Adsorption behavior of Cu-doped ZIF-67 for decomposition gases of organic insulator: A first-principles study

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Abstract. In order to detect the decomposition gas of organic insulator in gas insulated switchgear, Cu doped ZIF-67 material was proposed. In this paper, the gas adsorption process was analyzed by the first principle. The calculation indexes include density of States (DOS), adsorption energy (E_{ads}), charge transfer quantity (Q_t), Charge density difference (CDD), electron localization function (ELF), the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO). The results show that the adsorption capacity of Cu-ZIF-67 for CO and CO₂ is better than that of CF₄ in the single gas adsorption calculation. The adsorption energies of three single gases are -1.306eV, -1.597eV and -0.991eV, respectively. Therefore, this study provides excellent gas sensing materials and scientific theoretical calculation for selective detection and gas adsorption of decomposition gas.

1. Introduction
Gas insulated switchgear (GIS) is a kind of enclosed electrical equipment. GIS is generally composed of circuit breaker, disconnector, grounding switch connector and outlet terminal [1,2]. In addition, it is filled with insulation gas (such as SF₆) and with certain pressure. In recent years, due to urban construction, transportation and industrial upgrading. GIS has been widely applied. However, there are some security risks in the actual operation of GIS equipment, which needs further research [3,4].

In the long-term operation of GIS, partial discharge and overheating faults could happen, which can easily cause material decomposition [5]. The maintenance pictures of the damaged organic insulation part can be seen from the research in reference [6]. In addition, the organic insulator mainly contains C, H, O elements, and the decomposition gas products are mainly CO, CO₂ and CF₄ [7-9]. Therefore, some researchers began to study the detection of organic insulators, the main methods are Online detection, infrared imaging, spectral detection, gas sensing detection [10,11]. At present, gas sensitive detection method is a relatively new detection method, which can help to predict the damage of organic insulator [12-14].

At present, carbon nanotubes, graphene and metal oxide are the main gas sensing materials. Carbon nanofiber has been designed by Ghazala Zainab. Resultant PCNF nanofibers exhibited high surface area, superior CO₂ adsorption performance with CO₂ uptake of 3.11 mmol/g of sorbent. The cycle adsorption times were 50[15]. Cao-ZnO heterostructures were prepared in reference [16] and showed good selectivity in 10 interference gases. Due to the selectivity and sensitivity of traditional detection materials, its application has been limited. Therefore, this paper introduces a new type of metal organic framework material ZIF-67 to carry out the first principle adsorption analysis [17-19]. The adsorption mechanism of CO, CO₂ and CF₄ on Cu-ZIF-67 was studied to guide the feasibility of the materials.
2. Computation method

The first principle is a very popular computational theory, which has been applied to catalysis, adsorption and physical properties. All the theoretical calculation is completed in CASTEP code. The calculation quality level is the highest. The density scaling factor and energy cutoff are 1.5 and 350eV, respectively. Self-consistent field tolerance was set to \(5 \times 10^{-7} \text{eV/atom}\). Because the cluster is a planar structure, the k-point is set to \(1 \times 1 \times 1\) [20].

In the process of adsorption, gas molecules from fast to slow, until finally stop on the surface of the adsorption medium. The energy produced in this process was called adsorption energy \(E_{\text{ads}}\), Adsorption energy is used to describe the adsorption capacity of adsorbents to gas molecules. The calculation formula is

\[
E_{\text{ads}} = E_{\text{sur/gas}} - E_{\text{sur}} - E_{\text{gas}}
\]

Where \(E_{\text{sur/gas}}\), \(E_{\text{sur}}\) and \(E_{\text{gas}}\) represent the total energy of gas adsorbed on the surface of ZIF-67 material, surface of ZIF material and gas molecules respectively. When \(E_{\text{ads}}\) is greater than zero, the adsorption process is exothermic. In this paper, Mulliken charge was used to represent the charge change between the decomposition gas of organic insulator and the surface of ZIF-67. The charge transfer quantity \(Q_t\) is used to represent the electronic change and is defined as:

\[
Q_t = Q_a - Q_b
\]

Where \(Q_a\), \(Q_b\) represent the charge of gas molecules after adsorption and before adsorption respectively.

3. Results and discussion

3.1 Geometry and electronic properties of Cu-doped ZIF-67 clusters and gas molecules

![Geometry structure of undoped ZIF-67, Cu-ZIF-67 clusters, CO, CO2 and CF4](image)

ZIF-67 is a kind of MOF material with good stability and adsorption effect. ZIF-67 was prepared by the reaction of cobalt salt and dimethyl imidazole in methanol. The periodic ZIF-67 has a unit cell dimensions of 17.0993Å [23]. Each Co atom is connected to four 2-methylimidazoles. In order to reduce double counting, cluster model always has been used to analyze ZIF, which is proved to be a feasible strategy in many literatures. Consequently, the minimum cluster model was established to represent the adsorption properties of ZIF-67[24]. As shown in Figure 1, Geometry structure of undoped ZIF-67, Cu-ZIF-67 clusters, CO, CO2 and CF4. The bond length and bond angle have been marked in the figure.

The electronic properties of Cu-doped and undoped ZIF-67 are shown in Figure 2. The total density of States (TDOS) and the partial density of states (PDOS) are calculated. The red curve shifted to the right at -22eV, -19eV, -16eV, -13eV, and -8eV. The red and black curves pass through the Fermi level, which indicates that the effect of Cu-doped has little effect on the band gap. Cu doping provides unsaturated point for ZIF-67 and enhances the selective adsorption of target gas.
3.2 Adsorption analysis of CO, CO$_2$ and CF$_4$ on Cu-ZIF-67 surface

After the structural analysis in the previous section, we understand the metal sites Co of undoped ZIF-67 is saturated. We use transition metal doping to enhance the selective adsorption of gas molecules at unsaturated sites. Copper is a relatively cheap transition metal, which can reduce economic consumption and obtain better adsorption effect.

Figure 3 shows adsorption properties of CO, CO$_2$ and CF$_4$ adsorbed on Cu-ZIF-67. Figure 3 (a, d, g) shows the initial adsorption structure of CO, CO$_2$ and CF$_4$ on the surface of Cu-ZIF-67. The distance between atoms is less than 2.1Å and has been marked. Figure 3 (b, c) shows the TDOS and PDOS of CO adsorbed on Cu-ZIF-67, respectively. The density of states can not only reflect the information of band structure, but also analyze the hybridization between atoms. The hybrid orbital theory is based on the valence bond theory, which is helpful for the microscopic analysis between the molecular gas molecules and the adsorbent surface. From the TDOS, the coincidence degree of red curve and black curve is good, and the peaks of 4eV, -2.5eV, -7eV, -10eV are increased. The C-2p, O-2p, Cu-4p, Cu-4s orbitals have overlapping peaks at 2eV, -5eV and -8eV. However, the C-2p orbital and Cu-4p orbital have strong overlapping peaks. Taking CO as an example, there are obvious overlapping peaks between C-2p and O-2p, which caused by the triple bond between C and O atoms. Therefore, there may be chemical bonds on the surface of CO and Cu-ZIF-67. Figure (e, f) shows the TDOS and PDOS of CO$_2$ adsorbed on Cu-ZIF-67, respectively. From the TDOS, the coincidence degree of red curve and black curve is good. This indicates that the adsorption takes place at the atomic level, so it is necessary to analyze PDOS. We can clearly see that there are strong overlapping peaks in -1eV and 3eV, which contributed by C-2p, O-2p and Cu-4p orbitals. Therefore, it can be predicted that there may be chemical bonds on the surface of CO$_2$ and Cu-ZIF-67. On the contrary, we observed the TDOS and PDOS of CF$_4$ on Cu-ZIF-67, and there were no overlapping peaks between the orbitals, which indicated that there was no hybridization. Therefore, there is no chemical bond between CF$_4$ and Cu-ZIF-67.

After density of states analysis, $E_{ads}$ and $Q_t$ of CO, CO$_2$ and CF$_4$ adsorbed on Cu-ZIF-67 are calculated and shown in Figure 4. It can see from the figure that the absolute values of $E_{ads}$ for CO$_2$ and CF$_4$ adsorption by Cu-ZIF-67 are the maximum and the minimum, respectively. The $E_{ads}$ and $Q_t$ of Cu-ZIF-67 are -1.306eV and 0.368, respectively. Therefore, it is clear that Cu-ZIF-67 has better adsorption effect on CO and CO$_2$ by $E_{ads}$ and $Q_t$. But the $Q_t$ of CF$_4$ adsorbed on Cu-ZIF-67 is the maximum, further analysis is needed.
Figure 3 Adsorption properties of CO, CO$_2$ and CF$_4$ adsorbed on Cu-ZIF-67

Figure 4 $E_{\text{ads}}$ and $Q_t$ of CO, CO$_2$ and CF$_4$ adsorbed on Cu-ZIF-67 ($E_{\text{ads}}$ for eV, $Q_t$ for e)
To gain further insight into the adsorption properties of Cu-ZIF-67, Charge density difference (CDD), electron localization function (ELF), the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbital (LUMO) are calculated and shown in Figure 5. The CDD is a physical quantity reflecting the electron density between atoms. The higher value of the CDD, the greater the charge transfer between the gas molecules and the adsorbent surface. Red and blue represent high and low electron density, respectively. ELF is a physical quantity used to analyze the degree of electronic localization. ELF is an important criterion to describe chemical bonding. Red and blue represent high and low electronic localization, respectively. From the observation of CDD and ELF, the red region between CO, CO$_2$ and Cu-ZIF-67 all indicates that the high electron density and strong electron localization. All these indicate the existence of chemical bonds. On the contrary, the blue region between CF$_4$ and Cu-ZIF-67 indicates that the electron density is low and the degree of electron localization is weak. Furthermore, for a deeper understanding of the electronic changes caused by gas molecules adsorption on Cu-ZIF-67, frontier molecular orbitals (HOMO and LUMO) are analyzed. As can be seen from Figure 5 (a, b), the occupied orbits of CO and CO$_2$ are mainly concentrated in HOMO. the electronic density in LUMO is only distributed on the Cu-ZIF-67 monolayer. On the contrary, carbon tetrafluoride gas only concentrates on Cu-ZIF-67 surface in HOMO and LUMO. Therefore, it is proved that CO and CO$_2$ are strongly adsorbed on Cu-ZIF-67, while CF$_4$ is weak.

4. Conclusions

GIS is a common electrical equipment in power system. Due to high temperature and partial discharge, organic insulator decomposes. The main gas products are CO, CO$_2$ and CF$_4$. Therefore, this paper mainly uses Cu-ZIF-67 gas sensing material to study the detection ability of decomposition gas. In this paper, the adsorption behaviors of Cu-ZIF-67 clusters for CO, CO$_2$ and CF$_4$ gases were analyzed by first principles method. The interaction strength between gas molecules and gas sensitive materials was
analyzed by $E_{\text{ad}}$, $Q_i$, CDD, ELF, HOMO and LUMO. Results indicate that the copper on the metal site has strong adsorption ability for CO and CO$_2$, and may form chemical bonds. The adsorption energies of Cu-ZIF-67 for CO and CO$_2$ are -1.306eV and -1.597eV, respectively. On the contrary, Cu-ZIF-67 has weak adsorption on CF$_4$. Therefore, Cu-doped ZIF-67 can be a good adsorbent for CO and CO$_2$. This study provides a scientific direction for the detection and adsorption of organic ligand decomposition gases.

Acknowledgements
This work was financially supported by the National Natural Science Foundation of China (Grant numbers: 51907165, 52077177), and Chongqing graduate Scientific research innovation Project (Grant number: CYB20099).

References
[1] Darwish, A., Refaat, S.S., Abu-Rub., HToliyat, H.A. (2020) PD Signal Propagation in GIS: Ultra-High Frequency Detection-Based Modeling. IEEE Sens J.,20:9417-9426.
[2] Han, X.T, Guo, R.C, Shen, S.H., Li, J.H, Sun, W. (2020) Study on the combined characteristics of UHF and optical signals induced by partial discharge at spacer surface in GIS. IET Gener Transm Dis.,14:3332-3337.
[3] Zhuang, Y., Hu, X.T., Tang, B., Wang, S.W, Cui, AY. (2020) Effects of SF$_6$ decomposition components and concentrations on the discharge faults and insulation defects in GIS equipment. SCI REP-UK., 10: 1-12.
[4] Gui, Y.G., Sun, H., Wei, H.L., Duan, S.K, Tang, C., Zhang, X.X. (2019) Effect of Nickel Doping on Adsorption of SF$_6$ Decomposition Products over MoS$_2$ Surface. JOM.,71:3971-3979.
[5] Zhang, L., He, C., Guo, R.C., Yuan, W.Z., Li, J.H. (2020) Research on effectiveness of lightning impulses with different parameters for detecting protrusion defects in GIS. IEEE T Dielect El In.,27:1354-1362.
[6] Cheng, T.T.,Gao,WS,Liu,WD,Li,RP. (2018)Evaluation method of contact erosion for high voltage SF$_6$ circuit breakers using dynamic contact resistance measurement. Electr Pow Syst Res.,163:725-732.
[7] Wang,J.C.,Ding,WD.,Yan,J.Q.,Wang,Y.N.,Wang,Y.S.,Li,Z.C. (2017)Decomposition Characteristics of SF$_6$ under Overheating Conditions. IEEE T Dielect El In., 24:3405-3415.
[8] Zhong,L.P.,Ji,S.C.,Liou,K., Xiong, Q.,Zhu,L.Y. (2016)Decomposition Characteristics of SF$_6$ under Three Typical Defects and the Diagnostic Application of Triangle Method. IEEE T Dielect El In.,23:2594-2606.
[9] Zhang,X.X.,Gui,Y.G.,Zhang,Y.,Qiu,Y.J.,Chen,L.C. (2016)Influence of Humidity and Voltage on Characteristic Decomposition Components under Needle-plate Discharge Model. IEEE T Dielect El In.,230:2633-264.6.
[10] Shen,C.C.,Cai,XL., Sang,Y.B.,Zheng,T.C. (2020)Investigation of multispectral SF$_6$ stimulated Raman scattering laser. Chin Opt Lett.,18:1-5.
[11] Singh,A.,Bae, H.,Lee,S.,Shabbir,K., Huss-ain,T.,Lee,H. (2020)Highly sensitive and selective sensing properties of modified green phosphorene monolayers towards SF$_6$ decomposition gases. Appl Surf Sci.,512:1-9.
[12] Chen,W.L.,Gui,Y.G., Li,T.,Zeng,H.,Xu,L.N.,Ding,Z.Y.(2020)Gas-sensing properties and mechanism of Pd-GaNNTs for air decomposition products in ring main unit. Appl Surf Sci.,531:1-13.
[13] Pandey,D,Kamal,C, Dutt,R, Chakrabarti,A. (2020) Improved gas adsorption on functionalized aluminene surface: A first- principles study. Appl Surf Sci.,531:1-17.
[14] Mugutkar,A.B.,Gore,S.K.,Mane,R.S.,Patange,S.M.,Jadhav,S.S.,Shaikh,S.F. (2020)Structural modifications in Co-Zn nanoferites by Gd substitution triggering to dielectric and gas sensing applications. J Alloy Compd.,844:1-11.
[15] Zainab,G.,Babar,A.A.,Ali,N., Aboalhas-san,A.A.,Wang,X.F.,Yu,J.Y.,Ding,B. (2020)Electrospun carbon nanofibers with multi-aperture/opening porous hierarchical structure for efficient CO$_2$
adsorption. J Colloid Interf Sci.,561:659-667.
[16] Joshi,S, Jones,L.A.,Sabri,Y.M.,Bhar-gava,S.K.,Sunkara,M.V.,Ippolito,S.J. (2020)Facile conversion of zinc hydroxide carbonate to CaO-ZnO for selective CO$_2$ gas detection. J Colloid Interf Sci.,558:310-332.
[17] Son,Y.R.,Ryu,S.G.,Kim,H.S. (2020)Rapid adsorption and removal of sulfur mustard with zeolitic imidazolate frameworks ZIF-8 and ZIF-67. Micropor Mesopor Mat.,293:1-11.
[18] Qin,C,Wang,B,Wu,N,Han,C, Wu,CZ, Zhang,XS. (2020)Metal-organic frameworks derived porous Co$_3$O$_4$ dodecahedrons with abundant active Co$^{3+}$ for ppb-level CO gas sensing. Appl Surf Sci.,506:1-9.
[19] Cui,W.,Kang,X.L., Zhang,X.Y.,Zheng,Z., Cui,X.D. (2019)Facile synthesis of porous cubic microstructure of Co$_3$O$_4$ from ZIF-67 pyrolysis and its Au doped structure for enhanced acetone gas-sensing. Physica.,113:165-171.
[20] Wang,J.X.,Zhou,Q.,Lu,Z.R., Wei,Z.J., Zeng,W. (2019)Gas sensing performances and mechanism at atomic level of Au-MoS$_2$ microspheres. Appl Surf Sci.,490:124-136.
[21] Zhang,L,Sun,B,Zhang,Q.L.,Liu,H.F.,Liu,K.Z.,Song,H.F. (2020)Polaron modulation mechanism of H$_2$O and CO$_2$ adsorption on PuO$_2$(111) surface. Appl Surf Sci.,516:1-8.
[22] Mao,J,Guo,P,Zhang,T,Zhang,S.L,Liu,C. (2020)A first-principle study on hydrogen storage of metal atoms (M = Li, Ca, Sc, and Ti) coated B-40 fullerene composites. Comput Theor Chem.,1181:1-6.
[23] Liu,X.P.,Wang,B.H.,Cheng,J.,Meng,Q.M.,Song,Y.X.,Li,MH. (2020)Investigation on the capture performance and influencing factors of ZIF-67 for hydrogen sulfide. Sep Purif Technol.,250:1-9.
[24] Wang,H.F.,Zhao,L.M.,Xu,W.B.,Wang,S.P.,Ding,Q.Y.,Lu,X.Q.,Guo,W.Y. (2015)The properties of the bonding between CO and ZIF-8 structures: a density functional theory study, Theor Chem Acc.,134:1-9.