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# Design of Single-Atom Catalysts for Hg<sup>0</sup> Oxidation Using H<sub>2</sub>O<sub>2</sub>

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**ABSTRACT:** Hg<sup>0</sup> removal is the most difficult part in mercury purification due to its insolubility in water and strong volatility. Catalytic oxidation is the main method for Hg<sup>0</sup> removal. O<sub>2</sub> and hydrogen halides (HCl and H<sub>2</sub>S) are common oxidants for catalytic Hg<sup>0</sup> oxidation. However, previous studies showed that current catalytic oxidation routes have sluggish kinetics and may cause secondary pollution. Herein, we propose a new pathway for catalytic Hg<sup>0</sup> oxidation on the surface of single-atom catalysts (SACs) using the green oxidant H<sub>2</sub>O<sub>2</sub>. Some potential catalysts were screened by analyzing the adsorption and activation mechanism of H<sub>2</sub>O<sub>2</sub> on the surface of SACs. Spin-polarized density functional theory calculations with van der Waals corrections (DFT-D3) revealed that Zn<sub>1</sub>-N<sub>4</sub>-C has the lowest rate-determining step barrier (0.35 eV) among the analyzed systems. This study proposes a promising pathway for a kinetically facile catalytic Hg<sup>0</sup> oxidation, providing a new option for effective Hg<sup>0</sup> removal.



#### 1. INTRODUCTION

Mercury, as a heavy metal pollutant that is easily accumulated in biological organisms and difficult to degrade, is harmful to the ecological environment and human health. Mercury emission from coal combustion is one of the major sources of mercury in the atmosphere, accounting for ~21% of anthropogenic emission sources.<sup>1</sup> Mercury is present in flue gas in three forms: elemental mercury (Hg<sup>0</sup>), oxidized mercury (Hg<sup>2+</sup>), and particulate mercury (Hg<sup>P</sup>).<sup>2</sup> Hg<sup>0</sup> accounts for ~80% of the total mercury and is extremely stable, which is the difficult part of flue gas mercury removal.<sup>3</sup> At present, the main technologies for flue gas mercury removal are adsorption and catalytic oxidation,<sup>4</sup> where catalytic oxidation has become an emerging topic in recent years due to its low operating cost and high removal efficiency. Therefore, it is instructive to investigate the reaction mechanism of catalytic Hg<sup>0</sup> oxidation for mercury removal.

Catalysts play a critical role in catalytic oxidation reactions. Graphene-based single-atom catalysts (SACs) are widely used for atmospheric pollutant removal due to their high catalytic activity and selectivity in many reactions.<sup>5–7</sup> Zhao et al.<sup>8</sup> studied the adsorption of Hg<sup>0</sup> by doped-graphene and found that nitrogen-doped graphene-containing Pd clusters showed promising Hg<sup>0</sup> adsorption. Other reports<sup>9,10</sup> analyzed catalytic Hg<sup>0</sup> oxidation on graphene-based Pt SACs using O<sub>2</sub>; they showed that the Pt/3N-GN catalyst had excellent catalytic activity for catalytic Hg<sup>0</sup> oxidation, with a rate-determining step (RDS) barrier of 2.016 eV. Yang et al.<sup>11,12</sup> used a combined theoretical and experimental method to analyze the reaction mechanism of Fe SACs for the catalytic Hg<sup>0</sup> oxidation using O<sub>2</sub>; they found that Fe<sub>SA</sub>/DV-N<sub>4</sub> has the highest catalytic activity, with an RDS energy barrier of 2.34 eV. Our previous

study<sup>13</sup> predicted the catalytic activity of 3d, 4d, and 5d metal SACs (in the form of metal<sub>1</sub>– $N_4$ –C) for catalytic Hg<sup>0</sup> oxidation by the derived volcano activity plots; the results showed that Fe<sub>1</sub>– $N_4$ –C has the highest catalytic activity. However, it was found that the SACs catalyzed Hg<sup>0</sup> oxidations generally have high RDS energy barriers (>2 eV). Therefore, it is particularly important to explore other strategies to oxidize Hg<sup>0</sup> on SACs with more facile kinetics.

The selection of oxidant also significantly affects  $Hg^0$ removal. In addition to O2, hydrogen halides as HCl, HBr,<sup>15</sup> and  $H_2S^{16}$  are also used as the oxidants for  $Hg^0$ oxidation. However, the utilization of these acidic and toxic gases will not only cause secondary pollution but also cause pipeline corrosion. Hydrogen peroxide  $(H_2O_2)$  is a green oxidant that can be reduced to thermodynamically stable H<sub>2</sub>O in redox reactions. It was demonstrated that HO radicals generated from the gas-phase H2O2 have high reactivity on catalyst surfaces.<sup>17,18</sup> Li et al.<sup>19</sup> studied the catalytic oxidation of SO<sub>2</sub> on the surface of Al<sub>2</sub>O<sub>3</sub> by  $H_2O_2$  and found that  $H_2O_2$ has the lower energy barrier of  $H_2O_2$  decomposition (0.34 eV) and SO<sub>2</sub> oxidation (0.81 eV) on  $\gamma$ -Al<sub>2</sub>O<sub>3-x</sub>(110) surfaces. In addition, it was found that the decomposition of H<sub>2</sub>O<sub>2</sub> prefers breaking the O–O bond to form two HO\* on an  $Fe_3O_4(110)$ surface; HO combines with Hg<sup>0</sup> to form stable Hg(OH)<sub>2</sub>

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**Figure 1.** (a) 3d single TM atoms (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) considered in this study. (b, c) Top and side views of the optimized  $TM_1-N_3-C$  and  $TM_1-N_4-C$  structures. (d) Optimized adsorption geometries of  $H_2O_2$  on  $TM_1-N_3-C$ . (e-g) Optimized adsorption geometries of  $H_2O_2$  on  $TM_1-N_4-C$ . C, N, O, and TM atoms are denoted by brown, blue, red and purple, respectively.

which is more conducive to desorption.<sup>20</sup> Therefore,  $H_2O_2$  has a unique advantage in  $Hg^0$  oxidation. However, very few studies were reported regarding  $Hg^0$  oxidation on the SACs using  $H_2O_2$ . The reaction mechanism of  $H_2O_2$  activation and oxidation of  $Hg^0$  on the SACs surface was not well-understood. Therefore, it is urgently needed to study the reaction mechanism of the catalytic  $Hg^0$  oxidation on SACs using  $H_2O_2$ .

Herein, the activation mechanism of  $H_2O_2$  over 3d  $TM_1$ - $N_4$ -C and  $TM_1$ - $N_3$ -C SACs (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) were analyzed. The reaction mechanism for  $Hg^0$  oxidation using  $H_2O_2$  over  $TM_1-N_4-C$  was analyzed using spin-polarized density functional theory calculations with van der Waals corrections (DFT-D3). First, the adsorption configurations of  $H_2O_2$  on the  $TM_1-N_4-C$  and  $TM_1-N_3-C$ surfaces were analyzed. Second, the most stable dissociative adsorption configurations of H2O2 on the TM1-N4-C and  $TM_1-N_3-C$  were determined. Third, the dissociation processes of H<sub>2</sub>O<sub>2</sub> on TM<sub>1</sub>-N<sub>4</sub>-C and TM<sub>1</sub>-N<sub>3</sub>-C were analyzed by *ab initio* molecular dynamics (AIMD) simulations. Fourth, the activation processes of H<sub>2</sub>O<sub>2</sub> dissociation into 2HO\* on the catalyst surfaces were studied. Finally, the reaction mechanism of catalytic Hg<sup>0</sup> oxidation using H<sub>2</sub>O<sub>2</sub> on  $TM_1-N_4-C$  (TM= Cu and Zn) and Cu<sub>1</sub>-N<sub>3</sub>-C were studied, and the RDS barriers were determined. Most importantly, this work discusses a potential avenue to catalytically oxidize Hg<sup>0</sup> for Hg removal.

## 2. METHODS

All calculations were based on the spin-polarized DFT method using the Vienna *ab initio* simulation package (VASP). The

Perdew-Burke-Ernzerhof (PBE)<sup>21</sup> functional and projector augmented wave (PAW) method<sup>22</sup> were adopted for all DFT calculations. To acquire more accurate interactions between the gas molecules and catalyst surfaces, van der Waals interactions were included using the DFT-D3 framework.<sup>23</sup> A 5  $\times$  5 graphene with a vacuum layer of 15 Å was used to simulate the adjacent regions of SACs active center.<sup>24</sup> A  $4 \times 4$  $\times$  1  $\Gamma$ -centered *k*-point and 450 eV energy cutoff were adopted in geometric optimizations. A  $8 \times 8 \times 1$  k-point grid with  $10^{-5}$ eV self-consistent electron iteration as the convergence threshold was adopted to acquire electron energy ground state information.<sup>25</sup> The force convergence criteria were set to 0.02 eV/Å for each atom. The projected crystal orbital Hamiltonian population (pCOHP) method was employed to analyze the stability of chemical bonds in the system,<sup>26</sup> which was calculated using the LOBSTER package.<sup>27,2</sup>

To acquire transition states of the essential elementary steps, the climbing-image nudged elastic band (CI-NEB)<sup>29,30</sup> and improved dimer method (IDM)<sup>31</sup> were applied. The convergence criteria for the forces were set to 0.05 eV/Å. Vibrational frequency analyses were performed to validate the minima and transition state structures, which were analyzed with the limited displacements of  $\pm 0.02$  Å. To study the adsorption strength of gas molecules on the catalyst surfaces, adsorption energy ( $E_{ads}$ ) was calculated according to the following equation:

$$E_{ads} = E_{absorb} - E_{sur} - E_{gas} \tag{1}$$

Here the adsorption energy of HO\* is defined by referring to half of an  $H_2O_2$  molecule:

Table 1. Adsorption Energies  $(E_{ads})$  and Adsorption States of  $H_2O_2$  on the Analyzed Catalysts

catalyst	$E_{\rm ads}/{\rm eV}$	adsorption state	catalyst	$E_{\rm ads}/{\rm eV}$	adsorption state
$Sc_1-N_3-C$	-6.85	2HO*	$Sc_1-N_4-C$	-4.94	2HO*
$Ti_1-N_3-C$	-6.81	2HO*	$Ti_1-N_4-C$	-5.72	2HO*
$V_1 - N_3 - C$	-5.79	2HO*	$V_1-N_4-C$	-4.59	2HO*
$Cr_1-N_3-C$	-5.77	2HO*	$Cr_1-N_4-C$	-3.50	O*+H <sub>2</sub> O
$Mn_1 - N_3 - C$	-5.06	2HO*	$Mn_1-N_4-C$	-0.14	$H_2O_2$
$Fe_1-N_3-C$	-4.24	2HO*	Fe <sub>1</sub> -N <sub>4</sub> -C	-0.15	$H_2O_2$
Co <sub>1</sub> -N <sub>3</sub> -C	-3.88	2HO*	$Co_1-N_4-C$	-0.05	$H_2O_2$
Ni <sub>1</sub> -N <sub>3</sub> -C	-3.57	2HO*	$Ni_1-N_4-C$	-0.01	$H_2O_2$
Cu <sub>1</sub> -N <sub>3</sub> -C	-2.61	2HO*	$Cu_1-N_4-C$	-0.02	$H_2O_2$
$Zn_1-N_3-C$	-2.70	2HO*	$Zn_1-N_4-C$	-0.16	$H_2O_2$

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$$E_{ads}(OH) = E_{sur+HO} - E_{sur} - E_{H_2O_2}/2.$$
 (2)

 $E_{absorb}$ ,  $E_{sur}$ , and  $E_{gas}$  are the total energies of adsorption systems, catalyst surface, and gases, respectively.  $E_{sur+HO}$  is the total energy of the catalyst with adsorbed HO\*.  $E_{H_2O_2}$  is the total energy of an isolated  $H_2O_2$  molecule.

To determine the difficulty of Hg<sup>0</sup> catalytic oxidation and product desorption, reaction energy barrier  $(E_b)$  and reaction heat  $(\Delta E)$  in the reaction pathways were calculated according to

$$E_b = E_{TS} - E_{IS} \tag{3}$$

$$\Delta E = E_{\rm FS} - E_{\rm IS} \tag{4}$$

where  $E_{IS}$ ,  $E_{TS}$ , and  $E_{FS}$  are the total energies of the initial, transition, and final states, respectively.

The Gibbs free energy can be obtained via eq  $5^{32}$ 

$$G(T, P) = E_{ele} + ZPE + \Delta H - TS(T, P) + K_{\rm B}T \ln \frac{P}{P^0}$$
(5)

where  $E_{ele}$  is the system energy in the ground state, ZPS is the zero-correction energy,  $\Delta H$  is the enthalpy variation from 0 K to a given temperature, T is the temperature and TS(T,P) is the entropy of the system acquired from vibrational frequency,  $K_B$  is the Boltzmann constant, 8.6173303 × 10<sup>-5</sup> eV·K<sup>-1</sup>, and  $P^0$  is the standing pressure.

#### 3. RESULTS AND DISCUSSION

**3.1. Catalyst Models.** Graphene has various properties through carbon vacancies and nitrogen doping engineering.<sup>33</sup>



**Figure 2.** (a–d) Electronic density difference of  $H_2O_2$  adsorption on 4 SACs (the contour lines in plots are drawn at 0.004 e/Å<sup>3</sup> intervals) (e) Lowest unoccupied molecular orbitals (LUMO) of  $H_2O_2$ . (f–h) Highest occupied molecular orbitals (HOMO) of  $Cr_1-N_4-C$ ,  $V_1-N_4-C$  and  $Cu_1-N_3-C$ .



**Figure 3.** (a–d) Dissociative adsorption structures of  $H_2O_2$  on  $TM_1-N_3-C$  and  $TM_1-N_4-C$ . *C*, *N*, *O* and TM are denoted by brown, blue, red, and purple, respectively. (e–j) Relative Gibbs free energies of the dissociative adsorption configurations of  $H_2O_2$  on  $TM_1-N_4-C$  (TM = Mn, Fe, Co, Ni, Cu, and Zn) at 300 K.

Graphene substrates can be classified into two typical structures based on the number of carbon vacancies: singlevacancy graphene without a carbon atom and double-vacancy graphene without two adjacent carbon atoms. According to previous results, <sup>34,35</sup> SACs with four N-doped double-vacancy graphene substrates (DV-N<sub>4</sub>) and three N-doped single-vacancy graphene substrates (SV-N<sub>3</sub>) possess high stability. Therefore, we selected ten 3d TMs (TM = Sc-Cu, as shown Figure 1a) as the active center. SACs (TM<sub>1</sub>-N<sub>4</sub>-C, TM<sub>1</sub>-N<sub>3</sub>-C) were built by anchoring metal atoms on DV-N<sub>4</sub> and SV-N<sub>3</sub>. Top and side views of the optimized SACs structures are shown in Figure 1b,c. Considering the difference between DFT calculation and experiments, we compared the Fe loading rate of the calculation model with experimental results. The Fe loading rate in the calculation model (8.7 wt %) is similar to



**Figure 4.** (a–d) AIMD simulations on the energy variations and structures of the dissociative adsorption processes of  $H_2O_2$  on  $TM_1$ – $N_4$ –C (TM = Mn, Fe, Co, and Ni). (e) Activation pathways of  $H_2O_2$  on  $Zn_1$ – $N_4$ –C. *C*, *N*, *O*, and Zn are denoted by brown, blue, red, and green, respectively. (f) Relative Gibbs free energies variations in the activation of  $H_2O_2$  to HO\* on SACs at 300 K.

the previous experimental study (8.9 wt %),<sup>36</sup> suggesting that our DFT calculation model is reasonable and reliable.

3.2. Adsorption of H<sub>2</sub>O<sub>2</sub> on the Surface of SACs. Adsorption is usually a prerequisite for catalytic oxidation reactions.<sup>37</sup> In this study, all adsorption configurations after optimization are shown in Figure S1. The adsorption energy  $(E_{ads})$  and adsorption state of  $H_2O_2$  on SACs surface are shown in Table 1. H<sub>2</sub>O<sub>2</sub> spontaneously dissociates onto the surface of most catalysts except several  $TM_1 - N_4 - C$  (TM = Mn, Fe, Co, Ni, Cu, and Zn). The dissociation mechanisms can be divided into two types: two HO\* adsorbed on the metal and one  $O^*$  adsorbed on the metal with a free H<sub>2</sub>O molecule, which is consistent with the study by Liu et al.<sup>38</sup> Note that  $H_2O_2$  dissociates into 2HO\* on the surface of all ten  $TM_1$ -N<sub>3</sub>-C SACs. The adsorption geometries are shown in Figure 1d. Adsorption geometries of  $H_2O_2$  on  $TM_1-N_4-C$  are shown in Figure 1e–g.  $H_2O_2$  spontaneously dissociates into 2HO\* on  $TM_1 - N_4 - C$  (TM = Sc and Ti) and into one O\* with a H<sub>2</sub>O molecule on Cr1-N4-C. The absence of spontaneous dissociation of  $H_2O_2$  on  $TM_1-N_4-C$  (TM = Mn, Fe, Co, Ni, Cu, and Zn) may be due to the fact that the binding strength of H<sub>2</sub>O<sub>2</sub> on the catalyst surface is too weak to break the O-O bond.

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**Figure 5.** (a) Adsorption energies of HO\* on the SACs. (b) Calculated free energy diagrams of Hg<sup>0</sup> oxidation on  $Zn_1-N_4-C$   $Cu_1-N_4-C$ , and  $Cu_1-N_3-C$ . (c) Reaction pathways for the catalytic oxidation of Hg<sup>0</sup> on  $Zn_1-N_4-C$  using H<sub>2</sub>O<sub>2</sub>. C, N, O, and Zn are denoted by brown, blue, red, and green, respectively. (d) Electronic density difference of IS1, TS, and IM2 on  $Zn_1-N_4-C$  surface. (The contour lines in plots are drawn at 0.004e/Å<sup>3</sup> intervals.) (e) COHP analysis of the O–Fe bond in the desorption system. (f) COHP analysis of the O–Zn bond in IM2.

Considering the importance of electron transfer for understanding reaction mechanism,<sup>39</sup> we plotted the electronic density difference of the four adsorption configurations to visualize the electron transfer as shown in Figure 2a–d. The amount and direction of the charge transfer are marked. The O atom is surrounded by a yellow region in three dissociation configurations (Figure 2a–c), indicating that the O atom gains electrons and the metal atom loses electrons.  $H_2O_2$  has a small charge transfer area on the Ni<sub>1</sub>–N<sub>4</sub>–C surface (Figure 2d), indicating that a slight charge transfer has occurred. The calculated amount of charge transfer is consistent with the results of the above analysis.

The geometrical structure of SACs and the orientation of frontier molecular orbitals are both main factors affecting the adsorption conformation of  $H_2O_2$  on SACs surface.<sup>38</sup> As can be seen from Figure S1, both  $TM_1-N_3-C$  (TM = Sc-Zn) and  $TM_1-N_4-C$  (Sc-V) are nonplanar geometries with metal atoms standing out of the plane. The metal atoms exposed can fully contact and adsorb with OH radicals to form 2HO\*. The metal atoms of  $TM_1-N_4-C$  (TM = Mn-Zn) are embedded in the graphene layer and have weak adsorption of  $H_2O_2$ . Hence it can remain in the molecular state. Dissociative adsorption of  $H_2O_2$  on the SACs surface is related to the orientation of the frontier orbitals.<sup>40</sup> To facilitate discussion,

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catalyst	oxidant	functional	RDS energy barrier (eV)
Fe <sub>SA</sub> /DV-N <sub>4</sub>	O <sub>2</sub>	PBE-D3	2.34 <sup>11</sup>
Mn-doped g-C <sub>3</sub> N <sub>4</sub>	O <sub>2</sub>	PBE-D3	2.84 and 3.13 <sup>44</sup>
Fe <sub>2</sub> , Co <sub>2</sub> , Ni <sub>2</sub> @g-C <sub>3</sub> N <sub>4</sub>	O <sub>2</sub>	PBE-D3	2.79, 2.29, and 2.04 <sup>45</sup>
Pt/3N-GN	O <sub>2</sub>	PBE	2.0169
$Zn_1 - N_4 - C$	$H_2O_2$	PBE-D3	0.35
$Fe_3O_4$ (1 1 0)	$H_2O_2$	PBE	$1.67^{20}$
ZnO	lattice O	PW91	3.4 <sup>46</sup>
CuO (1 1 1)	O <sub>2</sub>	PW91	0.8047
CuCl <sub>2</sub> /TiO <sub>2</sub>	Cl	PW91	3.59 <sup>48</sup>
CuFe <sub>2</sub> O <sub>4</sub>	O <sub>2</sub>	PBE	1.2149
LaMnO <sub>3</sub>	HCl	PBE	0.74 <sup>50</sup>
MnFe <sub>2</sub> O <sub>4</sub>	HCl	PBE	2.20 <sup>51</sup>
RuO <sub>2</sub> /TiO <sub>2</sub>	HCl	PW91	$1.57^{52}$
$RuO_2(1\ 1\ 0)$	HCl	PW91	0.94 <sup>53</sup>
CeO <sub>2</sub> /TiO <sub>2</sub>	HCl	PBE	1.09 <sup>54</sup>
$CeO_2$ (1 1 1)	HCl	PBE	0.6255
Co <sub>3</sub> O <sub>4</sub>	HCl	PBE	0.67 <sup>56</sup>
VO <sub>x</sub> /TiO <sub>2</sub>	HCl	PBE	1.00 <sup>57</sup>
$V_2O_5/TiO_2$	HBr	PBE	0.69 <sup>58</sup>
MnO <sub>2</sub>	O <sub>2</sub>	PBE	1.86 <sup>59</sup>
$MoS_2$ (1 0 0)	HCl	PBE	0.53 <sup>60</sup>
$MnO_2$ (1 1 0)	HCl	PBE	$0.69^{61}$
CeO <sub>2</sub> –WO <sub>3</sub> /TiO <sub>2</sub>	HCl	PBE	$0.52^{62}$
Mn doped Fe <sub>3</sub> O <sub>4</sub> (1 1 1)	Cl	PBE	2.72 <sup>63</sup>
$V_2O_5 - TiO_2$ (001)	lattice O	PW91	$1.49^{64}$
$\delta$ -MnO <sub>2</sub>	O <sub>2</sub>	PW91	$1.68^{65}$
AgNPs	0	PBE	$1.62^{66}$
Cu-MOFs	Cl/Br	PBE	$1.92/1.82^{67}$
Pd (1 0 0)	HCl	PBE	0.70 <sup>68</sup>

Table 2. Summary	of the Catalysts,	Oxidants, DFT	' Functional, and	d RDS Energy	Barriers in	catalytic Hg	<sup>0</sup> Oxidation
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we have selected three representative SACs ( $Cr_1-N_4-C$ ,  $V_1-N_4-C$ ,  $Cu_1-N_3-C$ ) and plotted their highest occupied molecular orbitals (HOMO) as shown in Figure 2f-h. The HOMO of  $Cr_1-N_4-C$  and the lowest unoccupied orbitals (LUMO) of  $H_2O_2$  (Figure 2e) are well-matched in the vertical direction.  $H_2O_2$  on the  $Cr_1-N_4-C$  surface prefers to dissociate by vertical adsorption to form O\* and  $H_2O$ . The well-matched LUMO of  $H_2O_2$  and HOMO of SACs ( $V_1-N_4-C$  and  $Cu_1-N_3-C$ ) in the horizontal direction causes  $H_2O_2$  to prefer horizontal adsorption.  $H_2O_2$  dissociates in the horizontal direction to form 2HO\*. In summary, the geometry of SACs and the orientation of frontier molecular orbitals synergistically affect the adsorption and dissociation of  $H_2O_2$  on the SACs surface.

3.3. Stable Dissociative Adsorption Conformation of  $H_2O_2$ . Based on the above analyses,  $H_2O_2$  can dissociate or exist in a molecular form on SACs. However, these structures are not necessarily the lowest-energy structures. Meanwhile, HO generated by the dissociation of H<sub>2</sub>O<sub>2</sub> is more facile for  $Hg^0$  oxidation. To determine the most stable  $H_2O_2$  dissociative adsorption structure, we analyzed multiple dissociative adsorption geometries by DFT-D3 and the four typical configurations are denoted as A<sub>1</sub>, B<sub>1</sub>, A<sub>2</sub>, and B<sub>2</sub> (Figure 3ad). The adsorption configuration with a lower energy was identified as the stable structure. We calculated the relative Gibbs free energies at 300 K for the two dissociated structures (Figures 3e-j and S2 and Table S1). The above analyses can be used to identify a stable dissociative adsorption structure of H<sub>2</sub>O<sub>2</sub> on SACs. Stable dissociative adsorption structures are classified into the following two types: (i)  $H_2O_2$  dissociates to

two HO\* on TM<sub>1</sub>-N<sub>3</sub>-C (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) and TM<sub>1</sub>-N<sub>4</sub>-C (TM = Sc and Ti), and (ii)  $H_2O_2$  dissociates into one O\* with a  $H_2O$  molecule on TM<sub>1</sub>-N<sub>4</sub>-C (TM = V, Cr, Mn, Fe, and Co). From Figure 3h, it can be seen that the  $\Delta G$  for the dissociation of  $H_2O_2$  to  $A_2$  and  $B_2$  on Ni<sub>1</sub>-N<sub>4</sub>-C is >0. This indicates that  $H_2O_2$  cannot spontaneously dissociate on a Ni<sub>1</sub>-N<sub>4</sub>-C surface.

To further understand the most stable adsorption structure of H<sub>2</sub>O<sub>2</sub> on the SACs surface, we plotted the PDOS plots of H<sub>2</sub>O<sub>2</sub> before adsorption and two dissociated adsorption structures  $(A_2, B_2)$  on  $TM_1-N_4-C$  (TM = Mn, Fe, Co, Ni, Cu, and Zn) as shown in Figure S3. The PDOS peaks were all shifted after the adsorption of H<sub>2</sub>O<sub>2</sub>. The PDOS peak of the A<sub>2</sub>-type adsorption conformation on  $TM_1 - N_4 - C$  (TM = Mn, Fe, and Co) is shifted to the left (lower energy level), indicating that the  $A_2$ -type adsorption is more stable. The PDOS peaks of the A2-type and B2-type adsorption conformations on the Ni1-N4-C surface are shifted to the right (high energy level) compared to peaks before adsorption, suggesting that H<sub>2</sub>O<sub>2</sub> prefers not to dissociate on the Ni<sub>1</sub>-N<sub>4</sub>-C surface. The  $B_2$ -type adsorption conformation on the  $TM_1$ - $N_4$ -C (TM = Cu, Zn) surface is shifted to the left more compared to that before adsorption, indicating that the 2HO\* is more stable. It is remarkable that the PDOS plot of the B<sub>2</sub>type adsorption conformation of Zn<sub>1</sub>-N<sub>4</sub>-C has highly symmetric PDOS of spin-up and spin-down, suggesting that Zn<sub>1</sub>-N<sub>4</sub>-C may have unique properties when reacting with  $H_2O_2$ .

**3.4.** AIMD Simulations. Furthermore, AIMD simulations were performed at 300 K to analyze the  $H_2O_2$  adsorption

behavior. AIMD simulates the dissociative adsorption process of  $H_2O_2$  on  $TM_1-N_4-C$  (Mn, Fe, Co, and Ni), as shown in Figure 4a-d (others are shown in Figure S4). Results show that  $H_2O_2$  dissociates into 2HO\* after 100 fs on  $TM_1-N_3-C$  (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) and  $TM_1-N_4-C$  (TM = Sc and Ti).  $H_2O_2$  dissociates into one O\* with a  $H_2O$  molecule after 900 fs on  $TM_1-N_4-C$  (Cr, Mn, Fe, and Co). Similar analyses on Ni<sub>1</sub>-N<sub>4</sub>-C show that  $H_2O_2$  remains a molecular state after 3000 fs. The dissociation configurations of  $H_2O_2$  on the surface of SACs simulated by AIMD are consistent with the results from the calculated free energy diagram, providing more evidence on the dissociation behaviors of  $H_2O_2$ .

3.5. Activation Mechanism of H<sub>2</sub>O<sub>2</sub> on SACs. The stable dissociative adsorption structures of H<sub>2</sub>O<sub>2</sub> on SACs were acquired based on the above thermodynamic and kinetic analyses. The aim of this work is to oxidize Hg<sup>0</sup> using the HO generated by H<sub>2</sub>O<sub>2</sub>. Therefore, we herein consider the adsorption configuration that H<sub>2</sub>O<sub>2</sub> dissociates to 2HO\* on  $TM_1-N_3-C$  (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) and  $TM_1-N_4-C$  (TM = Sc, Ti, Cu, and Zn).  $H_2O_2$ dissociates directly into two HO\* on  $TM_1-N_3-C$  (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) and  $TM_1-N_4-C$  (TM = Sc and Ti) after structural optimization, which was also consistent with the AIMD simulations. Therefore, it can be considered that the activation of H2O2 to 2HO\* on these SACs is a near barrier-free process. The initial adsorption of  $H_2O_2$  on  $TM_1-N_4-C$  (TM = Cu and Zn) is in a molecular state, after which it dissociates into 2HO\*. The transition state of  $H_2O_2$  activation into 2HO\* on  $TM_1-N_4-C$  (TM = Cu and Zn) was searched by the CI-NEB method, and the energy variations of the activation process was acquired. The energy variations of the process of H<sub>2</sub>O<sub>2</sub> activation to 2HO\* on SACs are shown in Figure 4f. It can be seen that the energies of the activation processes of  $H_2O_2$  on  $TM_1-N_3-C$  (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) and  $TM_1-N_4-C$  (TM = Sc and Ti) are significantly lowered. The activation processes of  $H_2O_2$  on  $TM_1-N_4-C$  (TM = Cu and Zn) need to overcome the energy barriers of 0.46 and 0.11 eV, respectively. The activation pathways are shown in Figures 4e and S5. All these analyses provide important mechanistic insights to support the possibility of Hg<sup>0</sup> oxidation by HO\* on SACs.

In addition, we plotted the PDOS before and after activation of  $H_2O_2$  on all catalyst surfaces, as shown in Figures S6 and S7. The d orbitals of the metal atoms are all shifted, with  $TM_1$ –  $N_4$ –C and  $TM_1$ – $N_3$ –C (TM = Sc, Ti) shifted significantly to the right, corresponding to their more significant adsorption energy of  $H_2O_2$ . The p orbitals of the two O atoms ( $O^1$  and  $O^2$ ) in the 2HO\* type adsorption overlap significantly with the d orbitals of the metal atom, suggesting a significant interaction force between the metal atom and the HO radicals. The p orbital of the O atom ( $O^1$ ) in the O\*+ $H_2O_2$  type adsorption overlaps significantly with the d orbital of the metal atom, indicating the existence of a stable TM-O bond between the metal atom and the O atom. The results of the above analysis are consistent with the AIMD simulations, which demonstrate the stability of the dissociation adsorption structure.

**3.6. Reaction Mechanism of Catalytic Hg<sup>0</sup> Oxidation.** The above analyses found that  $H_2O_2$  can be activated to  $2HO^*$  on the SACs, indicating that  $H_2O_2$  can be used for the catalytic oxidation of Hg<sup>0</sup>. Previous studies found that combining HO with Hg<sup>0</sup> can form Hg(OH)<sub>2</sub>.<sup>41,42</sup> Therefore, the reaction path is determined as follows:  $H_2O_2$  activation generates  $2HO^*$ , which combines with  $Hg^0$  to form  $Hg(OH)_2$ . Finally,  $Hg(OH)_2$  desorbs from the catalyst surface. According to the Brønsted–Evans–Polanyi (BEP) relationship,<sup>43</sup> the transition state barrier can be well described using the adsorption energy. The formation of the oxidation product  $Hg(OH)_2$  is accompanied by the desorption of an individual HO\*. A higher adsorption energy of HO [ $E_{ads}(OH)$ ] on the catalyst surface corresponds to a higher energy barrier of  $Hg(OH)_2$  formation. In addition, a larger  $E_{ads}(OH)$  suggests a more sluggish  $Hg(OH)_2$  desorption. Therefore, we calculated  $E_{ads}(OH)$  on the catalyst surfaces, as shown in Figure 5a. It can be seen that the adsorption energies of HO\* on the surface of  $Cu_1-N_3-C$ ,  $Zn_1-N_4-C$ , and  $Cu_1-N_4-C$ , and  $Cu_1-N_4-C$ , and  $Cu_1-N_4-C$ , for further analysis.

The reaction mechanisms of catalytic Hg<sup>0</sup> oxidation on  $TM_1-N_4-C$  (TM = Cu and Zn) and  $Cu_1-N_3-C$  were studied by the CI-NEB method. The reaction path is shown in Figures 5c, S8, and S9. The activation energy barrier for  $H_2O_2$ , the formation energy barrier, and the desorption energy barrier for Hg(OH)<sub>2</sub> are denoted as  $E_{b1}$ ,  $E_{b2}$ , and  $E_{d}$ , respectively. The energy variations of the reaction are shown in Figure 5b. On  $Zn_1-N_4-C$ , the activation energy barrier of  $H_2O_2$  and the formation and desorption barriers of  $Hg(OH)_2$  are 0.11, 0.32, and 0.35 eV, respectively. Therefore, the RDS is  $Hg(OH)_2$ desorption. In contrast, the RDS of the H<sub>2</sub>O<sub>2</sub> catalyzed oxidation of Hg<sup>0</sup> on Cu<sub>1</sub>-N<sub>4</sub>-C is the formation step of  $Hg(OH)_2$  with a barrier of 0.76 eV.  $H_2O_2$  is spontaneously activated to 2HO\* on  $Cu_1 - N_3 - C_1$ , with  $Hg(OH)_2$  desorption as the RDS (1.21 eV). Based on the above analysis,  $Zn_1-N_3-$ C has the lowest RDS barrier for catalytic Hg<sup>0</sup> oxidation using  $H_2O_2$  (0.35 eV), indicating that this catalytic oxidation process may take place at room temperature. In addition, we also plotted the electronic density differences of IS1, TS1 and IM2 as shown in Figures 5d, S8b, and S9b. Obviously, the charge is transferred from the Hg atom to the O atom during the oxidation process, providing direct evidence for the oxidation of Hg<sup>0</sup>. Table 2 summarizes the catalysts, oxidants, and the corresponding RDS energy barriers for catalytic Hg<sup>0</sup> oxidation that have been reported in recent years; it can be seen that the RDS energy barrier for catalytic Hg<sup>0</sup> oxidation on Zn<sub>1</sub>-N<sub>3</sub>-C using  $H_2O_2$  is much lower than those reported in the literature. Therefore,  $Zn_1-N_4-C$  is considered to be one of the promising candidates for this important environmental reaction.

The high catalytic activity of  $Zn_1-N_4-C$  in the catalytic oxidation of  $Hg^0$  using  $H_2O_2$  is due to the ultralow desorption energy barrier of the oxidation products. To further investigate the bonding mechanism of Zn<sub>1</sub>-N<sub>4</sub>-C with oxidation products, we obtained information on the Zn-O bond by COHP (Crystal Orbital Hamilton Population) analysis. Compared to our previous study of  $Fe_1-N_4-C_2^{(1)}$  there is antibonding orbital occupation in the bond of O (p)–Zn (d), as shown in Figure 5e,f. It indicates that the O-Zn bond connecting the Hg(OH)<sub>2</sub> to  $Zn_1-N_4-C$  is unstable, making  $Hg(OH)_2$  extremely easy to desorb. Meanwhile, it also explains the ultrahigh catalytic activity of  $Zn_1-N_4-C$ . The excellent performance of  $Zn_1-N_4-C$  in the reaction is attributed to the moderate adsorption capacity, which is consistent with the Sabatier principle.<sup>43</sup> In the future, searching for moderate adsorption energy is the key to improving the catalytic activity.

# 4. CONCLUSION

In summary, we have studied the adsorption configurations of  $H_2O_2$  on  $TM_1-N_3-C$  and  $TM_1-N_4-C$  (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn), and determined the stable dissociative adsorption configurations of H<sub>2</sub>O<sub>2</sub> on these SACs using spin-polarized DFT-D3 calculations. We found that the adsorption conformation is related to geometry of SACs and the orientation of the frontier molecular orbitals. The stable dissociative adsorption structure of H2O2 on TM1-N3-C (TM = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, and Zn) and  $TM_1$ - $N_4$ -C (TM = Sc, Ti, Cu, and Zn) is 2HO\*, while the adsorption configuration on other  $TM_1 - N_4 - C$  (TM = Cr, Mn, Fe, and Co) is the formation of an O\* with a  $H_2O$ molecule. In addition, we selected TM<sub>1</sub>-N<sub>4</sub>-C (Sc, Ti, Zn, and Cu) and  $TM_1-N_3-C$  to analyze the mechanism of  $H_2O_2$ dissociation into 2HO\*. Finally, we selected Cu1-N4-C and two  $TM_1{-}N_4{-}C$  (TM= Cu and Zn) to analyze the reaction mechanism of Hg<sup>0</sup> oxidation using H<sub>2</sub>O<sub>2</sub> and found that Zn<sub>1</sub>- $N_4$ -C has an ultrahigh theoretical activity for the reaction. Meanwhile, COHP analysis revealed that the Zn-O bond between Zn<sub>1</sub>-N<sub>4</sub>-C and the oxidation product has obvious antibonding orbitals occupation, which makes the oxidation product extremely easy to desorb. Most importantly, this work analyses the catalytic oxidation of Hg<sup>0</sup> on a variety of SACs and discusses a new strategy for Hg<sup>0</sup> removal in industry.

# ASSOCIATED CONTENT

# **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.2c06266.

Optimized adsorption configurations of H<sub>2</sub>O<sub>2</sub> on SACs (Figure S1), the relative energies of the dissociative adsorption configurations of H<sub>2</sub>O<sub>2</sub> on SACs (Figure S2), calculated PDOS of the H<sub>2</sub>O<sub>2</sub> on SACs surface (Figure S3), AIMD simulations on the energy variations and structures of the dissociative adsorption processes of  $H_2O_2$  on SACs (Figure S4), initial and stable adsorption structures of  $H_2O_2$  on SACs (Table S1), the activation pathway of H2O2 on the Cu1-N4-C surface (Figure S5). PDOS analysis of H<sub>2</sub>O<sub>2</sub> on the SACs surface before and after activation (Figures S6 and S7), the reaction pathway and electronic density difference for the catalytic oxidation of Hg<sup>0</sup> on Cu<sub>1</sub>-N<sub>3</sub>-C surface (Figure S8), and the reaction pathway and electronic density difference for the catalytic oxidation of Hg<sup>0</sup> on the  $Cu_1 - N_4 - C$  surface (Figure S9) (PDF)

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## Notes

The authors declare no competing financial interest.

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