Adsorption of fatty acid and methanol via calcium sulfate-based catalyst using a density functional theory approach

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Abstract. This paper reports the molecular simulation of catalytic adsorption of the model compounds (simulated fatty acid and methanol) via the density functional theory (DFT) approach. The catalyst was prepared from an improved clean wet process using phosphorous rock as the raw materials. The adsorptions of the model compounds on the catalyst were simulated. The associated energies during adsorption were calculated. The proposed the detailed simulation offers great details of molecular adsorptions of the model compounds on the created crystallite lattice surface during adsorption.

1. Introduction

Ever since the announcement made by President Xi Jingping at the United Nations General Assembly in September 2020 [1], China has started to implement actions to significantly reduce CO₂ emissions before 2030 and realistically approach carbon neutrality prior to 2060 [2-5]. This means that the significant reduction in all industrial sector especially in manufacturing and energy production and consumption [6, 7]. The artificial ecological circulation economical paradigm of material recycling and energy cascade utilization re-emerge into horizon of both industry and academy under this new circumstance [8, 9]. In regard to material recycling and utilization, more focus should be on finding the utilizations of waste or high-value conversion of waste. To align with this, we recently developed an enhanced process for producing crystallite gypsum with less impurities and convert this by-product into a high-performance trans-esterification catalyst [10, 11]. By doing this, not only do we achieve the material recycling and high value conversion, but also find out a big opportunity for the renewable energy production such as for biodiesel preparation in a much more economical approach comparing that with the conventional catalytic processes such as using caustic soda or strong acid [12]. The reaction process normally involves with both transport and kinetics. Depending on which process is rate determining step (RDS), the process could be simplified by ignoring the process which occurs much faster than the other. For transesterification reaction, it is found that the transport normally plays quite important role in the entire process, especially when the chain length of the compounds is larger. As the long chain fatty acid playing a vital role over the entire process during the trans-esterification reaction,
the associated energies such as adsorption, transform energies etc., are critical in the subsequent intermediate reaction pathways, especially when the chain length of the compounds are larger. In addition, the in depth understanding of transport process, namely adsorption process, is also paramount to the reactor sizing [13]. The merit of using molecular simulation lies in its great advantages of presenting the possible and potential details of adsorptions on the surface of the catalyst, which will shed great information for the guidance of constructing the elementary kinetics. However, efforts of using molecular simulation through density functional theory to simulate the adsorption process using the catalyst that prepared from the above mentioned green process, to the best of authors’ knowledge, are still very limited, therefore, this initiates the reports of this work.

2. Experimental

2.1 Experimental
The catalyst was prepared through our recent reported clean process [14]. Through this process, the phosphate recovery can achieve over 95%, the prepared catalyst contained over 95% CaSO$_4$.2H$_2$O with some minor impurities. In this work, the catalyst was further calcined at 105 ºC for 20 minutes in fluidized bed. After oven dry at 100 ºC overnight, the crystallite phase of catalyst was characterized by the X-ray diffractometer (XRD), the surface characterization was conducted using ZEISS Sigma300 VP (UK), the element mapping was conducted using EDS. The detailed characterization result is shown in Figure 1.

![Figure 1](image_url)

**Figure 1.** Characterization of the prepared catalyst, a) SEM-EDS mapping, b) XRD spectrum.

From EDS mapping, the prepared catalyst was predominant with the main elements Ca, O and S. The SEM morphological characterization indicates that the prepared catalyst possesses a relative smooth surface with flaky shape. It is suggested that the morphology of the prepared catalyst is closely associated with the type of precursors and the way of precipitation and crystallization. XRD characterization shows that three strong peaks corresponding to 020, 121 and 141 planes. The small
broad and scattering peaks in the XRD spectra suggests the existence of crystallite impurities in the prepared catalyst.

2.2 DFT theory and calculation

As ionic sulfate groups are one of the most pivotal ionic functional groups that participating the transesterification reaction, the corresponding energies associated with adsorption on the crystallite 002 plane was calculated using DFT approach. In order to significantly reduce computational time used for simulation, the plane has been carefully chosen for adsorption simulation. In addition, the model fatty acid with carbon chain of 25 were used for fatty acid adsorption simulation, of which the general fatty acid chain length is approximate in 25. To build the crystal lattice, the corresponding crystallite structures are built and shown in Figure 2.

![Figure 2](https://example.com/figure2.png)

**Figure 2.** Crystallite structure of 020 plane catalyst, where the red ball refers to oxygen, white ball refers to hydrogen, yellow ball refers to sulfur, and green calcium.

The geometry optimization task parameters are summarized in the Table 1. With these theoretical setting, the XRD profile using DFT approach is calculated, and result is shown in Figure 3.

| Parameters                  | Values  |
|-----------------------------|---------|
| Energy convergence          | 2e-5    |
| Gradient convergence        | 4e-3 Å  |
| Displacement convergence    | 5e-3 Å  |
| Itteration                  | 100     |
| Max displacement            | 0.3 Å   |
| Density convergence         | 1e-5    |
| Charge mixing               | 2e-1    |

**Table 1.** Theoretical calculations of adsorption.
Figure 3. Simulated XRD profile using DFT approach for crystallite catalyst, where 020 refers to crystallite plane.

By comparing this simulated XRD profile with the XRD characterization (Figure 1b), the 020 plane is quite closely located at around 12 degrees indicating the constructed crystallite lattice could representative for catalyst adsorption process, although some differences do exist between simulated and experimental profile of the catalyst (CaSO$_4$.2H$_2$O). In this paper, to achieve stable structures, the energy of the structures were minimized. Prior to simulation, the geometry optimization was conducted to achieve the minimum energy structures. The annealing approach was employed during adsorption simulation. In this annealing approach, the local minimum will begin from the previous runs. Then the system will be heated up and the broader region around this local minimum region were explored. Afterwards, the investigated system will be repeated with the same approach to obtain the minimum energy once the temperature decreases [15].

3. Results and discussion
The Figure 4 is the simulation of adsorption of fatty acid and methanol by the constructed crystallite catalyst (002 plane). Clearly, with different locations, the model compounds present with different configurations in the space. The detailed adsorption energies with these four different configurations are shown in Figure 5. At the configuration 1, the total energy locates around -3 kJ/mol. In this configuration, the functional groups of the model compounds of fatty acid (ketone and hydroxyl groups) and methanol are closely facing each other, more importantly, these active functional groups are all facing towards the active surface of the catalyst gypsum. This is obvious for sulphate group of catalyst. By comparing among the depicted four configurations, the chance of occurring the transesterifications for the first configuration might be appreciably higher than the rest of three configurations, at least from physical distance perspective. This suggests that the configurations with relative larger total energies will tend to create the configurations of molecules that will approach the surface of active catalytic site with all potential active functional groups facing close to each other. In fact, without DFT simulation, it is quite challenging to figure out detailed adsorption process. Large numbers of reactions tend to follow the elementary reaction pathways that Michaelis-Menten reaction pattern describes, therefore, the reaction pathways are often potentially determined by the state of formed active intermediates [16]. Clearly, different adsorption configurations of model compounds that constructed during adsorption will lead to the proximity energy before catalytic reactions [17].
Figure 4. The 020 crystallite lattice adsorption simulation of model compounds (methanol and model fatty acid-carbon number=25).

Figure 5. The calculated total energies that associated with adsorption at different configuration.
Apart from total energy, other adsorption energies such as the adsorption, rigid and deformation energies are calculated and summarized as the following (Table 2 and Table 3):

**Table 2.** Theoretical calculations of associated energies during adsorption.

| Configuration types/- | Total/kJ.mol⁻¹ | Adsorption/ kJ.mol⁻¹ |
|-----------------------|----------------|---------------------|
| 1                     | -3.0828        | -32.4771            |
| 2                     | -2.8137        | -32.2079            |
| 3                     | -2.0695        | -31.4638            |
| 4                     | -1.2037        | -30.5980            |
| 5                     | -0.8775        | -30.2717            |
| 6                     | -0.6554        | -30.0497            |
| 7                     | -0.3014        | -29.6957            |
| 8                     | 0.0613         | -29.3330            |
| 9                     | 0.3444         | -29.0498            |
| 10                    | 0.5939         | -28.8004            |

**Table 3.** Theoretical calculations of associated energies during adsorption.

| Configuration types/- | Rigid /kJ.mol⁻¹ | Deformation/ kJ.mol⁻¹ |
|-----------------------|-----------------|-----------------------|
| 1                     | -30.7094        | -1.7677               |
| 2                     | -30.5901        | -1.6178               |
| 3                     | -29.9576        | -1.5061               |
| 4                     | -31.3443        | 0.7463                |
| 5                     | -30.7675        | 0.4957                |
| 6                     | -30.5229        | 0.4732                |
| 7                     | -30.2889        | 0.5932                |
| 8                     | -29.7922        | 0.4593                |
| 9                     | -29.9013        | 0.8515                |
| 10                    | -29.4723        | 0.6720                |

From theoretical calculation, one can determine different scenarios for model compounds adsorption, which will provide very insightful understanding about detailed mechanism during adsorption. As adsorption is the very critical step for transport prior reaction, the proposed DFT approach provides very useful tool for in-depth investigation of catalytic reactions for transesterification reaction such as biodiesel synthesis.

### 4. Conclusions

This paper proposed a DFT approach for insightful understanding the adsorption of fatty acid and methanol on the surface of catalyst. The prepared new catalyst was synthesized from a recently developed clean wet process using phosphorous rock as the raw materials. The energies (total,
adsorption, rigid and deformation) associated were calculated as the following: 0.59 to -3.08 (kJ.mol⁻¹), -32 to -28 (kJ.mol⁻¹), -30 to -29 (kJ.mol⁻¹), and 0.76 to -1.76 (kJ.mol⁻¹), respectively. The proposed the detailed simulation offers great details of potential configurations of the model compounds in the surface of catalyst during adsorption.

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