Ab initio Study of Structural Stability of Mo−S Clusters and Size Specific Stoichiometries of Magic Clusters

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Using first-principles calculations with ultrasoft pseudopotential formalism and the generalized gradient approximation for the exchange-correlation functional, we study the stability of Mo_nS_m ($n = 1-6$ and m ranging from n to $3n$) clusters and obtain the optimal stoichiometry for each n corresponding to the magic cluster. It is found that in this size range, the lowest-energy structures favor a core of metal atoms, which is covered by sulfur. In particular, we observe that for Mo_6S_{14} isolated clusters, a 3D structure is significantly lower in energy as compared to platelet structures found recently on Au (111) surface. The composition ratio between S and Mo in the magic clusters is less than 2 for $n = 3$ and greater than 2 for $n < 3$. The structural stability of the magic clusters arises from the optimization of the Mo−Mo and Mo− S bonding as well as the symmetry of the cluster. Addition of a terminal sulfur in a magic cluster generally lowers its binding energy. The presence of partially occupied d-orbitals in Mo atoms contributes to Mo−Mo bonding and for higher S concentration it leads to sulfur−sulfur bond formation. The variation in energy due to a change in the sulfur composition suggests that sulfurization of the magic clusters is generally more favorable than desulfurization.

1. Introduction

Currently there is a growing interest in understanding the properties of clusters and nanoparticles of different materials. Much progress has been made in the case of elemental clusters, but the study of clusters of alloys and compounds is more challenging because the number of possible configurations even for the same structure can become large. Also, the optimal stoichiometry of compound clusters with the magic behavior could be different from the bulk stoichiometry, particularly in the size range of less than a nanometer. This can be expected to be due to the differing charge states of metal atoms arising from different environments in clusters as compared to crystalline bulk. This could lead to novel structural features in clusters for various sizes and consequently to the evolution of interesting properties on the way to bulk behavior.

MoS_x clusters are used as catalyst for removing sulfur during petroleum refining process.[1] In bulk, there are three well-known stoichiometries MoS_2, Mo_2S_3, and MoS_3. Among these, MoS_2 and Mo_2S_3 crystallize in a hexagonal (space group P63/ mmc) and a monoclinic (P21/m) lattice,[2] respectively, whereas for MoS_3 an amorphous form has been observed.[3,4] In a model of the amorphous structure that gives good agreement with the experimental results, there are Mo− Mo as well as sulfur−sulfur bonds. This suggests that Mo− Mo bonds are preferred even for a higher concentration of S. This aspect we also find in our studies, and it differs from the behavior for MoO_3. The similarity of the layered structure of the crystalline MoS_2 with graphite has been exploited at the nanoscale, to develop fullerene like species,[5] nanotubes,[6] nanoflowers,[7] and nanoplatelets.[8] Also nanotubes[9] and nanorods[10] have been formed from Mo_2S_3, as it has a layered structure as well. Possibilities of hydrogen storage in these nanostructures have been explored.[11] Therefore, there is much interest in understanding the properties of nanostructures of MoS_x. Triangular-shaped nanoparticles of MoS_2 with about 4 nm width and monolayer thickness have been synthesized on Au (111) surface.[12] The atomic structure of such nanoparticles has been studied using bulk fragments of MoS_2. However, we have earlier shown[13] that bulk fragments of small clusters with the size of ∼1 nm are less stable compared to other structures in which clustering of Mo atoms is favored at the core and the surface is capped by S atoms. The higher stability of these clusters with a core of metal atoms is due to the presence of the partially occupied d-orbitals of Mo atoms. This result is also supported by the independent quantum mechanical calculations[14,15] that show the existence of Mo−Mo interactions in small clusters. Moreover, partial Mo−Mo bonding exists in bulk Mo_2S_3 with a bond distance of 2.84 Å.[17]

The presence of S atoms on the surface of Mo clusters could lead to a higher probability of addition or removal of sulfur atoms in such units. In order to understand the behavior of these clusters as the sulfur content is changed as well as to obtain the composition of the magic cluster for each size, we have studied a large set of cluster species. Experimentally often bulk MoS_2 is used[18,19] to produce MoS_x clusters. However, in the magic clusters, the composition ratio between S and Mo atoms could be higher or less than in bulk MoS_2. For the case of $n = 4$, the magic cluster, Mo_4S_6 has the S:Mo stoichiometry ratio of 1.5, and it has been synthesized. It has a large gap of about 2 eV between the highest occupied molecular orbital (HOMO) and

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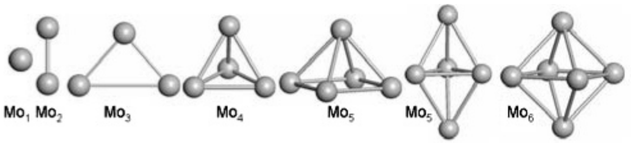

Figure 1. Cluster units of Mo_n used as core for the sulfide clusters. Geometries of the sulfide clusters Mo_nS_m, to be referred to as (n,m), are generated by addition of S atoms at terminal, edge, and face capping sites.

the lowest unoccupied molecular orbital (LUMO) and its structure has been predicted from density functional theory calculations.[18] Recently, negatively charged magic clusters $Mo_{13}S_{25}$ and $Mo_{13}S_{28}$ have also been obtained using laser evaporation technique.[19] These studies also reveal that the composition ratio between S and Mo for small MoS_x magic clusters is different from bulk. In this work, we aim to obtain the composition ratios between S and Mo atoms that correspond to the highest stability (magic clusters) of Mo_nS_m with $n = 1-6$. We study the structural stability of clusters with m ranging from n to $3n$ for each n. These results are further used to discuss sulfurization and desulfurization of magic clusters.

2. Computational Method

We perform first-principles calculations using an ultrasoft pseudopotential plane wave method[20] and generalized gradient approximation[21] with the Perdew−Wang exchange-correlation functional (PW91) as implemented in VASP.[22] The valence electronic configurations of Mo and S are described by $4d^55s^1$ and $3s^23p^4$, respectively. The cluster is kept in a large cubic cell of side, larger than 15 Å. The Brillouin Zone of this cell is sampled by the Γ point. For each size a few initial atomic configurations are considered and all structures are fully optimized for each size without any symmetry constraint using the conjugate gradient method. The optimization process is repeated until the force on each ion becomes less than 0.001 eV/Å. In order to reduce the computational time, initial calculations have been done without spin-polarization. The converged structures are re-optimized by performing spin-polarized calculations as the presence of partially occupied d-electrons in Mo atoms could give rise to magnetism in these clusters. The structural changes due to spin-polarization are quite small in all cases. Further calculations have been done for a few clusters using the projected augmented wave (PAW) method[23] implemented in the VASP program to verify the accuracy of the ultrasoft pseudopotentials. In all cases, the lowest energy isomer was found to be the same as obtained from the ultrasoft pseudo-potentials.

3. Results and Discussion

The initial structures of Mo_nS_m clusters are generated by capping S atoms on a core of Mo_n cluster. The geometries of Mo_n clusters used in this work are shown in Figure 1. These structures were found to be favored from our studies on stoichiometric MoS_2 clusters,[13] where we have generated and studied several initial configurations. The geometries of Mo_n clusters for $n = 1-6$ are point, line, triangle, tetrahedron, square pyramid, and octahedron, respectively. In addition, we also considered a trigonal bipyramid isomer of Mo_5 as its binding energy per atom (BE) is nearly degenerate with the square pyramid isomer. Our consideration of geometries of Mo_n units is also quite consistent with the results obtained from density functional calculations on Mo clusters.[24] For S atoms, we have considered face (S_F) or edge (S_E) or terminal (S_T) capping or a combination of these depending upon the composition.

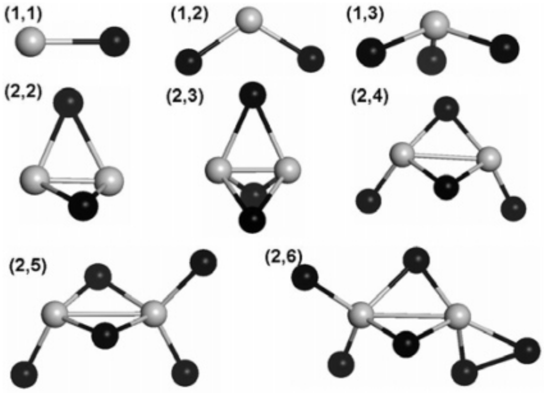

Figure 2. Most stable structures of Mo_1S_m and Mo_2S_m clusters with $m = n$ to $3n$. Grey (black) balls represent Mo(S) atoms. S−S bonding is observed for Mo_2S_6 cluster.

TABLE 1: BE (Unit, eV/atom) of the Lowest-Energy Isomers of Mo_nS_m Clusters, HOMO−LUMO Gap (eV), and Magnetic Moment (M) in μ_B

n	m	BE	Gap	M
1	1	2.10	0.00	4
1	2	3.16	0.55	2
1	3	3.57	0.33	0
2	2	3.53	0.90	0
2	3	3.91	1.55	0
2	4	3.94	0.35	2
2	5	4.09	0.77	0
2	6	4.04	0.90	0

The BE is used to identify the most stable stoichiometry, and it is obtained from

$$\mathrm{BE} = \frac{nE(\mathrm{Mo}) + mE(\mathrm{S}) - E(\mathrm{Mo}_n\mathrm{S}_m)}{n + m}$$

where E(Mo), E(S), and $E(Mo_nS_m)$ are the total energies of a Mo atom, a S atom, and Mo_nS_m cluster. The BE for the optimized most stable configuration for each Mo_nS_m is given in Table 1, and the corresponding atomic structures are shown in Figure 2 for $n = 1$ and 2. Other less stable structures are not discussed here. Some of these structures have been presented in our earlier work.[13]

To understand the bonding nature and the electronic and magnetic properties of Mo_1S_m ($m = 1-3$) clusters, S atoms are capped on an Mo atom as S_T atoms and the relaxed structures are shown in Figure 2. In all cases Mo−S bond is predominantly formed with the bond length of ~2.14 Å. The BE of these clusters increases with m (Table 1), and the highest stability is obtained for Mo_1S_3. This is the highest stoichiometry ratio in this series and it is nonmagnetic as all the valence electrons contribute to form Mo−S_T bonds in this case. Magnetic moments are, however, obtained for both Mo_1S_1 and Mo_1S_2 clusters (Table 1) as there are partially occupied d-orbitals on Mo atoms.

The stable structures of Mo_2S_m, $m = 2-6$ (Figure 2) show that two or three S atoms favor edge capping (S_E) of Mo_2 dimer and the remaining S atoms are placed at the S_T positions. In the case of $m = 3$, there is a 3-fold symmetric structure, and it has a large HOMO−LUMO gap of 1.55 eV as well as a large increase in the BE as compared to the $m = 2$ case. Capping of this structure with one S_T atom to achieve a 3-fold symmetric structure of Mo_2S_4 leads to a magnetic isomer (~2μ_B), which is about 0.6 eV higher in energy than the isomer shown in Figure

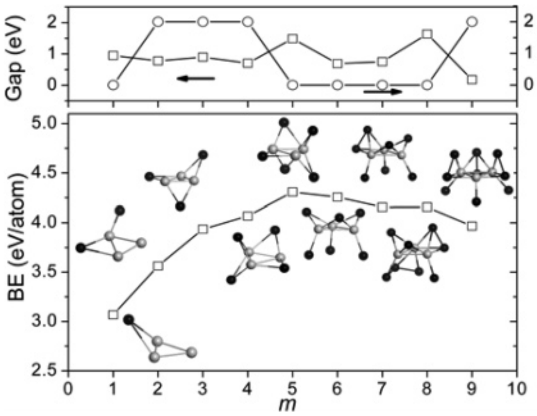

Figure 3. Most stable structures for Mo_3S_m clusters and their BE, HOMO−LUMO gap, and magnetic moments (*M*). Among Mo_3S_m clusters, Mo_3S_5 has the highest BE that leads to its magic behavior.

2. Furthermore, the addition of four S_E atoms around Mo_2 is quite unstable. This clearly shows that Mo_2 can accommodate only three S_E atoms. In the case of $m = 5$, capping of the Mo_2S_3 lowest energy isomer with two S_T atoms, one on each Mo atom, does not have the lowest energy as an occupied state lies above a large gap. Another isomer (shown in Figure 2) of lower symmetry has the lowest energy. In this isomer, one Mo atom has four sulfur atoms in a tetrahedral arrangement similar to the case of MoO_2 clusters,[25] and the Mo−Mo bond length is slightly elongated. However, in the case of $m = 6$, tetrahedral arrangement of sulfur around both the Mo atoms is not favored as Mo− Mo interactions are also important and an initial symmetric configuration with four S_T atoms around each Mo converges to the structure shown in Figure 2. In this structure, there is also a pair of sulfur atoms, and it reduces the BE of this cluster as compared to the case of $m = 5$. This result suggests that in Mo−S clusters complete sharing of *d* electrons with S atoms is not energetically favored. Therefore, there is a formation of sulfur−sulfur bond that leads to a small decrease in the BE. In this configuration of Mo_2S_6, the Mo−Mo, Mo−S_E, and S−S bond distances are 2.79, 2.34, and 2.08 Å, respectively. It is quite consistent with the earlier work on MoS_3 clusters[15] using the B3LYP density functional theory. Therefore, for $n = 2$ series, Mo_2S_5 is expected to be the magic cluster, since it has the highest BE. However, considering the second order difference in energy which is also used as a criterion for magic clusters[16] and the large HOMO−LUMO gap, we expect Mo_2S_3 to be also strongly abundant.

Structural stability of sulfide clusters with an Mo_3 triangle is studied by adding up to nine S atoms. In most cases, S atoms prefer edge capping positions of a triangle. But for Mo_3S_2, the lowest energy structure has one S_E and one sulfur atom which is displaced from S_E position toward the S_T position. This is due to the d−s−p hybridization. The angle between S_T−Mo−S_E is about 146°, which is close to one of the angles (∼136°) of d−s−p hybrid orbitals. The d−s−p hybridization is an important feature for bulk MoS_2[26]. The largest BE per atom is found for Mo_3S_5 and its HOMO−LUMO gap is also large (∼1.5 eV). Another isomer with a mixture of edge and face capping of S in Mo_3S_5 is quite unfavorable. It lies 1.18 eV higher than the lowest energy structure shown in Figure 3. In all structures, the bonding nature of Mo_3 triangle is preserved even with increasing number of S atoms. This is also due to the increasing BE of Mo clusters with size. Due to this behavior, one sulfur−sulfur bond is formed for $m \geq 7$ as expected from the earlier case also. This leads to lower BE of these clusters and also interestingly, 2 μ_B, magnetic moment is present in Mo_3S_9 due to the partially occupied d-orbitals in Mo atoms.

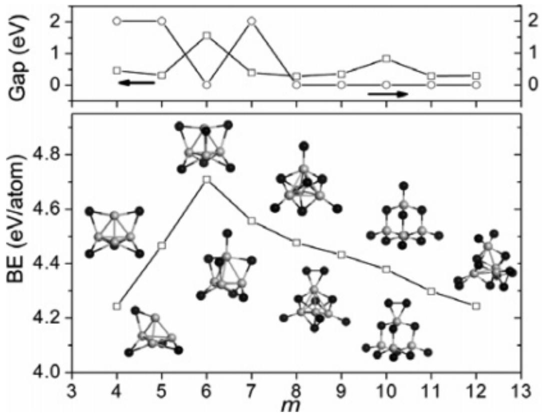

Figure 4. Same as in Figure 3 but for Mo_4S_m clusters. Mo_4S_6 has the highest stability.

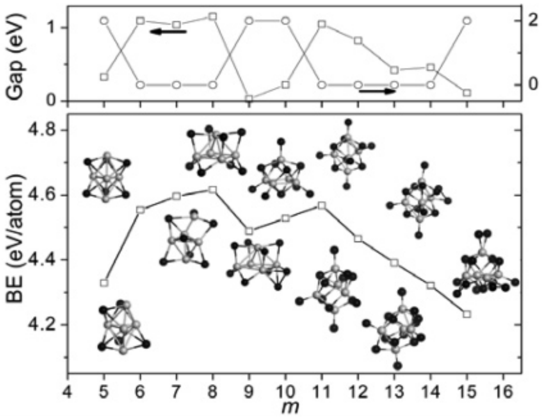

Figure 5. Same as in Figure 3 but for Mo_5S_m. Mo_5S_8 has the highest stability.

For Mo_4S_m, we studied clusters with $m = 4-12$. The relaxed structures, their BE, the HOMO−LUMO gap, and the magnetic moments are given in Figure 4. In these cases S atoms occupy either S_E or S_F sites. The largest BE in this series is found for Mo_4S_6. It is quite consistent with the experimental and theoretical findings of Bertram et al.[18] The HOMO−LUMO gap for this cluster is also large (∼1.57 eV). Addition of four S_T atoms in Mo_4S_6 cluster makes the Mo−Mo bonding in Mo_4 tetrahedron of Mo_4S_{10} weaker. The S atoms become tetrahedrally arranged around each Mo atom and the cluster has an overall tetrahedral symmetry. The high symmetry also leads to a large HOMO−LUMO gap of about 1.0 eV compared with the values for clusters with nearby stoichiometry. However, this cluster is not magic as the weaker Mo−Mo bonds reduce the BE of Mo_4S_{10}. Therefore, an important criterion for the stability of these clusters is the formation of strong Mo−Mo bonds and not just symmetry. Further addition of a sulfur atom leads to the formation of S−S bond in Mo_4S_{11}, supporting again the preference for the partially occupied d-orbitals in Mo atoms.

To study the structural stability with respect to increasing sulfur content on Mo_5 cluster, we considered two different isomers of Mo_5, namely, a square pyramid and a trigonal bipyramid because the BEs for the two isomers in the case of Mo_5S_{10} is quite comparable with each other.[13] The optimized atomic structures, BE, HOMO−LUMO gap, and the magnetic moments are shown in Figure 5. We find that Mo_5S_8 has the largest BE in this series with a square pyramidal structure. The HOMO−LUMO gap is also the largest (1.15 eV) in this series.

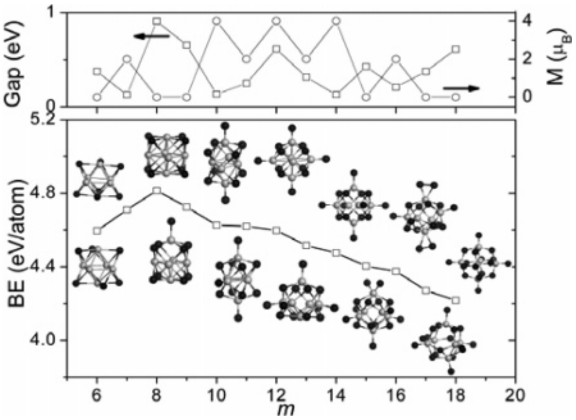

Figure 6. Same as in Figure 3 but for Mo_6S_m. Mo_6S_8 has the highest stability.

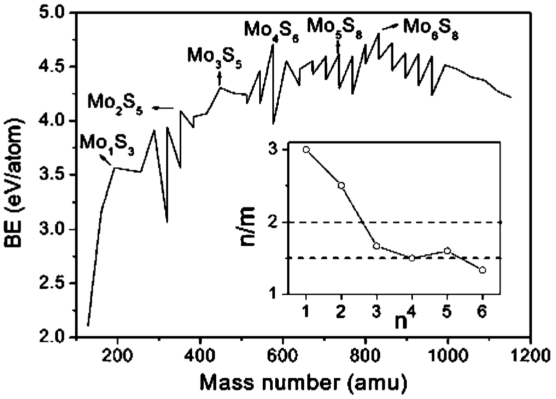

Figure 7. BE of the lowest-energy Mo_nS_m clusters with respect to their mass number. Most stable (magic) clusters of Mo_nS_m are marked. The BE of such clusters is significantly larger than the value for clusters with nearby mass numbers. The variation in the stoichiometry for different "n" is shown in the inset. The stoichiometry ratio is lower than 2 for $n > 2$.

This structure has 4-fold rotational symmetry with only S_E atoms as shown in Figure 5. For the same stoichiometry in the bipyramid isomer, two S_T atoms are required which increases the total energy by ~0.6 eV. However, in the case of Mo_5S_6 only the faces of the bipyramid are covered by S atoms. This leads to a 3-fold rotational symmetry of this cluster and a large HOMO−LUMO gap of 1.09 eV which again makes this isomer to be more favorable than the square pyramid. When five S_T atoms are added in Mo_5S_6 and Mo_5S_8, we obtain symmetric structures for Mo_5S_{11} and Mo_5S_{13} clusters, respectively. Interestingly, the BE of Mo_5S_{11} (4.57 eV/atom) is slightly higher compared to Mo_5S_6 (4.55 eV/atom), though in general S_T atoms tend to lower the BE. Also, in this case the HOMO−LUMO gap is large (1.05 eV), which suggests that this cluster has special stability. This is reflected as local maximum in the BE curve (Figure 5). In this case the two apex Mo atoms have tetrahedral arrangement of sulfur atoms while the remaining three Mo atoms have five neighboring sulfur atoms giving rise to a mixed bonding character. However, for Mo_5S_{13} (structure not shown) there is an abrupt decrease in BE by about 0.45 eV/atom compared to the value for Mo_5S_8, and this is not the lowest-energy isomer for this composition. As shown in Figure 5, an isomer based on trigonal bipyramid becomes lower in energy. Structures for other compositions are also shown in Figure 5. Both trigonal bipyramid and square pyramid isomers can be seen. The BE shows a sharp decrease with increasing number of S atoms beyond $m = 11$.

Most of the stable structures of Mo_6S_m show that in this case S_F atoms are preferred on an Mo_6 octahedron. Mo_6S_8 has the largest BE (~ 4.81 eV/atom) among all the clusters we have studied. It has also the largest HOMO−LUMO gap (0.91 eV) in this series. If edge capping of an octahedron is considered then we obtain Mo_6S_{12} cluster which is also a symmetric isomer but this does not have the lowest energy. Addition of six S_T atoms in S_E and S_F capped clusters of Mo_6 octahedron decreases the stability of these clusters significantly as it can be seen in Figure 6. For $m = 12$, 14, and 18 the lowest energy structures have D4h, Oh, and C4h symmetries, respectively. The former two isomers have face capped octahedra with four and six S_T atoms, respectively. In the case of $m = 18$, six S_T atoms are added on an edge capped isomer. For $m = 12$, there is a large HOMO−LUMO gap as well as a large magnetic moment of $4\mu_B$. However, for $m = 14$, the high symmetry leads to a small HOMO−LUMO gap due to the partially occupied HOMO which leads to Jahn−Teller distortion as well as a large magnetic moment of $4\mu_B$. For $m = 18$, the magnetic moment becomes zero and there is a significant HOMO−LUMO gap. In this case the structure attains MoS_3 stoichiometry and Mo−Mo bonding is reduced. However, among the structures we have studied in this case, we did not find preference for S−S bond formation.

Recently, triangular shaped platelet structures of Mo−S clusters have been obtained on Au (111) surface.[28] One of the smallest such platelet is for Mo_6S_{14} cluster. It is possible that with increasing S content, open structures of Mo−S clusters become favorable in order to increase the Mo−S interaction. As an example, S atoms can interact on both the sides of Mo planar structures, while in closed packed core in 3D structure; the Mo−S interaction takes place only on the outer surface. Energetically also, it is plausible as Mo−S interaction is more favorable compared to Mo−Mo interaction. In order to check this possibility, we considered platelet and 3-D isomers of Mo_6S_{14} and found the 3D isomers to be 5.57 eV lower in total energy as compared to platelet isomer (see Supporting Information). This result supports our findings that in the size range under consideration, a core of Mo atoms is most preferred.[29]

Figure 7 shows the BE of the stable clusters of Mo_nS_m as a function of the mass number of the clusters. The mass numbers for Mo and S atoms used in these calculations are 95.94 and 32.066 amu, respectively. The most stable clusters in each series of Mo_nS_m are marked and these have pronounced peaks among the nearby mass numbers except for Mo_5S_8 and should be magic. Indeed, Mo_2S_5 and Mo_4S_6 magic clusters have already been synthesized and have been found to show high abundances.[18,19] Also, Mo_2S_3 has been obtained as we find from our calculations. The composition ratio between S and Mo atoms for the most stable Mo_nS_m isomer is shown with respect to the number of Mo atoms in the inset of Figure 7. This ratio is always less than 2 for $n \geq 3$, and it comes around the stoichiometry of Mo_2S_3. This ratio decreases further for the $n = 6$ case. Therefore, for the small clusters there is substoichiometry of sulfur due to the preference of a core of Mo cluster. It would be of interest to know how the stoichiometry would change for the clusters with $n > 6$. A detailed study of this aspect is in progress. Our results also suggest that the small clusters of MoS_2 or MoS_3 should transform to magic clusters with substoichiometries by removal of S atoms.

It is important to discuss the reason for the sub-stoichiometric ratio of S in magic clusters that we have obtained. First, as discussed before the existence of Mo core in these clusters is due to the presence of partially occupied d-orbitals in Mo atoms.[13] Second, the preferential sites for S atoms on Mo clusters are either, edges or faces, rather than terminal sulfur atoms. The total number of sites for edge capping or face capping of Mo_n

clusters is less than 2*n* in these clusters, except for the octahedron. Note that Mo_6S_{12} has edge capping by sulfur and it is not favored.[13] Third, the occupation of additional S atoms other than S_E and/or S_F atoms should be on the terminal sites of Mo clusters[27] and it generally decreases the stability of the structure. Hence, the composition ratio between S and Mo atoms for the magic clusters is maintained always to be less than two in this size range.

Furthermore, in spite of the sub-stoichiometry, the magic clusters do not have any magnetic moment. The magic clusters have high symmetry, and the addition or removal of S atoms in such magic clusters leads to an asymmetric charge distribution and the development of magnetic moment in general. Such magnetic isomers always have lower structural stability. Thus, magnetic clusters are more likely to become magic cluster by addition or removal of S atoms depending upon the growth conditions. Moreover, we find from Figures 3−6 that addition of a S atom leads to energy gain which is much higher as compared to the value of BE of 2.65 eV/atom in S_2 molecule. Therefore Mo−S clusters can accept sulfur atoms. This is an important criterion for petrochemical refineries where Mo−S clusters are used as a catalyst for the removal of S content from the petroleum products.

4. Summary

In summary, we have explored stable structures of Mo_nS_m clusters with $n = 1-6$ and m ranging from n to $3n$ by considering various configurations of face, edge and terminal capping of sulfur atoms around a core of a Mo cluster using first principles calculations. From these results, magic clusters have been identified for each n. The stoichiometry ratios between S and Mo in the magic clusters are found to be less than 2 for $n \geq 3$ and close to 1.5 in the cases considered here. The reason for the stability of these magic clusters is explained. We find that the addition of S_T atoms generally leads to a decrease in the structural stability of clusters as it also weakens the Mo−Mo bonds. Also for higher S contents we find a tendency for the formation of S−S bonds that also weaken the stability of the clusters. The formation of S−S bond is indicative of the preference for Mo−Mo interactions due to the presence of the partially occupied d-orbitals in Mo atoms. Furthermore, the energy gain by addition of higher S contents is still much higher as compared to the binding energy in a sulfur molecule. This could still make it favorable for the removal of sulfur atoms by Mo−S clusters in petrochemical refineries.

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Supporting Information Available: Structures and description of Mo_6S_{14} isomers. This material is available free of charge via the Internet at http://pubs.acs.org.

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