

Methyl Butanoate Adsorption on MoS₂ Surface: A Density Functional Theory Investigation

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Abstract. Methyl butanoate is one of the compound which is obtained from triglyceride molecule. It has hydrocarbon components and hence may produce hydrocarbon through hydrodeoxygenation (HDO) or decarbonylation (DCO) processes. The first step to uncover the underlying mechanism of HDO or DCO is to find the active site of methyl butanoate adsorption over the catalyst. This study attempts to investigate the active site of methyl butanoate adsorption on MoS₂ surface. Stable bonding configuration for methyl butanoate adsorption on MoS₂ is investigated by using density functional theory (DFT). This investigation consists of geometry optimisation and adsorption energy calculations. The stable configuration of methyl butanoate adsorption on MoS₂ surface is found to be on top of Mo atom in Mo-edge surface.

1 Introduction

Hydrotreating is a catalytic hydrogenation process which is aimed to remove the content of sulfur, nitrogen, oxygen and metals [1]. The hydrotreating catalyst consists of at least 2 metals (Mo or W), and (Co or Ni) as promoters.

Molybdenum disulfide (MoS₂) catalysts are well known as catalyst for refinery processes, especially for hydrodesulfurization (HDS) reactions. In HDS catalytic reactions, Mo-based catalyst reduces sulfur-containing compound from the feed stock. In advanced application, MoS₂ with Co / Ni as a promoters is used for production processes of hydrocarbon from feed stock with ultralow sulfur content for transportation fuels [2-7].

HDS process has a negative effect, especially air pollution and acid rain. It also cause the depletion of fossil fuel reserves. The solution for this problem is to find the alternative fuels. One of the alternative is palm oil based biofuel which is produced from organic material.

In order to improve the catalysts, a detailed understanding of the active site of MoS₂ surface and its interactions with typical molecules is a necessity. Experimental and theoretical studies of the catalysts has been done by many scientist [8-18]. Nevertheless, to the best of our knowledge, the catalytic interactions of MoS₂ with methyl butanoate have never been reported before.

Methyl butanoate (C₅O₂H₁₀) is an adsorbate derived from triglyceride (palm oil compound). It can be transformed into hydrocarbon with different cetane number, by hydrodeoxygenation (HDO) and decarbonylation (DCO) reactions. The main problem in hydrotreating process is catalytic activity. The first step to unveil further evidence is to investigate the interaction between methyl butanoate and MoS₂ surface. This study will be a first effort to do so. The density functional theory (DFT) [19], [20] based on ab initio computational method will be used for this purpose.

2 Computational details

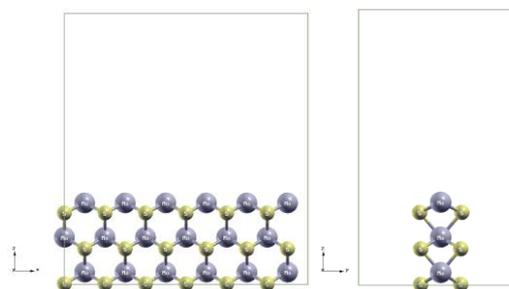


Fig. 1. Mo-edge MoS₂ surface. Mo atom (grey), S atom (gold)

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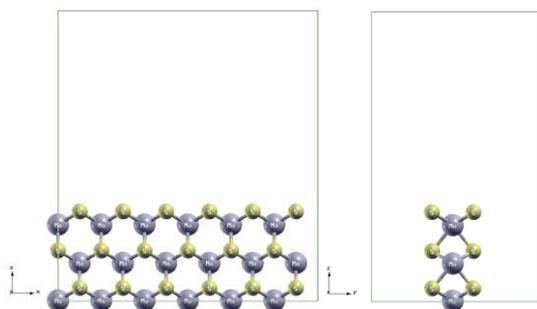


Fig. 2. S-edge MoS₂ surface. Mo atom (grey), S atom (gold)

The calculations are implemented in the open Source Package for Research in Electronic Structure, Simulation and Optimization (Quantum ESPRESSO) [21]. The ultrasoft pseudopotential method is employed to describe the interaction between ion cores and electrons. The electron exchange correlation is treated by a generalized-gradient approximation (GGA) based on Perdew, Burke, and Ernzerhof (PBE) functional [22]. The planewave basis set with a cut-off energy of 500 eV is used for all calculations. Supercell for this study is (18.96 x 12.29 x 21.28) Å³. The Monkhorst-Pack method [23] is used to sample k-point by using 3 x 1 x 1 grid.

Figures 1 and 2 show the structure of MoS₂ surface. We use Mo-edge and S-edge (0001) model from Lauritsen et al [18]. In our model, the surface consists of 54 atoms; namely 18 Mo atoms and 36 S atoms. There are 6 layers in the surface. The difference between M-edge and S-edge is in the top of layer. In Mo-edge, the top of layer consist of Mo atoms, while in S-edge, the top of layer consist of S atoms. To prevent the interaction between molecules and periodicity of the system, we use vacuum space of ~16 Å.

Based on chemical formula, methyl butanoate consists of 17 atoms; namely 5 carbon atoms, 2 oxygen atoms, and 10 hydrogen atoms. Figure 3 shows the methyl butanoate model.

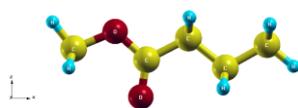


Fig. 3. Methyl butanoate model. C atom (yellow), O atom (red), H atom (light blue)

Interaction between MoS₂ surface and methyl butanoate are displayed in Figures 4 and 5. We choose this adsorption configuration because of the possibility of adsorption of methyl butanoate.

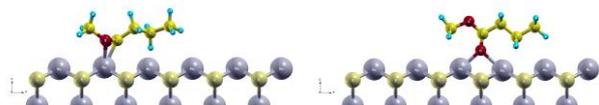


Fig. 4. Methyl butanoate adsorption on Mo-edge MoS₂ surface. Left: Methyl butanoate on the Top of Mo atom. Right: Methyl butanoate on the bridge of two Mo atom.

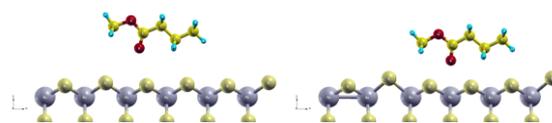


Fig. 5. Methyl butanoate adsorption on S-edge MoS₂ surface. Left: Methyl butanoate on the Top of S atom. Right: Methyl butanoate on the hollow of four S atom.

3 Results and discussion

3.1. Geometry optimisation

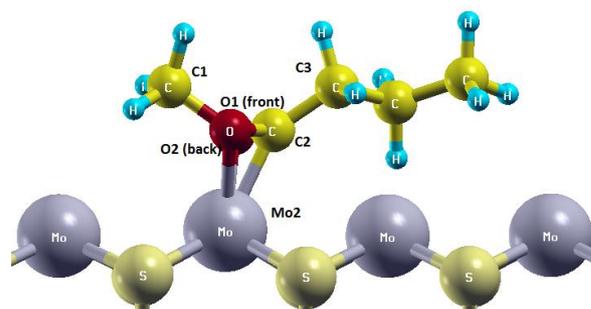


Fig. 6. Final position of methyl butanoate on Mo-edge surface (Top Mo site).

Figure 6 shows the final position of top Mo site. After the interaction with MoS₂ surface, the methyl butanoate molecule structure is slightly changed. In this figure, Mo₂ stands for the second Mo atom on the top of layer. For methyl butanoate, C₁, C₂, C₃ stands for the first, the second and the third C atoms, while O₁ and O₂ stand for the front and the back O atoms respectively.

Table 1. Geometry optimisation of Top Mo site (Mo-edge).

Bonding	Initial distance (Å)	Final distance (Å)	Δr (Å)
C ₁ -O ₁	1.4552	1.4515	-0.0037
C ₂ -O ₂	1.3061	1.2901	-0.0160
C ₂ -C ₃	1.5183	1.5077	-0.0106
O ₁ -Mo ₂	2.4122	2.2460	-0.1662
O ₂ -Mo ₂	2.1942	2.2119	0.0177

Note: (+) bond's weakening

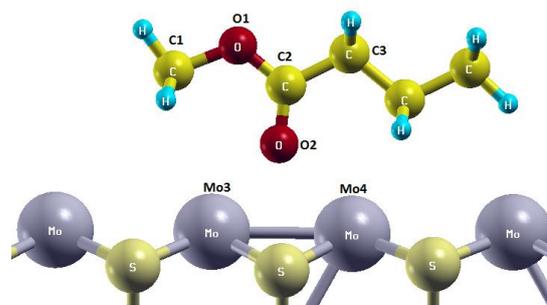


Fig. 7. Final position of methyl butanoate on Mo-edge surface (Bridge Mo site).

Figure 7 shows the final position of bridge Mo site. Similarly after interaction with MoS₂ surface, the methyl butanoate molecule structure is slightly changed. In this figure, methyl butanoate adsorbs in the bridge of two Mo atoms, with label Mo₃ and Mo₄. The position of those two Mo atoms in the top of layer are in the third and fourth place from the left.

Table 2. Geometry optimisation of Bridge Mo site (Mo-edge).

Bonding	Initial distance (Å)	Final distance (Å)	Δr (Å)
C ₁ -O ₁	1.4314	1.4564	0.0250
C ₂ -O ₂	1.2233	1.2537	0.0304
C ₂ -C ₃	1.5117	1.5021	-0.0096
O ₂ -Mo ₃	2.0224	2.3451	0.3227
O ₂ -Mo ₄	2.1731	2.4510	0.2779

Note: (+) bond's weakening

In top Mo site, only O₂-Mo₂ is elongated, indicating bond's weakening while other bonds are shortened after the interaction with the surface as shown in Table 1. Meanwhile, in bridge Mo site, only C₂-C₃ is shortened while other bonds are elongated as observed in Table 2. The O₂-Mo₃ bond length is stretched from previous value of 2.0224 Å to 2.3451 Å, indicating the presence of an active site on the surface and the occurrence of charge transfer or electron flow. Further discussion in the next section will clarify this observation.

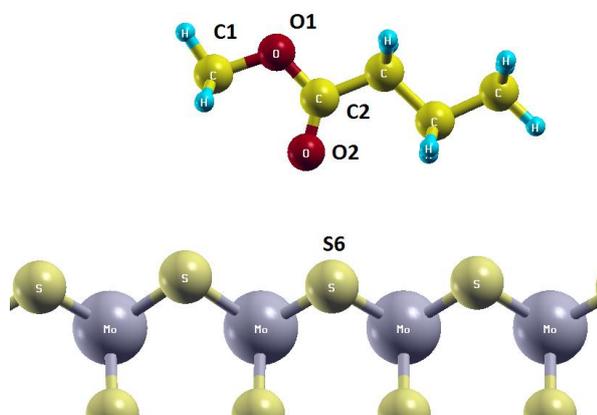


Fig. 8. Final position of methyl butanoate on S-edge surface (Top S site).

Table 3. Geometry optimisation of Top S site (S-edge).

Bonding	Initial distance (Å)	Final distance (Å)	Δr (Å)
C ₁ -O ₁	1.4314	1.4462	0.0148
C ₂ -O ₁	1.3662	1.3626	-0.0036
C ₂ -O ₂	1.2233	1.2156	-0.0077
C ₁ -C ₂	2.3661	1.5094	-0.0023
O ₂ -S ₆	1.7002	3.3458	1.6456

Note: (+) bond's weakening

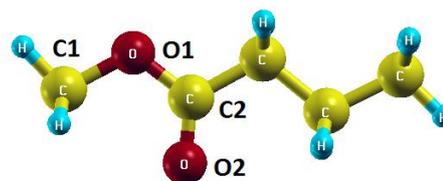


Fig. 9. Final position of methyl butanoate on S-edge surface (Hollow S site).

Table 4. Geometry optimisation of Hollow S site (S-edge).

Bonding	Initial distance (Å)	Final distance (Å)	Δr (Å)
C ₁ -O ₁	1.4314	1.4498	0.0184
C ₂ -O ₁	1.3662	1.3528	-0.0134
C ₂ -O ₂	1.2233	1.2187	-0.0046
C ₁ -C ₂	2.3661	2.3518	-0.0143
O ₂ -Mo ₄	2.0941	2.8486	0.7545

Note: (+) bond's weakening

Figure 8 and 9 shows the final position of methyl butanoate adsorption on S-edge surface. After the interaction with S-edge surface, methyl butanoate molecule away from the surface. There are no bond between the methyl butanoate and surface. With oxygen atom as a reference, we can measure atomic distance between O atom in methyl butanoate with sulphur atom in surface. For Top S site, the distance between O atom and S atom is around 1.64 Å, while in hollow site, the distance between O atom and S atom is around 0.75 Å.

3.2. Adsorption Energy

Adsorption energies are computed by optimized gas-phase methyl butanoate, optimized MoS₂ surface and optimized MoS₂/methyl butanoate according to:

$$E_{\text{ads}} = E_{\text{MoS}_2/\text{methyl butanoate}} - (E_{\text{MoS}_2} + E_{\text{methyl butanoate}}) \quad (1)$$

E_{ads} = adsorption energy, $E_{\text{MoS}_2/\text{methyl butanoate}}$ = total energy of methyl butanoate on MoS₂ surface, E_{MoS_2} = total energy of MoS₂ surface and $E_{\text{methyl butanoate}}$ = total energy of isolated methyl butanoate.

Table 5. Adsorption energies of methyl butanoate on MoS₂.

Surface	Site	Adsorption energy (eV)
Mo-edge	Top Mo	-2.79
	Bridge Mo	-1.29
S-edge	Top S	-0.31
	Hollow S	-0.47

From our calculations for Mo-edge surface, methyl butanoate prefer to adsorb in Top Mo. The adsorption energy on top Mo site is 2.79 eV, while in bridge Mo site is 1.29 eV. For S-edge surface, methyl butanoate prefer to adsorb in hollow site, with the adsorption energy in this site is -0.47 eV.

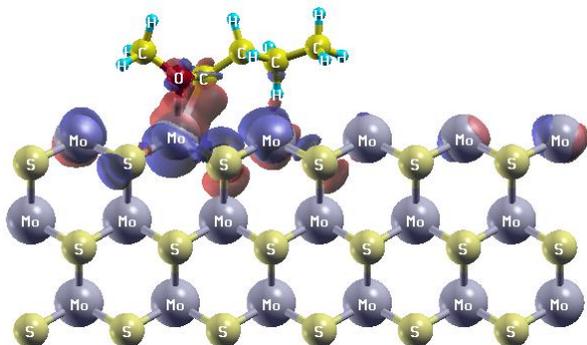


Fig. 10. Charge density difference at top Mo site. Red: charge accumulation. Blue: charge depletion. Isosurface = 0.01

Table 6. Charge density in specific atom at top Mo site

Atom	Initial Charge (e)	Final Charge (e)	Charge Difference (e)
O ₁	4.6658	4.6961	0.0303
C ₂	2.5539	2.6950	0.1411
Mo ₂	6.7726	6.8713	0.0987
Mo ₃	6.7725	6.8864	0.1139

Note: (-) transfer electron, (+) receive electron.

In Figure 10, the charge density concentrated near the bonding of Mo₂-O₂ and Mo₃-C₂. There are electron charge accumulation at that site, represent by red contour. There is an accumulation of charge between O₁-Mo₂ atoms. This indicates the presence of bonding between methyl butanoate molecules with Mo atom from MoS₂ surface. Methyl butanoate transfer charge around 0.04e to the surface. This is facilitated by the interaction of d orbitals from the surface with p orbitals of the methyl butanoate molecule.

Table 7. Charge density in specific atom at bridge Mo site

Atom	Initial Charge (e)	Final Charge (e)	Charge Difference (e)
O ₂	4.7139	4.7046	-0.0093
Mo ₃	6.7725	6.8580	0.0855
Mo ₄	6.7725	6.8480	0.0755

Note: (-) transfer electron, (+) receive electron.

Figure 11 shows the electron charge density of bridge Mo site. In this case, we can't see the red contour near surface and methyl butanoate. This indicates that the bonding between methyl butanoate and MoS₂ surface at this site are weaker than that at top Mo site. These results are consistent with Table 7.

Figures 12 and 13 show the electron charge density of top S site and hollow S site. Both of them show that

there are no bonding between methyl butanoate and surface. There is no significant difference for the charge density between before and after adsorption.

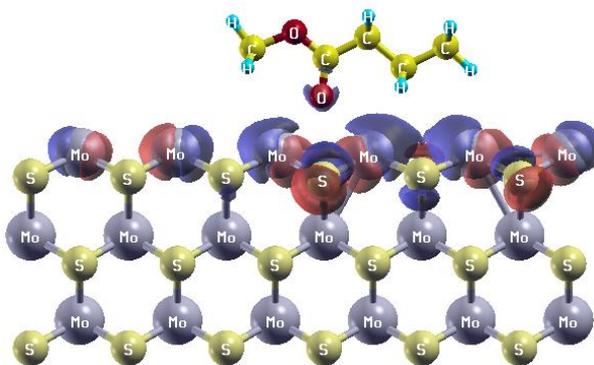


Fig. 11. Charge density difference at bridge Mo site. Red: charge accumulation. Blue: charge depletion. Isosurface = 0.01

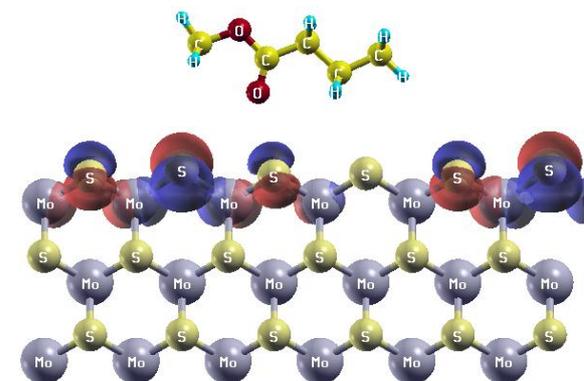


Fig. 12. Charge density difference at top S site. Red: charge accumulation. Blue: charge depletion. Isosurface = 0.01

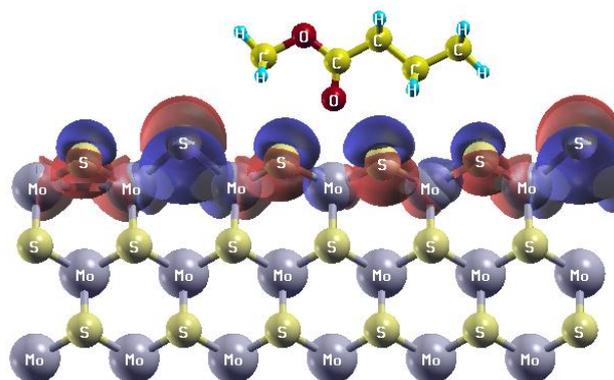


Fig. 13. Charge density difference at hollow S site. Red: charge accumulation. Blue: charge depletion. Isosurface = 0.01

4 Conclusion

Methyl butanoate prefers to adsorb on top Mo site, with the adsorption energy is around -2.79 eV. In this site, methyl butanoate forms a bond with the surface, and yields some shortened chemical bonds. Charge density plots show that there are some charge accumulations around Mo₂ of the surface, and at the vicinity of O₁ and C₂ of the methyl butanoate. At bridge site, charge density

plots show that there is charge depletion between atom Mo₃ and atom O₂. Although it has charge depletion between molecule and surface, but there are no bond's formed between the molecule and the surface. The adsorption energy in this site is around -1.29 eV. This value does not only correspond to charge density, but also corresponds to Coulombic interaction between atom O₂ and atom Mo₃. For S-edge surface, the presence of S atoms on the top of layer make the molecule away from the surface because of the Coulombic interaction between S atom and O₂ atom.

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