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Coordination engineering for single-atom catalysts in bifunctional oxidation NO and mercury

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ABSTRACT

Catalytic oxidation of NO and Hg⁰ in flue gas is essential for environmental protection. Some state-of-the-art single-atom catalysts (SACs) have shown good catalytic performance for NO and Hg⁰ in both theoretical and experimental aspects. However, the catalytic activity of currently reported catalysts for the oxidation NO and Hg⁰ still need to be promoted. Here, we report a method to reduce the reaction energy barrier via doping different pblock elements to regulate the coordination environment of single-atom cobalt catalysts. Through spin polarization density functional theory calculations, 64 stable structures were obtained from 122 SACs with different coordination environments. To analyze their catalytic activity performance for oxidation NO and Hg^0 , the adsorption energy for O₂, O, and NO was calculated. The results show that the coordination environment can effectively regulate the adsorption energy of O₂ (-0.24 to -1.98 eV) and O (0.40 to -3.65 eV). Four potentially high-activity catalysts were obtained based on their suitable adsorption energies for O_2 and O atoms. Further-more, the energy barriers for catalytic oxidation of NO and Hg^0 over $Co_1P_2C_2$ -pen are 0.98 and 2.14 eV, respectively, which are 0.33 and 0.42 eV lower than Fe₁N₄ currently reported in the experiment. Moreover, by microkinetic modeling, the turnover frequency (TOF) of these four catalysts in the catalytic oxidation of NO and Hg^0 were calculated. Finally, pCOHP and charge transfer characteristic of $Co_1P_2C_2$ -pen is calculated to reveal its origin of high activity from the electronic structure. $Co_1P_2C_2$ -pen can be used for the bifunctional catalytic oxidation of NO and Hg⁰. Most importantly, this study shows that adjusting the coordination environment of the active metal center can significantly improve the catalytic activity of SACs in the catalytic oxidation NO and Hg^0 .

1. Introduction

Flue gas from coal combustion in coal-fired power plants contains many toxic pollutants, such as nitrogen oxide (mainly NO) and mercury (Hg⁰), leading to serious environmental problems [1–5]. The NO and Hg⁰ can cause respiratory diseases and seriously endangers human health [6–8]. Mercury in flue gas mainly exists in three forms: elemental mercury (Hg⁰), mercury oxide (Hg²⁺), and particulate mercury (Hg^p) [9]. Wet flue gas desulfurization (WFGD) and electrostatic precipitators (ESP) can effectively remove Hg²⁺ and Hg^p [10]. However, Hg⁰ is difficult to capture due to its low solubility and strong volatility. Therefore, developing a safe, economical, and efficient method for the collaborative removal of NO and Hg^0 in coal-fired power plants is particularly important. Oxidizing NO and Hg^0 to NO₂ and Hg^{2+} by O₂ in flue gas, and then those oxidates can be easily removed through integration adsorption in the alkaline solution. Therefore, developing the high activity of the catalyst is essential for the pollutant removal technology of catalytic oxidation.

Graphene based single-atom catalysts (SACs) are an emerging catalyst material that has shown great potential in many catalytic fields such as thermal catalysis, electrocatalysis, and even photocatalysis [11–13]. In terms of thermal catalytic oxidation, SACs showed excellent catalytic

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activity and product selectivity. Chen et al. [14] studied the catalytic oxidation of CO by Ni metal atoms loaded with N-doped graphene and found that Ni₁N₁C₂ has excellent catalytic performance for the catalytic oxidation of CO through transition state calculations and microkinetic modeling. Yang et al. [15] conducted systematic research on graphenebased SACs for O₂ catalytic oxidation of Hg⁰, providing new insights for removing mercury pollution from coal-fired power plants. Liu et al. [16] found that under the Langmuir Hinshelwood (LH) mechanism, Pd metal atoms supported on graphene exhibit good catalytic activity for the catalytic oxidation of CO at low temperatures. The theoretical results of Liu et al. [17] show that Fe₁N₂ has excellent catalytic performance in the catalytic oxidation of CO, and LH is the dominant reaction mechanism. Dong et al. [18] explored the adsorption characteristics of single-atom cobalt catalysts for NO and O2 when different numbers of N atoms were doped with graphene and found that Co₁N₃ may be a potential catalyst for the oxidation of NO. Yang et al. [19] have studied the catalytic oxidation of NO over carbon-based single-atom iron catalysts and found that it is a promising catalyst for NO oxidation. In experimental, Yang et al. [20] showed that Fe₁N₄ exhibited excellent catalytic oxidation activity for NO and Hg⁰ at low temperatures. Although SACs have been proven to be a promising catalyst for the catalytic oxidation of NO and Hg⁰ both theoretical and experimental, the activity regulation strategy for NO and Hg⁰ oxidation is still very lacking.

Recently, several studies have shown that the catalytic activity of SACs can be further improved by introducing defects and p-block elements (e.g., B, N, O, P, and S) into graphene. In terms of theoretical research, Tang et al. [21] regulated the coordination environment by codoping B and N in single-atom cobalt catalysts and found that they had excellent catalytic activity for the oxidation NO and CO. Li et al. [22] regulated the coordination environment by co-doping N and O in a single-atom manganese catalyst, and found that the number of N and O atoms in the manganese coordination environment determines the adsorption energy of Hg^0 . Yang et al. [12] found that doping *p*-block elements in single-atom iron catalysts can effectively regulate the adsorption free energy of intermediates in oxygen evolution reactions (OER), thereby regulating the activity of the catalysts for OER. In terms of experimental research, Tang et al. [23] successfully synthesized a single-atom molybdenum catalyst with O and S coordination, and found that this catalyst can significantly promote ORR. Li et al. [24] synthesized single-atom platinum catalysts with N and O coordination in their experiments and found excellent hydrogen evolution reaction (HER) activity. Yuan et al. [25] achieved co-doping of N and P in single-atom iron catalysts and found that the catalyst exhibits excellent ORR activity. Chen et al. [26] introduced N, S, and P into single-atom iron catalysts and found that the ORR performance of the catalyst was significantly improved after doping with heteroatoms. The doping of *p*block elements can regulate the coordination environment of SACs, and then adjust the adsorption of the reaction gas to improve the catalytic activity of catalysts. However, there are still challenges in reducing the energy barriers for catalytic oxidation NO and Hg⁰ by optimizing the composition of the active centers of the catalysts.

Motivated by the above landscape, herein, we aim to analyze the adsorption properties of reaction intermediates such as O_2 , O, and NO of single-atom cobalt catalysts in different coordination environments, and to screen single-atom cobalt catalysts with excellent bifunctional catalytic oxidation NO and Hg⁰. We constructed 122 single-atom cobalt catalysts for spin-polarized density functional theory calculations with van der Waals corrections (DFT-D3). First, 122 single-atom cobalt catalysts based on different coordination environments with B, N, O, P, and S were designed. Second, 64 stable configurations were identified by stability analysis. Third, by analyzing the adsorption energies of these structurally stable catalysts for O_2 , O, and NO, we found four potential catalysts for the catalytic oxidation of NO and Hg⁰ in a bifunctional manner. Fourth, through the calculation of the reaction path and microkinetic modeling, it is found that $Co_1P_2C_2$ -pen has the highest catalytic activity for the catalytic oxidation of NO and Hg⁰

four catalysts. This "design & screening" study by tuning the local coordination environment provides important theoretical guidance for exploring the experimental synthesis of new high-activity catalysts for the oxidation of NO and Hg^0 .

2. Computational and modeling methods

In this work, all density functional theory (DFT) calculations were performed using the Vienna ab initio simulation package (VASP 5.4.4) [27-29]. In detail, the projected enhanced wave (PAW) method was used to describe the interaction between the nucleus and valence electrons, and the Perdew-Burke-Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation [30-32]. Spin polarization was considered to obtain the precise electron ground state energy. To accurately describe the interaction between the gas and the catalyst surface, dipole corrections and DFT-D3 were both considered [33]. We constructed 5 \times 3 $\sqrt{3}$ \times 1 (12.33 \times 12.88 \times 20.00 Å) graphene as the catalyst carrier and set the vacuum layer to 20.00 Å, which can effectively avoid the interaction between mirror images [34]. To ensure the rationality of the calculation, k-point and truncation energy tests were conducted, and the test results are shown in Fig. S1. Taking into account both actuarial accuracy and computational time, the k-point grid and truncation energy are selected as $2 \times 2 \times 1$ and 450 eV, respectively. The force convergence criterion in geometric optimization was set to -0.02eV/Å. At the same time, a k-point grid of $4 \times 4 \times 1$ was used for electronic self-consistent calculations, and the convergence standard was set to 10⁻⁵ eV.

To accurately obtain the transition state configuration and energy of NO and Hg⁰ oxidation, a method combining the climb-image nudged elastic band (CI-NEB) [35,36] and an improved dimer method (IDM) [37] was adopted. The CI-NEB method is used to obtain a rough geometric structure of the transition state with a force of -0.5 eV/Å. Subsequently, IDM was used to obtain an accurate transition state configuration with a convergence criterion of -0.05 eV/Å. In addition, to confirm the correctness of the obtained transition state, we ensure that the accurate transition state configuration has only one virtual frequency in the correct vibration direction, and the calculated finite displacement is ± 0.02 Å. The projected crystal orbital Hamiltonian population (pCOHP) was analyzed using the LOBSTER [38-40] package to study the strength between chemical bonds. Bader charge analysis is used to calculate the amount of charge transfer in the adsorption system. In detail, we obtained the calculated valence electron value of each atom through DFT calculation, and then subtracted the calculated valence electron value of each atom from the pseudo potential to obtain the corresponding Bader charge. The calculation equations for binding energy, adsorption energy, and energy barrier are respectively shown in Supporting Information (equations 1–3).

3. Results and discussion

3.1. Catalyst model

Two-dimensional SACs based on graphene structures have been widely used to model carbon-based SACs. Herein, we remove two adjacent carbon atoms in the graphene structure to form a vacancy and then load a cobalt atom on the vacancy to form single-atom cobalt catalysts. Furthermore, different numbers of *p*-block elements (e.g., B, N, O, P, and S) were used to replace the four C atoms coordinated with the cobalt atom, thus regulating the coordination environment of singleatom cobalt catalysts. The doping sites of *p*-block elements in the catalyst are shown in Fig. 1a. Interestingly, when two identical *p*-block elements are doped, three different coordination configurations exist (pen, hex, and opp). Taking the B-atom doped system as an example, when doped with two B atoms, three coordination configurations $Co_1B_2C_2$ -pen, $Co_1B_2C_2$ -hex, and $Co_1B_2C_2$ -opp will be generated, as shown in Fig. S1. Based on these results, we constructed 122 single-atom



Fig. 1. (a) Schematic diagram of *p*-block elements doping sites. (b) Calculated binding energies of 122 single-atom cobalt catalysts with different coordination environments. The dashed line represents the cobalt clusters of cohesive energy at -5.27 eV. (c) Side face O₂ adsorption energy in different coordination environments. (d) O atom adsorption energy in different coordination environments.

cobalt catalysts by adjusting the number and position of coordination *p*block elements. The detailed configurations of these structurally optimized single-atom cobalt catalysts are shown in Figs. S2–S19.

It is necessary to explore the structural stability of these catalysts. Binding energy is an important descriptor to evaluate the stability of SACs, which is of great significance to evaluate the difficulty of catalyst experimental synthesis. Therefore, we calculated the binding energies of these 122 catalysts. Fig. 1b shows the overall distribution of the binding energies of these 122 catalysts (the detailed binding energy values of these catalysts are shown in Table S1). The horizontal axis in Fig. 1b represents the number of catalysts produced under different doping atomic systems. The more negative the binding energy value, the more stable the catalyst. According to previous reports [41], the cohesion energy of cobalt clusters is -5.27 eV. When the calculated binding energy is more negative relative to -5.27 eV, it indicates that the catalyst has better thermodynamic stability [42]. Therefore, we screened out catalysts with a negative binding energy than -5.27 eV. Finally, 64 stable catalyst configurations were identified.

From Fig. 1b, we can find that when the O atom is used as the coordination atom, most of the catalysts show low binding energy. Especially when the number of coordination O atoms increases, the binding energy shows a downward trend. Therefore, we believe that the doping of O atoms will pose a threat to the stability of the catalyst.

3.2. Adsorption properties

The adsorption energy of O_2 and O is important to reflect the catalytic activity of SACs on NO and Hg⁰ [43,44]. In addition, considering that NO participates in the oxidation process, we calculated the adsorption energies of these 64 single-atom cobalt catalysts for O_2 , O, and NO. The coordination and adsorption energies of these 64 stable catalysts are shown in Fig. 1c-d and Table S2. It is worth noting that in the process of catalyst adsorption of oxygen molecules, two different adsorption energies of these two configurations are expressed as $E_{ads}(O_{2side})$ and $E_{ads}(O_{2end})$, respectively. Interestingly, the calculation results show that O_2 tends to adsorb on the catalyst in a side face configuration.

It is obvious from Fig. 1c-d that regulating the coordination environment of single-atom cobalt catalysts can significantly adjust the adsorption energy of O₂ (-0.24 \sim -1.98 eV) and O (0.40 \sim -3.65 eV). Therefore, regulating the coordination environment of the SACs can significantly adjust the adsorption strength of these reactants, thereby adjusting the catalytic oxidation activity of the catalysts.

Our previous work showed that when the adsorption energy of SACs achieves -0.41 eV and -0.47 eV for O₂ and O, respectively, they will show optimal catalytic activity for the oxidation NO and Hg⁰ [45,46].

Based on these studies, we found four potential high-activity catalysts ($Co_1P_2C_2$ -pen, $Co_1N_1C_1P_2$ -pen, $Co_1S_1N_1P_2$ -pen, and $Co_1S_1N_1C_2$ -hex) among the 64 catalysts through adsorption energy analysis, as

shown in Fig. 2 and Table 1. It can be seen that the adsorption energy of these four catalysts, whether O_2 or O, is very close to our above optimal adsorption energy.

3.3. Reaction pathway analysis

For the four potentially high-activity catalysts we screened, we calculated their catalytic oxidation reaction pathway of NO and Hg⁰, which will further clarify their specific catalytic activities. It should be noted that for the oxidation Hg⁰, the product may be mercury oxide (HgO) or mercury oxide clusters (HgO)₂. (HgO)₂ can be divided into two types: (HgO)₂-chain and (HgO)₂-ring according to different forms. Previous studies [15] have shown that the (HgO)₂-chain has the highest thermodynamic stability among the three mercury oxidation products. In addition, Jayasekharan, T. et al. reported a study on the characterization of (HgO)_n⁺ by laser desorption ionization time of flight mass spectrometry (LDI-TOFMS) thereby confirming the existence of (HgO)_n⁺ clusters [47]. Therefore, in our calculation of the catalytic oxidation pathway of Hg⁰, the (HgO)₂-chain is considered the final oxidation product.

According to previous reports [45,46,48], the Eley-Rideal (ER) reaction mechanism is thought to favor the oxidation NO and Hg⁰. Therefore, when calculating the oxidation reaction pathways of NO and Hg⁰, the ER mechanism is taken as the dominant reaction mechanism. We show the oxidation reaction pathways and energy barriers of $Co_1P_2C_2$ -pen to NO and Hg⁰ in Fig. 3, respectively. Following the extremely similar reaction pattern, the reaction pathways and free energy diagrams of the remaining three catalysts are shown in Figs. S20–S28.

It can be seen that in Fig. 3a, O_2 is pre-adsorbed on the Co atom, and then the O_2 adsorbed by NO attacks generates an energy barrier of 0.08 eV for generating the first NO₂. The second NO then attacks the residual O atoms on the catalyst to generate the second NO₂, and this process will produce an energy barrier of 0.27 eV. It is noted that desorption of the generated second NO₂ from the catalyst only needs to overcome the 0.98 eV energy barrier to complete the catalytic cycle. Therefore, in the oxidation of NO on Co₁P₂C₂-pen, the rate-determining step (RDS) is desorption process of the second NO₂, and the energy barrier of 0.98 eV needs to be overcome.

In the oxidation of Hg^0 (Fig. 3b), Hg atoms attack O_2 to generate O-Hg-O structures, and this process requires overcoming a 2.01 eV energy barrier. Then the second Hg atom is adsorbed on the O-Hg-O structure to form the final oxidation product (HgO)₂-chain. Finally, the (HgO)₂-chain overcomes the energy barrier of 2.14 eV to desorb, thus completing the catalytic cycle on $Co_1P_2C_2$ -pen. It can be found that the desorption of the (HgO)₂-chain is the RDS of the entire Hg⁰ oxidation process, and the energy barrier of 2.14 eV needs to be overcome.

We summarize in Table 2 the RDS when these four catalysts catalyze the oxidation NO and Hg^0 , respectively. Among the four catalysts, it is obvious that $Co_1P_2C_2$ -pen has the lowest RDS for the catalytic oxidation



Fig. 2. Coordination configurations for four potentially highly activity single-atom cobalt catalysts.

Table 1

Adsorption energy performance of O2 and O by four potentially high-activity catalysts. (Adsorption energy unit: eV).

SACs	Δq_{Co} (e)	d-band center	Electronegativity	$E_{ads}(O_{2side})$	$E_{ads}(O_{2end})$	$E_{ads}(O)$
Co ₁ P ₂ C ₂ -pen	-0.36	-1.36	5.30	-0.55	-0.44	-0.60
Co1N1C1P2-pen	-0.36	-1.12	5.64	-0.65	-0.61	-0.47
Co ₁ S ₁ N ₁ C ₂ -pen	-0.65	-0.62	6.17	-0.63	-0.62	-0.45
Co ₁ S ₁ N ₁ C ₂ -hex	-0.60	-0.53	6.17	-0.65	-0.47	-0.41



Fig. 3. (a) Catalytic oxidation cycle of NO on $Co_1P_2C_2$ -pen. (b) Catalytic oxidation cycle of Hg⁰ on $Co_1P_2C_2$ -pen.

Table 2

The four catalysts RDS and TOF/s of oxidation NO and $\rm Hg^0,$ respectively. The temperature is 400 K and the oxygen pressure is 0.05 bar.

SACs	RDS		TOF/s	TOF/s		
	Oxidation NO	Oxidation Hg ⁰	Oxidation NO	Oxidation Hg ⁰		
Co ₁ P ₂ C ₂ -pen Co ₁ N ₁ C ₁ P ₂ - pen	0.98 eV 1.23 eV	2.14 eV 2.25 eV	$\begin{array}{c} 6.70\times10^6\\ 1.57\times10^6\end{array}$	$\begin{array}{c} 3.23 \times 10^{\text{-18}} \\ 3.17 \times 10^{\text{-19}} \end{array}$		
Co ₁ S ₁ N ₁ C ₂ - pen	1.36 eV	2.32 eV	1.51×10^4	$4.09\times 10^{\text{-}21}$		
Co ₁ S ₁ N ₁ C ₂ - hex	1.24 eV	2.22 eV	8.63×10^4	1.35×10^{18}		

NO and Hg^0 . Therefore, $Co_1P_2C_2$ -pen is a high-activity bifunctional catalyst for catalytic oxidation of NO and Hg^0 .

3.4. Microkinetic modeling

To evaluate the activities of these four catalysts under flue gas conditions, microkinetic modeling was constructed based on the kinetic parameters and methods in the Supporting Information. Herein, we choose temperature (T) and pressure (P) as the two descriptors and [log (TOF)] as the reaction evaluator. The microkinetic modeling analyses of the oxidation NO and Hg⁰ of these four catalysts are shown in Fig. 4, respectively. $Co_1P_2C_2$ -pen exhibits the best catalytic activity among the four catalysts in the temperature range of approximately 400 K, which is close to the temperature of coal-fired flue gas emitted in actual operation [49].

To further describe the activity behavior of these four catalysts under the actual working conditions of coal-fired power plants, we calculate their specific TOF values under simulated flue gas conditions. According to previous reports [49], the flue gas temperature and pressure at the tail of the coal-fired power plant flue are 400 K and 1 bar, respectively. In addition, according to relevant research [50], the partial pressure of O₂ in coal-fired flue gas accounts for approximately 5% of the total pressure of the flue gas. Therefore, under the actual flue gas conditions with a temperature of 400 K and an O₂ pressure of 0.05 bar, we calculated the specific TOF values of the catalytic oxidation NO and Hg⁰ of these four catalysts based on the above microkinetic modeling, as shown in Table 2. Under simulated flue gas atmosphere, Co₁P₂C₂-pen exhibited the highest TOF for both NO and Hg⁰ oxidation.

3.5. Electronic characteristic analysis

Fe₁N₄ is a widely reported SACs in the field of multi catalysis, and it is necessary to compare the activity of Co₁P₂C₂-pen and Fe₁N₄. We show the oxidation reaction pathways and energy barriers of Fe₁N₄ to NO and Hg⁰ in Figs. S29–S31, respectively. Co₁P₂C₂-pen has a significant advantage of low RDS, with oxidation RDS of NO and Hg⁰ being 0.33 and 0.42 eV lower than it, respectively. During the oxidation of NO and Hg⁰ by Co₁P₂C₂-pen and Fe₁N₄, the oxidation product NO₂ and (HgO)₂-chain desorption are the RDS of the entire oxidation reaction. Therefore, it is necessary to analyze the binding strength between the oxidation product (NO₂ and (HgO)₂-chain) and the two catalysts (Co₁P₂C₂-pen and Fe₁N₄) to reveal the intrinsic mechanism of Co₁P₂C₂-pen having a lower RDS.

Projected crystal orbital Hamiltonian group (pCOHP) analysis can quantitatively describe the bonding strength between atoms [38]. Here, the integral pCOHP (IpCOHP) of atomic pairs is obtained by integrating pCOHP below the Fermi level to more quantitatively analyze the binding strength between oxidation products and catalysts [51]. The integral region above the Fermi level represents the nonbonding contribution of the empty orbit. From Fig. 5, we can find that the IpCOHP value of Fe₁N₄ (-3.00 and -3.76 eV) for NO₂ and (HgO)₂-chain bonding is greater than that of Co₁P₂C₂-pen (-2.25 and -3.08 eV) for them. This means that compared to Co₁P₂C₂-pen, Fe₁N₄ has a greater bonding contribution of the two oxidation products, resulting in the difficulty of dissociation of the two oxidation products.

In addition, we analyzed the charge transfer of $Co_1P_2C_2$ -pen and Fe_1N_4 in the bonding process of these two oxidation products, as shown in Table 3. It can be seen that compared with Fe_1N_4 , the change of coordination environment significantly reduces the amount of charge transfer of Co atoms, and reduces the interaction between oxidation products and catalysts. This is conducive to the smooth dissociation of oxidation products, thus effectively reducing the RDS in the oxidation process. Therefore, Fe_1N_4 has are higher RDS than $Co_1P_2C_2$ -pen.

The charge transfer analysis results in Table 3 are consistent with the pCOHP analysis results in Fig. 5. Both of them further elucidate the internal mechanism of regulating the coordination environment to reduce the oxidation barrier from the perspective of electronic structure.

To further demonstrate the activity advantage of $Co_1P_2C_2$ -pen in the bifunctional catalytic oxidation NO and Hg^0 , we compare the RDS with



Fig. 4. (a)-(d) are microkinetic modeling analyses of the overall flue gas pressure and temperature functions in the process of catalytic oxidation NO by $Co_1P_2C_2$ -pen, $Co_1N_1C_1P_2$ -pen, $Co_1S_1N_1C_2$ -pen, and $Co_1S_1N_1C_2$ -hex, respectively; (e)-(h) are microkinetic modeling analyses of the overall flue gas pressure and temperature functions in the process of catalytic oxidation Hg⁰ by $Co_1P_2C_2$ -pen, $Co_1N_1C_1P_2$ -pen, $Co_1S_1N_1C_2$ -hex, respectively; (e)-(h) are microkinetic modeling analyses of the overall flue gas pressure and temperature functions in the process of catalytic oxidation Hg⁰ by $Co_1P_2C_2$ -pen, $Co_1N_1C_1P_2$ -pen, $Co_1S_1N_1C_2$ -hex, respectively.

previous reports on the catalytic oxidation NO and Hg^0 , as shown in Table 4. Co₁P₂C₂-pen exhibits excellent catalytic activity for the oxidation of NO and Hg^0 compared with previous literature reports [45,46,48,52–56].

4. Conclusion

Through analyzing 122 single-atom cobalt catalysts with different coordination environments, promising single-atom structures with high catalytic activity for the bifunctional oxidation NO and Hg^0 were obtained. By comparing binding energy and cohesive energy, 64 thermodynamically stable catalysts were identified. Regulating the coordination environment of single-atom cobalt, the adsorption energies of O₂ (-0.24 to -1.98 eV), O (0.40 to -3.65 eV), and NO (-1.01 to -2.75 eV) can be effectively adjusted. According to the adsorption energy of O₂ and O, four potential single-atom catalysts, namely Co₁P₂C₂-pen, Co₁N₁C₁P₂-pen, Co₁S₁N₁C₂-pen, and Co₁S₁N₁C₂-hex, were successfully screened for the bifunctionally catalytic oxidation NO and Hg⁰. Based on the energy barrier in the rate-determining step (RDS), Co₁P₂C₂-

pen has the lowest energy barrier among those catalysts (0.98 and 2.14 eV for NO and Hg⁰ oxidation, respectively). Microkinetic modeling also further shows that Co₁P₂C₂-pen exhibits the highest turnover frequency value in the catalytic oxidation NO and Hg⁰ (6.70×10^6 /s and $3.23 \times 10^ ^{18}/\text{s}$ for NO and Hg^0 oxidation, respectively). Compared to the $\text{Fe}_1\text{N}_4,$ Co₁P₂C₂-pen has the significant advantage of low RDS barrier, with oxidation RDS barrier of NO and Hg⁰ being 0.33 and 0.42 eV lower than it, respectively. pCOHP and charge transfer analysis show that Co₁P₂C₂pen has lower bonding contribution and less charge transfer amount for oxidation products compared to Fe1N4. This further reveals the intrinsic mechanism that Co1P2C2-pen has a low catalytic oxidation energy barrier. Compared with the catalysts reported so far for catalytic oxidation of NO and Hg⁰, Co₁P₂C₂-pen exhibits lower RDS barrier advantages. Most importantly, regulating the coordination environment is an effective approach for improving the catalytic activity of SACs in the catalytic oxidation NO and Hg⁰.



Fig. 5. (a)-(b) pCOHP of NO₂ bonding with $Co_1P_2C_2$ -pen and Fe_1N_4 , respectively; (c)-(d) pCOHP of (HgO)₂-chain bonding with $Co_1P_2C_2$ -pen and Fe_1N_4 , respectively. The green and purple integration regions represent antibonding contributions and bonding contributions, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Table 3
The amount of charge transfer when $Co_1P_2C_2$ -pen and Fe_1N_4 bond with NO_2 and
(HgO) ₂ -chain.

SACs	Δq (Metal atom) (e)	Δq (NO ₂) (e)	Δq ((HgO) ₂ -chain) (e)
Co ₁ P ₂ C ₂ -pen	-0.48/-0.63	+0.41	+0.43
Fe ₁ N ₄	-1.09/-1.29	+0.47	+0.49

Table 4

RDS for the catalytic oxidation NO and Hg^0 by various catalysts are reported in the literature. (Unit: eV).

Catalysts	Oxidation NO	Oxidation Hg ⁰	Functional	Software
LaMnO ₃ (001)[52]	2.29		PBE	CASTEP
Co ₁ CNT-N ₃ [48]	1.65		PBE	VASP
LaCoO ₃ (011)[53]	2.63		PBE	DMol ³
Ce-doped	2.50		PBE	DMol ³
LaCoO ₃ (011)[53]				
Fe ₁ V _B -BN[54]		2.91	PBE	CASTEP
Mn ₁ g-C ₃ N ₄ [55]		2.84/3.13	PBE	VASP
Ni ₁ g-C ₃ N ₄ [56]		2.59	PBE	VASP
Co1g-C3N4[56]		2.92	PBE	VASP
Sc ₁ N ₄ [46]		4.89	PBE	VASP
Ti ₁ N ₄ [45, 46]	3.60	4.98	PBE	VASP
V ₁ N ₄ [45, 46]	2.85	4.98	PBE	VASP
Cr ₁ N ₄ [45, 46]	1.74	3.12	PBE	VASP
Fe ₁ N ₄ [45, 46]	1.33	2.40	PBE	VASP
Co ₁ N ₄ [45, 46]	1.49	2.73	PBE	VASP
Co ₁ P ₂ C ₂ -pen [This	0.98	2.14	PBE	VASP
work]				

CRediT authorship contribution statement

Weijie Yang: Funding acquisition, Investigation, Methodology, Writing – review & editing. Binghui Zhou: Data curation, Validation, Visualization, Writing – original draft. Liugang Chen: Investigation, Methodology. Ruiyang Shi: Conceptualization, Investigation, Methodology. Hao Li: Methodology, Visualization. Xiaoshuo Liu: Methodology, Supervision, Writing – review & editing. Zhengyang Gao: Funding acquisition, Project administration, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.

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