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Adsorption characteristics of Co-anchored different graphene substrates toward O₂ and NO molecules



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ABSTRACT

The adsorption characteristics of O_2 and NO on Co-anchored different graphene-based substrates (single vacancy, double vacancy and N atoms doped) have been investigated using density functional theory. The geometric stability of the single atom catalysts, adsorption configurations of gas molecules, adsorption energies, electronic structure and thermodynamic analysis have been performed. Co/vacancy-graphene shows high thermodynamic stability through calculating and comparing the binding energy of Co-anchored single atom catalysts and the cohesive energy of Co bulk. For O_2 adsorption, it prefers to form two chemical bonds with the Co atom, and electron transfer dominates the formation of the strong chemical ionic bonds. While on Co single and double vacancy graphene substrates, N atom in NO invariably bonds to the Co atom, with electron transfer and orbital hybridization dominating the process of bonding formation respectively, afterwards ionic and covalent bonds formed between gas molecule and the metal atom. Additionally, electro-negativity and partial *d*band centre are good descriptors of adsorption energies and can well reveal the relationship of adsorption energy with adsorption activity and the electronic structure. Co/single vacancy-graphene substrate with three pyridine nitrogen atoms (Co/SV-N123) is a promising catalyst in catalytic oxidation of NO. The results can provide reference for the further study of the NO oxidation mechanism on the Co/GN surface as well as the new nonnoble-metal catalysts design.

1. Introduction

Nitric oxide (NO), one of the main components of nitrogen oxides (NOx), mainly comes from anthropogenic fossil fuel combustion. Because of the complex formation mechanism of NO, it is difficult to effectively inhibit its production [1]. Furthermore, NO is poorly soluble in water, which increases the difficulty of removal, so effectively oxidation of NO to good water soluble NO₂ has always been a continued technology roadmap. Pt and Pd are the typical noble catalysts for NO catalytic oxidation due to their high activity and stability, but the high cost prevents their widespread utilization [2]. As a novel catalyst, single atom catalysts (SACs) exhibit high catalytic activity and even more reactive than metal clusters or particles, and have becoming a hot research topic [3–5]. Narula1 et al. [6] conducted experimental study and the results showed that single θ -Al₂O₃ supported platinum atoms have high catalytic activity with NO oxidation and the oxidation activity is as good as fully formed platinum particles.

In recent years, graphene has been currently researched and applied in many fields by reason of the unique physical and chemical properties [7–9]. Some experimental and theoretical researches have shown that graphene especially defective graphene with the vacancies can be excellent supports for single atom catalysts. Synthesized SACs with non-noble-metal atoms anchored on graphene-based substrates (TM/GS) can further reduce the catalysts cost [10–14]. Therefore, taking advantage of the graphene, TM/GN catalysts have been investigated in a wide range of fields such as toxic gas monitor [15–18], CO₂ reduction [19,20], catalysts, bio-devices and other applications [21–27]. Recent studies revealed that SACs with the single atoms (Au [28], Cu [29], Pd [30], Pt [31]) embedded on graphene have shown high catalytic activity for CO oxidation.

As we all know, the adsorptive ability of reactants on the catalyst determines the reaction pathway which will prevent or promote the subsequent reaction or even induce a new rate-determining step. Lee et al. [15] investigated the magnetic characteristics while gas (N₂, O₂, NO₂, SO₂) adsorption on the Pt embedded graphene system. Shi et al. [18] calculated the adsorption characteristics of HCN on graphene embedded with Fe, Mn and Cr atoms based on the first principle, and found the adsorption energy decrease as follows: Fe-(-1.36 eV) > Cr-

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Received 12 November 2018; Received in revised form 21 February 2019; Accepted 27 February 2019 Available online 04 March 2019 0169-4332/ © 2019 Published by Elsevier B.V. (-0.86 eV) > Mn-(-0.60 eV). In our previous work, single iron atom embedded on graphene (incorporated with single vacancy, double vacancy and four nitrogen atoms) shows high adsorption activity for toxic gases (NO₂, NH₃, SO₃ and H₂S). Meanwhile, CO and NO competitive adsorption behaviors are also calculated and analyzed, and the results suggest that it is almost impossible for CO adsorption when both CO and NO present [32,33]. In addition, oxidizing reaction paths of NO on the single-vacancy graphene embedded Fe atom were systematically studied [34].

Recent experimental researches confirm that single atom Co has been successfully anchored on the graphene supports [35,36]. Tang et al. [16.37] demonstrated that the interaction between Co atom and the pristine graphene substrates is much weaker than the graphene with single vacancy, although the binding energy of Co/pri-graphene is larger than the cohesive energy of Co bulk, the Co atoms are still easy to move and aggregate to Co bulk. Then, they also investigated the adsorption behavior and reaction activity of CO and O₂ molecules on the Co-anchored graphene with single vacancy. According to the theoretical studies [38,39], four pyridinic nitrogen-doped graphene exhibited high electro-catalytic activity during oxygen reduction reaction. Zhang et al. [40] explored the CO and O₂ gas molecules adsorption properties on the Co, Mo, B atoms incorporated N4 centres. However, there is a lack of systematically study about the impact of vacancies location and doped nitrogen number on the Co/GN geometries, electronic properties and adsorption-activities. Thus, in order to achieve this, first of all, in the light of the vacancies location, the supported graphene are divided into two types, single vacancy graphene and double vacancy graphene, on the basis of the above, combining the number and position of doping nitrogen, there are eleven kinds of graphene based substrates.

In this work, detailed studies of the adsorption properties of O_2 and NO on Co-anchored different graphene-based substrates (single vacancy, double vacancy, and nitrogen doped) have been presented. Firstly, eleven kinds of Co/GN were constructed and the magnetic properties of the system were analyzed. Secondly, the adsorption geometries parameters and adsorption energies of O_2 and NO on Co-anchored graphene were calculated, and the electrons transfer mechanism was interpreted. Thirdly, in order to further analyze the adsorption activity, the system electro-negativity (*X*) and partial d-band centre were introduced and the relationships with the adsorption energy were discussed. Finally, in order to analyze the temperature effect on the adsorption characteristics, Gibbs free adsorption energies of gas molecules on the eleven different Co/GN configurations were calculated.

2. Computational details

All the DFT calculations were performed utilizing the Vienna ab initio simulation package (VASP) [41,42]. In order to improve the calculation efficiency, the projector augmented wave (PAW) pseudopotentials were used to replace the core electrons [43]. The exchange and correlation interactions were described by the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) function [44]. Since the chemical bonding of gas molecules on the Coanchored graphene substrates was the concerned, the calculation results utilizing GGA potential which does not include the influence of the van der Waals (vdW) interaction may be reasonable enough.

In light of the electronic structure of Cobalt atom, the spin polarization was taken into account to attain the ground state energy. In keeping with previous research, a 4×4 supercell of graphene with periodic boundary conditions was built as catalyst supports, and the vacuum layer was set to 15 Å to avoid the interaction among mirror images [16,32].

The Kohn-Sham orbitals were expanded using plane waves expansion and the kinetic energy cutoff was set as 500 eV and the convergence precision criterion for the electronic self-consistent iteration calculation was taken to be 10^{-5} eV. The Brillouin zone (BZ) optimization integration was sampled with a 7 × 7 × 1 Γ -centred Monkhorst-

Pack (MP) grid and a $15 \times 15 \times 1$ Γ -centred MP grid was used for the calculation of the final density of states (DOS).

During the geometry optimizations, all atoms were allowed to fully relax in all directions with the conjugate gradient method and the maximum force was set to 0.02 eV/Å. The C–C bond value after optimization in graphene is 1.42 Å, which is in accordance with the previous experimental and theoretical results [45–47].

For the optimized structure of the Co anchored on different graphene support systems, the binding energy (E_b) between Co atom and substrates was defined as the following expression:

$$E_{\rm b} = E_{\rm sub} + E_{\rm Co} - E_{\rm sub+Co} \tag{1}$$

where E_{sub+Co} represents the total energy of Co/GN catalysts, E_{sub} and E_{Co} are the energy of graphene-based supports and the energy of Co atom.

The adsorption energy of molecules (O_2 and NO) on the Co/GN substrates was obtained from the expression:

$$E_{\rm ads} = E_{\rm Co/GN} + E_{\rm gas} - E_{\rm Co/GN-gas}$$
⁽²⁾

where $E_{Co/GN}$, E_{gas} and $E_{Co/GN-gas}$ are the energy of Co decorated graphene supports, the energy of gas molecules and the total energy of the system for gas with adsorbed supports respectively.

3. Results and discussion

3.1. Geometries and electronic properties of Co/GN

First, the most stable geometries of Co/GN are investigated. According to the numbers and locations of the doping nitrogen atoms as well as the carbon atom vacancies, there are eleven kinds of graphene based substrates, as shown in Fig. 1. The corresponding geometries data and binding energies are summarized in Table 1.

As shown in Fig. 1, the graphene embedded with Co atoms (Co/GN) are divided into two categories corresponding to the number of vacancies: one substitutes single carbon vacancy with a Co atom in the graphene lattice (Co/SV-GS), while the other replaces double carbon vacancy. In Co/SV-GS, the doping number of nitrogen atom increased from zero to three, and the number increased from zero to four in Co/DV-GS.

In our work, the optimized geometry parameters of Co/SV-GN and Co/SV-N1234 are in good agreement with the previous results, which can guarantee the rationality and effectiveness of the following calculation. However, there are slight differences of binding energy and transferred electrons between the calculated results and previous research data, which may be caused by the different single atom surface coverage and the parameters setting. Because of the larger atomic radius, the anchored Co atom protrudes outside from the graphene substrates. The embedded height of Co atom changes with the doping of N atoms. For Co/SV-GN, the doped N atoms increase embedded height to some extent, but for Co/DV-GN, a decreasing tendency presents with N atoms doped.

In the study of Liu and Huang [48], O₂ dissociation on the Pt single atom graphene support, the charge of the Pt atom is an important parameter that determines the adsorption and the catalytic activity. Co atom may have similar properties. For Co anchored on the graphene supports containing single and double vacancies as well as N doping, more electrons transferred from Co atom to the dangling bonds of the neighboring N and C atoms may facilitate their interaction. By comparing the binding energy of Co atom placed on the pristine graphene (1.61 eV), Co anchored on defective graphene with N atoms dopant systems have larger binding energy (4.799 eV to 8.229 eV), illustrating that these dopants at graphene exhibit relatively high stability. But Co atoms are still easy to move and aggregate to Co bulk, so the stability of the Co/GN configurations needs to be further confirmed. The cohesive energy value of Co bulk in experiment is 4.43 eV [49], which is smaller than the binding energies of Co/GS, suggesting that Co/GS



Fig. 1. The optimized structures of Co atom anchored on different graphene supports.

configuration would be stable enough to be utilized in chemical reaction. The binding energy of Co/SV-GS decreases gradually with N atom doping, which is consistent with the tendency in the Pt/SV-GS [48] and Fe/SV-GS [50]. While for Co/DV-GS, the binding energy does not show a gradual increase with N atom doping, suggesting that both the number of carbon vacancies and the dopant atom in the graphene sheet affect the stability of the single atom catalysts together. In order to further analyze the origin of high stability of Co/GS configurations, the projected density of states are plotted in Fig. S1 (Supporting information). According to the DOS plots of the spin up and spin down channels, it's clearly asymmetric which indicates that Co/SV-GS exhibit magnetic characters, that accordance with the previous results [37,51]. The broadened partial DOS (PDOS) of Co d-orbital states strongly hybridized with the C p-orbital states (or N p-orbital states)

Table 1

The binding energy (E_b , eV), embedded height of Co atom (h, Å), bond length of Co–C or Co–N (d, Å), the Bader chargers carried by Co atom (q, e) and the magnetic moment M (μ B) for Co/GS.

| Supports | $E_{\rm b}~({\rm eV})$ | h (Å) | d _{Со-С} (Å) | $d_{\text{Co-N}}$ (Å) | <i>q</i> (e) | <i>M</i> (µB) |
|-------------|------------------------|----------------|-----------------------|-----------------------|----------------|---------------|
| Co/SV-GN | 7.61(8.51[16]) | 1.24(1.21[16]) | 1.77(1.77[16]) | - | 0.50(0.68[16]) | 0.90 |
| Co/SV-N1 | 6.13 | 1.18 | 1.77 | 1.78 | 0.58 | 0.00 |
| Co/SV-N12 | 5.67 | 1.27 | 1.76 | 1.82 | 0.64 | 1.00 |
| Co/SV-N123 | 4.80 | 1.37 | - | 1.832 | 0.74 | 2.22 |
| Co/DV-GN | 6.48 | 0.60 | 1.94 | - | 0.61 | 1.00 |
| Co/DV-N1 | 7.49 | 0.46 | 1.91 | 1.96 | 0.73 | 2.00 |
| Co/DV-N12 | 8.23 | 0.00 | 1.87 | 1.90 | 0.73 | 1.05 |
| Co/DV-N13 | 7.99 | 0.24 | 1.88 | 1.90 | 0.76 | 1.08 |
| Co/DV-N14 | 7.49 | 0.19 | 1.84 | 1.94 | 0.74 | 1.00 |
| Co/DV-N123 | 7.91 | 0.02 | 1.84 | 1.90 | 0.75 | 0.55 |
| Co/DV-N1234 | 7.58(8.55[40]) | 0.00(0.00[40]) | 1.88(1.85[40]) | - | 0.82(1.06[40]) | 0.87 |



Fig. 2. Adsorption geometries of O₂ on Co/GN.

and overlap with the total DOS of Co/SV-GS near the Fermi level (E_F). In comparison, the spin up and spin down channels of the Co/SV-N1 are symmetrical, indicating that the magnetic moment is zero (0 µB) in the Co/SV-N1 and that the N atom dopant can modulate the magnetic character. In Co/DV-GS, the hybridized states between anchored Co atom and the C p-orbital states (or N p-orbital states) are not obvious. However, the strong hybridization between the total DOS of Co/DS and the PDOS of Co d-orbital states still exists and induces larger DOS peaks around the Fermi level (E_F) especially in Co/DV-N12, indicating that the electronic states overlap between Co atom and graphene-based supports enhance their interaction.

As an important reference, the Co d-orbital states of the Co/GN

system are further analyzed (Fig. 2, Supporting information). It is found that Co d-orbital spin up and spin down channels are effectively regulated by the number as well as location of doped N atoms. Compared with Co/SV-GS and Co/DV-GS, the doping N atoms extremely induce the d-orbital DOS peak significantly increased around the Fermi level (E_F).

3.2. Adsorption of gas molecules on Co/GN

Next, the adsorption of NO and O_2 gas molecules on the Co/SV-GN and Co/DV-GN has been investigated. The possible adsorption sites were optimized in order to find out the most favorable geometries



Fig. 3. Adsorption geometries of NO on Co/GN.

configurations. The most energetically favorable configurations of O_2 and NO adsorption on Co/SV-GN and Co/DV-GN systems are shown in Figs. 2–3. The corresponding geometries parameters are summarized in Table S1 (Supporting information).

As shown in Fig. 2(a)–(k), for O_2 molecule, it prefers to form two chemical bonds with the Co atom and the O–O bond is parallel to the support surface or somewhat tilted on the Co/GS support surface except for Co/DV-N1234. In Fig. 3(a)–(k), it shows that the end-on configuration is favorable for NO molecule and the N atom in NO is bonded to the Co atom, and the adsorbed NO is nearly vertical for the NO on the Co/DV-GS. For the stable configuration of each chemisorbed gas molecule, the anchored Co atom was pulled out of the graphene support, and the bond length (d, in Å) between atoms in gas molecule was elongated (with O–O bond length of 1.21 Å for O₂ gas molecule, with N–O bond length of 1.15 Å for NO gas molecule). The adsorption of gas molecules on Co/SV-GS still exhibits magnetic property. However, for NO adsorbed on Co/DV-GS, there is no magnetic property and magnetic moments are almost zero.

It is supposed that the charge redistribution between gas molecules and the support systems can induce the geometric changes. Based on the Bader charge analysis [52], the electrons transferred during the adsorption process are plotted in Fig. 4.

From Fig. 4, it is found that electrons transfer from Co atom as well as graphene support to the gas molecules, although gas molecules form chemical bonds with the Co atom during the adsorption process, which



(a)O₂ adsorption on Co/GS

(b) NO adsorption on Co/GS



implies that Co atom not only serves as the electron donor but also as an electron transfer bridge. At the same time, the graphene-based substrates act as the catalyst atom anchor and electron donor.

The number of adopter electrons of O_2 molecule is larger than that of NO molecule in the Co/GS. In the Co/SV-GS, the transferred electrons increase gradually with the doped N atoms, meanwhile the number of electrons transferred from Co atom and from the graphenebased substrates is almost the same except for Co/SV-N123. While in Co/DV-GS, no obvious growth trend of transferred electrons with the doped N atoms was observed. The number of transferred electrons from the Co atom is smaller than from the graphene-based substrates.

The charge transfer between NO and metal centres can be described in terms of the Blyholder model of sigma donation and pi back-donation [53]. Blyholder described CO bonding to the transition metal in terms of molecular orbital theory in which CO bonds to the metal by donation of electrons from the 5 σ level to the metal with back-donation of metallic *d* electrons to the anti-bonding $2\pi^*$ orbital of CO. The chemisorptions of NO on the transition metals may be considered to be similar to that of CO. According to the Blyholder model, when NO bonds with the Co atom, the 5 σ orbital is hybridized with the unoccupied state of the metal electron, then some of the 5 σ electrons of NO are transferred to the metal space orbit, which mainly occurs in between the Nterminus of the NO molecule and the metal atom. On the other hand, the $2\pi^*$ orbital of NO may be orbitalized with the electronic state of the metal surface (mainly the d-electron state of the metal), and the result is that the $2\pi^*$ orbital of the NO molecule obtains part of the electron from the metal, which is the so called back-donation. Simultaneously, due to the pi back-donation of the metal, the anti-bonding orbital of NO is partly filled with the transferred electrons which slightly weaken the N–O bond from 1.15 Å in the gas state to 1.18–1.20 Å.

According to the matching requirements of the orbital direction, the 5 σ electron of NO is mainly at the nitrogen end, so the interaction of NO with the Co atom is mainly achieved by bonding the N atom with the metal atom. On the other hand, the $2\pi^{*}$ orbital is parallel to the N–O bond axis, which coincides with the d-orbital of the metal. Therefore, the Blyholder model can explain why NO prefers to form the end-on adsorption configuration and the N atom in NO is bonded to the Co atom, which is in agreement with the adsorption geometries of NO on Co/GS of Fig. 3.

In order to visually describe the electron transfer in the adsorption process of NO and O_2 gas molecules on the Co/SV-GS and Co/DV-GS, the most stable adsorption configurations are selected as research object, then the electron density difference of O_2 adsorption on Co/SV-N123 and Co/DV-GN, NO adsorption on Co/SV-N123 and Co/DV-N1 are plotted in Fig. 5.

In Fig. 5, the gas molecules and the Co atom are surrounded by



Fig. 5. The electron density difference of the most adsorption stable configurations (the contour lines in plots are drawn at $0.003 e/Å^3$ intervals).

Fig. 6. Adsorption energies of O2 and NO on Co/GN.

yellow and blue-green color, which represent the gain and loss electrons respectively. O_2 and NO molecules are mainly surrounded by yellow color, which suggests that O_2 and NO molecules gain electron. The larger the surrounded yellow area, the more electrons are obtained. The yellow area surrounding the gas molecule on Co/SV-N123 is larger than on the other configurations, indicating that gas molecule obtains more electrons on Co/SV-N123, which is in good agreement with the results of Bader charge analysis. The HOMO and LUMO orbitals for the most stable configurations are also plotted, as shown in Fig. S3 (Supporting information).

To analyze the adsorption strength of O_2 and NO on the eleven different Co/GN configurations, the histogram of adsorption energies are plotted, as shown in Fig. 6.

In our research, the adsorption energy (E_{ads}) of O₂ on the Co/DV-N1234 is 0.702 eV, Zhang et al. [40] investigated O₂ adsorption on the Co dopant incorporated N4 centres (D-GN4), and the adsorption energy is 0.67 eV, which suggests that our calculations are reasonable and efficient. Moreover, in the research of Lee et al. [15], the adsorption of O₂ on the surface of Pt/SV-GN is 1.487 eV which is smaller than the E_{ads} of O₂ on the Co/SV-GN. By comparing with the research of Gao et al. [32], the O₂ adsorption energy on the Fe/SV-GS is higher than on Co/SV-GS, which indicates that Co atom is less active than Fe atom but not worse than Pt atom for O₂ adsorption.

From Fig. 6, the O_2 has the largest adsorption energy (2.43 eV) on the Co/SV-N123. For Co/SV-GS, the adsorption energy increases with the number of doped N atoms, while for Co/DV-GS the adsorption energy as a whole shows a declining trend with the N atoms doping number. When O2 adsorbed on the Co-anchored graphene doped with two nitrogen atoms, contraposition has the largest adsorption energy (1.14 eV) among the three configurations, while the right orthoposition and the left orthoposition have similar values (0.87 eV and 0.90 eV respectively). By comparing, it is found that NO adsorption energies have the same increasing tendency on Co/SV-GS but no significant downtrend on Co/DV-GS. Instead, for Co/DV-GS, the largest adsorption energy (2.50 eV) occurs on Co/DV-N1 configuration. It is worth noting that NO molecule adsorbs more actively on two types surfaces (Co/SV-GS and Co/DV-GS) than the O2 molecule. It is suspected that this may be related to the electronic configuration characteristics of gas molecules. According to the frontier orbital theory, the symmetry of the frontier orbit (the highest electron-occupied molecular orbital (HOMO) and the lowest empty molecular orbital (LUMO)) in the molecule plays a decisive role in the reaction process. For NO molecular, the electronic configuration is $[(\sigma_1 s)^2 (\sigma_1 s)^2 (\sigma_2 s)^2 (\sigma_2 s)^2 (\pi_2 p_y)^2 (\pi_2 p_z)^2 (\sigma_2 p$

 $(\pi^*2p_y)^1]$. There is an unpaired electron in the system and the frontier orbit is asymmetrical, which may easily form new chemical bonds with unpaired electrons of the substrate. While for O_2 molecular, the electronic configuration is $[(\sigma 1s)^2(\sigma^2 1s)^2(\sigma^2 2s)^2(\sigma^2 2p_x)^2(\pi 2p_y)^2(\pi 2p_y)^2(\pi 2p_y)^2(\pi 2p_y)^1(\pi^2 2p_z)^1]$. There are two unpaired electrons and the ground state of O_2 is a triplet state. At the same time the orbits are symmetrically, which makes it difficult to overlap with the orbit of the substrate.

In the same Co/GV configuration, NO adsorption energy is always larger than O_2 especially on the Co/DV-GS. Based on the Bader charge analysis before, the adopter electrons of NO molecule is always lesser than that of O_2 molecule. It is indicated that although adsorption energies exhibit correlation with the electrons transfer, but the intrinsic properties of the Co/GN sheets that dominates the adsorption strength is uncertain. In order to explore this issue in depth, adsorption-activity of the Co/GN sheets and electronic structure analysis have been performed.

3.3. Adsorption-activity and electronic structure analysis

It is known that the electro-negativity quantifies the electron affinity of certain elements when the corresponding covalent bond is formed. For O_2 and NO adsorption on the Co/GS support surface, chemical bonds are formed with the Co atom. In the research of Bligaard and Nørskov [54], it has been proved that the occupied electrons of the metal *d* orbital (θ_d) have a significant influence on the adsorption strength. Considering the redistribution of θ_d caused by the interaction between single atom and gas molecules, electro-negativity was introduced as an additional factor added to θ_d . Actually, local environment of the metal active centre may impact adsorption activity. So the single transition metal atom and its nearest neighbors are considered as the active centre.

Many previous experimental and theoretical researches [55-61] show that the realistic active sites of single transition-metal atom anchored on graphene with different local coordination (C and N hybrid coordination) environments are actually isolated single atom coordinated by C, N or hybrid of C and N. In the reference [61], it is found that the modified electro-negativity of single metal atom with different coordination environments can exhibit a linear relationship when plotted against adsorption energies. As a universal descriptor, modified electro-negativity of SACs. Therefore, the single transition-metal atom and its nearest neighboring atoms are considered together as the active centre and the system electro-negativity (X) as a descriptor was introduced as following:

$$X = \theta_{\rm d} \times (E_{\rm M} + n_{\rm C} \times E_{\rm C} + n_{\rm N} \times E_{\rm N}) \tag{3}$$

where θ_d is the occupied electron number of d orbitals of metal atom; E_M , E_C and E_N are the electro-negativity of metal atom, C atoms and N atom; n_C and n_N are the number of C atoms and N atoms adjacent to the embedded metal atom.

 E_{ads} versus *X* is plotted in Fig. 7. For O₂ and NO adsorbed on Co/SV-GS, it is found that the descriptor *X* exhibit a linear relationship with the adsorption energy, and an increase in *X* corresponds to an increase in adsorption strength, which can be attributed to the charge redistribution of active sites binding with O₂ molecule. As for O₂ adsorption on Co/DV-GS, it shows an opposite trend. E_{ads} presents a decreasing function of *X*. But for NO adsorbed on Co/DV-GS, the correlation coefficient is only 0.37. The reason for this phenomenon may be related to the bonding mechanisms during chemical adsorption: one is ionic bond which is dominated by charge transfer, and the other is covalent bond dominated by orbital hybridization. System electro-negativity (*X*) is more suitable to describe the ionic bond, but not for covalent bonds.

To further analyze the origin of the structure stability of gas adsorption on Co/GN systems, the partial density of states (PDOS) was

Fig. 7. The linear fitting relation between adsorption energy and system electro-negativity X.

analyzed, as shown in Fig. S4 (Supporting information). PDOS plots for the most stable adsorption configurations were shown in Fig. 8.

By comparing the PDOS plot of gas adsorbed on Co/GS, the PDOS of Co d-orbital states strongly hybridize with the local density of states (LDOS) of NO and the TDOS of the Co/DV-GS, illustrating that the Co dshell electrons play a vital role in enhancing the substrate and adsorbate interaction. In addition, the TDOS channels of adsorbed NO on Co/DV-GS become symmetric, indicating that NO adsorbed on Co/DV-GN exhibits nonmagnetic and that NO can effectively regulate the magnetic property of the Co/DV-GS, which makes it possible as a gas sensor for NO detection.

Based on the above discussion, for O_2 adsorption on Co/GS, system electro-negativity (X) can describe the adsorption energy well, indicating that the adsorption-bonding mechanism of O_2 on Co/SV-GS and Co/DV-GS substrates are mainly dominated by electron transfer. While for NO adsorbed on Co/SV-GS and Co/DV-GS substrates, there are two bonding mechanisms: electron transfer and orbital hybridization dominate the process of bonding formation respectively.

Previous studies [62,63] show that d-band centre (ε_d) has a close relationship with the transition-metal surface activity. In order to find out the intrinsic relationship between the adsorption energies and the

electronic structure, d-band centre (ε_d) has been performed. The expression is as follows:

$$\varepsilon_d = \frac{\int_{-\infty}^{+\infty} n_d(\varepsilon) \cdot \varepsilon \cdot d\varepsilon}{\int_{-\infty}^{+\infty} n_d(\varepsilon) d\varepsilon}$$
(4)

where $n_d(\varepsilon)$ is the electron density, ε is the d states of Co atom in Co/GS.

According to the ε_d value, the adsorption energies of NO on Co/DV-GS linear fitting relationship against ε_d were plotted, and the relationship regression fitted from data is shown as follows:

$$E_{\rm ads} = 1.090 \times \varepsilon_d + 3.156 \quad (R^2 = 0.006)$$
 (5)

The correlation shows that no linear relationship exists between adsorption energy and ε_d . As well known, the *d* orbital includes five individual orbits, and in most cases not all the five orbits participate in the adsorption process [64]. Therefore, we tried to improve the d-band model by utilizing the individual d orbital instead of the weighted average value of the five total orbitals. The five individual d-band centres for Co/DV-GS are listed in Table 2. Correlation coefficients of linear fitting between E_{ads} and five individual *d*-band centre of Co atom are listed in Table 3.

The correlation coefficients indicate that almost no linear

relationship exists between adsorption energies and three partial *d*band centre (d_{yz} , d_{xz}). During interaction with NO gas molecule, Co atom is partial to use the d_{xy} and d_{x2-y2} orbitals. Since d_{xy} , d_{x2-y2} orbitals involved the adsorption interaction with the gas molecule, the contribution of each individual d-band was considered during the new dband centre calculation. The expression was modified as follows:

$$\varepsilon_d^p = \frac{\sum\limits_{i=1}^n \varepsilon_d^i \cdot n_d^i}{\sum\limits_{i=1}^n n_d^i}$$
(6)

where $\epsilon_d^{\ i}$ is the centre of each individual *d* orbital, $n_d^{\ i}$ is the electron number of corresponding *d* orbital. The electron numbers of d_{xy} , d_{x2-y2} orbital are listed in Table 4 as well as the calculated partial *d*-band

centre (ε_d^{P}).

The linear fitting relationship between the partial d-band centre and the adsorption energies is established, as presented in Fig. 9. It seems that the partial d-band centre can be a good descriptor of the adsorption activity for NO adsorbed on Co/DV-graphene, indicating that the hybridization between Co d-orbital and the NO gas molecule plays a leading role during the bond formation process.

3.4. Thermodynamic analysis

As temperature has great effects on the adsorption characteristics in practical applications, the thermodynamic analysis was conducted at different temperatures. The adsorption energy was replaced by Gibbs free adsorption energy (ΔG), which is calculated as follows [65–67]:

(b) O₂ on Co/DV-GN

Fig. 8. Partial DOS (PDOS) of the most adsorption stable configurations.

(d) NO on Co/DV-N1

Fig. 8. (continued)

| Table 2 | | | | | | | |
|---------------------|--------|--------|-------|------|----|-------|------|
| The five individual | d-band | centre | of Co | atom | on | Co/DV | -GS. |

| Systems | d_{xy} (eV) | d_{yz} (eV) | d_{xz} (eV) | d_z^2 (eV) | d_{x-y}^{22} (eV) |
|--|--|--|--|--|---|
| Co/DV-GN Co/DV-N1 Co/DV-N12 Co/DV-N13 Co/DV-N14 Co/DV-N123 Co/DV-N1234 | -0.917 -1.031 -0.888 -0.824 -0.843 -1.035 -1.408 | $-1.112 \\ -1.012 \\ -0.554 \\ -0.561 \\ -0.627 \\ -0.499 \\ -0.725$ | -1.071 -0.9387 -0.648 -0.578 -0.72 -0.546 -0.815 | $\begin{array}{c} - \ 0.987 \\ - \ 1.023 \\ - \ 0.815 \\ - \ 0.7 \\ - \ 0.907 \\ - \ 0.571 \\ - \ 0.758 \end{array}$ | $\begin{array}{r} -0.848 \\ -0.933 \\ -0.828 \\ -0.772 \\ -0.789 \\ -1.017 \\ -1.431 \end{array}$ |
| | | | | | |

Table 3

The correlation coefficients of linear fitting between $E_{\rm ads}$ and five partial d-band centre.

| Systems | $\varepsilon_d (d_{\rm xy})$ | $\varepsilon_d \left(d_{\mathrm{yz}} \right)$ | $\varepsilon_{d}\left(d_{\mathrm{xz}}\right)$ | $\varepsilon_{d} (d_{\mathrm{z2}})$ | $\varepsilon_d \; (d_{\rm x2-y2})$ |
|----------------|------------------------------|--|---|-------------------------------------|------------------------------------|
| \mathbb{R}^2 | 0.74 | 0.01 | 4×10^{-5} | 0.21 | 0.82 |

Table 4The electrons number of d_{xy} , d_{x2-y2} orbitals and the partial *d*-band centre $(\varepsilon_d^{\rm P})$.

| Systems | $\varepsilon_d^{\ i}(d_{xy})$ | $\varepsilon_d^{i}(d_{x-y}^{22})$ | $\varepsilon_d^{\mathrm{P}}$ |
|-------------|-------------------------------|-----------------------------------|------------------------------|
| Co/DV-GN | 1.71 | 1.42 | -0.886 |
| Co/DV-N1 | 1.71 | 1.37 | -0.987 |
| Co/DV-N12 | 1.64 | 1.30 | -0.861 |
| Co/DV-N13 | 1.67 | 1.26 | -0.802 |
| Co/DV-N14 | 1.68 | 1.34 | -0.819 |
| Co/DV-N123 | 1.66 | 1.23 | -1.027 |
| Co/DV-N1234 | 1.63 | 1.14 | -1.417 |
| | | | |

$$\Delta G = G_{\rm Co/GN-gas} - G_{\rm Co/GN} - G_{\rm gas}$$
⁽⁷⁾

$$G_{\rm gas} = E_{\rm ele} + ZPE + RT - TS \tag{8}$$

$$G_{\text{solid}} = E_{\text{ele}} + ZPE - TS \tag{9}$$

where $G_{\rm Co/GN-gas}$, $G_{\rm Co/GN}$ and $G_{\rm gas}$ are the Gibbs free energy of the adsorbed system, Co/GN substrates and gas molecules respectively, $E_{\rm ele}$ is

∆G/eV

Fig. 9. The linear fitting relation between E_{ads} and partial d-band centre (ε_d^{P}) for NO adsorbed on Co/DV-GS.

the ground state energy of the calculated system, ZPE is the zero correction energy which can be obtained by frequency calculation, R is the universal gas constant, T is the thermodynamic temperature, S is the

entropy of the calculated system which can also be obtained by frequency calculation. The adsorbed system and Co/GN substrates are treated as solid, so $G_{Co/GN-gas}$ and $G_{Co/GN}$ can be calculated through Eq. (9).

In order to analyze the temperature effect on the adsorption characteristics, the Gibbs free adsorption energy of O₂ and NO on the eleven different Co/GS configurations were calculated, the Gibbs free adsorption energy versus temperature are plotted, as shown in Fig. 10. (For detailed data, please refer to the Tables S2 and S3 in the Supporting information).

From Fig. 10, with temperature rising, the Gibbs free adsorption energy increases gradually from negative to positive. When the value of ΔG is negative, indicating that adsorption can occur spontaneously, and the smaller the value, the greater the adsorption strength. By comparing O2 adsorption, it is not thermodynamic favor on the Co/DV-GS, and the adsorption process cannot occur spontaneously when the temperature is above 650 K. In terms of Co/SV-GS, the adsorption process can occur spontaneously within the researched temperature range when adsorbed on the Co/SV-N12 and Co/SV-N123. In detail, O2 is more liable to adsorbed on the Co/SV-N123 at the same temperature due to the smaller Gibbs free adsorption energy compared with other catalysts. For NO adsorption, the process can occur spontaneously when the temperature is below 850 K and 720 K respectively. Similarly, the process of NO adsorbed on the Co/SV-N12 and Co/SV-N123 can always

(c) NO on Co/SV-GS

(d) NO on Co/DV-GS

Fig. 10. The ΔG of gas molecules as a function of temperature in Co/GS.

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occur spontaneously within the researched temperature range. Except for Co/DV-N123 and Co/DV-N1234, the difference of Gibbs free adsorption energy on several other Co/DV-GS catalysts is very small and exhibits similar thermodynamic properties.

According to the study of gas adsorption and thermodynamic analysis, it is predicted that Co/SV-N123 may be the most promising catalyst for NO oxidation. Firstly, during the progress of fossil fuel combustion, the content of NO is much smaller than O₂, so it is reasonable to select O₂ adsorption as the initial reactant in the reaction mechanism. Secondly, in the study of Yang et al. [34], for NO and O₂ reaction mechanism on the surface of Fe/SV, the adsorbed O₂ is the initial reactant and NO interacts with adsorbed O₂ on the surface of Fe/ SV. Co atom may have similar properties, so it is reasonable that oxygen is the initial reactant to be adsorbed. Thirdly, it is expected that the activated oxygen can promote the oxidation reaction of NO. The bond length of O₂ on Co/SV-N123 is the largest, which suggests that the activation effect on Co/SV-N123 surface is more significant than on others. Moreover, thermodynamic analysis shows that the Gibbs free adsorption energies of gas on Co/SV-N123 are all negative within the researched temperature range, and adsorption can occur spontaneously.

4. Conclusions

Based on the first-principle, the adsorption geometric configurations, electrons transfer characteristic, adsorption energy, electronic structure and thermodynamic analysis have been performed to investigate the adsorption behavior of O₂ and NO on the single Co atom catalysts with different graphene-based substrates. Firstly, according to the binding energy and cohesive energy calculation and discussion, the Co anchored on different graphene supports along with doped N atoms show high stability. Secondly, for the O2 and NO adsorbed on the Co/ GS systems, it is found that O2 on the Co/GS gain more transferred electrons but smaller adsorption energies compared with that of NO gas molecule. Meanwhile, when O2 adsorbed on Co/SV-GS and Co/DV-GS substrates, charge transfer-based ionic bonds are formed between gas molecule and the metal atom. While for NO adsorption, two different bond formation mechanisms exist. For NO adsorbed on Co/SV-GS, ionic bonds are formed which dominated by electron transfer, but on Co/DV-GS, orbital hybridization dominates the process of bonding formation and covalent bonds are formed. In addition, system electro-negativity (X) is found to be more suitable to describe the adsorption energies that mainly dominated by electron transfer, while partial d-band centre can well reveal the relationship of adsorption energies and the electronic structure of SACs. Furthermore, thermodynamic analysis indicates that Co/SV-N123 may be the most promising catalyst for NO oxidation. Finally, it is hoped that our work can provide reference for the further study of the NO oxidation mechanism as well as new non-noble-metal catalysts design.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.02.238.

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