



## Research article

# Reaction and free-energy pathways of hydrogen activation on partially promoted metal edge of CoMoS and NiMoS: A DFT and thermodynamics study



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## ABSTRACT

Understanding of molecular hydrogen (H<sub>2</sub>) activation mechanism on MoS<sub>2</sub>-based catalysts is crucial for enhancement of catalytic hydrotreating processes. In this work, H<sub>2</sub> activation reaction pathways including adsorption, dissociation, and diffusion phases on metal edge of partially Co-promoted MoS<sub>2</sub> (CoMoS) and partially Ni-promoted MoS<sub>2</sub> (NiMoS) catalysts under hydrotreating conditions have been investigated using density functional theory and thermodynamic calculations. Here, investigation of H<sub>2</sub> adsorption on CoMoS and NiMoS catalysts shows that H<sub>2</sub> molecule prefers to adsorb on the promoter site rather than the sulfur site, while the H<sub>2</sub> molecule adsorbs firmly on CoMoS but substantially weaker on NiMoS. H<sub>2</sub> dissociation is the rate-determining step for both CoMoS and NiMoS catalysts and the activation energy ( $E_a$ ) of rate-determining step for both catalysts is identical ( $E_a = 0.79$  eV). However, thermodynamic result indicates that CoMoS is more reactive toward H<sub>2</sub> activation than NiMoS (free energy of activation ( $\Delta G^\ddagger$ ) at 575 K = 0.65 and 1.14 eV for CoMoS and NiMoS, respectively). In terms of diffusion, hydrogen atom migrates relatively easy ( $E_a < 0.55$  eV) on both CoMoS and NiMoS surfaces. Partial charge analysis reveals that both heterolytic and homolytic H<sub>2</sub> dissociation characteristics are observed on CoMoS and NiMoS depending on the reaction site. In addition, dissociated hydrogen atoms are more stable in terms of thiol group (S—H) on CoMoS while metal-hydrogen pairs (Mo—H and Ni—H) are more stable on NiMoS.

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## 1. Introduction

In the search for highly efficient catalytic materials for hydrotreating processes [1], which is an established refinery process for reducing sulfur, nitrogen and aromatic content from petroleum feedstocks, effective materials with more active and selective properties have been developed to attain the increasing demand for cleaner fuels and to meet with more stringent environmental regulations [2–5]. Among them, Co-promoted MoS<sub>2</sub> (CoMoS) and Ni-promoted MoS<sub>2</sub> (NiMoS) on a high-surface area  $\gamma$ -alumina have met both requirements and have been major catalytic materials in refinery processes for over six decades [6–12]. Adding Co or Ni promoters into MoS<sub>2</sub> significantly increase the reactivity for hydrotreating processes such as hydrodesulfurization (HDS), hydrodenitrogenation (HDN), and hydrodeoxygenation (HDO) [13–24]. These processes require H<sub>2</sub> activation on catalyst surface before

the occurrence of the key reactions. Therefore, understanding of H<sub>2</sub> activation mechanism is one of the most crucial steps to enhance performance of CoMoS and NiMoS catalysts.

There have been several investigations on the hydrogen adsorption and activation on MoS<sub>2</sub> catalysts [15,16,25–29]. Some studies showed that MoS<sub>2</sub> with promoter have higher reactivity toward hydrogen activation than the unpromoted MoS<sub>2</sub> [15,16,27,28]. However, a few studies have investigated on reaction pathway of hydrogen activation reaction. Prodhomme and colleagues [26] studied a free-energy profile of H<sub>2</sub> reduction on metal edge (M-edge) and sulfur edge (S-edge) of unpromoted-MoS<sub>2</sub> catalyst. Huang et al. reported hydrogen activation on promoted and unpromoted ReS<sub>2</sub> surfaces [30]. Sun et al. studied reaction pathway of hydrogen activation using the active sites on 100% Co-promoted S-edge and 100% Ni-promoted M-edge of MoS<sub>2</sub> [16]. However, recent studies suggested that the thermodynamically stable M-edge of CoMoS and NiMoS structures contained only 50% of promoter atoms [31,32]. This partially promoted MoS<sub>2</sub> catalyst has been shown to have superior reactivity in HDO reaction [31–35]. Additionally, the ratio of sulfide groups on partially promoted CoMoS and NiMoS were

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reported to be deviated from the previous studies [15,16,27,28]. These might be keys factor contributing to the higher performance of H<sub>2</sub> activation on promoted MoS<sub>2</sub>. However, to the best of our knowledge, there is no report on hydrogen activation reaction pathway on partial Co- and Ni-promoted M-edge MoS<sub>2</sub> catalysts, along with a systematic comparison of partially promoted CoMoS and NiMoS in term of H<sub>2</sub> activation reaction.

In this work, the nature of sites dissociating H<sub>2</sub> on M-edge, which are the active sites of CoMoS and NiMoS creating the active hydrogen species in the hydrotreating processes, will be explored. Here, important reaction pathways including hydrogen adsorption, dissociation, diffusion steps, along with H<sub>2</sub> dissociation characteristics, energetic and charge properties of all intermediates, and transition states will be thoroughly studied. In addition, the most favorable hydrogen activation pathway including thermodynamic contributions for CoMoS and NiMoS will be identified and systematically compared.

## 2. Computational methodology

### 2.1. Density functional theory (DFT) calculation

All periodic boundary calculations were performed based on the density functional theory (DFT) [36] using the Vienna Ab initio Simulation Package (VASP) [37]. For improvement of the calculation efficiency, core electrons were treated by the projector augmented wave (PAW) pseudo-potential [38] and the generalized gradient approximation (GGA) of the Perdew, Burke, and Ernzerhof (PBE) [39] functional was employed for the exchange-correlation terms. The geometry optimization was obtained when the force convergence criterion of 0.05 eV/Å was achieved with the criterion for electronic self-consistent field iteration of 10<sup>-5</sup> eV. The Brillouin zone integration was performed using a 2 × 2 × 1 Monkhorst-Pack grid [40] for the *k*-point sampling with the cut-off energy of 400 eV and Methfessel-Paxton smearing energy of 0.1 eV [41]. Van der Waals interaction was added using the DFT-D3 method of Grimme [42]. Transition states (TS) of reactions were calculated using the climbing-image nudged elastic band (CI-NEB) [43] and dimer method [44], in which all of the TS were confirmed as the first-order saddle points based on the single imaginary frequency of vibrational analysis.

### 2.2. Structures of partially promoted metal edge of CoMoS and NiMoS

Throughout this work, active phases on metal edge (M-edge) structure of CoMoS and NiMoS systems under hydrotreating conditions were

considered in accordance with the previous studies [31,32]. Here, CoMoS system contains 50% Co promoter substitution on Mo atoms with 25% S coverage in alternate configuration (—Co—Mo—Co—Mo—, see Fig. 1(a), (c), (e)). Note that there were two stable 50% Co-promoted M-edge configurations in CoMoS, but the alternate configuration is chosen due to its reportedly reactive toward HDO in the previous study [45]. For NiMoS, the system contains 50% Ni promoter substitution with 12.5% S coverage (Fig. 1(b), (d), (f)). This partially promoted NiMoS was reported as highly reactive for HDS reactions [17]. The simulation was performed using an orthorhombic supercell with vacuum space added in the *x* and *z* directions to avoid interactions among periodic images. The resulting lattice parameters of simulation supercell are *a* = 13.12 Å, *b* = 12.73 Å, and *c* = 24.18 Å. The two lower atomic layers of CoMoS and NiMoS were fixed to simulate bulk constraints while the rests were allowed to relax.

By partially substituting Mo atoms on the M-edge of MoS<sub>2</sub> with Co and Ni promoter atoms, smaller atomic radii of Co and Ni (1.52 and 1.49 Å, respectively, compared to 1.90 Å of Mo) has triggered the surface readjustment on the M-edge of CoMoS and NiMoS. For CoMoS, substituted Co atom in the alternate Mo—Co—Mo—Co— configuration [31] couples Co to one of the Mo atom, while increasing the distance to another Mo atom on the opposite site. In particular, Fig. 1(a) shows that Co1 atom moves close to Mo1 atom (2.95 Å) but apart from Mo2 (3.50 Å). Likewise, Co2 pairs with Mo2 atom (2.95 Å) and moves away from Mo1 (3.50 Å). This surface alteration certainly affects the possibility that hydrogen dissociates and diffuses. Therefore, we address this asymmetric structure by investigating dissociation and diffusion for both short and long Co—Mo directions in the CoMoS section. For NiMoS, the optimized pairing Mo—Ni—Ni—Mo configuration [31] shows that structure between Mo1—Ni1 and Mo2—Ni2 are indistinguishable. Thus we do not distinguish direction of reaction between Mo1—Ni1 and Mo2—Ni2 in NiMoS study.

### 2.3. Adsorption energy and partial charge analysis

Adsorption energy ( $E_{\text{ads}}$ ) of H<sub>2</sub> is defined as

$$E_{\text{ads}} = E_{\text{catalyst}+\text{H}_2} - E_{\text{catalyst}} - E_{\text{H}_2} \quad (1)$$

where  $E_{\text{catalyst}}$  is the total energy of clean CoMoS and NiMoS surfaces,  $E_{\text{H}_2}$  is the total energy of free hydrogen (H<sub>2</sub>) molecule, and  $E_{\text{catalyst}+\text{H}_2}$  is the total energy of CoMoS and NiMoS surface after H<sub>2</sub> adsorption. Noted that more negative  $E_{\text{ads}}$  implies more stable adsorption.

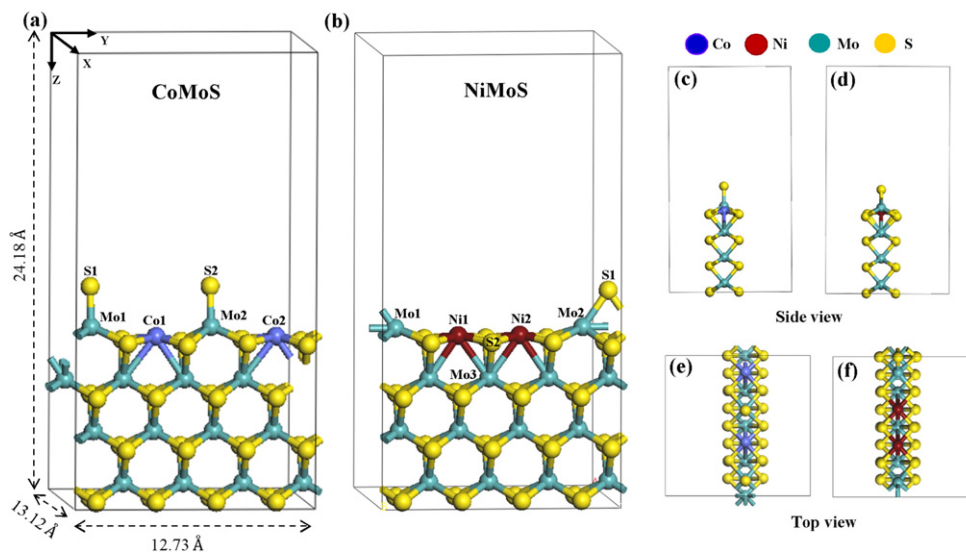


Fig. 1. Supercell configurations of 50% promoted CoMoS with 25% sulfidation and 50% promoted NiMoS with 12.5% sulfidation used in all calculations in this study: (a)–(b) (100)-direction views; (c)–(d) (010)-direction views; and (e)–(f) (001)-direction views of CoMoS and NiMoS, respectively.

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