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Influence of sulfur vacancy on thiophene hydrodesulfurization mechanism at different MoS_2 edges: A DFT study

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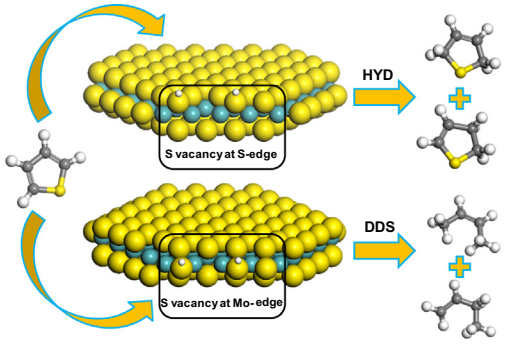
HIGHLIGHTS

- The formations of sulfur vacancy at different MoS_2 edges were studied.
- The influence of sulfur vacancy on DDS and HYD pathways was investigated.
- The interaction energies were assessed by dispersion corrected methods (DFT + D).
- Sulfur vacancy at Mo-edge was favored to DDS pathway with lower reaction barriers.
- A detailed reaction network of thiophene HDS was proposed.

GRAPHICAL ABSTRACT



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ABSTRACT

The detailed hydrogenation (HYD) and direct desulfurization (DDS) pathways of thiophene over the sulfur vacancy of different MoS_2 edge structures were investigated by density functional theory (DFT) calculations. The interaction energies were evaluated by dispersion corrected methods (DFT + D). Innovatively, a detailed thiophene hydrodesulfurization (HDS) reaction network over the sulfur vacancy was proposed, involving most of products which could be detected in the experiments. Taking the influence of sulfur vacancy into consideration, it could be found that the sulfur vacancy at Mo-edge was more beneficial for the formation of intermediates and products contained in DDS pathway by comparing the reaction barriers of DDS and HYD pathways. The HYD reaction pathway, which involved hydrogenation to 2-hydrothiophene followed by hydrogenation to 2,3-dihydrothiophene and 2,5-dihydrothiophene, could proceed with a mild reaction barrier at the S-edge with the creation of sulfur vacancy. The results also showed that butane could be formed at both S and Mo edges with relatively high reaction barriers of 52.60 kcal/mol (Mo-edge, DDS), 53.99 kcal/mol (S-edge, DDS) and 58.07 kcal/mol (Mo-edge, HYD), however, the formations of 1-butene and 2-butene were much more favored with energy barriers of 33.45 kcal/mol (S-edge HYD) and 35.20 kcal/mol (Mo-edge DDS), respectively. These results demonstrated that the sulfur vacancy at the different edges of MoS_2 catalysts had a great impact on the overall HDS reaction routes. Based on the systematic calculations, the contribution of sulfur vacancy to the formation of certain intermediates and products was clearly orientated, which provided theoretical guidance for designing highly active catalysts for HDS technology.

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1. Introduction

As the global energy consumption rapidly increases, the environmental regulations have been tightened in many countries to reduce the sulfur contents of transportation fuels to a ultra low level (≤10 ppm) (Knudsen et al., 1999; Turaga and Song, 2003; Stanislaus et al., 2010). As the most effective method in large-scale for the low-sulfur gasoline production, hydrofining technology is still widely utilized by many refineries though adjusting the operation conditions and developing highly efficient hydrodesulfurization (HDS) catalysts, wherein the exploitation of novel catalysts is one of the important focuses to realize the upgrading of the desulfurization technologies. For example, excellent HDS performance could be achieved by synthesizing novel supports (Cao et al., 2014; Gao et al., 2015a, 2015b; Klimova et al., 2008), addition of chelating agents (Wu et al., 2014; Castillo-Villalón et al., 2014), and utilization of new active metals (Infantes-Molina et al., 2013; Zhang et al., 2016). Researches on the HDS mechanism could help us to well understand the HDS catalysis processes, then to assist the improvement of catalysts. Based on the current studies, two basic HDS reaction routes have been identified for the removal of sulfur: hydrogenation (HYD) followed by sulfur removal and direct desulfurization (DDS) (Weber and Veen, 2008). Most of experimental studies together showed that: (a) S-containing compounds such as thiophene (T), benzothiophene (BT) and dibenzothiophene (DBT) were hydrodesulfurized mainly through the DDS route, (b) 4,6-DMDBT (with large molecular size and steric hindrance from the alkyl substituents) preferred the HYD pathway in HDS (Cristol et al., 2004). Despite numerous experimental researches (Schweiger et al., 2002; Toulhoat et al., 1999; Raybaud, 2007; Krebs et al., 2008; Kogan et al., 2012; Rangarajan and Mavrikakis, 2015, 2016) on the HDS mechanism, it has, however, not been possible to resolve a number of fundamental issues due to the existing limitations and difficulties in the characterization, for instance, some intermediates of HDS and the structures of active sites are difficult to be determined. For these reasons, the mechanism of the DDS and HYD pathway is still being disputed.

In addition, it has been recognized that the most widely-used industrial HDS catalysts are composed of TMS (Transition Metal Sulfides) and the catalytically active sites in the HDS processes located on the surface of the active MoS_2 or Co (Ni)-promoted MoS_2. In order to provide theoretical guidance for designing highly active catalysts for HDS technology, therefore, this kind of active sites has been widely studied by DFT calculations (Moses et al., 2009; Lauritsen and Besenbacher, 2015; Rangarajan and Mavrikakis, 2016, 2017). Based on the previous studies, the activation of edges and C—S bond scission required the formation of sulfur vacancy. For example, by atom-resolved scanning tunneling microscopy (STM), Tuxen et al. found that DBT molecule could adsorb directly through its sulfur atom at sulfur vacancies (Tuxen et al., 2012). In addition, Lauritsen et al. also revealed that sulfur vacancies on the edges played an important role in the interactions between sulfur-containing compounds and the surfaces of catalysts (Lauritsen and Besenbacher, 2015). By DFT calculations, Rangarajan et al. studied the adsorption of nitrogen- and sulfur-containing compounds on the sulfur vacancy of the edges (Rangarajan and Mavrikakis, 2016). Considerable researches have shown that the existence of sulfur vacancy at the edges can affect the adsorption behavior of sulfur compounds.

Therefore, density functional theory (DFT), as a useful approach has been extensive applied to investigate HDS mechanism, such as the hydrogen activation on Mo-based sulfide catalysts, the adsorption modes of thiophene on the MoS_2 edges, and C—S bond breaking of thiophene through their interaction with the metal sulfide catalyst surfaces. Sun et al. studied the formation and stable structures of surface hydrogen species on unpromoted and nickel-promoted MoS_2 catalyst surfaces by investigating the adsorption and dissociation of molecular hydrogen and hydrogen sulfide (Sun et al., 2005). Prodhomme et al. also investigated a series of various reaction pathways for H_2S and H_2 dissociative adsorption and associative desorption, as well as various hydrogen diffusion processes occurring at both 50% coverage of MoS_2 Mo-edge and 100% coverage of S-edge (Prodhomme et al., 2011). These researches provided a lot of information on the thermodynamic stability and activation pathways of hydrogen on MoS_2 edges and some new insights of the surface chemical species: sulfur vacancies, sulfur dimers and S—H group, etc. Among these surface species, as the initial active sites sulfur vacancies were speculated to be involved in the elementary steps of HDS reactions. However, the formation of sulfur vacancies and its function to the HDS reactions are still controversial.

Therefore, some theoretical and microscopy researches had been performed to study the influence of the sulfur vacancies on the adsorption modes of S-containing compounds. Cristol et al. studied the thiophene adsorption on different edges of MoS_2 by the DFT calculations, in their research, both η^1 and η^5 adsorption energies on the vacancies were calculated (Cristol et al., 2006). From the observation by Lauritsen et al., η^5 adsorption geometry could occur at fully saturated edges due to the special electronic environment, but an η^1 binding of thiophene to a vacancy might be represented (Lauritsen et al., 2004). Recently, Lauritsen et al. found that the interaction of thiophene with sulfur vacancies might participate in the complete desulfurization of thiophene under HDS conditions (Lauritsen and Besenbacher, 2015). Therefore, it could be concluded that the sulfur vacancy had a certain effect on the catalytic activity, offering chemisorption sites to the sulfur-containing compounds and lowering the activation barrier of the HDS reaction. However, few computational chemistry studies focused on the influence of the sulfur vacancy on the HDS mechanism.

Based on the previous studies, it was shown that the sulfur vacancy had influences on the adsorption configurations of the S-containing compounds, therefore, its effects on the HDS mechanism still need to be studied in detail. Moses et al. presented the DFT calculations of the reaction pathways for both of HYD and DDS routes in the HDS of thiophene over different MoS_2 edge structures. In this report, the C—S bond scission, could occur at the equilibrium Mo(10−10) edge without the creation of sulfur vacancies, but they found that sulfur vacancies at the S(−1010) edge were active sites for the DDS and HYD pathways (Moses et al., 2007). In another report, Moses et al. studied the thiophene HDS mechanism over the cobalt-promoted MoS_2, they found that the Co—Mo—S equilibrium structure contained sulfur vacancies, promoting an increase in the hydrogenation activity and also of the relative importance of the DDS pathway (Moses et al., 2009). In short, sulfur vacancies affected the barrier of hydrogenation reactions and the C—S bond scission reactions. Based on experimental studies of the thiophene HDS reactions by Wang et al., it was evidenced that the products of the thiophene HDS reactions were relatively complex, including butadiene, butane and other intermediates (Wang and Iglesia, 2010). However, a systematic understanding of the thiophene HDS mechanism on the various possible edges of MoS_2 active phase with the sulfur vacancies has not been reported. The researches on the sulfur vacancies will refresh our understanding of the structure of active sites, providing better explanations of desulfurization products analysis and an important direction for the design of highly active HDS catalysts.

In this paper, the formation of the sulfur vacancy over the different MoS_2 edges and the detailed HYD and DDS processes of