Formaldehyde Molecules Adsorption on Zn Doped Monolayer MoS$_2$: A First-Principles Calculation

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Based on the first principles of density functional theory, the adsorption behavior of H$_2$CO on original monolayer MoS$_2$ and Zn doped monolayer MoS$_2$ was studied. The results show that the adsorption of H$_2$CO on the original monolayer MoS$_2$ is very weak, and the electronic structure of the substrate changes little after adsorption. A new kind of surface single cluster catalyst was formed after Zn doped monolayer MoS$_2$, where the ZnMo$_3$ small clusters made the surface have high selectivity. The adsorption behavior of H$_2$CO on Zn doped monolayer MoS$_2$ can be divided into two situations. When the H-end of H$_2$CO molecule in the adsorption structure is downward, the adsorption energy is only 0.11 and 0.15 eV and the electronic structure of adsorbed substrate changes smaller. When the O-end of H$_2$CO molecule is downward, the interaction between H$_2$CO and the doped MoS$_2$ is strong leading to the chemical adsorption with the adsorption energy of 0.80 and 0.98 eV. For the O-end-down structure, the adsorption obviously introduces new impurity states into the band gap or results in the redistribution of the original impurity states. All of these may lead to the change of the chemical properties of the doped MoS$_2$ monolayer, which can be used to detect the adsorbed H$_2$CO molecules. The results show that the introduction of appropriate dopant may be a feasible method to improve the performance of MoS$_2$ gas sensor.

Keywords: first-principles calculation, monolayer MoS$_2$, H$_2$CO, adsorption energy, gas sensitivity

INTRODUCTION

In recent years, two-dimensional (2D) materials have attracted much attention due to their unique physical, chemical and electrical properties (Abbasi and Sardroodi, 2018a; Abbasi and Sardroodi, 2018b; Wu et al., 2018; Abbasi, 2019; Abbasi and Sardroodi, 2019). Among them, monolayer MoS$_2$ belongs to hexagonal system, which is a typical 2D layered transition metal sulﬁde with sheet structure similar to graphene (Pan et al., 2020). It has been studied due to the excellent electronic structure, chemical and thermal stability, high surface activity and high strength (Xu et al., 2013). Compared with the zero gap of graphene, single-layer MoS$_2$ has considerable direct band gap, which is suitable for light emitter, energy conversion and solar cell (Yu et al., 2016). Meanwhile, MoS$_2$ has
large specific surface area, surface activity and excellent adsorption capacity, so it is a special gas storage material or gas sensing material source (Zhang et al., 2017; Zhang et al., 2018; Zhou et al., 2018; Chen et al., 2019; Kathiravan et al., 2019; Tan et al., 2020). These excellent properties make the monolayer MoS2 have potential applications in the field of gas sensing.

However, due to the lack of free bonds on the surface of intact MoS2, which is chemically inert (Wang et al., 2013), the interaction with most gas molecules is limited to physical adsorption (Wanno and Tabtimsai, 2014), resulting in weak interaction between the adsorbent and monolayer MoS2, and the change of electronic properties is not obvious, and the original MoS2 cannot detect H2CO gas molecule (Ma et al., 2016a). Therefore, it is an effective and feasible method to adjust the electronic structure, chemical activity and sensitivity of MoS2 by introducing appropriate dopants into defect sites (Ma et al., 2016c; Sharma et al., 2018; Cui et al., 2019; Guo et al., 2019; Ren et al., 2019; Zhang et al., 2019; Guo et al., 2020; Zheng et al., 2020). For example, Lolla et al. have shown that Fe and Co doped monolayer MoS2 can enhance the adsorption of O due to the partial occupation of d-orbitals on Fermi level, and the introduction of doping significantly improves the catalytic activity of MoS2 monolayer (Lolla and Luo, 2020). (Abbas et al., 2018) proposed that compared with the original monolayer MoS2, N and P doped atoms can enhance the sensing sensitivity of monolayer MoS2 to O2 and NO gas molecules (Abbas et al., 2018). (Sahoo et al., 2016) have shown that the original monolayer MoS2 is inert to gas molecules such as NH3 and NO2, and the detection sensitivity of antisite doped with MoS2 for these gas molecules and other chemical substances is significantly improved (Sahoo et al., 2016). Luo et al. have shown that Al, Si and P doped atoms increase the orbital hybridization effect between NO2, NH3 molecules and monolayer MoS2, and promote the electron transfer. The doped monolayer MoS2 has better adsorption performance than the undoped monolayer MoS2 (Luo et al., 2016). Ma et al. have shown that when Au, Fe, CO and Ni are doped into the monolayer MoS2, the charge transfer occurs, the distance between the adsorbed molecule and the dopant is shortened, the adsorption energy is increased, and the gas sensitivity to H2, CO, NO and O2 is increased (Ma et al., 2016b; Kwak et al., 2018; Kwon et al., 2018; Wang et al., 2019a). Au doped monolayer MoS2 has high charge transfer and strong orbital hybridization ability. Doping Au atoms affect the electronic structure of MoS2 monolayer, thus improving the adsorption capacity, so that the adsorption structure of C2H4 and C2H4 molecules on Au doped MoS2 monolayer is relatively stable (Qian et al., 2020). In conclusion, although there are some reports on the surface activity of doped monolayer MoS2, the adsorption of formaldehyde on the surface of transition metal Zn doped MoS2 has not been confirmed. Therefore, the geometry, electronic structure and small molecule adsorption of different transition metal atom doped monolayer MoS2 system can be obtained by theoretical simulation method, which has guiding significance for the study of the unique gas sensing properties, adsorption properties and chemical activities of transition metal atom doped monolayer MoS2.

At present, toxic gas molecules are one of the main problems of environmental pollution. H2CO is a common toxic gas. H2CO is widely used in household materials (Chung et al., 2013; Salthammer, 2013). Long term exposure to H2CO will irritate the eyes and throat, make breathing difficult, and even pose a serious threat to the lungs. Therefore, it is of great significance to detect and control H2CO in home, residence and scientific research (Lara-Ibeas et al., 2020; Song et al., 2020; Zhou et al., 2020). Based on the first principle calculation, this paper studies the changes of the configuration, geometric stability and electronic structure of MoS2 substrate caused by the adsorption of H2CO on the original and Zn doped monolayer MoS2 gas after the S vacancy is filled with Zn dopant, and the adsorption energy, adsorption structure and charge transfer of gas molecules are analyzed. This study is helpful to find suitable chemical modification methods to improve the performance of MoS2 based gas sensors, and has important scientific significance and application prospects for the design of high-efficiency gas sensing materials.

**computing method**

All calculations were carried out using the first principle method, which was carried out by Vienna *Ab-initio* Simulation Package (VASP) and projector enhanced wave (PAW) method of DFT (Qian et al., 2019; Wang et al., 2019b). The configuration of transition metal Zn doped MoS2 monolayer was optimized. The generalized gradient approximation (GGA) and perdue-Burke-Ernzerhof (PBE) are used to calculate the exchange correlation energy. The C 2s2p, Zn 3dd5s and O 2s2p states are regarded as valence electrons. In the process of geometric optimization, all internal coordinates are allowed to relax under a fixed lattice constant, and the energy cutoff for plane waves is set to 450 eV. The Brillouin domain integral uses 3 × 3 × 1 (Monkhorst and Pack, 1976) monkhorst pack (MP) grid and 0.1 eV Gaussian smear. The convergence criterion is 10−5 eV. When the force applied to the atom is less than 0.01 eV Å−1, the optimized structure is obtained. The calculated lattice constant of MoS2 is 3.18 Å, which is well consistent with the experimental and theoretical value of 3.20 and 3.18 Å (Ataca and Ciraci, 2011; Le et al., 2014). Dispersive interactions are not included because we are concerned about the effects of chemical bonds and gas molecules on the electronic and magnetic properties of MoS2. This method has been used to study gas adsorption on atom doped MoS2 (Ma et al., 2016a). MoS2 cell is constructed as a 4 × 4 supercell, in which one S atom is replaced by a Zn doped atom, with a total of 48 atoms, including 16 Mo atoms, 31 S atoms and one Zn atom. In order to avoid the interaction between the MoS2 monolayer and its periodic image, a vacuum space of 18 Å was added perpendicular to the MoS2 layer. The binding energy (E_b) between metal atom and support is defined as $E_b = E_{\text{tot}} (\text{MoS}_2-S) + E_{\text{tot}} (\text{M} + \text{MoS}_2), \text{M} = \text{Zn}$. Here, $E_{\text{tot}} (\text{M} + \text{MoS}_2)$ and $E_{\text{tot}} (\text{S})$ are the total energy of M/MoS2 catalyzed, energy of MoS2 vacancy S-based carrier and the energy of single metal atom, respectively. Positive values indicate that the reaction gives off heat. In addition, the adsorption energy ($E_{\text{ads}}$) was calculated to describe the interaction strength between gas and gas/MoS2 catalyst. According to the formula $E_{\text{ads}} = E_{\text{tot}} (\text{M} + \text{MoS}_2) + E_{\text{tot}} (\text{gas}) - E_{\text{tot}} (\text{gas-M/MoS}_2)$, $E_{\text{tot}} (\text{M} + \text{MoS}_2)$, $E_{\text{tot}} (\text{gas})$ and $E_{\text{tot}} (\text{gas-M/MoS}_2)$ are the energy of M/MoS2 catalyzed, the energy of
gas and the total energy of adsorption system respectively. According to this definition, positive adsorption energy represents exothermic adsorption. The density of states (DOS) is calculated by using the K point $5 \times 5 \times 1$ with higher density. The results of DOS were analyzed by P4vasp. Bader charge (Henkelman et al., 2006) was used to analyze the charge transfer. The 3D visualization program Vesta (Momma and Izumi, 2011) was used to visualize all molecular structures, and the electron density difference was obtained to analyze the electron transfer direction. The electron density difference is defined as $\Delta \rho = \rho_{\text{gas-M/MoS}_2} - \rho_{\text{M/MoS}_2} - \rho_{\text{gas}}$, where $\rho_{\text{gas-M/MoS}_2}$, $\rho_{\text{M/MoS}_2}$ and $\rho_{\text{gas}}$ represent the electron density of adsorption system, M/MoS$_2$ catalyst and gas, respectively. The PAW results based on VASP processing and the COHP diagram of LOBSTER 4.0.0 (Local Orbital Basis Suite Towards Electronic-Structure Reconstruction) (Maintz et al., 2016) were used to analyze the bonding.

RESULTS AND DISCUSSION

Properties of Zn Doped Monolayer MoS$_2$ (Zn-MoS$_2$)

Seen from Supplementary Figure S1A, nine possible adsorption sites were considered for H$_2$CO adsorb on the original MoS$_2$ surface, where $T_{\text{S}}, T_{\text{Mo}}, T_{\text{Mo}}, H_1/H_2$ and $B_1/B_2/B_3$ represent the top of S and Mo atoms, hexagonal ring center and bridge sites. The $T_{\text{SV}}$ represent the top site of Zn doped the S vacancy. As depicted in Supplementary Figure S1B, the band structure and total density of states (TDOS) of the original monolayer MoS$_2$ show that the original MoS$_2$ monolayer is a non-magnetic semiconductor with a direct band gap of 1.74 eV, which is well consistent with the results reported in the literature value of 1.74 eV (Dimple et al., 2017). The calculated binding energy of Zn doping on MoS$_2$ surface is 0.5 eV, which indicates that this structure is easy to form under thermodynamic equilibrium conditions due to the exothermic process. As shown in Figure 1B, the charge accumulation and loss can be observed in both Zn and Mo atoms, which means that chemical bonds are formed between Zn and Mo atoms in the ZnMo$_3$, clusters, which can be used as a new surface single cluster catalyst (SCC) (Ma et al., 2018) to study the adsorption performance of H$_2$CO molecules.

For the average bond length between Zn dopant and adjacent Mo atoms, the calculated average bond length of Zn-Mo is 2.65 Å, which is larger than that of S-Mo bond in original monolayer MoS$_2$ with the value of 2.41 Å. As exhibited in Figure 1A, accordingly the expansion of Zn-Mo bond relative to S-Mo bond makes the doped Zn atom protrude 0.26 Å above the S-plane. The electron transfer between dopant and MoS$_2$ is calculated by Bader charge analysis. The trend of charge transfer is consistent with that of element electronegativity (Allred, 1961). The paulin electronegativity of Mo is 2.16, which is greater than that of Zn (1.65). Accordingly, Zn dopant loses electrons and carries a positive charge of 0.35 e.
The charge distribution of Zn-MoS$_2$ can be confirmed from Figure 1B. It is easy to see that Zn atoms are surrounded by cyan, which indicates that Zn atoms lose electrons. In addition, the magnetic moment of Mo$_2$S$_2$ is produced by Zn doping, the total magnetic moment of the single-layer Mo$_2$S$_2$ is 2.00 $\mu_B$, only 0.1 $\mu_B$ is located on the doped Zn atom, which indicates that the magnetic moment of the system mainly comes from Mo atom. In order to further understand the electronic and magnetic properties of Zn-MoS$_2$, the total DOS (TDOS) and projected DOS (PDOS) of Zn-MoS$_2$ spin polarization are given in Figure 1C. It can be seen from Figure 1C that an asymmetric DOS peak appears near the Fermi level, which is obviously different from the perfect Mo$_2$S$_2$ monolayer. This is consistent with the fact that the Zn-MoS$_2$ system is paramagnetic ($2.0 \mu_B$). Compared with Mo$_2$S$_2$ monolayer Supplementary Figure S1B, the spin down channel of Zn-MoS$_2$ maintains the zero gap semiconductor characteristics of Mo$_2$S$_2$, but the spin up channel presents a non-zero density of states near Fermi level which indicates that the Zn-MoS$_2$ system is semimetallic. Seen from the PDOS shown in Figure 1C, the degree of spin asymmetry of the 4$d$ orbit of Mo is greater than that of the 3$d$ orbit of Zn. This is consistent with the fact that the magnetic moment is mainly located on Mo atoms near Zn doping. In addition, since the asymmetric DOS peak is dominated by the 4$d$ orbit of Mo, it can be expected that the spin charge density is mainly distributed on Mo atoms. Therefore, as shown in Figure 1B, the spin charge density of Zn-MoS$_2$ system is mainly concentrated around Mo atom. In addition, Figure 1C also shows that near the Fermi level, the 3$p$ state of Zn atom is hybridized with the 4$d$ orbital of Mo, indicating the interaction between metal atom and S-vacancy.

Adsorption of H$_2$CO on Original MoS$_2$ Monolayer

In order to obtain a stable configuration, various possible initial adsorption structures were considered Supplementary Figure S1A. The interaction between H$_2$CO and original Mo$_2$S$_2$ is very weak, and the stable configuration obtained belongs to physical adsorption. In this work, only the configuration with the largest and most stable adsorption energy is discussed. The adsorption energy, charge transfer and other related parameters are shown in Table 1, and the geometric electronic structure is shown in Figure 2.

### Adsorption of H$_2$CO on Zn Doped Monolayer MoS$_2$ (Zn/H$_2$CO)

Finally, four stable configurations of H$_2$CO adsorption structure on Zn-MoS$_2$ were obtained, including Zn/H$_2$CO-(a), Zn/H$_2$CO-(b), Zn/H$_2$CO-(c) and Zn/H$_2$CO-(d). The structure parameters are shown in Figure 3, and the other related parameters are shown in Table 1.

#### Configuration of the Adsorbed Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b)

As shown in Figure 3A-B, the adsorption energies of Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b) are 0.98 and 0.80 eV, respectively. The distance between the O atoms of the adsorbed molecule and Zn dopant is 1.98 and 1.95 Å, respectively, indicating that the

| Configuration | $E_{ad}$ (eV) | $Q_a$ | $Q_Zn$ | $M$ ($\mu_B$) | $d_{z-Zn}$ (Å) | $D_{Zn-Mo}$ (Å) | $h$ (Å) |
|---------------|--------------|-------|--------|---------------|----------------|----------------|--------|
| S/H$_2$CO     | 0.04         | 0.01  | 0.00   | 0.00          | 3.13           | 2.41           | 0.00   |
| Zn/H$_2$CO-(a)| 0.98         | 0.00  | 0.00   | 0.00          | 2.02           | 1.98           | 2.70   |
| Zn/H$_2$CO-(b)| 0.85         | 0.00  | 0.00   | 0.00          | 2.00           | 1.95           | 2.70   |
| Zn/H$_2$CO-(c)| 0.15         | 0.00  | 0.00   | 0.00          | 2.00           | 1.95           | 2.70   |
| Zn/H$_2$CO-(d)| 0.11         | 0.00  | 0.00   | 0.00          | 2.00           | 1.95           | 2.70   |

For M ($\mu_B$), the values inside and outside the brackets are the magnetic moment of the adsorbed molecule and the magnetic moment of the whole cell, respectively. It should be noted that S/H$_2$CO refers to the configuration shown in Figure 3A, and the dopant of this configuration is actually S atom.
The molecule has strong adsorbed ability. The interaction between the adsorbed H$_2$CO and the substrate makes the geometry of H$_2$CO change obviously, the C-O bond length of H$_2$CO increased by 0.04 Å and the C-H bond length decreased by 0.02 Å. The average bond length of Zn-Mo on the substrate Zn-MoS$_2$ increases from 2.41 to 2.70 Å, and the distance between the dopant Zn and the S-plane is 0.33 and 0.28 Å larger than that of the substrate Zn-MoS$_2$, respectively. In addition, Bader charge analysis showed that H$_2$CO was the electron acceptor of Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b), and the electron transfer between Zn-MoS$_2$ substrate and H$_2$CO was 0.05 and 0.09 e, respectively, this is mainly due to the doping of Zn atoms (0.51 and 0.53 e), it may be due to the difference of electronegativity between O (3.44) and Zn (1.65).

The difference of charge density of the final configuration of Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b) is shown in Figures 4A,B to further understand the interaction between H$_2$CO molecule and Zn doped monolayer MoS$_2$. The yellow area is the electron accumulation area, and the cyan area is the electron consumption area. As shown in Figure 4A, the electron transfer is not only located on the C and O atoms of H$_2$CO adsorption, but also on the O-Zn bond, which is consistent with the strong adsorption capacity of H$_2$CO. In addition, the loss of electrons on the C-O bond leads to the weakening of the C-O bond, which makes the O atom protruding above the S plane chemically active to other molecules, including H$_2$CO itself. For the adsorption of Zn/H$_2$CO-(b), it can be found that the adsorption behavior is similar to that of Zn/H$_2$CO-(a), as shown in Figure 4B, which will not be further discussed.

In order to further understand the adsorption behavior of H$_2$CO on Zn-MoS$_2$ surface. Figures 5A–D displayed the spin-polarized total densities of states (TDOS) (upper panels) and corresponding DOS projected on 3d states of Zn atom, adsorbed H$_2$CO gas molecules and the isolated H$_2$CO gas molecules after H$_2$CO adsorption on Zn-embedded monolayer MoS$_2$.

The TDOS of Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b) systems are shown in Figures 5A,B. Compared with Zn-MoS$_2$, due to the hybridization of Zn atoms and H$_2$CO molecules, the charge is transferred from the matrix to the adsorbed H$_2$CO molecule, resulting in a new DOS peak at CBM for the TDOS of Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b) systems. It can be observed that the occupied state PDOS of the adsorbed H$_2$CO molecule Figures 5A,B, below is much lower panels than Fermi level, and the induced impurity state is produced, which reveals the reaction between Zn-MoS$_2$ monolayer and H$_2$CO molecule. For Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b) configurations, the molecular orbitals of adsorbed H$_2$CO are delocalized relative to the isolated H$_2$CO in the gas phase. The 3d orbital of Zn atom is coupled with H$_2$CO in the range of 9.60–0.00 eV. The interaction between H$_2$CO molecule and Zn atom leads to charge transfer. Zn/H$_2$CO-(a) and Zn/H$_2$CO-(b) structures have higher adsorption energy, which indicates that the adsorption is
chemisorption, which is suitable for gas removal under H₂CO adsorption. The results show that, compared with undoped MoS₂, doping Zn atoms in the defective monolayer MoS₂ is beneficial to the adsorption of H₂CO. We use crystal orbital Hamiltonian populations (COHP) to analyze the interaction between different O-Zn/H-Zn bonds by means of a pair of atomic orbital bonding or antibonding states (van Santen and Tranca, 2016; Steinberg and Dronskowski, 2018; Tsuji and Yoshizawa, 2018). Moreover, through the integration of COHP (ICOHP), we can get a precise value of bond strength. The positive and negative values of ICOHP represent the anti bonding state and bonding state respectively. The smaller the ICOHP value, the stronger the bond strength.

Figures 6A-D shows the -COHP curve and the integral (ICOHP) value of the O-Zn and H-Zn bonds in the structured Zn/H₂CO-(a) and Zn/H₂CO-(b) systems and the Zn/H₂CO-(c) and Zn/H₂CO-(d) systems, respectively. It can be seen from Figures 6A,B that when H₂CO is adsorbed to Zn-MoS₂, there are a small amount of O-Zn bonding orbitals (-COHP values) at Fermi level, and the orbitals above Fermi level belong to anti bonding orbitals. In other words, the O-Zn bond is enhanced after H₂CO adsorption, which is consistent with the increase of C-O distance (Figures 4A,B). The O atoms in the two adsorption systems have strong binding with Zn atoms (ICOHP value is small), which also shows that these phases are stable.

**Configuration Adsorption of Zn/H₂CO-(c) and Zn/H₂CO-(d)**

As shown in Figures 3C,D the Zn/H₂CO-(c) and Zn/H₂CO-(d) configurations with adsorption energies of 0.15 and 0.11 eV, respectively, are much less stable than those of Zn/H₂CO-(a) and Zn/H₂CO-(b), and the H atoms point to the doped Zn atoms. Different from the configurations of Zn/H₂CO-(a) and Zn/H₂CO-(b), the adsorption energies are also very different, similar to the adsorption on the original monolayer MoS₂. Therefore, the orientation of H atom or O atom in H₂CO can be used to determine the adsorption energy. At the same time, in Figures 3C,D the interaction between the adsorbed molecules and the substrate is also different due to the different orientations of hydrogen atoms, i.e., the angle of C-H-Zn is different. In the two structures, the distance between H and Zn atoms is 2.02 Å.

Therefore, the strong covalent bond or ionic bond between the two atoms can be eliminated. The weak electrostatic attraction of negatively charged H atom (0.06 e) and positively charged Zn atom
(0.33 e) should be combined, which is consistent with the weak adsorption of Zn/H₂CO-(c) and Zn/H₂CO-(d) configurations.

Compared with H₂CO in the gas phase, the geometry and substrate of the adsorbed state are only slightly changed. The C-O bond of H₂CO decreased by 0.01 Å. In addition, for Zn/H₂CO-(c) and Zn/H₂CO-(d), there is a small electron transfer (0.07 and 0.08 e) between the adsorbed H₂CO and the substrate, and the molecule has a small magnetic moment of 0.01 µB. The adsorption of Zn/H₂CO-(c) and Zn/H₂CO-(d) is weaker than that of Zn/H₂CO-(a) and Zn/H₂CO-(b), indicating that the probability of occurrence of the latter two configurations is much higher than that of the former two. For the adsorption of Zn/H₂CO-(c) and Zn/H₂CO-(d) configurations, the charge density difference diagram shows that there is almost no electron accumulation between the adsorbed molecule H₂CO and the Zn doped MoS₂ monolayer (Figures 4C,D). It is further confirmed that the adsorption capacity of H₂CO on the substrate is weak, which is consistent with the small adsorption energy and large distance mentioned above.

Further analyzing the adsorption behavior of H₂CO on the Zn-MoS₂ surface, it can be seen from Figures 5C,D above that the TDOS of the Zn/H₂CO-(c) and Zn/H₂CO-(d) systems do not show induced impurity state near the Fermi level, and the DOS curves of the adsorbed H₂CO of the Zn/H₂CO-(c) and Zn/H₂CO-(d) systems overlap slightly with the 3d orbitals of the Zn atoms (Figures 5C,D, below), shows that the interaction between H₂CO and Zn-MoS₂ is weak, the bonding between H-Zn atoms is weak, and the ICOHP negative value is large (Figures 6C,D), resulting in only 0.07 and 0.08 e being transferred from the adsorbed H₂CO molecule to the final substance. The H-Zn strength in Zn/H₂CO-(c) system is higher than that in Zn/H₂CO-(d) system, indicating that Zn/H₂CO-(c) system is more stable than Zn/H₂CO-(d) system. This conclusion is consistent with the previous calculation of adsorption energy (Table 1). In terms of magnetic properties, the total magnetic moment of the whole adsorption system did not change after adsorption of H₂CO by Zn-MoS₂ (Zn/H₂CO-(c) and Zn/H₂CO-(d) were 2.00 µB), which was consistent with the small adsorption energy of Zn/H₂CO-(c) and Zn/H₂CO-(d).

CONCLUSION

In conclusion, according to the first principles calculations, we have studied the effects of Zn doping S vacancy on the electronic structure, magnetic properties and chemical activity of monolayer MoS₂. The calculation of binding energy shows that Zn atoms are closely bound to S-defects, which is mainly due to the hybridization between dopant atoms and their nearest Mo
FIGURE 5 | (A–D) shows the total spin polarized density of states (TDOS) of Zn/H₂CO–(A), Zn/H₂CO–(B), Zn/H₂CO–(C) and Zn/H₂CO–(D) systems (upper panels), and the projected density of states (PDOS) of H₂CO adsorbed by Zn-MoS₂ (lower panels). Purple curve, H₂CO in adsorption state; orange dotted line, H₂CO in gas phase; blue curve, d-projected PDOS for Zn atom. The positive and negative values of DOS indicate spin up and spin down, respectively. The Fermi level is marked with a black dotted line.

FIGURE 6 | (A–D) figure shows the negative crystal orbital Hamilton density (-COHP) on the Zn/H₂CO–(A) and Zn/H₂CO–(B) system O-Zn bond and the Zn/H₂CO–(C) and Zn/H₂CO–(D) system H-Zn bond, respectively. The red filled area is the O-Zn/H-Zn bonding area, and the green filled area is the O-Zn/H-Zn antibonding. Fermi energy level marked with black dotted line.
atoms. Finally, a new single cluster catalyst on ZnO-Mo surface is formed, which improves the selectivity of MoS2 surface. By embedding Zn atoms, the magnetic properties of MoS2 monolayer can be adjusted and the spin magnetic moment of Zn4Mo2 is 2.00 μB. The electronic properties of MoS2 are also changed by the impurity states induced in the band gap. The effects of H2CO adsorption and doping on the chemical activity of MoS2 monolayers were further investigated. It was found that the H-end downward adsorption of H2CO in the original monolayer MoS2 and Zn doped monolayer MoS2 was very weak, and the electronic structure of the two substrates changed little after adsorption, indicating that the two systems were not sensitive to H2CO. When the O atom in H2CO molecule faces to the substrate, the adsorption capacity is strong, and the adsorbed H2CO is effectively activated. DOS analysis showed that the electronic structure of Zn-MoS2 could be changed by introducing impurities in the band gap when the O-terminal of H2CO molecule was adsorbed downward. At the same time, the magnetic properties of Zn-MoS2 system are also adjusted. The COHP diagram shows that Zn atoms are strongly bonded with O atoms. This study shows that Zn doping is a promising method to optimize the electronic structure, magnetic properties and chemical activity of MoS2, which provides a promising way to improve the electronic properties of MoS2 materials.

AUTHOR CONTRIBUTIONS

CH: conceptualization, methodology, funding acquisition, supervision, project administration. GZ: formal analysis. JH: writing—original draft, investigation, formal analysis, methodology. LF: supervision, funding acquisition, project administration. GD: formal analysis. HY: software.

DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding authors.

FUNDING

This study was funded by the Natural Science Foundation of China (Nos. 21603109 and 21876104), the Henan Joint Fund of the National Natural Science Foundation of China (No. U1404216), Transformation of Scientific and Technological Achievements Programs of Higher Education Institutions in Shanxi (No. 2020CGG032), Cultivation Plan of Young Scientific Researchers in Higher Education Institutions of Shanxi Province.

SUPPLEMENTARY MATERIAL

The Supplementary Material for this article can be found online at: https://www.frontiersin.org/articles/10.3389/fchem.2020.605311/full#supplementary-material.

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Conflict of Interest: The authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.