American Academic Scientific Research Journal for Engineering, Technology, and Sciences
ISSN (Print) 2313-4410, ISSN (Online) 2313-4402
http://asrjetsjournal.org/

Acetone Adsorption to Co_3O_4（111）Surface: A Density Functional Theory (DFT) Study

Yanyun Feng[a*], Haiming Zhang[b], Peng Lu[c], Xiaomin Jia[d]

[a,b,c,d] *School of physical science and technology, Tiangong University, Tianjin 300387, China*
[a]*Email: 1784023659@qq.com,* [b]*Email: zhmtjwl@163.com,* [c]*Email: lupeng@tiangong.edu.cn*
[d]*Email: 1767306505@qq.com*

Abstract

Acetone, as one of VOCs, is not only polluting to the environment, but also harmful to humans. Therefore, detecting acetone is an important topic in the field of gas sensing. The carbonyl functional group determines the chemical properties of acetone. Aldehydes also contain carbonyl functional group. In this paper, we have calculated adsorption energy, adsorption distance and transfer charge by DFT. The results showed that the top of Co^{3+} on Co_3O_4 (111) surface has the best selectivity for sensing acetone. Our study contributes to the further study of the sensing properties of p-type metal oxide semiconductor sensors.

Keywords: Acetone; Carbonyl functional group; Co_3O_4(111) surface; DFT methods; Sensing mechanism.

1. Introduction

Volatile organic compounds (VOCs) can pollute the environment and harm human health. Acetone is one of VOCs and one of the gas in human respiration. It is used as a respiratory marker for non-invasive diagnosis of diabetes mellitus[[1]]. Therefore, the detection of acetone is important for environmental safety and human health. In recent decades, many metal oxides (ZnO, In_2O_3, Fe_2O_3, SnO_2, MnO_2, WO_3) have been used in sensitive studies of acetone[2, 5]. Among them, Co_3O_4 crystal, as a typical p-semiconductor, has the advantages of high cost-effectiveness, low pollution and good stability. Many experimental and theoretical results prove that Co_3O_4 has great potential to detect VOCs in the field of gas sensing. At the experimental level, Yao and colleagues synthesized four Co_3O_4 nanocatalysts with main exposure (100), (111), (110) and (112) surfaces by hydrothermal method[[6]]. At the theoretical level, Liu and colleagues studied and reported on the ability of Co_3O_4 to improve acetone response and gas sensitivity by doping W and Mn atoms[[7]]. Some researchers also found that the preferential growth of Co_3O_4 (111) surface favors the formation of Co_3O_4 octahedra[8, 11]. In summary, we can guess that (111) surface is special for Co_3O_4 and according to previous reports on acetone adsorption, the top of Co^{3+} has the best selectivity for sensing acetone[[12]].

---

* Corresponding author.

To our knowledge, the functional group of acetone molecule is the carbonyl group (O=C). Its chemical properties are expressed in the carbonyl group. Inspired by this, we have studied the selectivity of Co_3O_4(111) surface to formaldehyde and butanone gas molecules that also contain carbonyl group, to better understand the mechanism of gas sensitivity of Co_3O_4 special surface to acetone.

In this paper, the adsorption properties of acetone on Co_3O_4 (111) surface were studied based on density functional theory (DFT). The adsorption energy, adsorption distance and transfer charge were calculated to study the effect of carbonyl group on adsorption of acetone from the theoretical level. The research method is universal and can be used as an effective research route.

2. Computational methods and modeling

All density functional theory (DFT) calculations are implemented with Cambridge Serial Total Energy Package (CASTEP) contained in the Materials Studio (MS) software[13]. The generalized-gradient approximation (GGA) of Perdew, Burke, and Ernzerh (PBE) of exchange-correlation functional is used for geometry optimization and adsorption properties[13]. For Co_3O_4 bulk geometry optimizations, a Monkhorst-Pack grid of 5 × 5 × 5 was used to sample the first Brillouin zone of k space for better accuracy. For the slabs geometry optimizations, the Monkhorst−Pack grid was 3 × 3 × 1. The cutoff energy of 400 eV was applied, and the convergence threshold parameters for the optimization were 1×10^{-5} Ha (energy), 0.03 eV/ Å (force), and 1×10^{-3} Å (displacement), respectively[14]. When the structure of Co_3O_4 bulk was optimized, fixed the bottom three atoms and relaxed the top three atoms.

In this study, the Co_3O_4 (111) surface structure was derived from a 2 × 2 × 1 supercell block, with 56 atoms ($Co_{24}O_{32}$). Then, a 15 Å vacuum was added above layers to simulate the surface[15]. The fully relaxed bulk structure parameters of Co_3O_4 (111) surface are a = b = 11.58 Å, c = 18.70 Å and α = β = γ = 90°. Adsorption energy and transfer charges are utilized to analyze the stability of acetone gas adsorbed on the Co_3O_4 (111) surface. The adsorption energy (E_{ads}) and transfer charges (Q_t) were calculated as follow:

$$E_{ads} = E_{Co_3O_4} + E_{acetone} - E_{acetone/Co_3O_4} \quad (1)$$

$$Q_t = Q_a - Q_b \quad (2)$$

Where $E_{acetone/Co_3O_4}$ is the total energy of acetone gas molecule adsorbed on the Co_3O_4 (111) surface, $E_{acetone}$ and $E_{Co_3O_4}$ are the energy of acetone gas molecule in a big box and the Co_3O_4 slab, respectively. A positive value of E_{ads} indicates that the adsorption process is exothermic, while a negative value of E_{ads} indicates that the adsorption process is endothermic[[15]]. In formula (2), Q_a and Q_b represent the amount of charge before and after adsorption of gas molecules, respectively[[16]]. If $Q_t > 0$, it represents that electrons transfer from acetone gas molecule to Co_3O_4 surface. If $Q_t < 0$, it represents that electrons transfer from the Co_3O_4 surface to acetone gas molecule. In addition, we have mapped the charge density difference (CDD) to better clarify electron interactions and charge transfer between gas molecules and adsorbents[17].

3. Results and discussion

3.1. Construction of references

In order to investigate configurations of acetone adsorbed on Co_3O_4 (111) surface, We firstly analyzed the characteristics of Co_3O_4 crystal structure. The space group of Co_3O_4 crystal is Fd-3m (227). As is shown in Figure 1, there are two kinds of cobalt atoms in Co_3O_4 crystal, namely Co^{2+} (Co fills the tetrahedral void) and Co^{3+} (Co fills the octahedral void). As is shown in Figure 2 (a), the terminating surface of Co_3O_4 (111) surface contains Co^{3+} and Co^{2+}. Referring to previous reports, the O atom of acetone usually attaches to metal atom vertically downward[18, 19]. Therefore, as is shown in Figure 2 (b), the top of Co^{3+} atom are selected as the adsorption sites of gas molecules.

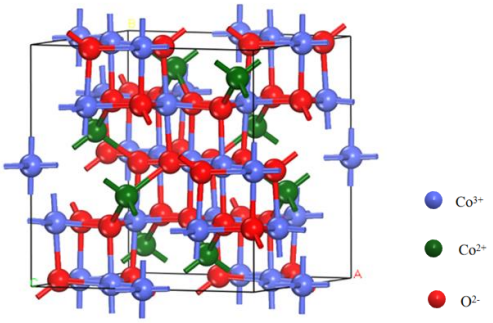
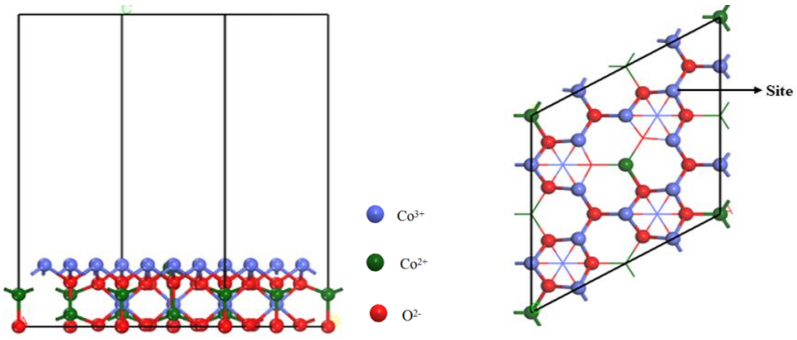


Figure 1: Side view of the structure of Co_3O_4 (2×2) supercell.



(a) (b)

Figure 2: Optimal configuration of Co_3O_4(111) surface: (a) side view; (b) Top view.

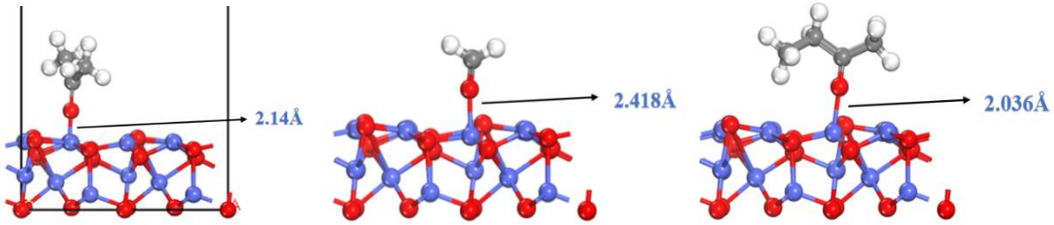
3.2. Adsorption properties

As is shown in Figure 3, these are adsorption configurations of gas on Co_3O_4 (111) surface. The adsorption energy, transfer charge and Co-O bond length parameters calculated by each adsorption configuration are listed in Table 1. From table 1, it can be found that all three adsorption energy are positive. It indicates that the adsorption processes are exothermic, and each adsorption system is spontaneously adsorbed. By comparison (Table 1), it can be found that the adsorption energy of acetone is relatively larger than the remaining two. It illustrates that acetone molecules is more easily adsorbed to Co_3O_4. In addition, the Co-O bond lengths (2.14 Å,

2.418 Å, 2.036 Å) are all less than the Van der Waals radius (3.0-5.0 Å)[[20]]. It illustrates that a chemical bond is formed between the Co atom of Co_3O_4 and the O atom of gas.

Table 1: Parameters of adsorption properties of gas molecular on the surface of Co_3O_4 (111).

Model	Adsorption energy (*eV*)	Distance(*Å*)	Transferred electrons(*e*)
Acetone	1.86	2.140	0.16
Formaldehyde	1.10	2.418	0.11
Butanone	1.28	2.036	0.09

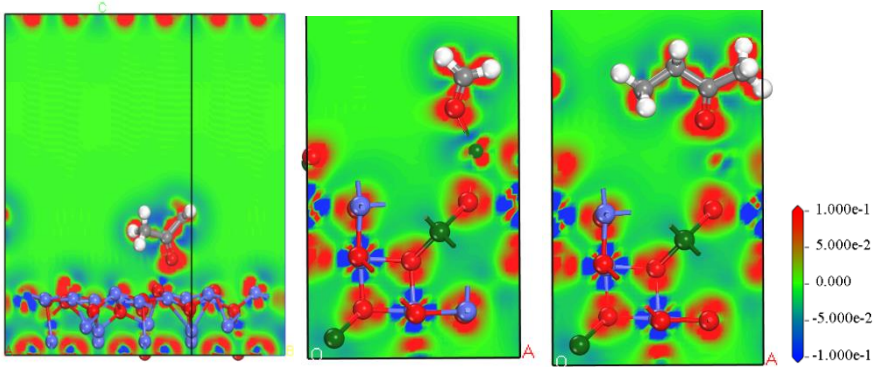


(a) (b) (c)

Figure 3: Adsorption configuration of gas molecular on Co_3O_4(111) surface: (a) Acetone; (b) Formaldehyde; (c) Butanone.

3.3. Hirshfeld charge analysis

Hirshfeld charge refers to the description of the affinity strength of an atom or intramolecular electron in a system. The hirshfeld charge analysis of gas molecule on Co_3O_4 (111) surface are reported in the Figure 4. Here, the green region denotes the neutral zone, the bule region denotes trapped electrons, and the red region denotes the loss of the electrons[21]. It is clear that the O atoms of acetone molecule and the Co atom regions of the Co_3O_4 are more blue and red than the others. It indicates that the number of electrons transferred during this adsorption process is higher, indicating that acetone molecules are more easily adsorbed to Co_3O_4 (111).



(a) (b) (c)

Figure 4: Differential charge diagram of gas adsorption to Co_3O_4(111) surface: (a) Acetone; (b) Formaldehyde; (c) Butanone.

4. Conclusion

Acetone, formaldehyde and butanone all contain carbonyl functional groups. The influence of adsorption properties of Co_3O_4 (111) toward them have been studied by DFT. The most stable adsorption structures and adsorption characteristic parameter (the adsorption energy, transfer charges and adsorption distances) have been calculated to analyze the gas sensing performance of gas molecular adsorbed Co_3O_4 (111). The results showed that Co_3O_4 (111) surface had the best selectivity for acetone. This report contributes to the further study of the associated sensing property of p-type metal oxide semiconductor gas sensors.

Acknowledgements

This work was financially supported by the Municipal Education Commission Scientific Research Program of Tianjin City (2019KJ029).

References

[1] Xiaofeng Wang, et al. "Prussian Blue analogue derived porous $NiFe_2O_4$ nanocubes for low-concentration acetone sensing at low working temperature." *Chemical Engineering Journal*, vol. 338, pp. 504-512, Jan. 2018.

[2] Xiao Chang, et al. "Metal-organic frameworks derived ZnO@ MoS_2nanosheets core/shell heterojunctions for ppb-level acetone detection: Ultra-fast response and recovery." *Sensors and Actuators B: Chemical*, vol. 304, pp. 127430, Nov. 2019.

[3] Yang Liu, et al. "Hierarchical SnO_2 nanostructures made of intermingled ultrathin nanosheets for environmental remediation, smart gas sensor, and supercapacitor applications." *ACS applied materials & interfaces*, vol. 6.3, pp. 2174-2184, Jan. 2014.

[4] Thomas Waitz, et al. "Ordered mesoporous In_2O_3: synthesis by structure replication and application as a methane gas sensor." *Advanced Functional Materials*, vol. 19.4, pp. 653-661, Jan. 2019.

[5] Shuai Liang, et al. "Highly sensitive acetone gas sensor based on ultrafine α-Fe_2O_3 nanoparticles." *Sensors and Actuators B: Chemical*, vol. 238, pp. 923-927, June. 2016.

[6] Junxuan Yao, et al. "Facet-dependent activity of Co_3O_4 catalyst for C_3H_8 combustion." *ChemCatChem*, vol. 11.22, pp. 5570-5579, Oct. 2019.

[7] Dongliang Liu, et al. "Theoretical study on W-Co_3O_4 (1 1 1) surface: Acetone adsorption and sensing mechanism." *Applied Surface Science*, vol. 566, pp. 0169-4332, July. 2021.

[8] Filip Zasada, et al. "Periodic DFT and HR-STEM studies of surface structure and morphology of cobalt spinel nanocrystals. Retrieving 3D shapes from 2D images." *The Journal of Physical Chemistry C*, vol. 115.14, pp. 6423-6432, Feb. 2011.

[9] Filip Zasada, et al. "Periodic density functional theory and atomistic thermodynamic studies of cobalt spinel nanocrystals in wet environment: molecular interpretation of water adsorption equilibria." *The Journal of Physical Chemistry C*, vol. 114.50, pp. 22245-22253, Oct. 2010.

[10] Filip Zasada, Witold Piskorz, and Zbigniew Sojka. "Cobalt spinel at various redox conditions: DFT+ U investigations into the structure and surface thermodynamics of the (100) facet." *The Journal of*

Physical Chemistry C, vol. 119.33, pp. 19180-19191, Nov. 2015.

[11] Filip Zasada, et al. "Mono-and diatomic reactive oxygen species produced upon O_2 interaction with the (111) facet of cobalt spinel at various conditions—molecular DFT and atomistic thermodynamic investigations." *The Journal of Physical Chemistry C*, vol. 122.48, pp. 27528-27539, Sep. 2018.

[12] R. A. P. Ribeiro, et al. "Theoretical approach for determining the relation between the morphology and surface magnetism of Co_3O_4." *Journal of Magnetism and Magnetic Materials*, vol. 453, pp. 262-267, Nov. 2017.

[13] Yamian Mo et al. "Acetone adsorption to $(BeO)_{12}$,$(MgO)_{12}$ and $(ZnO)_{12}$ nanoparticles and their graphene composites: A density functional theory (DFT) study." *Applied Surface Science*, vol. 469, pp. 962-973, Nov. 2018.

[14] Shengli Zhang, et al. "First-principles study of field emission properties of graphene-ZnO nanocomposite." *The Journal of Physical Chemistry C*, vol. 114.45, pp. 19284-19288, Oct. 2010.

[15] Cortés-Arriagada Diego, Nery Villegas-Escobar, and Daniela E. Ortega. "Fe-doped graphene nanosheet as an adsorption platform of harmful gas molecules (CO, CO_2, SO_2 and H_2S), and the co-adsorption in O_2 environments." *Applied Surface Science*, vol. 427, pp. 227-236, Aug. 2017.

[16] Hongcheng Liu, et al. "The adsorption and sensing performances of Ir-modified MoS2 monolayer toward SF_6 decomposition products: a DFT study." *Nanomaterials*, vol. 11.1,pp. 100, Nov. 2011.

[17] Xianyong Pang, et al. "Structure sensitivity of CO oxidation on Co_3O_4: a DFT study." *ChemPhysChem*, vol. 14.1, pp. 204-212, Jan. 2013.

[18] Yue Cao, et al. "Acetone sensing mechanism of PdO-modified hexagonal WO_3 (001) surface: DFT calculations." *Applied Surface Science*, vol. 495, pp. 143532, July. 2019.

[19] Jinzhen Han, et al. "The effect of simultaneous Al-doping and Pt-decoration on the sensitivity of a ZnO nanocluster toward acetone." *Materials Science in Semiconductor Processing*, vol. 121, pp. 105312, July. 2020.

[20] Zhen Zhou, et al. "Energetics and electronic structures of AlN nanotubes/wires and their potential application as ammonia sensors." *Nanotechnology*, vol. 18.42, pp. 424023, May. 2015.

[21] C. J. Liu, et al."Response characteristics of lead phthalocyanine gas sensor: effect of operating temperature and postdeposition annealing."Journal of Vacuum Science & Technology A: Vacuum, Surfaces, and Films, vol.14.3, pp.753-756, May. 1996.