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Removal of surface sulfur from MoS_x cluster under CO adsorption

Tao Zeng [a], Xiao-Dong Wen [a], Yong-Wang Li [a,*], Haijun Jiao [a,b,*]

[a] *State Key Laboratory of Coal Conversion (SKLCC), Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan, Shanxi 030001, China*
[b] *Leibniz-Institut für Organische, Katalyse an der Universität Rostock e.V., Albert-Einstein-Strasse 29a, 18059 Rostock, Germany*

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Abstract

Removal of bridging sulfur from the Mo edge of a $Mo_{20}S_{43}$ cluster has been investigated at the level of density functional theory. It is found that the reductive removal of bridging sulfur is not favored energetically but becomes favorable under CO adsorption. Due to the strong adsorption, CO can help the reductive removal of surface sulfur, and in turn, the reduced Mo edge can favor and facilitate the hydrogenation process of CO.

Keywords: DFT; Sulfur removal; MoS_x; CO adsorption

1. Introduction

Molybdenum sulfide (MoS_x) in combination with transition metals as a promoter is a widely used catalyst in CO hydrogenation (HYD) and hydrodesulfurization (HDS) processes for producing cleaner fuels and fuel additives [1]. In contrast to metallic catalysts, MoS_x has the advantage of excellent resistance to sulfur poisoning. To understand the reaction mechanisms, Delmon et al. proposed the "remote-control" model and indicated that the source of activated H atoms can be enriched by a promoter [2], and that these hydrogen atoms can remove surface sulfur to produce coordinatively unsaturated sites (CUS) on Mo, which are essential to HYD and HDS [2a,3].

Theoretically, Raybaud et al. [4], Cristol et al. [5] and Byskov et al. [6] performed systematic calculations on the removal of surface sulfur by hydrogen and Sun et al. [7] summarized their results. They found that the [3–3] surface, where both the Mo(1 0 $\bar{1}$ 0) and S($\bar{1}$ 0 1 0) edges are half covered by bridging sulfur, can be formed easily, but that its further reduction is thermodynamically unfavorable. Li et al. [8] studied the effect of removing surface sulfur for understanding the activation mechanism of HDS/HYD catalysts on the basis of a Mo_7S_{24} cluster model. Paul and Payen [9] studied the vacancy formation mechanism on the surfaces of MoS_x nano-crystallites of active phases in HDS process, and the dynamic equilibrium on these surfaces.

CO adsorption and activation on MoS_x have been investigated experimentally and theoretically. Müller et al. [10], Elst et al. [11] and Peri [12] reported a characteristic broad band at 2070 cm^{-1} with a tail extent to 2000 cm^{-1} in the IR spectra of adsorbed CO on MoS_x. It has been generally believed that this band is attributed to CO adsorbed on two-fold CUS at Mo [13]. Maugé et al. [14] attributed the red-shift from 2143 cm^{-1} of free CO to the surface back donation. Travert et al. [15] performed a systematic computation of CO adsorption on various kinds of MoS_x surfaces, and assigned the observed IR frequencies to different adsorption modes. Recently, Zeng et al. [16] used simplified but still representative stoichiometric and non-stoichiometric $Mo_{16}S_x$ clusters (x = 29, 32, 34 and 38) for CO adsorption and activation to model the changes of surface structure and composition. They found that end-on CO adsorption modes on the corner and

* Corresponding authors. Tel.: +49 3811281135; fax: +49 38112815000.
E-mail address: haijun.jiao@ifok-rostock.de (H. Jiao).

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edge sites are populated equally at low CO concentration, but the corner sites are predominant at high CO coverage. However, it is possible that at high CO coverage, the composition of these edges might change, and so will act as the catalytic center. They also identified the 2070–2000 cm^{-1} band as the corner and edge CUS at Mo and showed that the S-naked Mo edge adsorbs and activates CO to the largest degree, and should be the potential catalytic center for CO HYD. Indeed, S-naked Mo edges have been considered as one of the most active sites [17,18]. However, due to the strong interaction with bridging sulfur, the formation of such edges is unlikely under H_2 atmosphere.

In this paper, we focus on the formation of the S-naked Mo edge under the influence of both H_2 and CO, setting off from the results of CO adsorption [16], and confirm the catalytic centers on the Mo edge under real CO/H_2 HYD conditions, using DFT calculation.

2. Models and methods

2.1. Models

The structure of MoS_2 is a closely packed layered sandwich with each Mo atom co-ordinated by six sulfur atoms in a prismatic unit, and Mo atoms in a plane situated between two sulfur planes [19]. Small MoS_2 slabs are responsible for the catalytic activities of HYD [3a,3c,20]. Two primary surfaces, Mo(1 0 $\bar{1}$ 0) and S($\bar{1}$ 0 1 0), are located on a MoS_x slab, as shown in Fig. 1. The active phase of HYD over MoS_x has long been known to be highly dispersed MoS_x crystals in nano-size with boundaries in all-crystallographic directions. More recently, the scanning tunneling microscopy revealed a truncated hexagon form for MoS_x cluster under excess hydrogen [21]. This result indicates that a cluster model similar to a hexagon, rather than a periodic model, should be

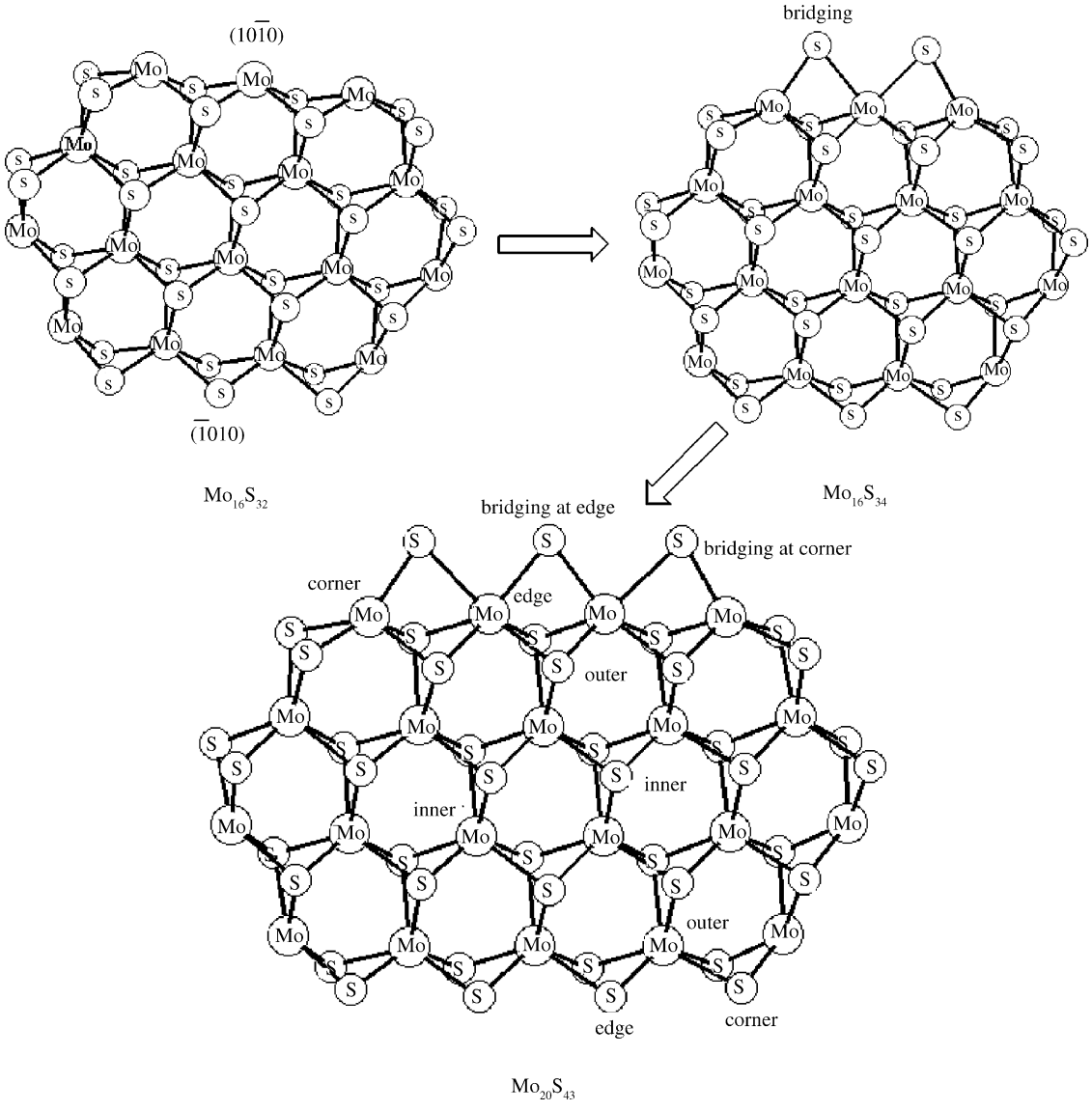

Fig. 1. MoS_x cluster models.