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Structure and Energy of $\text{Mo}_{27}\text{S}_x\text{C}_y$ Clusters: A Density Functional Theory StudyXiao-Dong Wen,[†] Zhi Cao,[†] Yong-Wang Li,[†] Jianguo Wang,[†] and Haijun Jiao^{*,†,‡}

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For understanding the carburization processes of MoS_x catalysts, the structures and energies of $\text{Mo}_{27}\text{S}_x\text{C}_y$ cluster models have been computed at the level of density functional theory. The surface sulfur atoms on the Mo edge and S edge as well as bulky sulfur atoms have been replaced by atomic carbon, and the corresponding structures have S/C ratios in the range of 0.8–55. The formation of all $\text{Mo}_{27}\text{S}_x\text{C}_y$ structures is favored thermodynamically. It is also found that the formation of CS and C_2 bridging units is more favored than the individual or separated replacements and that the formation of C_2 bridging units is more favored than that of CS units. In contrast, the replacement of sulfur on the Mo edge is least favored. Furthermore, the replacement of the bulky sulfur on the Mo edge is equally favored as those of sulfur on the S edge. For aiding further experimental studies, the C=S and C=C stretching frequencies have been computed.

1. Introduction

Because of the worldwide environmental regulations on minimum sulfur content in fuel, it is desired to remove sulfur-containing organic compounds from fuel. The widely used catalysts in oil refinery for hydrogenation, hydrodesulfurization (HDS), and hydrodenitrogenation (HDN) reactions are molybdenum sulfides (MoS_x). To understand the catalytic activity of MoS_x , it is necessary to have full insight into the structure and composition of the MoS_x surfaces.

One of the problems is the role of carbonaceous species on the activity of hydrotreating catalysts. In 1982, Hallie et al.¹ found an enhanced activity in HDS and HDN conversion of a vacuum gas oil by using CS_2 instead of $\text{H}_2/\text{H}_2\text{S}$ as a sulfiding agent. Early evidence for structural carbon was found by Chianelli and Pecoraro,^{2,3} and they found that a RuS_2 catalyst stabilized for 1000 h in a catalytic environment exhibited a $\text{RuS}_{2-x}\text{C}_x$ phase with carbon replacing sulfur atoms on the surface. In addition, Seiver and Chianelli⁴ showed that layered transition metal sulfides such as MoS_2 and WS_2 catalysts have the same behavior. Using a ^{14}C radiotracer element, Bussell and Somorjai⁵ suggested that the clean $\text{Mo}(100)$ surface of a single crystal can be changed into a carbided surface with carbon atoms occupying the 4-fold hollow sites. By using a density functional theory (DFT) method, Liu et al.⁶ investigated the sulfur adsorption and sulfidation of metal carbides and found that the sulfidation of $\text{TiC}(001)$, $\text{VC}(001)$, $\text{MoC}(001)$, and $\text{TaC}(001)$ is endothermic at 1/4 S monolayered coverage, and this endothermic property becomes stronger with increased coverage.

It has long been recognized that the activation of hydrotreating catalysts in the presence of crude oil was more efficient than the gas-phase procedure. Hallie et al.⁷ have shown that there is a strong dependency of the HDS activity on the nature of the sulfiding agent (RSH , $\text{CH}_3\text{—S—S—CH}_3$, and CS_2). Chianelli and Pecoraro² have found that the catalyst activity using $(\text{NR}_4)_2\text{—}$

MoS_4 (R = alkyl group) as the precursor for catalyst preparation was higher than that using ammonium heptamolybdate $(\text{NH}_4)_6\text{—Mo}_7\text{O}_{24}$. Kasztelan et al.⁸ suggested that the proposed replacement of S atoms on the edges by carbon could be ascertained through crystallographic considerations. Chianelli et al.⁹ proposed that carbon could play an important role in the stabilized structure of active catalysts. Their results indicated that the MoS_2 edge area and the activity increase with the increased carbon content of the catalyst. Therefore, they proposed that the excess sulfur on the surface was replaced by carbon to give stoichiometric $\text{MoS}_{2-x}\text{C}_x$ as the stabilized catalyst composition.

It is well-known that active catalysts, prepared from the treatment of oxide catalysts with organosulfide, have a higher HDS activity, suggesting the modified sulfide structure by carbon. Rueda et al.¹⁰ have observed that the use of hydrocarbons as solvent or surfactant modifies the texture, providing higher specific surface areas and lower stacking for MoS_2 particles, as well as better stability during catalytic tests in the course of the synthesis of bulk MoS_2 catalysts. Berhault et al.¹¹ investigated bulk MoS_2 and proposed that such carbide-like species were formed on the surface of MoS_2 particles by using synchrotron X-ray diffraction (XRD), infrared (IR), and electron energy loss spectroscopy (EELS). Neither XRD nor IR experiments did reveal the presence of a bulk carbide phase after treatment with $(\text{CH}_3)_2\text{S}$ up to 793 K, but surface sensitive EELS techniques indicated the formation of Mo—C bonds at the surface of $(\text{CH}_3)_2\text{S}$ treated MoS_2 particles. They proposed the active catalysts as sulfide-supported transition metal carbides, $\text{RuS}_{2-x}\text{C}_x$ and $\text{MoS}_{2-x}\text{C}_x$, in which the value of x depends on the surface area of the catalysts. Completely coordinated bulk sulfur atoms could not be replaced easily by carbon except under severe experimental conditions.

Recently, Glasson et al.¹² have concluded that one identifiable beneficial effect of carbon was the geometry. However, structural effects may not be excluded. They assumed the thermal, geometrical, supportive, and chemical effects as to the role of C-containing molecules during the sulfidation process. They suggested that carbon deposit was one reason for catalyst

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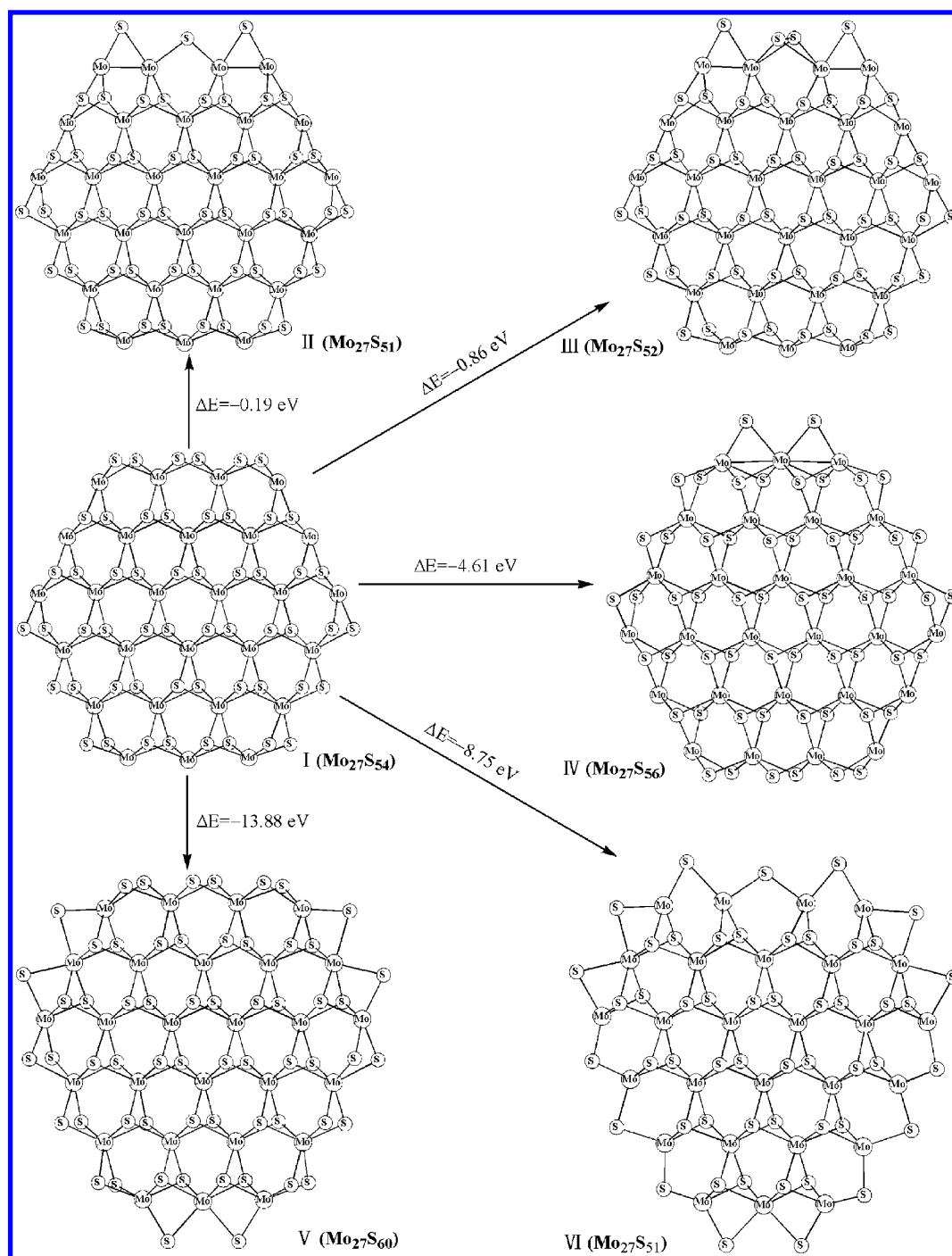


Figure 1. Different Mo_{27}S_x cluster models.

deactivation and that the presence of organic thiocompounds ($\text{CH}_3\text{—S—S—CH}_3$, tertiononyl-pentasulfide, etc.) or gas oil during the sulfidation process was recognized to enhance the activity.

Despite this experimental evidence, the structures of $\text{MoS}_{2-x}\text{C}_x$, especially the location of carbon atoms on the surface, are still not clear. The DFT method can offer detailed information for the fine structural models of MoS_xC_y . The carburization processes are performed on Mo edge (33% sulfur coverage), S edge (100, 67, and 50% sulfur coverage), and bulk $\text{Mo}_{27}\text{S}_{54}$ cluster, respectively. In this work, the carburization structures and their formation energies are discussed to understand the structural carbon in the MoS_2 catalyst.

2. Model and Methods

2.1. Surface Models. There are intensive studies looking into the surface structure and stability of MoS_x catalysts. Lauritsen et al.¹³ found that the morphology of MoS_x nanoclusters as catalysts in fact might be very complex by using scanning tunneling microscopy (STM). By using DFT methods, Byskov et al.¹⁴, Raybaud et al.^{15,16}, Cristol et al.^{17,18} and Sun et al.^{19,20} have reported the surface structure of MoS_x catalysts on the basis of periodic models, and they found that it is energetically not favored to obtain the Mo edge and S edge of MoS_x surfaces with sulfur coverage less than 50%, and adding sulfur atoms to the bare Mo edge is exothermic up to 50% sulfur coverage. We also have computed the surface structure and stability of different MoS_x clusters instead of periodic models.²¹ These

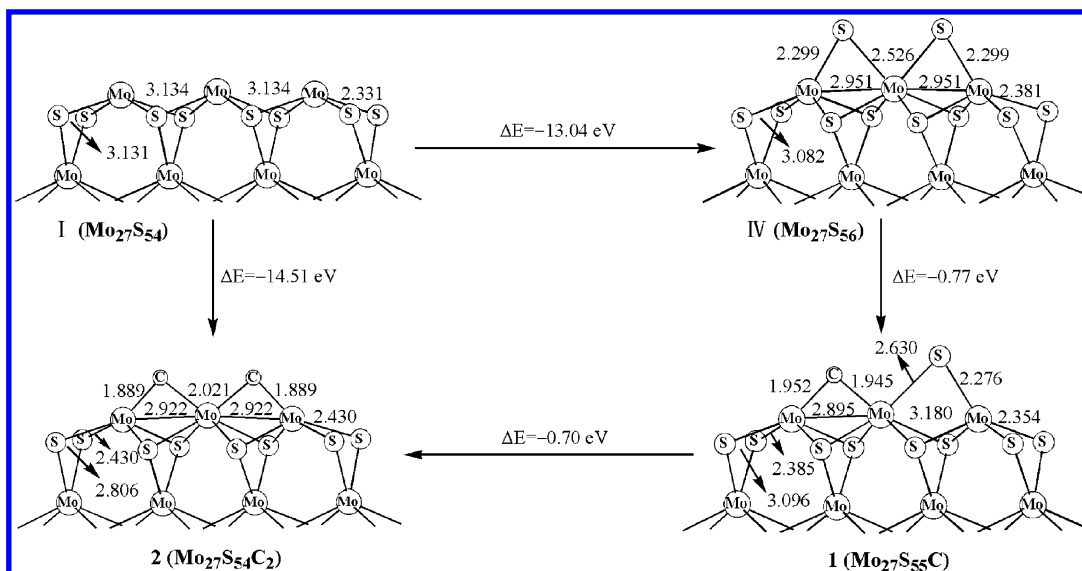


Figure 2. Carburization on Mo edge.

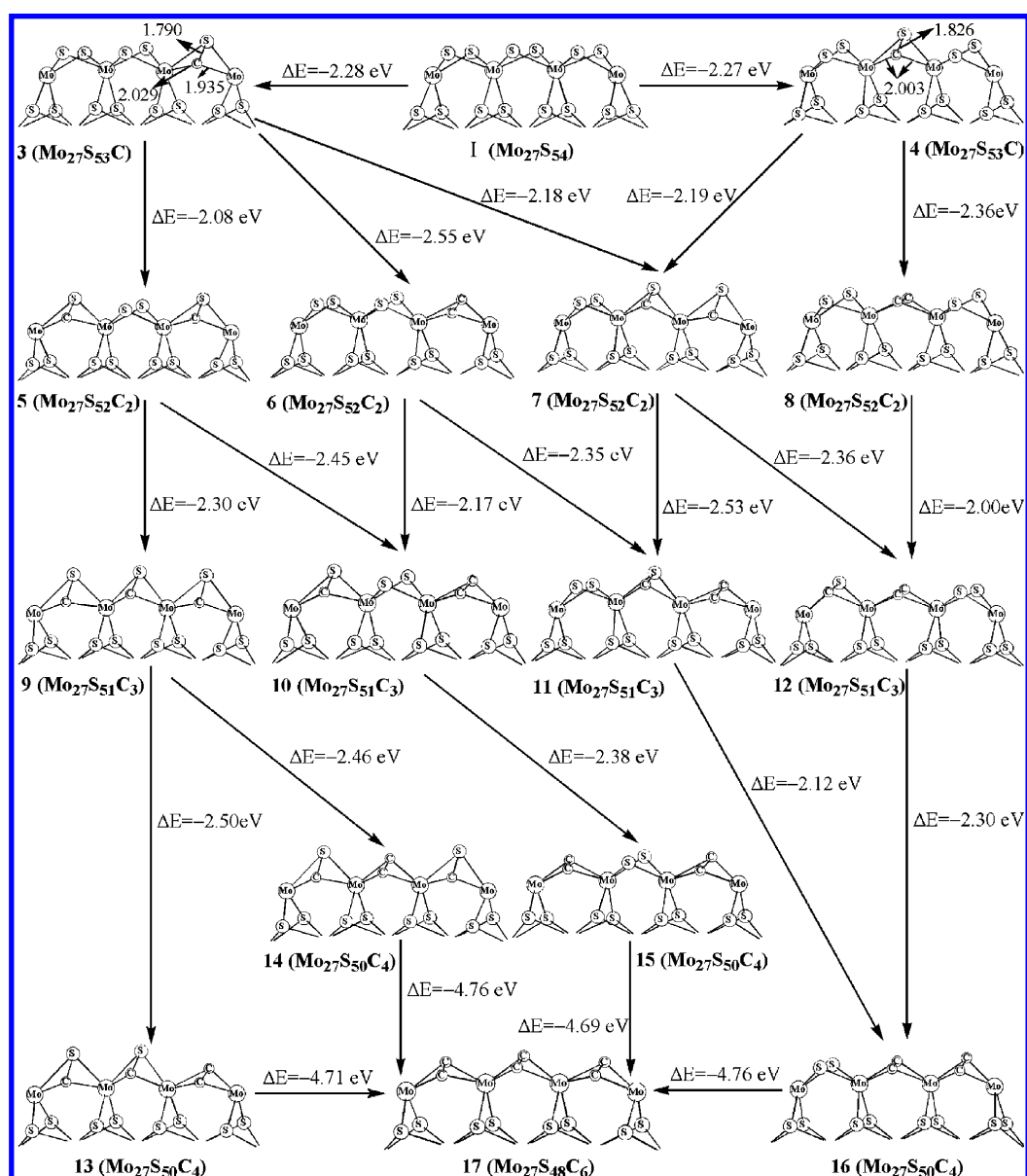


Figure 3. Carburization on S edge with 100% sulfur coverage.

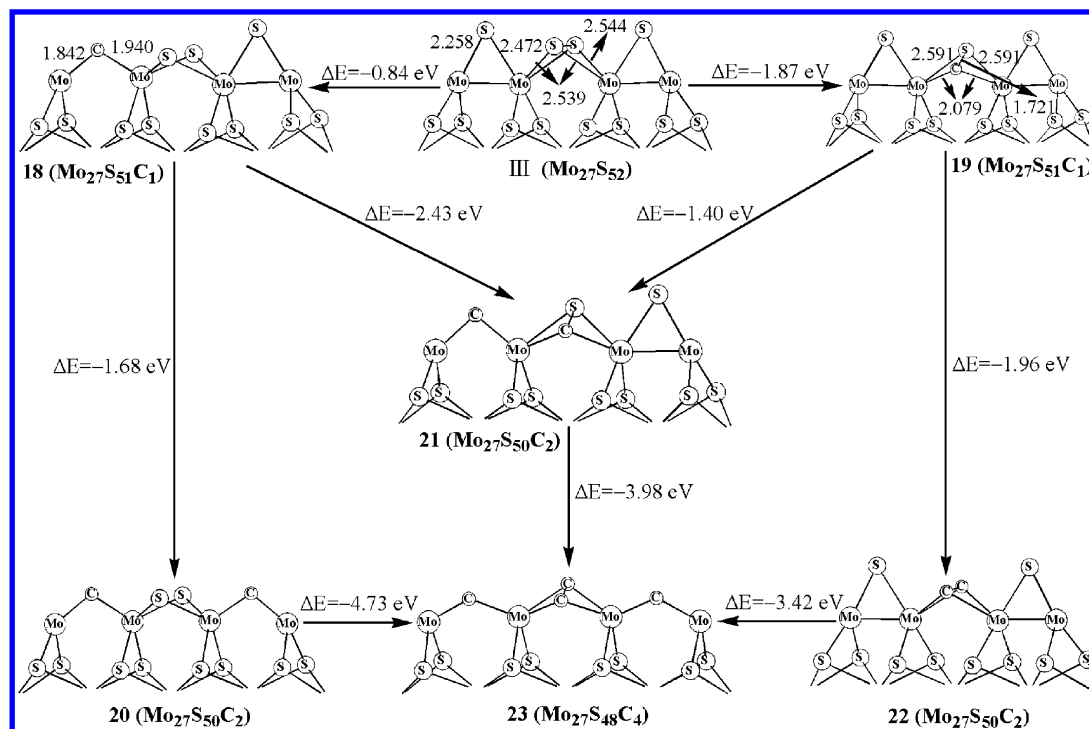


Figure 4. Carburization on S edge with 67% sulfur coverage.

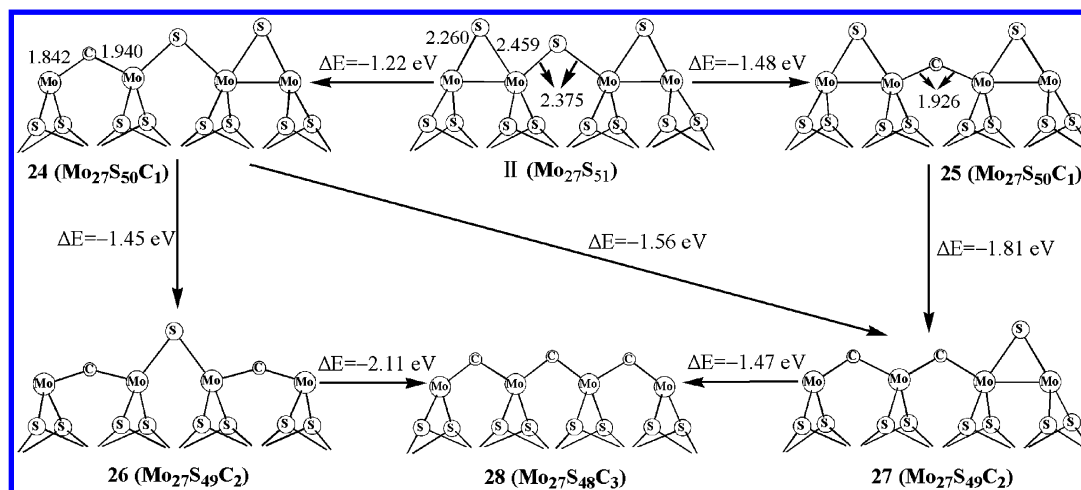
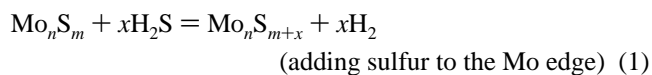


Figure 5. Carburization on S edge with 50% sulfur coverage.

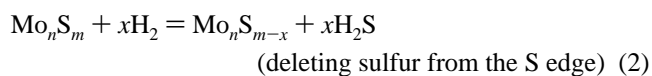
results show that adding sulfur to the Mo edge is always exothermic and that deleting corner sulfur from the S edge is exothermic for 67% (**III**) and 50% (**II**) sulfur coverage. However, our results do not agree fully with the results obtained by using the periodic slab model, which shows that the removal of sulfur from the S edge is always endothermic. This energetic discrepancy comes from the difference between cluster and period models since the cluster model has both edge and corner sulfur atoms, while the periodic model has only edge sulfurs. Removing the corner sulfur is much easier than that of the edge sulfur.

In our current work, we used the stoichiometric ($\text{Mo}_{27}\text{S}_{54}$) and nonstoichiometric (Mo_{27}S_x) clusters to model the surfaces. $\text{Mo}_{27}\text{S}_{54}$ (**I**) with 0% sulfur Mo edge and 100% sulfur S edge, $\text{Mo}_{27}\text{S}_{56}$ (**IV**) with two bridging S atoms on the Mo edge (33% sulfur coverage on Mo edge), $\text{Mo}_{27}\text{S}_{51}$ (**II**) with three bridging S atoms on the S edge (50% sulfur coverage on S edge), and $\text{Mo}_{27}\text{S}_{52}$ (**III**) with 67% sulfur coverage on the S edge are shown in Figure 1. In our previous study,²¹ we reported various Mo_{27}S_x clusters. On the basis of eqs 1 and 2, the formation of $\text{Mo}_{27}\text{S}_{56}$

(**IV**), $\text{Mo}_{27}\text{S}_{51}$ (**II**) and $\text{Mo}_{27}\text{S}_{52}$ (**III**) is exothermic by 4.61, 0.19 and 0.86 eV.



$$\Delta E_0(\text{Mo}) = [E(\text{Mo}_n\text{S}_{m+x}) + E(x\text{H}_2)] - [E(\text{Mo}_n\text{S}_m) + E(x\text{H}_2\text{S})]$$



$$\Delta E_0(\text{S}) = [E(\text{Mo}_n\text{S}_{m-x}) + E(x\text{H}_2\text{S})] - [E(\text{Mo}_n\text{S}_m) + E(x\text{H}_2)]$$

Apart from these clusters with sulfur coverage on the individual Mo and S edges, we also have chosen structures with changed sulfur coverage on both edges at the same time (Figure 1) (e.g., $\text{Mo}_{27}\text{S}_{60}$ (**V**) with 100% sulfur coverage on the S edge

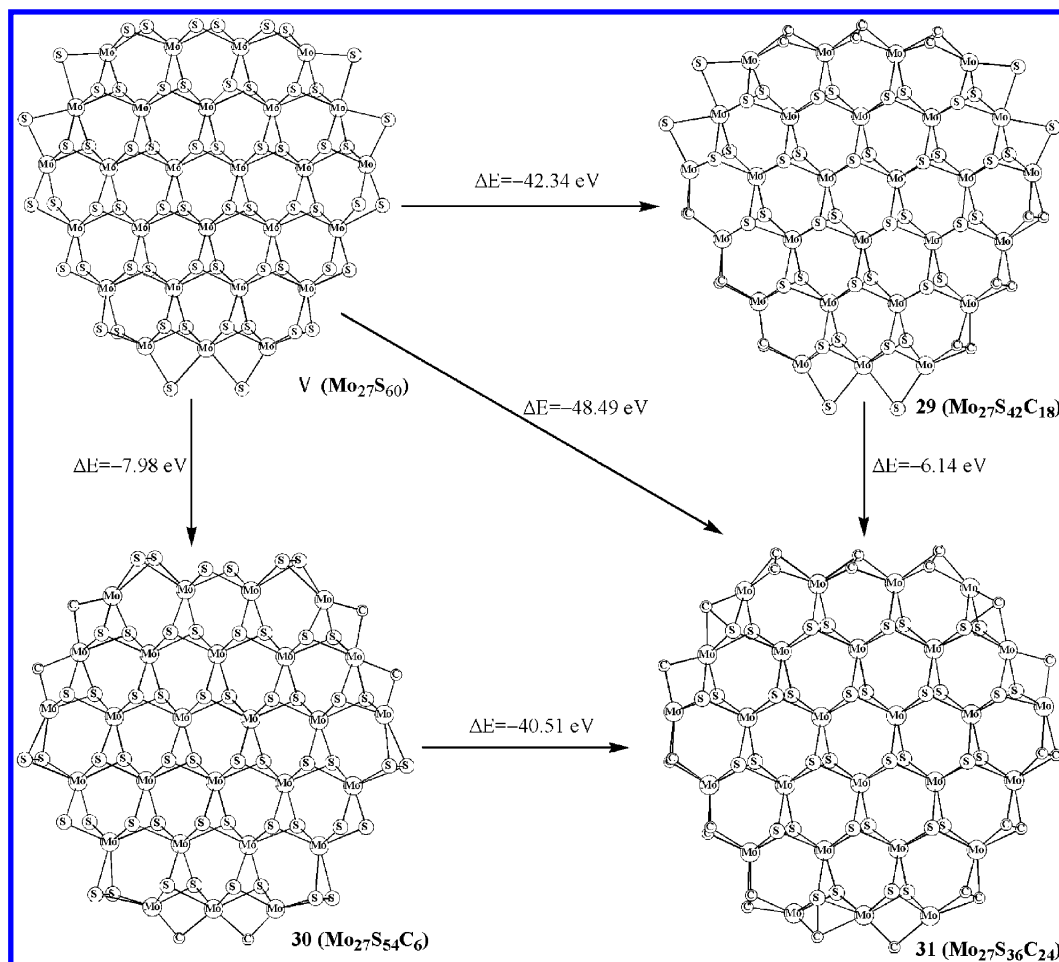
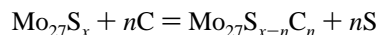


Figure 6. Carburization on $\text{Mo}_{27}\text{S}_{60}$ with 33% sulfur Mo edge and 100% sulfur S edge.

and 33% sulfur coverage on the Mo edge and $\text{Mo}_{27}\text{S}_{51}$ (VI) with 50% sulfur coverage on the S edge and 33% sulfur coverage on the Mo edge). The formation energies of $\text{Mo}_{27}\text{S}_{60}$ (V) and $\text{Mo}_{27}\text{S}_{51}$ (VI) are -13.88 and -8.75 eV from $\text{Mo}_{27}\text{S}_{54}$ (I), respectively. The carburization process was first studied on the Mo edge with 33% sulfur coverage, followed by different sulfur coverages on the S edge (100, 67, and 50% sulfur coverage). The carburization process on both Mo edge and S edge at the same time was also examined. Finally, the replacement for the bulk S atom in $\text{Mo}_{27}\text{S}_{54}$ by the C atom was also reported.

In our work, we used the atom formation energy in eq 3 to investigate the carburization process, in which we have used atomic carbon and sulfur as references.²² On the basis of eq 3, the more negative the atom formation energies, the more favorable the process.



$$\Delta E_f = [E(\text{Mo}_{27}\text{S}_{x-n}\text{C}_n) + nE(\text{S})] - [E(\text{Mo}_{27}\text{S}_x) + nE(\text{C})] \quad (3)$$

2.2. Methods. All calculations were performed with the program package DMol³ in the Materials Studio 2.2 of Accelrys Inc. In DMol³, the physical wave functions are expanded in terms of accurate numerical basis sets.²³ We have used the doubled numerical basis set with polarization functions for other elements (DNP), while the effective core potential (ECP) is used for molybdenum. The generalized gradient corrected functional by Perdew and Wang (GGA-PW91) was used,²⁴ and the medium quality mesh size was used for the numerical integration. The

tolerances of energy, gradient, and displacement convergence were 2×10^{-5} au, 4×10^{-3} au/Å, and 5×10^{-3} Å, respectively. The real space cutoff of atomic orbitals was set at 5.5 Å, and a Fermi smearing of 0.0005 was used to count the orbital occupancy. In our work, all structures were fully optimized and relaxed without any constraints. The computed total energies (E_{tot} , au) for all structures are listed in the Supporting Information.

3. Results

3.1. Partially Covered Mo Edge. The carburization processes are shown in Figure 2. The formation energy for $\text{Mo}_{27}\text{S}_{56}$ (IV) of -13.04 eV is used for comparison. The first substitution step from $\text{Mo}_{27}\text{S}_{56}$ (IV) to form $\text{Mo}_{27}\text{S}_{55}\text{C}$ (1) is exothermic by 0.77 eV, and the second step from 1 to $\text{Mo}_{27}\text{S}_{54}\text{C}_2$ (2) is exothermic by 0.70 eV. Both steps have nearly the same formation energies, indicating that the sulfur and carbon atoms on the surface are roughly independent. In addition, it is obvious to see that carburization is more favored than sulfidation on the surface. It shows that a direct carburization on the Mo edge of $\text{Mo}_{27}\text{S}_{54}$ (I) also is favored thermodynamically by -14.51 eV. The result shows that the C atom is more favored than the S atom to bond with Mo. It is interesting to note that our results agree well with the finding by Liu et al.⁶ They found that the sulfidation of metal carbides, TiC(001), VC(001), MoC(001), and TaC(001), is endothermic, in agreement with experiments.²⁵

The changes of the surface structure (Mo–Mo distance and Mo–S distance) by carburization are shown in Figure 2. The Mo–Mo bond length is 3.134 and 2.951 Å in $\text{Mo}_{27}\text{S}_{54}$ (I) and

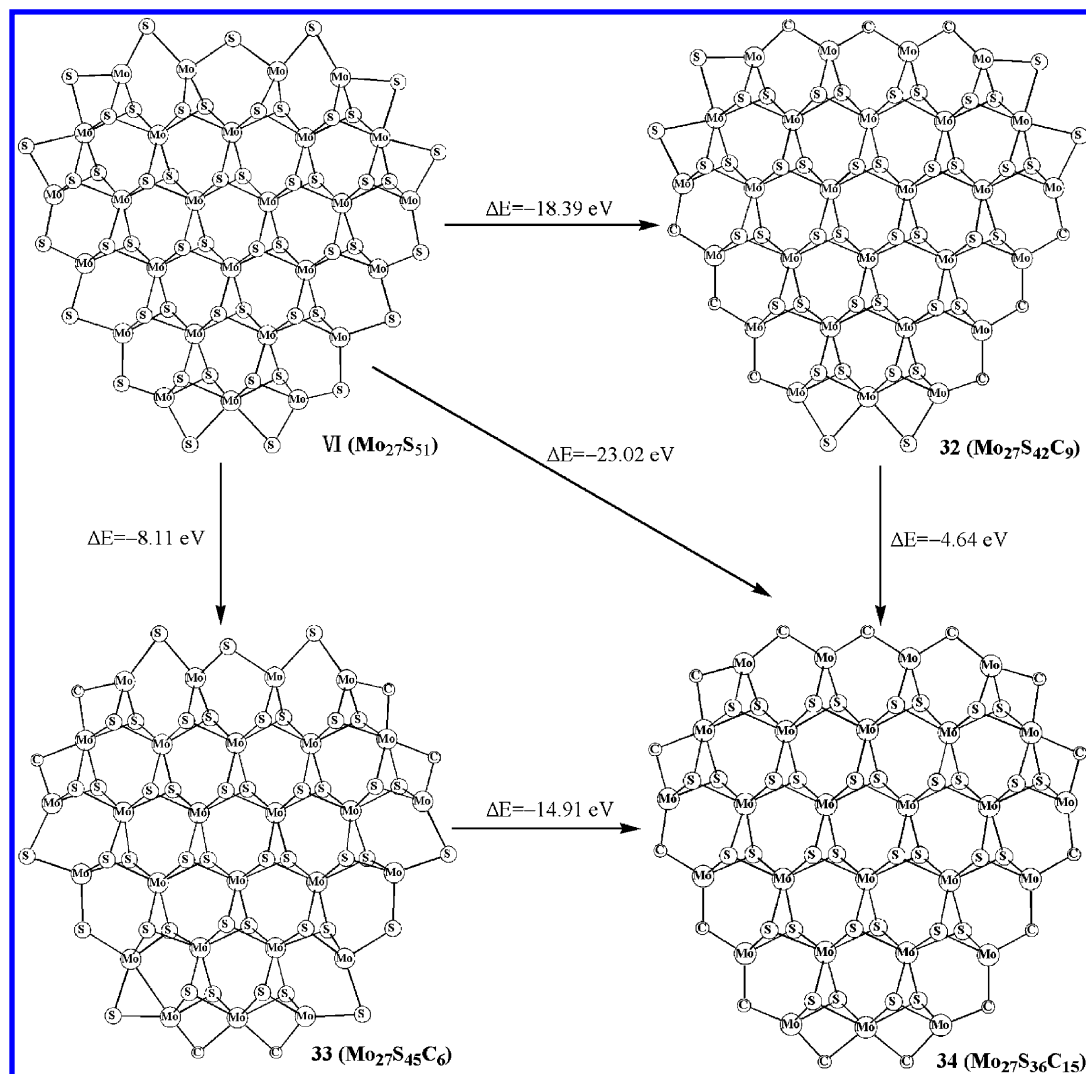


Figure 7. Carburization on $\text{Mo}_{27}\text{S}_{51}$ with 33% sulfur Mo edge and 50% sulfur S edge.

$\text{Mo}_{27}\text{S}_{56}$ (**IV**), respectively, while it becomes shorter in **2** (2.922 Å). The Mo–C distances are 1.889 and 2.021 Å.

3.2. 100% Covered S Edge. There are two structures for replacing one S atom on the 100% covered S edge by one carbon atom in $\text{Mo}_{27}\text{S}_{54}$ (**I**). Structures **3** and **4** with one corner S atom and one edge S atom replaced are shown in Figure 3, respectively. In **3**, the Mo(c)–C and Mo(o)–C bond lengths are 1.935 and 2.029 Å, respectively. In **4**, the Mo(o)–C bond lengths are 2.003 Å. It is interesting that the C atom bonds with the neighboring S atom; the distance is 1.790 Å in **3** and 1.826 Å in **4**. Both replacements are exothermic and have the same formation energies.

For replacing two sulfur atoms on the surface, there are four structures (**5**–**8**). As shown in Figure 3, **5** has two corner S atoms replaced, while **7** has one corner and one edge S atoms replaced. Compounds **6** and **8** have a C_2 replacement at the same corner and edge. The formation energy shows that C_2 replacement at the same corner (**6**, –2.55 eV) and at the same edge (**8**, –2.36 eV) is more favored than those at corner/corner (**5**, –2.08 eV) and corner/edge (**7**, –2.19 eV), respectively. Indeed, both theoretical^{6,26–28} and experimental²⁹ studies revealed the formation of a C_2 unit in the sulfidation process of transition metal carbides.

As shown in Figure 3, there are four structures for replacing three sulfur atoms by carbon atoms (**9**–**12**). In **10**–**12** there is one C_2 bridging unit and one single carbon atom on the corner

or edge, while **9** has three single carbon atoms on the same side of the molecule plane. The formation energy shows that the C_2 bridging unit is more favored than the single C replacement (**10**/–2.45 eV vs **9**/–2.30 eV) and that the C_2 bridging unit at the corner is more favored than at the edge (**11**/–2.53 eV vs **12**/–2.36 eV). In addition, we have also computed the four-carbon (**13**–**16**) and full carbon (**17**) replacement. All these processes are favored thermodynamically.

3.3. Partially Covered S Edge. Figure 4 shows the replacement of a 67% covered S edge in $\text{Mo}_{27}\text{S}_{52}$ (**III**). For one carbon replacement, it shows clearly that the formation of CS bridging units (**19**, –1.87 eV) is more favored than a single carbon bridge (**18**, –0.84 eV). This behavior is also indicated by the formation energies of **21** and **20** of –2.43 and –1.68 eV, respectively. That the formation of the C_2 bridging unit is more favored is also indicated by the formation energy of **22** (–1.96 eV) as compared to **21** (–1.40 eV) from **19**. The full replacement shown in **23** is also highly exothermic.

Figure 5 shows the replacement of a 50% covered S edge in $\text{Mo}_{27}\text{S}_{51}$ (**II**). For one carbon replacement, there are two possible structures (**24** and **25**). The formation energy difference shows that the edge bridging carbon (**25**, –1.48 eV) can be more easily formed than the corner one (**24**, –1.22 eV). This relationship is also confirmed by the additional S replacement in **24** (i.e., the formation of **27** (–1.56 eV) is more easily attained than that of **26** (–1.45 eV)). The full replacement is shown in **28**.

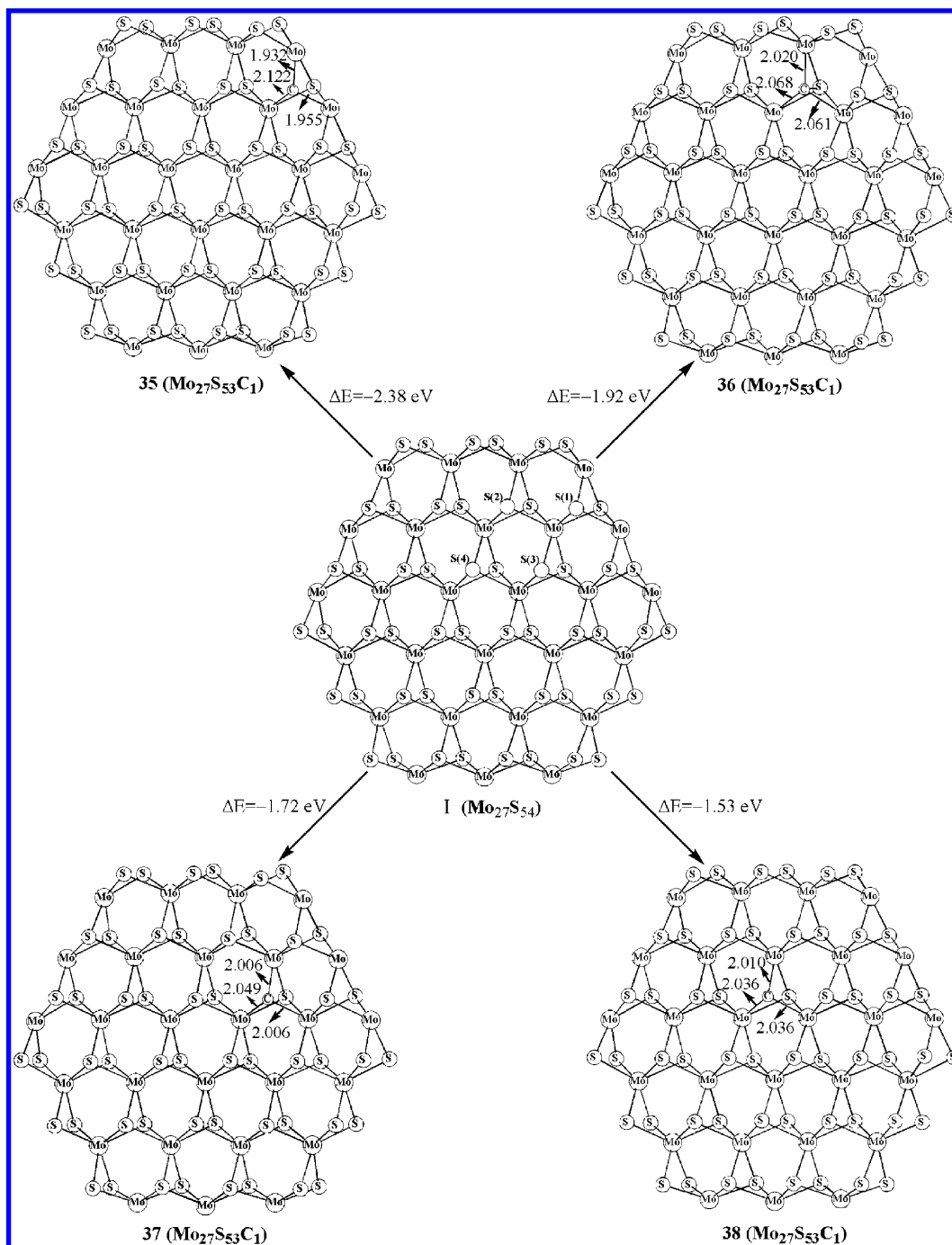


Figure 8. Carburization on the bulk of $\text{Mo}_{27}\text{S}_{54}$.

Apart from the individual replacement of S on the Mo edge and S edge, we have also computed the replacement of S at both edges at the same time. Figure 6 shows the replacement of S in $\text{Mo}_{27}\text{S}_{60}$ (V) with a 100% covered S edge and 33% covered Mo edge. It shows that sulfur on the S edge can be more easily replaced than S on the Mo edge, as indicated by the formation energy per replaced S (29/S, -2.35 eV vs 30/S, -1.33 eV). Therefore, the sulfur on the S edge should be first replaced. The full replacement is shown in 31.

Figure 7 shows the replacement of S in $\text{Mo}_{27}\text{S}_{51}$ (VI) with a 33% covered Mo edge and 67% covered S edge. Despite the partially covered S edge, the replacement of sulfur on the S edge is more easily attained than that on the partially covered Mo edge, as indicated by the formation energy per replaced S (32/S, -2.04 eV vs 33/S, -1.35 eV). The same energetic

behavior is also indicated by the formation of the fully replaced 34, deduced from 32 and 33 (-0.77 vs -1.65 eV, respectively).

3.4. Replacing the Bulky S in $\text{Mo}_{27}\text{S}_{54}$. In addition to the replacement of surface sulfur on the Mo edge and S edge, it is interesting to show the possibility for replacing the bulky sulfur. As shown in Figure 8, there are four types of bulky sulfur atoms in $\text{Mo}_{27}\text{S}_{54}$ (I). The first bulky sulfur is S_1 to the Mo edge, and the second type is S_2 close to the S edge. The third type is S_3 , which is one line deeper than S_1 , and the fourth type is S_4 , which is one line deeper than S_2 .

The replacement of S_1 is much easier than that of S_2 , as indicated by the formation energy of 35 (-2.38 eV) and 36 (-1.92 eV). Comparably, the replacement of S_3 and S_4 is very difficult (37, -1.72 eV and 38, -1.53 eV, respectively).

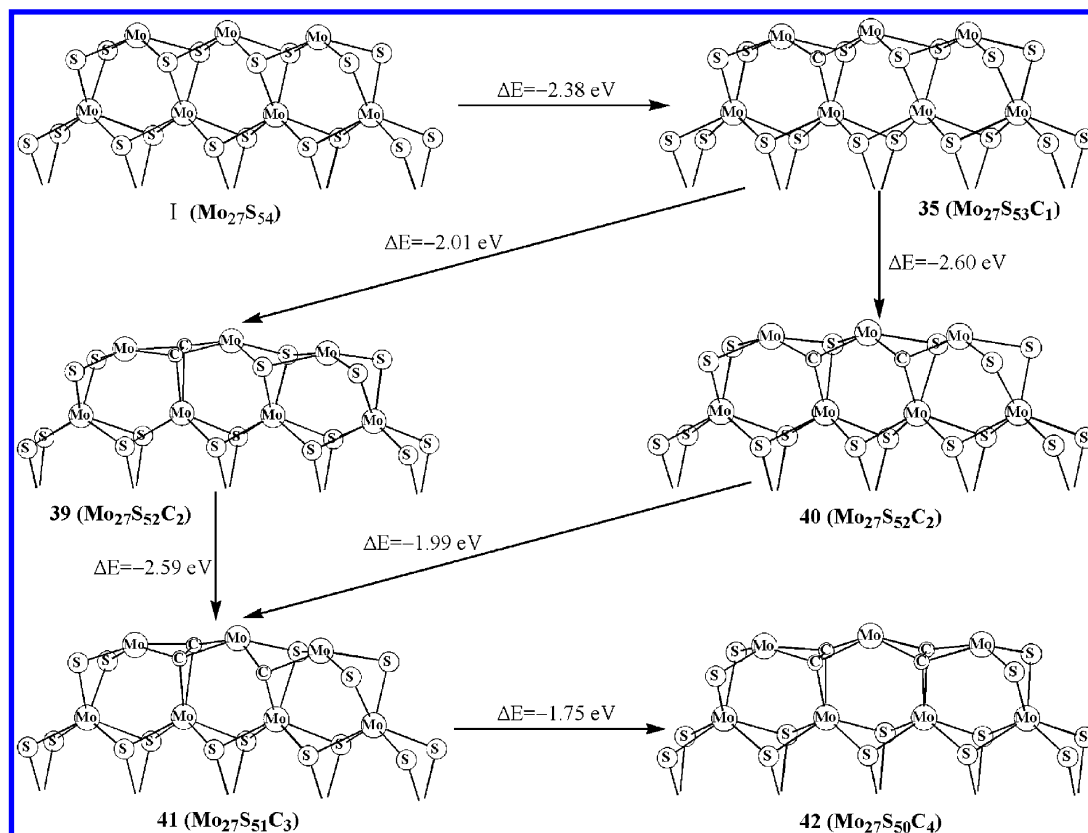


Figure 9. Carburization on the bulky S_1 atoms of $\text{Mo}_{27}\text{S}_{54}$.

Therefore, S_1 is the type of bulky sulfur that can be replaced most easily.

On this basis, the replacement of other S_1 atoms is also reported. Structures **39** and **40** with replacing two S_1 atoms at different sides and at the same site are shown in Figure 9, respectively. The formation energy shows that replacing two S_1 atoms at the same side (**40**, -2.60 eV) is more favored than that at different sides (**39**, -2.01 eV). The same result is shown in **41** (-2.59 vs -1.99 eV). In addition, the replacement of four S_1 atoms (**42**, -1.75 eV) is also exothermic.

It is interesting to note that the replacement of S_1 is as favorable as that of sulfur on the S edge; therefore, concurrent replacement of both sulfur types could be possible. For that, we have also computed the replacement edge S atoms at 100% sulfur covered S edge and bulky S_1 atoms in the $\text{Mo}_{27}\text{S}_{54}$ cluster. As shown in Figure 10, the replacement of S atoms at the 100% S edge (**44/S**, -2.29 eV) and S_1 atoms (**43/S**, -2.17 eV) are easy. The full replacement of 30 S atoms shown in **45** ($\text{Mo}_{27}\text{S}_{24}\text{C}_{30}$) is also exothermic.

4. Conclusion

To understand the carburization process of the MoS_x catalyst, we have carried out systematic investigations into the replacement process of the surface sulfur on the Mo edge and S edge as well as bulky sulfur. On all surfaces, replacement of surface sulfur by a carbon atom is thermodynamically favored, indicating that carburization is more favored than sulfidation on the surface of catalysts. For surface sulfur on the S edge with different coverages, it is found that the higher the sulfur coverage, the easier the replacement by carbon. Further comparison shows that the formation of CS and C_2 bridging units is more favored than individual or separated replacements. In contrast, the replacement of sulfur on the Mo edge is least favored. Apart from these results, the most surprising finding

is that the replacement of the bulky sulfur on the Mo edge is as equally favored as those of sulfur on the S edge. It is worth noting that sulfur replacement favored by carbon is supported by the endothermic sulfidation of transition metal carbides.⁶ The favored formation of a C_2 unit is also supported by theoretical studies^{6,26–28} and experimental findings.²⁹

Experimentally, two carburization processes are usually known. One is the pretreatment of the sulfide active phase with a different sulfiding agent (i.e., RSH , $\text{CH}_3\text{—S—CH}_3$, $\text{CH}_3\text{—S—S—CH}_3$, or other alkylpolysulfides).¹¹ The other process is the pretreatment of MoS_2 catalysts with $(\text{NR}_4)_2\text{MoS}_4$ (R = alkyl group).² The pretreated catalysts have higher HDS activity or beneficial effect of carbon. Chianelli et al.³⁰ have observed an increase of HDS activity by a factor of 2.5–3 for carbon-containing precursors as compared to a standard MoS_2 samples, and they attributed the enhanced activity to the formation of smaller and less stacked crystallites (i.e., carbon strongly increases the morphological properties and structurally modifies the MoS_2 particles).

XRD and IR experiments¹¹ did not reveal the presence of a bulk carbide phase after a treatment, while EELS techniques showed the formation of Mo—C bonds at the surface of $(\text{CH}_3)_2\text{S}$ treated MoS_2 particles. Therefore, they suggested that a carburization process seemed to occur by replacing some sulfur atoms by carbon without phase segregation, and the MoS_2 active edge sites would then be first involved in this replacement.

For general comparison and aiding further experimental studies, these frequencies of C=S and C=C bridging units of these structures (**13–16**) with replacing four sulfur atoms by carbon atoms have been computed. The C=S frequency is 689 cm^{-1} at the corner site and 631 cm^{-1} at the edge site in **13**, and that of C=C is 1245 cm^{-1} . In **14**, the stretching frequencies for C=S and C=C are 689 and 1309 cm^{-1} , respectively. The frequencies for C=C at the corner sites are 1265 and 1243 cm^{-1}

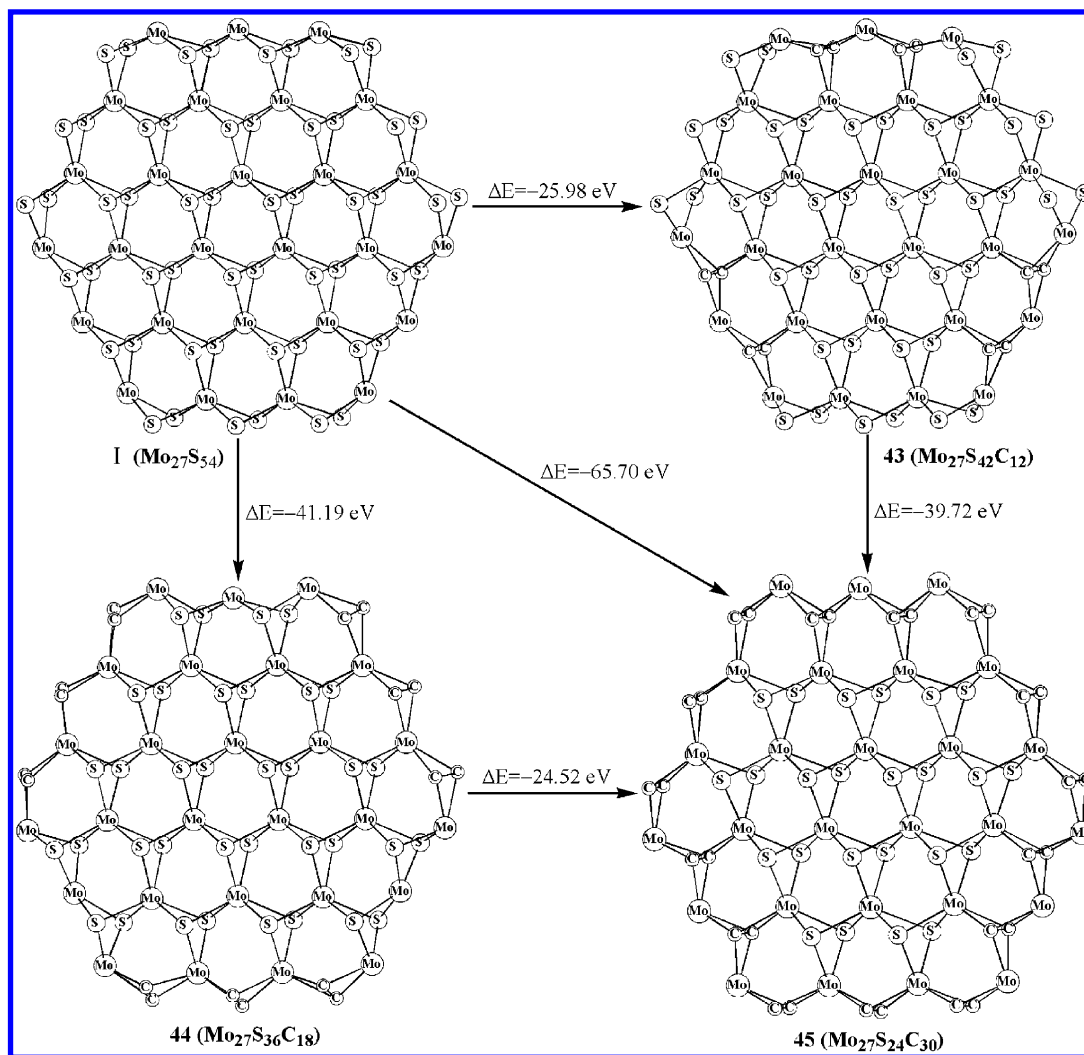


Figure 10. Carburization on 100% sulfur coverage S edge and bulky S_1 atoms of $Mo_{27}S_{54}$.

in **15**, respectively. In **16**, the frequencies for C=C at the corner and edge sites are 1029 and 1305 cm^{-1} , respectively. Experimentally, Berhault et al.¹¹ have reported the evolution of IR spectra of MoS_2 by $(CH_3)_2S$ treatment. In the mid-IR region, a very broad band at 1093 cm^{-1} (from 1000 to 1300 cm^{-1}) and a minor signal at 830 cm^{-1} are observed, and they suggested that these peaks are related to the intermediary products of $(CH_3)_2S$ decomposition as a $(C_xS)_n$ polymer species. It is also worth noting that most of our computed C=C frequencies for **13**, **15**, and **16** are in the experimental range.¹¹ Despite this agreement, further studies from theory and experiment are needed for detailed comparison.

Berhault et al.¹¹ proposed three MoS_xC_y catalysts with different S/C ratios; $MoS_{2.05}C_{1.12}$ (S/C = 1.83), $MoS_{1.96}C_{1.17}$ (S/C = 1.68), and $MoS_{1.82}C_{0.22}$ (S/C = 8.27). In our work, carburization structures with different S/C ratios (from 0.8 to 55) were reported. In these structures, the S/C ratios of **15** (S/C = 8.00) and **25** (S/C = 9) are close to that of $MoS_{1.82}C_{0.22}$ (S/C = 8.27). In addition, structures **26** (S/C = 1.50) and **44** (S/C = 2.00) have close S/C ratios to those of $MoS_{1.96}C_{1.17}$ (S/C = 1.68) and $MoS_{2.05}C_{1.12}$ (S/C = 1.83).

In addition, Berhault et al.¹¹ suggested that MoS_2 particles can be progressively modified by carburization starting on the surface and progressively modified by the bulk structures. In our studies, carburization for the bulk S_1 atom is more favored, while that of inner bulk S atoms is not favored. Our model

cluster, $Mo_{27}S_{24}C_{30}$ (**45**), with a fully carbonized S edge and S_1 bulky sulfur, represents the most favored full carburization.

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Supporting Information Available: Total electronic energies, bond lengths for all models, and carburization structures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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