Journal of Catalysis 358 (2018) 131–140

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Modeling the adsorption of sulfur containing molecules and their hydrodesulfurization intermediates on the Co-promoted MoS_2 catalyst by DFT

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ARTICLE INFO

Article history:
Received 16 August 2017
Revised 30 November 2017
Accepted 2 December 2017

Keywords:
Hydrodesulfurization
Hydrogenation
Catalysis
Methylthiol
Thiophene
Dibenzothiophene
4,6-Dimethyldibenzothiophene
CoMoS
Adsorption
DFT

ABSTRACT

Achieving ultra-deep hydrodesulfurization means enabling removal of the last fractions of sulfur, contained in refractory molecules, from oil. Improving the state-of-the-art Co-promoted MoS_2 (CoMoS) catalyst or the development of novel catalysts is crucial for this. Improving CoMoS requires more insight in the way sulfur containing molecules interact with it. Herein, we model the adsorption of sulfur containing molecules on the S-edge, M-edge, corner and basal plane of CoMoS using density functional theory. The obtained adsorption configurations and energies point to a preference towards physisorption at the S-edge and chemisorption in vacancies at the M-edge and corner. Smaller molecules, such as thiophene and methylthiol, were found to prefer vacancies when adsorbing while larger, sterically hindered molecules as 4,6-dimethyldibenzothiophene prefer physisorption on the brim of the edges or the basal plane through van der Waals interactions. Hydrogenation generally leads to a preference towards adsorption at vacancies for thiophene and dibenzothiophene while for 4,6-dimethyldibenzothiophene hydrogenation leads to preferential adsorption on the S-edge brim, possibly explaining why 4,6-dimethyldibenzothiophene does not get desulfurized directly but follows a hydrogenation route. Thiolate formation energies were also calculated for the different molecules and used to predict which sites are most likely to be involved in breaking carbon-sulfur bonds. The thiolate formation energies show the inert nature of the basal plane towards breaking carbon-sulfur and sulfur-hydrogen bonds. Additionally, activation energies for thiophene and dibenzothiophene carbon-sulfur bond scission indicate that both molecules follow the direct desulfurization route on under-coordinated sites or vacancies.

1. Introduction

Hydrodesulfurization (HDS) is performed in refineries in order to reduce sulfur contents of oil prior to its distribution [1–3]. Reducing sulfur contents of oil decreases SO_2 emissions upon combustion. SO_2 emissions are associated with the formation of acid rain and decreasing air quality, due to this there are regulations that limit SO_2 emissions and sulfur contents of fuels. These regulations are getting stricter with time, causing a need for new or further improvement of current state-of-the-art HDS catalysts [4–6].

The cobalt promoted MoS_2 hydrodesulfurization catalyst (CoMoS) has been the topic of many studies in the past decade. These studies have uncovered several structural aspects such as hexagonal particle shape, position of cobalt promoters, edge and corner sulfur coverage, metallic character of edges, sulfur vacancy formation energies [7–21]. Furthermore, a number of studies address adsorption of various sulfur and nitrogen containing molecules representing oil feeds in HDS. These studies gave insight on how different molecules interact with CoMoS, addressing issues of surface poisoning as well as suggesting mechanisms and reaction pathways that these molecules follow during HDS [22–24,10,25–29].

HDS can be described with the following equation:

$$R - SH + H_2 \leftrightarrow R - H + H_2S \qquad (1)$$

Abbreviations: HDS, hydrodesulfurization; CoMoS, Co-promoted MoS_2; DFT, density functional theory; DDS, direct desulfurization; HYD, hydrogenation; DBT, dibenzothiophene; 4,6-DMDBT, 4,6-dimethyldibenzothiophene.

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https://doi.org/10.1016/j.jcat.2017.12.001
0021-9517/

Here, R represents the main body of an organic molecule [1–3]. Although Eq. (1) seems very simple, the mechanism of HDS can get very involved and its complexity increases with the complexity of the molecule that is being desulfurized. Two pathways for hydrodesulfurization have been identified and reported in the literature, the direct desulfurization (DDS) and hydrogenation (HYD) pathways [22,23,12]. In DDS, the molecule is desulfurized directly, using the least amount of hydrogen necessary to break the carbon-sulfur (C—S) bonds. In HYD, a series of hydrogenation steps precedes the C—S bond cleavage. These hydrogenation steps saturate organic molecules with hydrogen, turning π-bonds to σ-bonds which is speculated to increase the "flexibility" of some organic molecules, particularly those containing benzene rings, which in return allows them to adsorb stronger at the active sites. The difference between DDS and HYD is further illustrated in Fig. 1.

Although many studies were performed on the adsorption of various molecules on CoMoS, most studies address structure and adsorption separately. Information on the fundamental connection between atomic scale structure and adsorption configurations is lacking. Furthermore, most studies address adsorption of non-hydrogenated molecular species on the edges of CoMoS exclusively, neglecting the role of corner sites. Additionally, in order to describe adsorption of larger molecules computationally, inclusion of van der Waals (vdW) interactions is needed. This was made possible by the recent development of various exchange-correlation functionals that include long range vdW interactions [30,31]. In the present work we model the adsorption of sulfur containing molecular species and their HDS intermediates on CoMoS. Furthermore, we base our model systems on previous work performed with density functional theory (DFT) in which the equilibrium atomic scale structure and active sites of an ideal CoMoS particle at HDS conditions were determined [32]. This approach makes it possible to identify the role that each active site has in HDS, determining if some sites are active only towards particular molecular species and argue whether a specific molecular species can get desulfurized directly through the DDS mechanism or if it needs to go through a series of hydrogenation steps prior to the removal of sulfur. Another benefit of basing the present adsorption models on established structures is ensuring that all the sites are treated in a systematic and rational way without speculating whether a certain type of defect or sulfur vacancy is present at a given site under HDS conditions.

2. Materials and methods

2.1. Total energy calculations

Total energy calculations were performed using the DFT code GPAW employing grid mode with a spacing of 0.18 Å [33,34]. To treat exchange and correlation and to get an ensemble of 2000 energies used for uncertainty estimation the BEEF-vdW functional was used [30,31]. The systems representing various molecules adsorbed on the sites of CoMoS were modeled by taking the surface structures from our previous study [32], where the active and inert sites of CoMoS relevant for HDS conditions were identified, and relaxing various molecules on them. In previous work [32] the active S-edge is a 4 × 4 stripe terminated by sulfur monomers periodic in the x direction separated by 13 Å of vacuum in the y and 15 Å in the z direction. The M-edge is modeled similarly, with the difference that it is terminated by sulfur monomers having single sulfur vacancies. The corner is modeled as a stepped stripe continuous in the x direction and, similarly to the edges, separated in the y and z direction. It exposes 3 Co atoms at the S-edge side and 2 Mo atoms at the M-edge side. The basal plane is modeled as a 4 × 4 sheet periodic in the x and y directions separated by 15 Å of vacuum in the z direction and is considered inert. The surface models are shown in Fig. 2. The Brillouin zone of the edges and corner models were sampled with 2, 1, 1 k-points in the x, y and z directions respectively, while the basal plane was sampled with 2, 2, 1 k-points. The same sampling was kept for the adsorption systems in the present work. All the molecules were modeled as single molecules centered in a box with sufficient empty space added in the x, y and z directions respectively. All the structures were optimized until the maximum force was lower than 0.05 eV/Å.

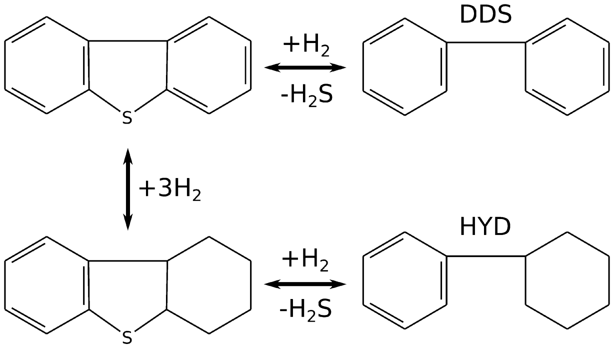

Fig. 1. Scheme showing the difference between the DDS and HYD pathways using DBT as example. Adopted from Prins et al. [23].

2.2. Free energy corrections

HDS conditions have been taken from Ref. [25] as 573 K, 38 atm of H_2 and 0.13 atm of H_2S. The adsorption free energy of the considered molecular species (ΔG_X) was calculated as follows:

$$\Delta G_X = G_{X^*} - G_X - G_* \tag{2}$$

where G_{X^*} is the free energy of a molecule X adsorbed on a specific site, G_X is the free energy of molecule X and G_* is the free energy of the site without the molecule adsorbed on it.

Thiolate formation free energies (ΔG_T) were calculated on each site as follows for methylthiolate:

$$\Delta G_T = G_{T*} + \frac{1}{2}G_{H_2} - G_X - G_* \tag{3}$$

while for the rest of the thiolates the calculations were performed as:

$$\Delta G_T = G_{T*} - G_X - \frac{1}{2}G_{H_2} - G_* \tag{4}$$

where G_{T*} is the free energy of the thiolate adsorbed on a specific site, G_{H_2} is the free energy of a hydrogen molecule, G_X is the free energy of the intact molecule X and G_* is the electronic energy of the site without the thiolate adsorbed on it. The formation of a thiolate from methylthiol is associated with breaking the sulfur-hydrogen (S—H) bond by the removal of a hydrogen atom from the initial molecule. For the rest of the molecules, thiolate formation is associated with breaking the C—S bond by the addition of a hydrogen atom to the molecule. This is the reason behind the difference between Eqs. (3) and (4).

The free energy of the adsorbed species has been obtained from the calculated vibrational frequencies of the adsorbate and the harmonic approximation [35] as follows:

$$G_{X^*} = E_{X^*} + ZPE_{X^*} + \Delta U^{0,T}_{X^*} - TS^{T}_{X^*} \tag{5}$$

where E_{X^*} is the electronic energy, ZPE_{X^*} is the zero-point energy contribution, $\Delta U^{0,T}_{X^*}$ is the change in internal energy when going