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Full Length Article

Promoted effect of cobalt on surface (0 1 0) of MoS_2 for CO methanation from a DFT study

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ABSTRACT

In light of the good performance of Mo-based catalysts for sulfur-resistant CO methanation, we investigated the reaction mechanism over pure MoS_2 in a previous study, in which the Mo-edge from (0 1 0) surface of MoS_2 was found inactive due to the difficulty in S-vacancy creation. It was generally recognized that Co is a good additive on Mo-based catalyst for CO methanation. Thus, we focused on promoting the Mo-edge by presenting a group of cobalt substituted surface models via DFT simulation. These models were all reconstructed by performing a thermodynamic investigation on the numbers of the created S-vacancies according to the reaction condition of CO methanation from experimental data. Based on the discussion of reaction pathways over four determined surfaces, we found that a substitute ratio of 0.25 and 0.50 in ortho-position can exhibit the highest catalytic activities, but a substitute ratio of 0.50 in meta-position exhibits the optimum stability in the overall reaction.

1. Introduction

The sulfur resistant nature of MoS_2 makes itself a notable catalyst active component in the direct methanation of syngas (a mixture of CO and H_2), which contributes to producing substitute natural gas (SNG) to meet the year by year increased demand for natural gas.

To exhibit the activity of MoS_2 moieties, the number of S-vacancies is a very important measurable indicator. According to Nørskov et al. [1], an S-vacancy is to remove one S atom to exposure the metal (i.e. Mo atom) sites for chemisorption of CO molecule and dissociated H_2. Furthermore, the possibility of S-vacancy formation has a close connection with the binding energy of S atom to the surface metal atoms of MoS_2 moieties.

Generally, S-vacancies are more likely created on edge surfaces of MoS_2 than the basal plane ((0 0 1) cleaved surface), for that the edge surfaces are terminated with unsaturated atoms but the surface atoms into basal plane are fully coordinated with stability. Through our previous study [2], the reaction mechanism of CO methanation based on different unsaturated edge surfaces had been fully discussed. These surfaces had been reconstructed beforehand by considering the basic reaction conditions such as the atmosphere and the temperature. The simulated results from reconstructed (0 1 0) and (1 1 0) surfaces were compared, which shows that the Mo edge of (0 1 0) surface has the least favorable promoted effect on CO methanation for the reason most partly from the hardness of the S-vacancy formation.

The transition metal elements had been proposed to have possibilities to possess promoted effect on Mo—S phase for their lower binding energies with S atom, according to Byskov et al. [3] Moreover, among them, Fe, Co and Ni could have more significant performances when incorporated in the original MoS_2 moieties. The discussions were firstly took and then widely cited for hydrodesulfurization (HDS) reaction [4].

In Byskov et al.'s studies, by using the Newns Anderson model, these three transition metal elements (Fe, Co, Ni) as promoted assistant respectively were discussed. The presence of transition metal atom is a replacement of surface exposure Mo atom in the unsaturated edge surface of MoS_2. Their results showed that S-vacancy is still hard to be created in Fe—Mo—S phase, because the anti-bond in incorporated Fe atom is crossing the fermi level and then obtains higher binding energy for Fe—S bond than that in Co and Ni.

In the later studies, Travert et al. [5] had a further discussion on comparing promoted effects of Co and Ni. They had pointed out that the Ni—S bond is too much weaker to active the H_2. Whereas to produce single H atom with one free electron by activating H_2 is definitely a very important step for CO methanation.

Co—Mo—S phase was firstly proposed by Topsøe et al. [6], and since then Co incorporated significantly promoting both creating S-vacancies and catalytic activity of Co—S phase were confirmed by Duchet et al. [7] and Vissers et al. [8] in successive.

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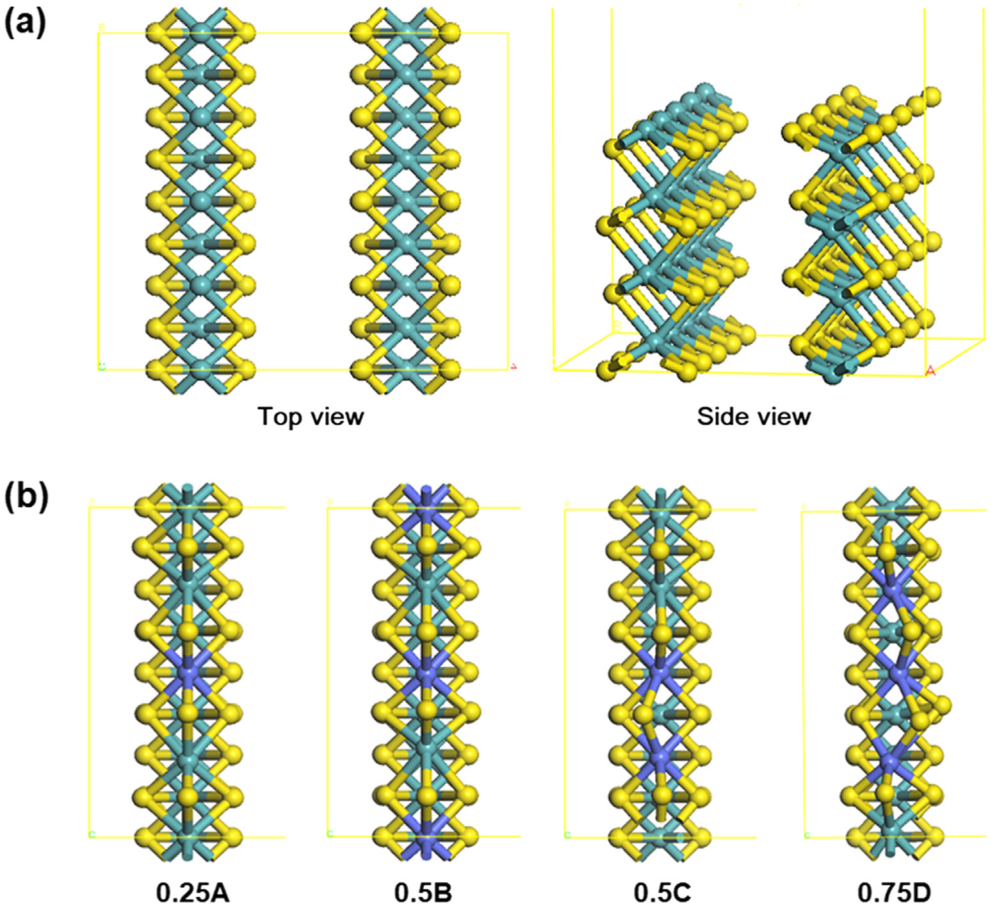

Fig. 1. (a) The original pure MoS_2 model of the cleaved (0 1 0) surface. (b) The primarily reconstructed surface structures of Mo edge by different Co atom substituted ratios and arrangements; The number of 0.25–0.75 is the relative ratio of Co atoms compared to surface Mo atoms (blue = Mo, yellow = S, purple = Co). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

The periodical model of MoS_2 in DFT (density function theory) study was initially constructed by Byskov et al. [9], by replacing the target Mo with Co atom, the advantage of the substituted model was revealed. Lately, Travert et al. [5] investigated the number of S-vacancies in variety of substituted surfaces from different substituted ratio by employing the method in Cristol et al.'s studies [10,11]. Additionally, Raybaud et al. [12,13] and Travert et al. [5] had revealed that surface Mo atoms on Mo edge is more likely to be replaced by Co than that on S edge. It is proved that to promote the Mo edge is both feasible and valuable. Thus, we focus our work on promoting the Mo edge of (0 1 0) MoS_2 surface with the aforementioned proofs as bases in this study. A methanation condition of atmosphere and temperature is to be considered for redistributing the ratio of the surface S atoms based on substituted models by different ratio and arrangement of incorporated Co atoms. Then the reaction mechanism will be investigated by DFT simulations.

2. Computational methods

For the calculations carried out herein, CASTEP [14,15] module implemented in the Materials Studio 6.1 software (Accelrys Software, Inc.), and the gradient-corrected periodic DFT method was employed [16]. All major calculations, including geometry optimization and transition state (TS) searches, were carried out utilizing the CASTEP module with a plane-wave basis set. In addition, all calculations were performed using the generalized gradient approximation and the Perdew-Burke-Ernzerhof exchange correlation functional [17]. A cut-off energy of 340 eV and a Vanderbilt ultrasoft pseudopotential [18] were adopted to describe the core electrons and nuclei of the atoms within the structures [19]. During geometry optimization, electronic energy minimization was performed using the Pulay density mixing scheme [20].

The convergence criteria of self-consistent field tolerance, energy tolerance, maximum displacement tolerance, and maximum force tolerance for geometry optimization were set as 5.0×10^{-7} eV/atom, 5.0×10^{-6} eV/atom, 5.0×10^{-4} Å, and 0.01 eV/Å, respectively. TS searches were performed using the complete LST/QST [21] search protocol, with the RMS force convergence, self-consistent field tolerance, and smearing set as 0.1 eV/Å, 1.0×10^{-6} eV/atom, and 0.1 eV, respectively. The k-points in the CASTEP checkbox were set at $1 \times 1 \times 1$ through a convergence test. On account of the magnetic property of Co element, the spin polarization was checked during the whole calculation jobs.

The model was built to a size of $1 \times 4 \times 4$ (Fig. 3, vacuum slab not contained) with two relaxed upper units along the z-axis. Testing was carried out based on the surface energies of different cleaved surface sizes, and the adsorption energies of the reactants and products on differently sized cleaved surfaces.

3. Results and discussion

3.1. Periodic model and thermodynamic investigation

Being employed from our previous studies, the basic model in this study was a periodic model created using the primitive cell of 2H structurep [22]. For that Ab initio quantum chemistry approaches (in another word, the first principles methods [16]) are best for characterizing the large unit of hexagonal MoS_2, the periodic model we used which contains only one hundred atoms approximately, has a good performance in DFT simulation.

Based on the pure MoS_2 periodic model, the bare surface Mo atoms on the Mo edge can be easily substituted by Co atoms in different ratios