

# Reply to “Comment on ‘Density Functional Theory Study of Triangular Molybdenum Sulfide Nanocluster and CO Adsorption on It’”

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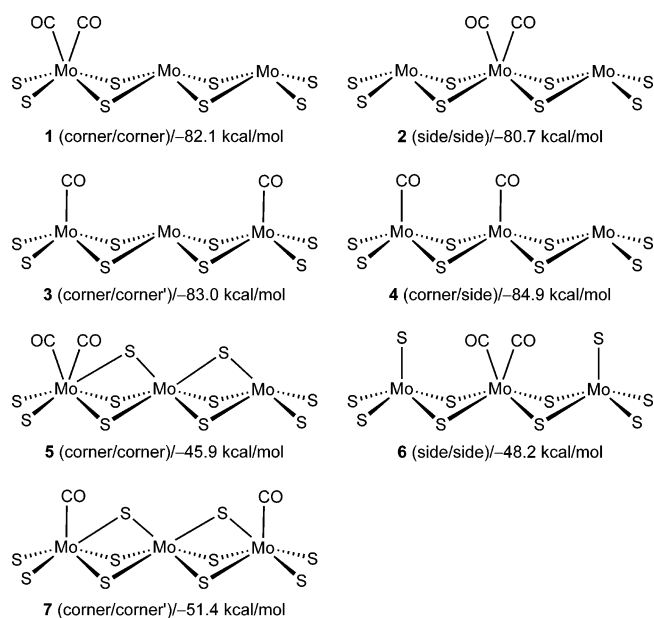
Molybdenum sulfides ( $\text{MoS}_x$ ) are widely used catalysts in oil refineries for hydrogenation, hydrodesulfurization, and hydrodenitrogenation reactions.<sup>1,2</sup> The increasing demand for cleaner fuels requires hydro-treating catalysts with higher activity and selectivity, and consequently a rationalized understanding of the activities and surface structures of  $\text{MoS}_x$  catalysts is essential.

Characterization of active surface species by the adsorption of probe molecules is informative, and infrared (IR) spectroscopy of adsorbed probe molecules is used widely to study the surface properties of catalysts. The chemisorption of CO or NO molecules provides important experimental insight into the surface structures of the active sites on hydrodesulfurization catalysts. However, the discussion about the location and nature of the active surface sites for CO adsorption is still controversial, and IR study alone is not sufficient to give the final answer. Fortunately, density functional theory calculations can provide information on the structure and stability of the active surface sites and CO adsorption on them at the molecular level. Direct comparison between theory and experiment will provide more realistic and reliable schemes about the active surface sites for catalysts.

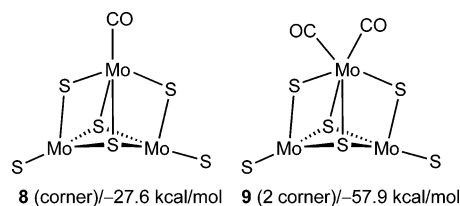
It is well known that structure determines the activities and properties. On the basis of the sulfiding condition, two topological structures of  $\text{MoS}_x$  can be formed, for example, truncated hexagonal structures at low  $\text{H}_2\text{S}/\text{H}_2$  ratios and triangular structures at high  $\text{H}_2\text{S}/\text{H}_2$  ratios.<sup>3</sup> Once the cluster is formed, changing the  $\text{H}_2\text{S}/\text{H}_2$  ratio can only affect the surface structure, not the morphology. The corresponding catalytic activity and CO adsorption should reflect the differences in the structures.

Experimentally, Travert et al.<sup>4–6</sup> have reported the IR spectra of adsorbed CO on a series of  $\text{Mo}/\text{Al}_2\text{O}_3$ ,  $\text{CoMo}/\text{Al}_2\text{O}_3$ , and  $\text{NiMo}/\text{Al}_2\text{O}_3$  sulfided catalysts. In addition, they also carried out the corresponding theoretical calculations using the periodic model. On the basis of the experimental spectra on  $^{12}\text{CO}/^{13}\text{CO}$  adsorption experiments, they found a single and symmetrical band at  $2112\text{ cm}^{-1}$ , which is characteristic of CO adsorption on the  $\text{MoS}_2$  phase. They proposed that this band was due to monocarbonyl adsorption rather than dicarbonyl adsorption.

To understand the structural differences, we have recently carried out systematic density functional theory studies on the CO adsorption on both hexagonal<sup>7</sup> and triangular clusters.<sup>8</sup> For CO adsorption on the Mo site of the hexagonal stoichiometric cluster ( $\text{Mo}_{16}\text{S}_{32}$ , Figure 1), we have found that two monocarbonyl adsorption in vicinal or separated positions (3 and 4) are



**Figure 1.** CO adsorption on the stoichiometric (1–4) and nonstoichiometric (5–7) clusters.



**Figure 2.** CO adsorption at the triangular corner of the nonstoichiometric cluster.

energetically more favored than the dicarbonyl adsorption in germinal position (1 and 2) by 2.8–4.2 kcal/mol. These energetic differences indicate the predominance of monocarbonyl adsorption over dicarbonyl adsorption. This agrees well with the experimental results by Travert et al.<sup>4</sup>

In addition, we have also computed CO adsorption on the nonstoichiometric cluster ( $\text{Mo}_{16}\text{S}_{34}$ , Figure 1). Our computed results show once again the predominance of two monocarbonyl adsorption (7) over dicarbonyl adsorption (5 and 6) by 3.2–5.5 kcal/mol. This finding is in agreement with the experimental results.<sup>4</sup> It is also interesting that our computed results are closer to the experimental results than the theoretical results that Travert et al.<sup>4</sup> obtained from periodic model. Indeed, Travert et al. found that both monocarbonyl and dicarbonyl adsorption with the same adsorption energies are equally populated. On this basis, there is no controversy between our computation and the experimental as well as theoretical results by Travert et al.

For CO adsorption on the corner site of the triangular nonstoichiometric cluster ( $\text{Mo}_{28}\text{S}_{84}$ , Figure 2), however, we have found that the dicarbonyl adsorption (9) is stronger than twice the monocarbonyl adsorption (8) by 2.7 kcal/mol,<sup>8</sup> indicating that the dicarbonyl adsorption is more energetically favored than the monocarbonyl adsorption. This energetic difference is in contrast to those of the hexagonal clusters. In addition, we have also computed the CO stretching frequencies. The CO stretching frequency of the monocarbonyl adsorption (8,  $2049\text{ cm}^{-1}$ ) is lower than the experimental value, whereas that of the dicarbonyl adsorption (9,  $2102\text{ cm}^{-1}$ ) is close to the experimental

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value. On the basis of the calculated adsorption energies, we can say that hexagonal clusters prefer monocarbonyl adsorption, whereas the triangular clusters prefer the dicarbonyl adsorption.

However, none of the computed CO stretching frequencies of the monocarbonyl and dicarbonyl adsorptions on the stoichiometric and nonstoichiometric hexagonal clusters in our calculations and in the calculations of Travert et al. are close to the experimentally detected characteristic band at  $2112\text{ cm}^{-1}$ . Considering this disagreement, one might ask the question about the right structures of the active surface sites of the  $\text{MoS}_x$  catalysts for CO adsorption used in calculations. In our recent work,<sup>9</sup> we have studied the structure and stability of  $\text{MoS}_x$  surfaces under the variation of the  $\text{H}_2\text{S}/\text{H}_2$  ratio. It clearly shows that the stability of individual surface structure depends on the  $\text{H}_2\text{S}/\text{H}_2$  ratio. It is therefore expected that different surface structures should have different CO frequencies.

For the hexagonal cluster model and the periodic model, the computed frequencies are underestimated by around  $60\text{--}70\text{ cm}^{-1}$  compared to the experimental values. It is important to note that the computed frequencies are scaled by an empirical factor deduced from the comparison between the computed and detected frequency of free CO molecule ( $2124$  vs  $2143\text{ cm}^{-1}$ ). The most suitable scaling factor should be deduced from the computed and detected frequencies of well-defined structures, but such defined structures are not available yet. By adding  $60\text{--}70\text{ cm}^{-1}$  to the computed IR data, there are perfect agreements between the calculated data and the experiment, not only for monocarbonyl but also for dicarbonyl as well as for full CO adsorptions. In turn, such agreements show that IR cannot be a sufficient method for identifying individual adsorption models.

Considering that the computed IR data for the triangular cluster could also be underestimated by  $60\text{--}70\text{ cm}^{-1}$ , the corrected CO stretching frequency for monocarbonyl adsorption (**8**) should be  $2110\text{--}2120\text{ cm}^{-1}$ , whereas those of the dicarbonyl adsorption (**9**) should be  $2170\text{--}2180\text{ cm}^{-1}$  for the symmetric and  $2145\text{--}2150\text{ cm}^{-1}$  for the asymmetric modes. These stretching frequencies are larger than that of free CO ( $2143\text{ cm}^{-1}$ ) and belong to the category of nonclassic metal carbonyl systems,<sup>10</sup> which is beyond the scope of our study. Nevertheless, further experimental studies are desired to verify these theoretical results.

In addition, Travert et al. also doubted our theoretical results of the sulfur removing process under CO adsorption. The goal of our research is the understanding of the poisoning process of  $\text{H}_2\text{S}$ .<sup>11</sup> It is important to note that our computed results are on the basis of multiple or full CO adsorptions and the availability of activated hydrogen on the nonstoichiometric hexagonal cluster, and this reaction can take place only at very high CO and  $\text{H}_2$  partial pressures, compared to  $\text{H}_2\text{S}$ . In contrast, Travert et al.<sup>4</sup> studied the removal of adsorbed CO by  $\text{H}_2\text{S}$ , and

they used a very high  $\text{H}_2\text{S}$  partial pressure, compared to CO. This is just the reverse reaction of our model system. Therefore, it is easy to understand why our computed results are not supported by the experimental study by Travert et al. Considering the computed equilibrium,<sup>11</sup> the  $\text{CO}/\text{H}_2\text{S}$  exchange reaction could be adjusted by changing the  $\text{CO}/\text{H}_2\text{S}$  partial pressure; that is, high  $\text{CO}/\text{H}_2\text{S}$  partial pressure leads to the removal of adsorbed  $\text{H}_2\text{S}$ , whereas low  $\text{CO}/\text{H}_2\text{S}$  partial pressure leads to the removal of adsorbed CO. On the basis of these, there is no controversy between our analysis and the results by Travert et al. Nevertheless, further studies for the understanding of the  $\text{H}_2\text{S}$  poisoning processes are needed.

In conclusion, structures determine adsorption properties. At low CO coverage, hexagonal clusters prefer monocarbonyl adsorption over dicarbonyl adsorption on the stoichiometric and nonstoichiometric Mo sites, and dicarbonyl adsorptions do exist at high CO coverage. In contrast, triangular clusters prefer dicarbonyl adsorption over monocarbonyl adsorption at the corner position of the nonstoichiometric S site. The fact that dicarbonyl adsorptions have not been observed in experiment can be attributed to the structures that are not formed on the employed experimental conditions. Further intensive and extensive theoretical studies are highly desired for the understanding of the surface structures and their catalytic activity, and in turn, these studies will help in the design of new novel catalysts.

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