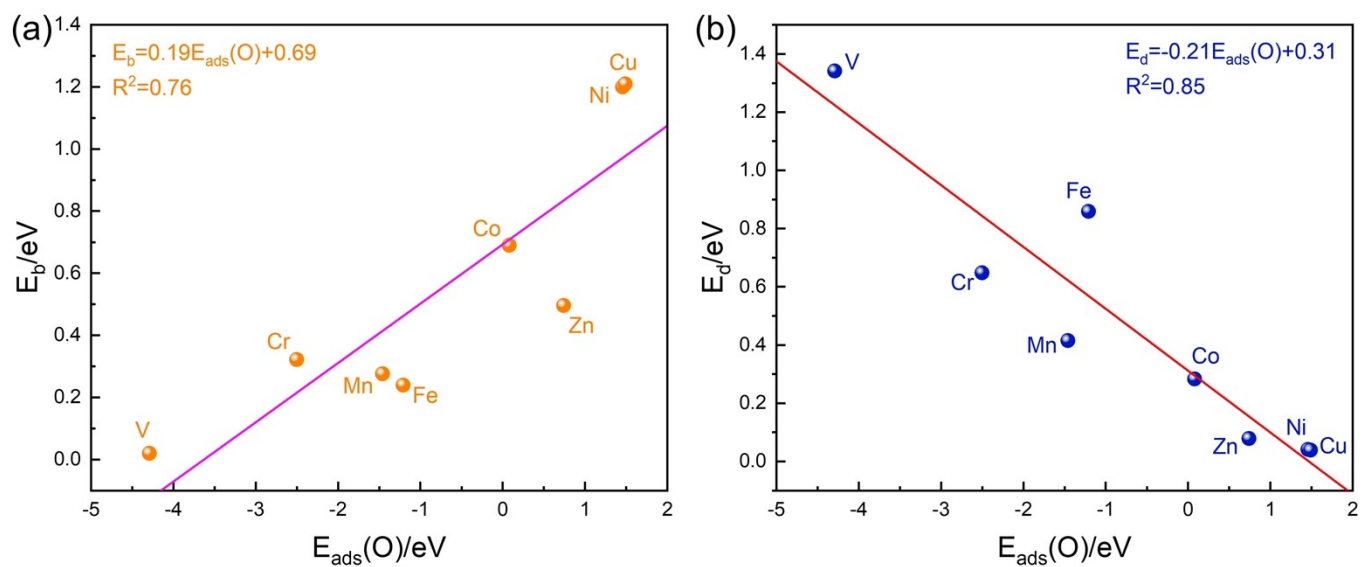
Fig. S10 Correlations analyses of (a) E_b vs $E_{ads}(O)$, (b) E_d vs $E_{ads}(O)$.

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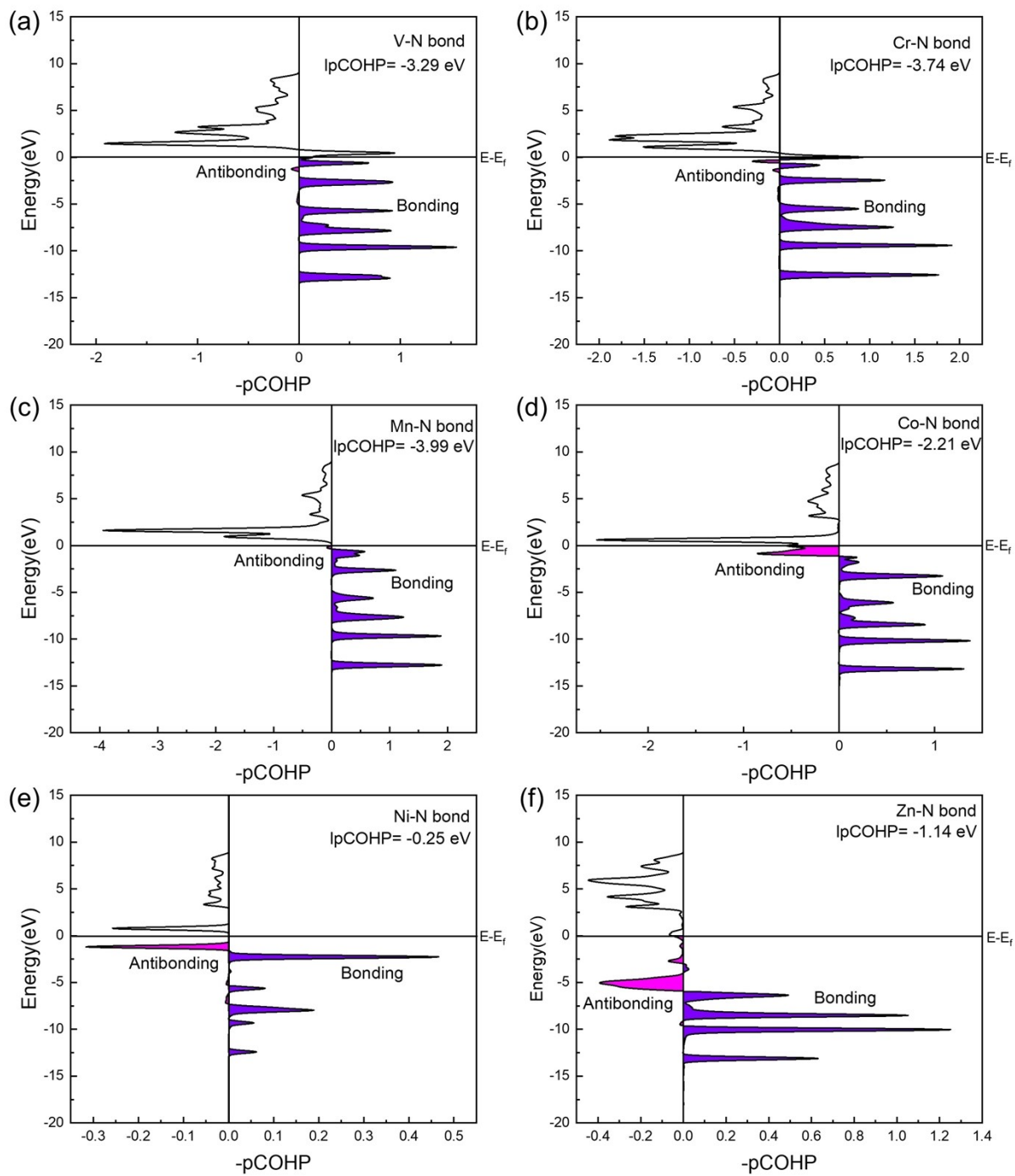
Fig. S11 COHP analysis between different SACs and HNO$_2$.

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(a) 1.97 e V-N$_4$-C

(b) 1.88 e Cr-N$_4$-C

(c) 1.80 e Mn-N$_4$-C

(d) 1.91 e Co-N$_4$-C

(e) 2.88 e Ni-N$_4$-C

(f) 2.21 e Zn-N$_4$-C
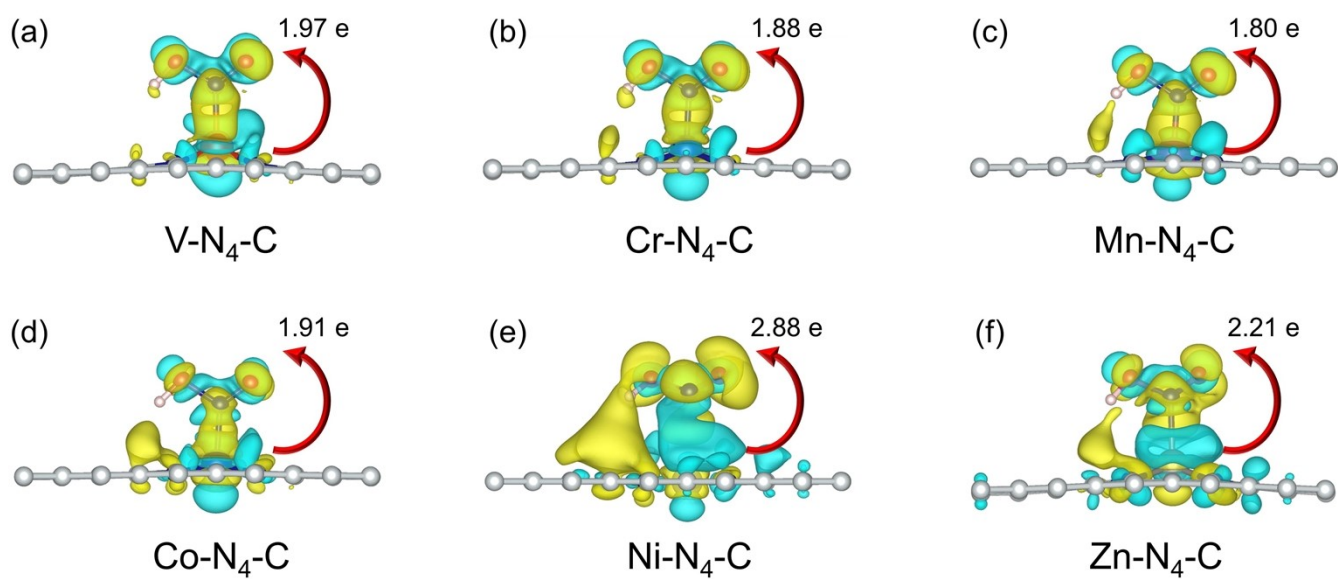
Fig. S12 Electronic density difference between different SACs and HNO$_2$ Contour lines in the plots are drawn at 0.001 e Å^{-3} intervals.

101 **Table S2.** Charge transfer (Q) of the central TM and the bond length (d) between TM and HNO_2 gas molecule

102 on different SACs.

Catalysts	Q(e)	d(Å)
V-N$_4$-C	-1.57	1.97
Cr-N$_4$-C	-1.42	1.88
Mn-N$_4$-C	-1.33	1.80
Fe-N$_4$-C	-1.12	1.77
Co-N$_4$-C	-1.04	1.91
Ni-N$_4$-C	-0.87	2.88
Cu-N$_4$-C	-0.95	2.95
Zn-N$_4$-C	-1.21	2.21

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