Supplementary Information

Understanding Trends in the Mercury Oxidation Activity of Single-Atom Catalysts

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Microkinetic modeling methods

In this study, we employed a microkinetic framework based on the Sabatier analysis[1] to find an upper bound of the overall reaction rate of Hg^0 oxidation. The Sabatier rate[1] is the reaction rate when each elementary reaction is assumed to be optimal, which can well reflect the catalytic reaction ability of the surface. This process is similar to the previously reported modeling for oxidation reactions[2, 3]. Based on the discussions in the main text, the reaction of Hg^0 oxidation can be divided into the following four elementary steps:

$$O_2 + * \rightleftarrows O_2* \quad \text{(R1)}$$

$$O_2* + Hg \rightleftarrows HgO* \quad \text{(R2)}$$

$$HgO* + Hg \rightleftarrows (HgO)_2* \quad \text{(R3)}$$

$$(HgO)_2* \rightleftarrows (HgO)_2 + * \quad \text{(R4)}$$

where R1 is assumed to be in equilibrium. The forward rate constants of the remaining steps are given by:

$$k_i = v_i exp\left[\frac{-\triangle G_{ai}}{KT}\right] = v_i exp[\frac{-(E_{ai} - T \triangle S_{ai})}{KT}], \quad (2)$$

where v_i is the prefactor, E_{ai} is the activation energy, and $\triangle S_{ai}$ is the entropy difference between the transition state and the initial state, k is the Boltzmann constant, and T is the temperature. v_i is estimated by kT/h, where h is the Planck's constant.

Assuming R1 is in equilibrium, this gives:

$$\theta_{O_2} = \frac{1}{1 + K_1 p(O_2)}, \quad (5)$$

where K_i is the equilibrium constant of R1, $p(O_2)$ is the partial pressure of O_2. K_i was calculated by:

$$K_1 = Exp[\frac{-G_1}{kT}], \quad (6)$$

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 estimated by the minimum reaction rate among R2-R4 as a function of O adsorption energy:

$$r_S = Min[r_2^{S_{max}}, r_3^{S_{max}}, r_4^{S_{max}}]. \quad (7)$$

Finally, the volcano activity plot is plotted as:

$$A = kTLn[r_S h/kT]. \quad (8)$$

References

1. T. Bligaard, J. K. Nørskov, S. Dahl, J. Matthiesen, C. H. Christensen and J. Sehested, The Brønsted–Evans–Polanyi relation and the volcano curve in heterogeneous catalysis, *Journal of Catalysis*, 2004, **224**, 206-217.
2. H. Li, A. Cao and J. K. Nørskov, Understanding Trends in Ethylene Epoxidation on Group IB Metals, *ACS Catalysis*, 2021, **11**, 12052-12057.
3. H. Falsig, B. Hvolbaek, I. S. Kristensen, T. Jiang, T. Bligaard, C. H. Christensen and J. K. Norskov, Trends in the catalytic CO oxidation activity of nanoparticles, *Angewandte Chemie International Edition*, 2008, **47**, 4835-4839.

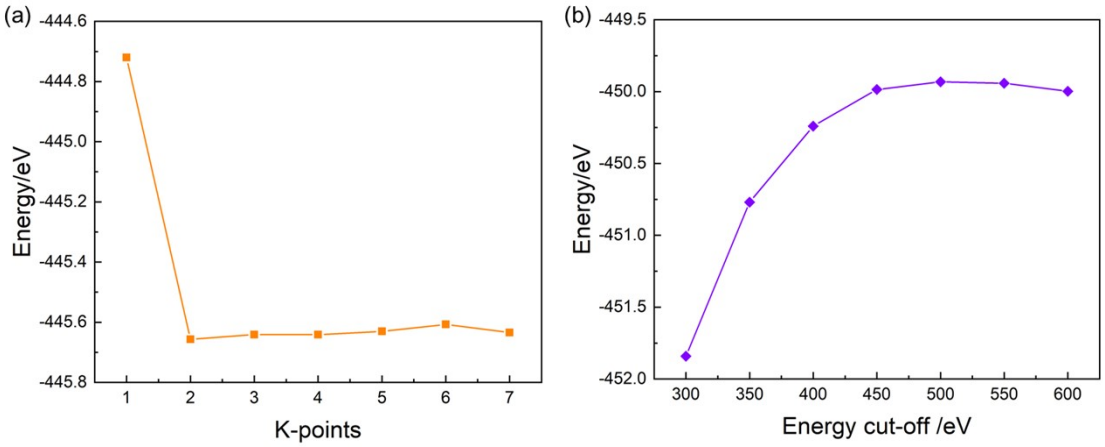

Figure. S1. Parameter test calculations on the settings of (a) *k*-points test (b) energy cutoff.

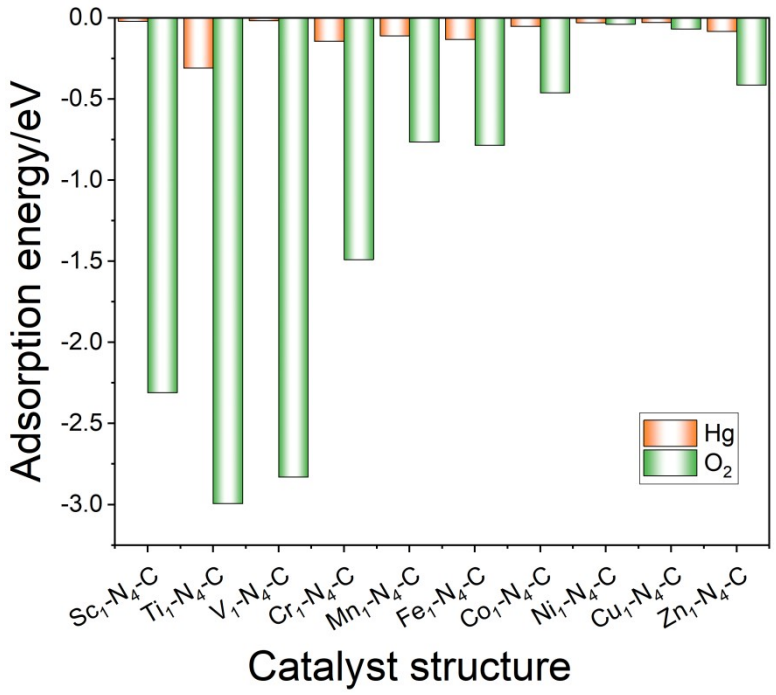

Figure S2. Adsorption energy of O_2 and Hg^0 on ten single-atom catalysts

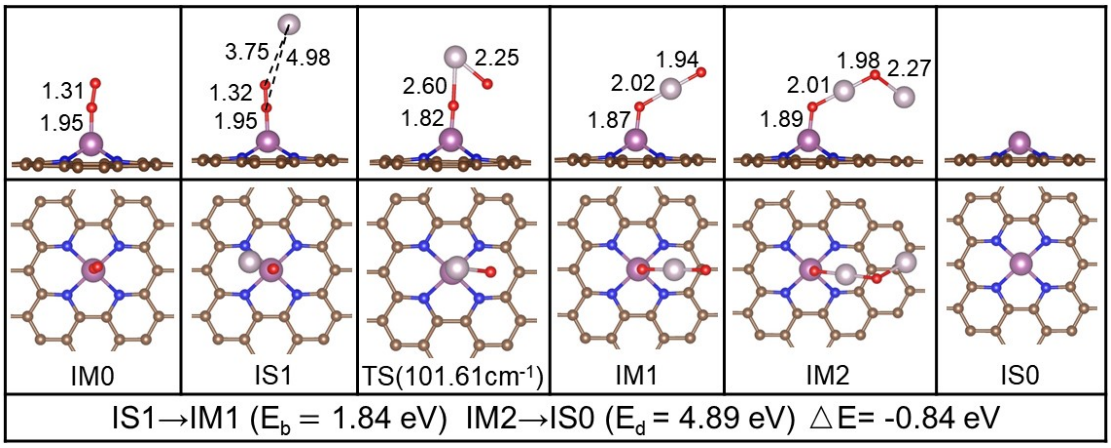

Figure S3. Reaction pathway of catalytic oxidation of Hg^0 on Sc_1-N_4-C. C, N, and Sc are denoted by brown, blue, and pink, respectively.

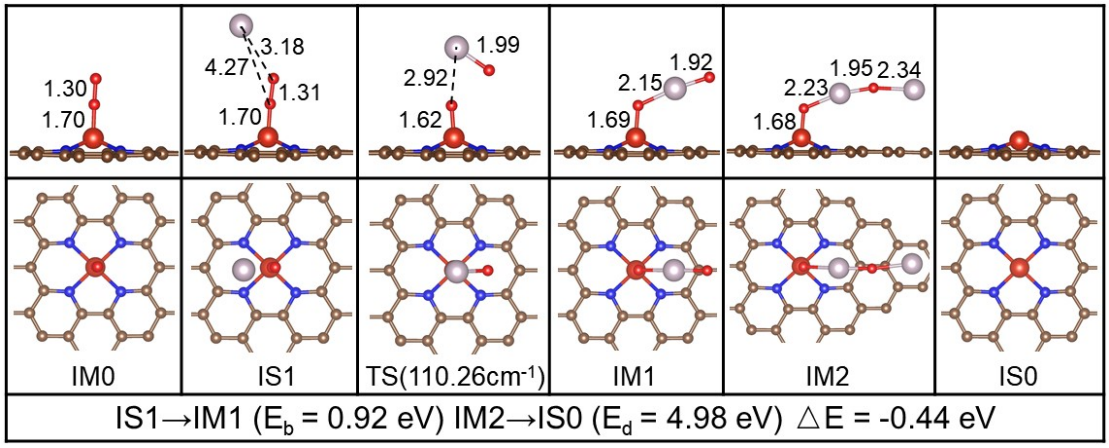

Figure S4. Reaction pathway of catalytic oxidation of Hg^0 on V_1-N_4-C. C, N, and V are denoted by brown, blue, and red, respectively.

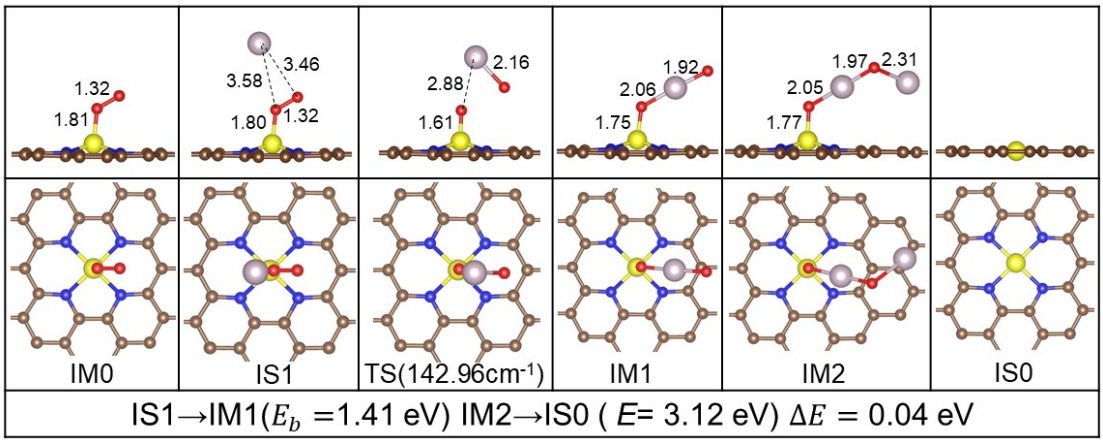

Figure S5. Reaction pathway of catalytic oxidation of Hg^0 on Cr_1-N_4-C. C, N, and Cr are denoted by brown, blue, and yellow, respectively.

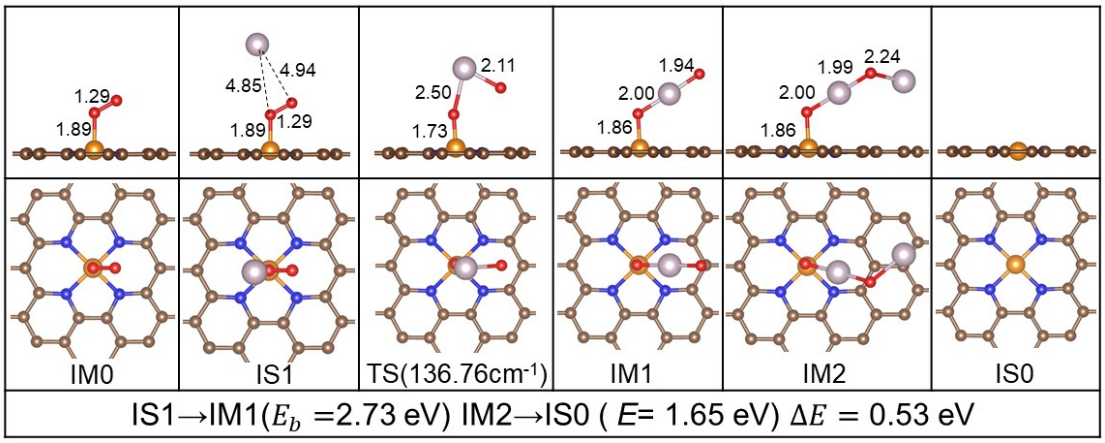

Figure S6. Reaction pathway of catalytic oxidation of Hg^0 on Co_1-N_4-C. C, N, and Co are denoted by brown, blue, and orange, respectively.

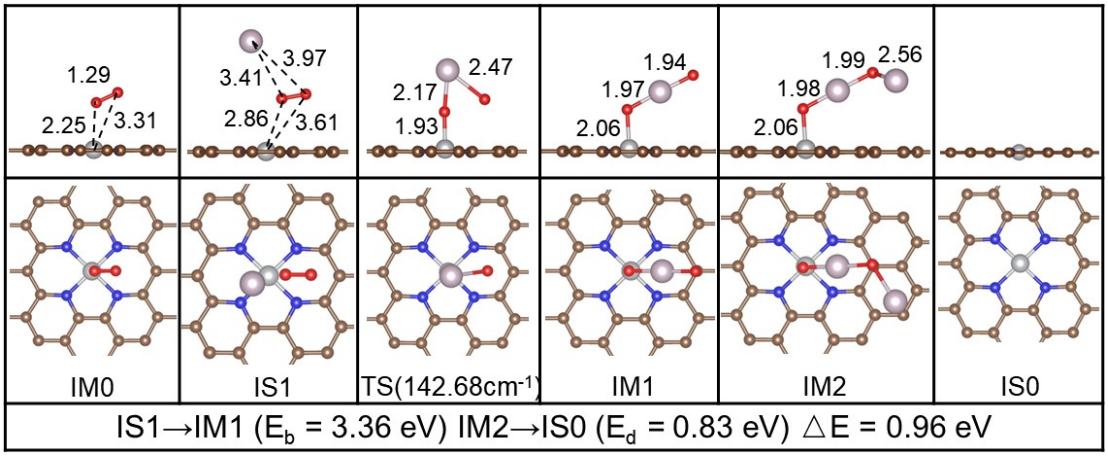

Figure S7. Reaction pathway of catalytic oxidation of Hg^0 on Ni_1-N_4-C. C, N, and Ni are denoted by brown, blue, and light grey, respectively.

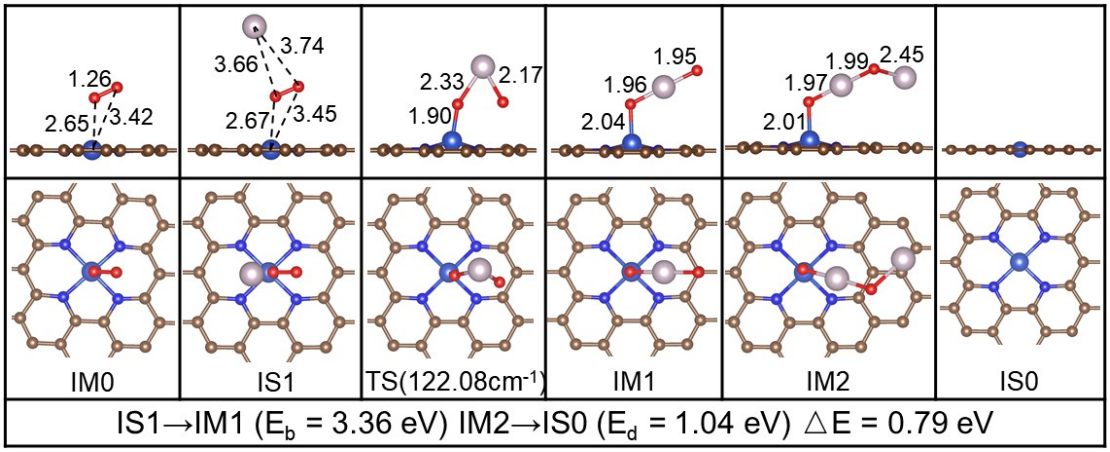

Figure S8. Reaction pathway of catalytic oxidation of Hg^0 on Cu_1-N_4-C. C, N, and Cu are denoted by brown, blue, and light blue, respectively.

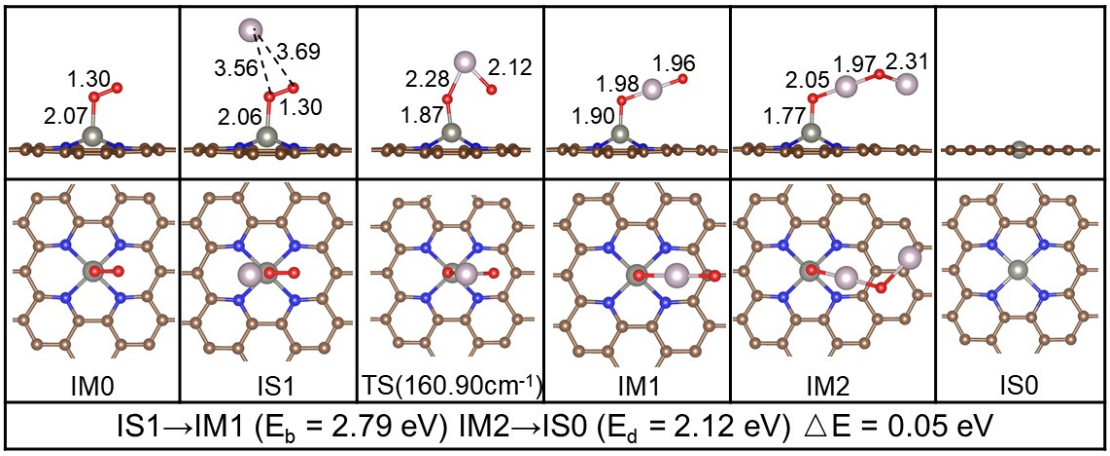

Figure S9. Reaction pathway of catalytic oxidation of Hg^0 on Zn_1-N_4-C. C, N, and Zn are denoted by brown, blue, and grey, respectively.

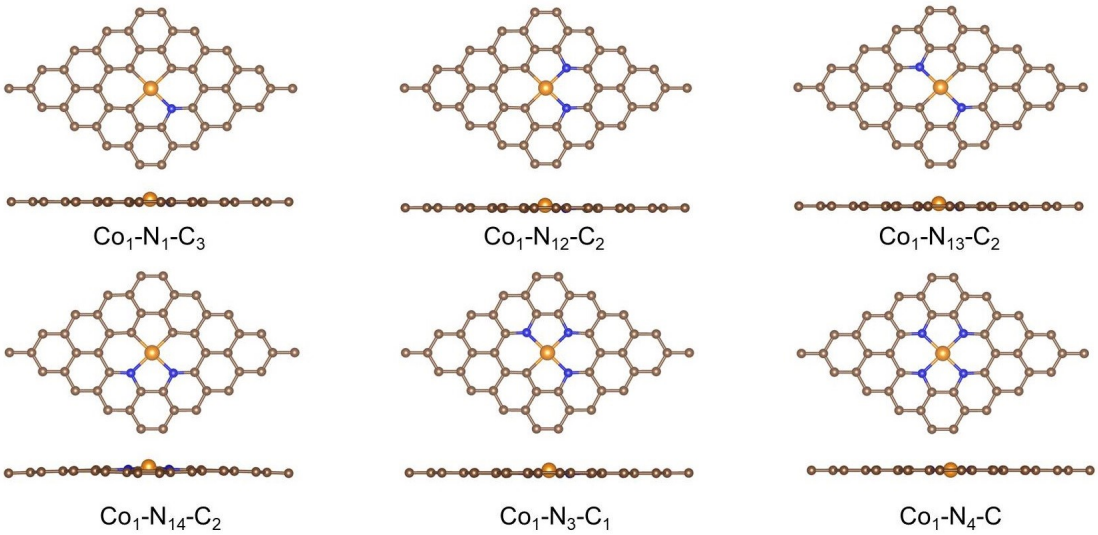

Figure S10. Optimized geometric structures of six Co-N-C catalysts. C, N, and Co are denoted by brown, blue, and orange, respectively.

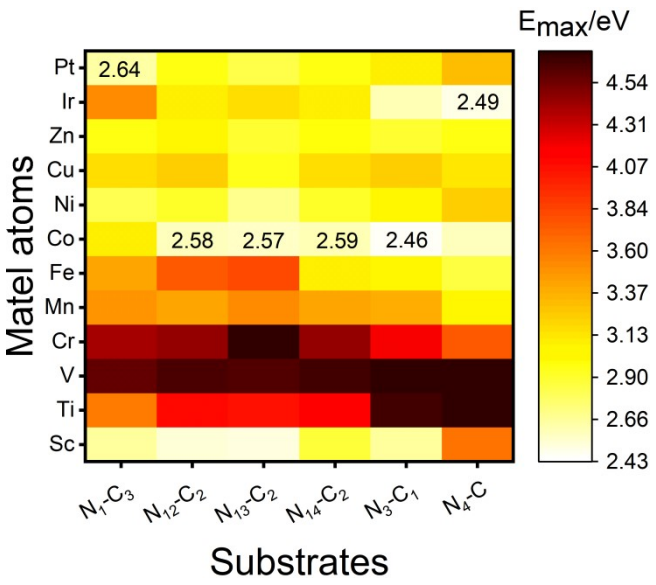

Figure S11. Predicted rate-determining step barriers for 72 SACs in the catalytic oxidation of Hg^0.

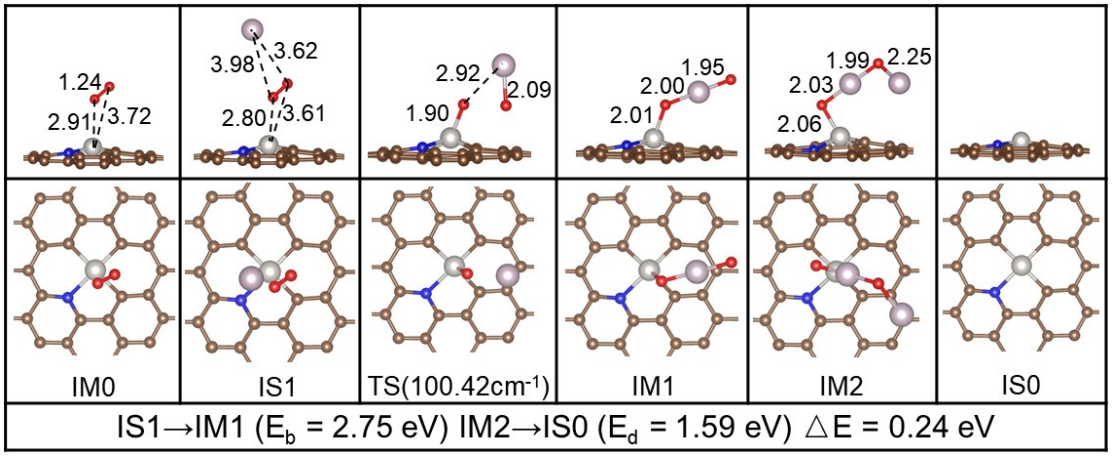

Figure S12. Reaction pathway of catalytic oxidation of Hg^0 on Pt_1-N_1-C_3. C, N, and Pt are denoted by brown, blue, and silver white, respectively.

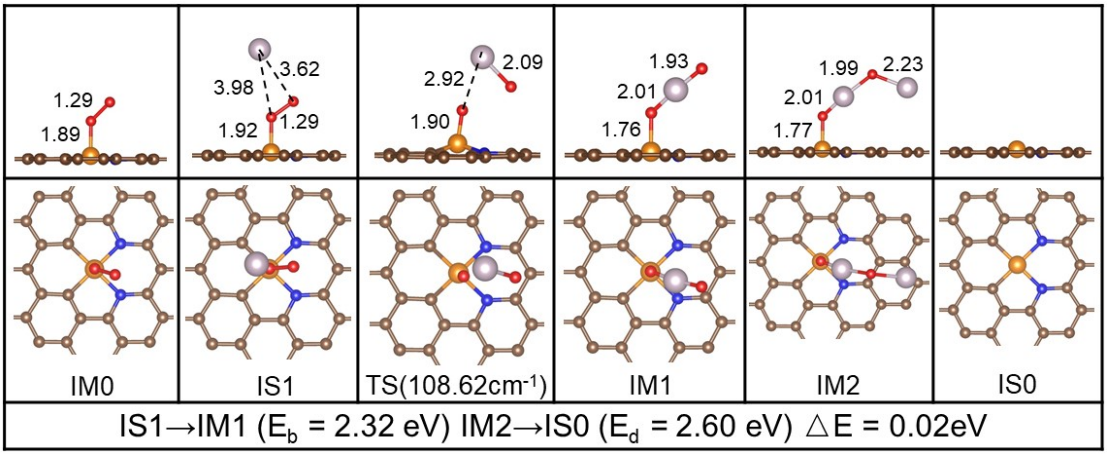

Figure S13. Reaction pathway of catalytic oxidation of Hg^0 on Co_1-N_{12}-C_2. C, N, and Co are denoted by brown, blue, and orange, respectively.

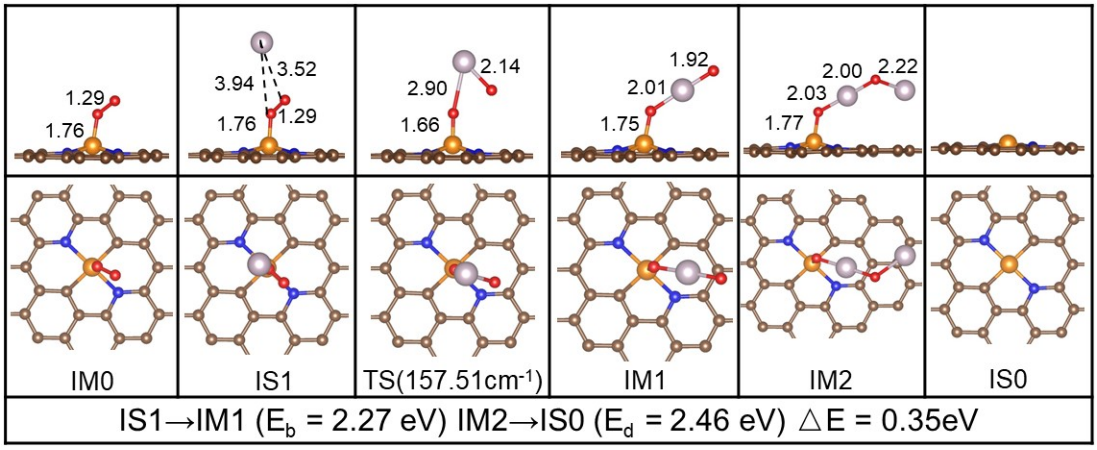

Figure S14. Reaction pathway of catalytic oxidation of Hg^0 on Co_1-N_{13}-C_2. C, N, and Co are denoted by brown, blue, and orange, respectively.

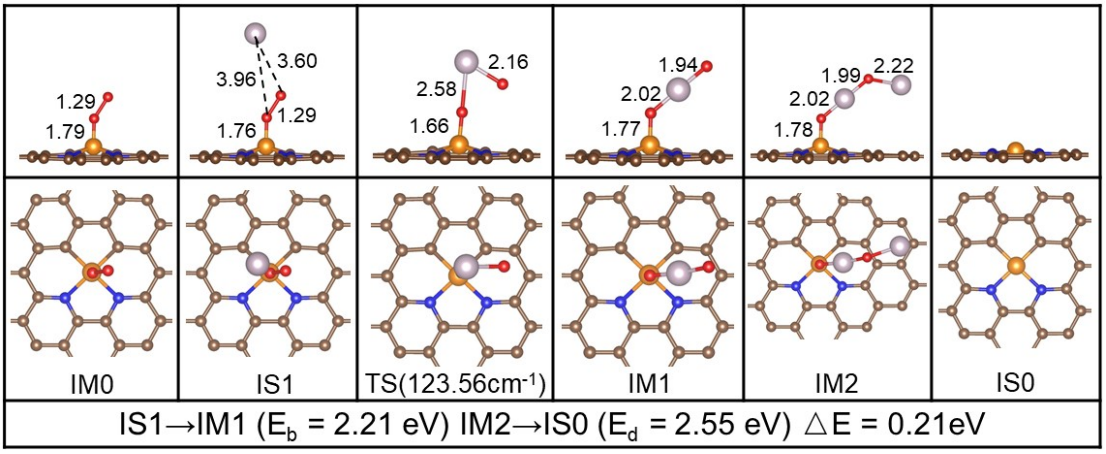

Figure S15. Reaction pathway of catalytic oxidation of Hg^0 on Co_1-N_{14}-C_2. C, N, and Co are denoted by brown, blue, and orange, respectively.

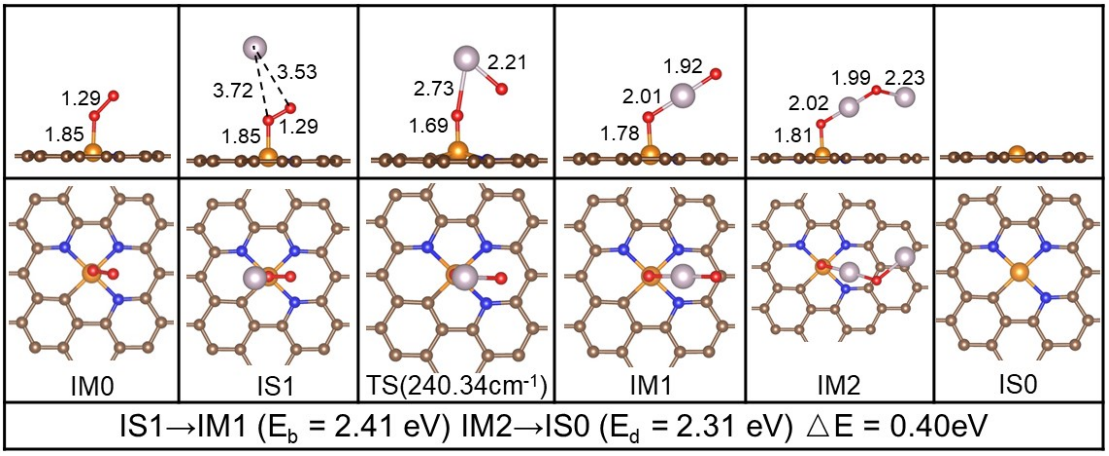

Figure S16. Reaction pathway of catalytic oxidation of Hg^0 on Co_1-N_3-C_1. C, N, and Co are denoted by brown, blue, and orange, respectively.

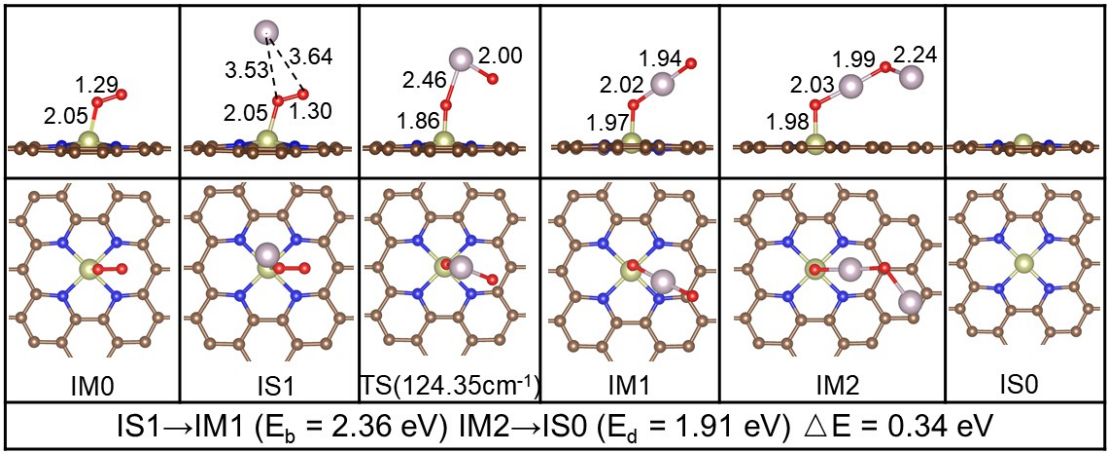

Figure S17. Reaction pathway of catalytic oxidation of Hg^0 on Ir_1-N_4-C. C, N, and Ir are denoted by brown, blue, and light yellow, respectively.