

Sulfurization of MoO₃ in the Chemical Vapor Deposition Synthesis of MoS₂ Enhanced by an H₂S/H₂ Mixture

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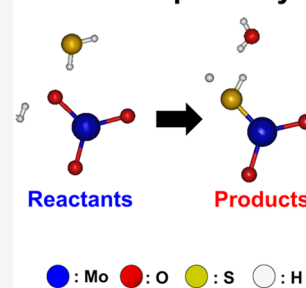
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Supporting Information

ABSTRACT: The typical layered transition metal dichalcogenide (TMDC) material, MoS₂, is considered a promising candidate for the next-generation electronic device due to its exceptional physical and chemical properties. In chemical vapor deposition synthesis, the sulfurization of MoO₃ powders is an essential reaction step in which the MoO₃ reactants are converted into MoS₂ products. Recent studies have suggested using an H₂S/H₂ mixture to reduce MoO₃ powders in an effective way. However, reaction mechanisms associated with the sulfurization of MoO₃ by the H₂S/H₂ mixture are yet to be fully understood. Here, we perform quantum molecular dynamics (QMD) simulations to investigate the sulfurization of MoO₃ flakes using two different gaseous environments: pure H₂S precursors and a H₂S/H₂ mixture. Our QMD results reveal that the H₂S/H₂ mixture could effectively reduce and sulfurize the MoO₃ reactants through additional reactions of H₂ and MoO₃, thereby providing valuable input for experimental synthesis of higher-quality TMDC materials.

Reaction pathways



Two-dimensional and layered materials like graphene, transition metal dichalcogenide (TMDC), and hexagonal boron nitride have received a great amount of attention due to possible explorations of new functional and stacked nanostructures.^{1–3} In particular, a monolayered MoS₂ is a promising material for the next-generation electric device due to its outstanding physical and chemical properties.^{4–8} These characteristics allow MoS₂-based materials to be applicable to a wide range of nanostructured electronics and optoelectronics.^{9,10} For mass production of common layered materials, chemical vapor deposition (CVD) is generally used,^{11,12} and this process is highly scalable and reproducible, compared to other methods, such as physical vapor deposition, mechanical exfoliation, and hydrothermal synthesis.^{13–15} During CVD synthesis, the sulfurization of MoO₃ powders with sulfur precursors is an essential reaction step in which MoO₃ powders are vaporized, reduced, sulfurized, and converted to MoS₂ crystals.^{16–20} As such, it is vitally important to understand atomic level reactions of MoO₃ and the sulfur precursors. Many studies have been conducted to investigate the sulfurization reactions of MoO₃ powders and condensed sulfur powders or H₂S gas precursors.^{21–24} More importantly, recent experimental studies suggested the use of H₂ carrier gas for the effective sulfurization of the MoO₃ powders.^{25–27} For example, Kumar et al.²⁷ reported that the sulfurization of MoO₃ could be achieved during the first reduction step by H₂ carrier gas followed by the conversion step to MoS₂ by H₂S precursors. Albiter et al.²⁸ used the H₂S/H₂ mixture as a catalyst preparation to sulfurize MoO₃ nanorods. The computational results provided by Misawa et al.²⁹ supported these experimental results. They concluded that the MoO₃ surface must be reduced by an effective reducing agent, such as H₂, to

facilitate the subsequent sulfurization reactions. However, the effects of H₂ gas on the sulfurization process of MoO₃ are still uncertain. This is because the atomic-scale resolutions of the reaction pathways for the reactions of MoO₃ and the H₂/H₂S mixture have yet to be obtained. In that sense, atomic scale modeling and simulations, such as molecular dynamics simulations, enable us to study reaction dynamics of complex materials.^{30,31} Here, we perform quantum molecular dynamics (QMD) simulations based on the density functional theory^{32,33} to investigate the sulfurization of the MoO₃ flake using an H₂S/H₂ mixture. Our goal is to clarify the reaction pathways for the reduction/sulfurization processes of the MoO₃ flake with and without H₂ molecules. Below, we discuss our QMD methods, followed by results and discussion and our conclusions in this study.

For QMD simulations, we used highly parallelized simulation software that was developed by the authors.³⁴ Specifically, we used the projector-augmented-wave (PAW) method³⁵ to calculate the electronic states of simulated systems, and the generalized gradient approximation³⁶ was employed for the exchange-correlation energy with nonlinear core corrections.³⁴ Also, the DFT-D method was used for the semiempirical correction of the van der Waals interaction.³⁷ Projector functions were generated for the 2s and 2p states of

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the O atoms, the 1s state for H, the 3s and 3p states of the S atoms, and the 3d, 4s, and 4p states of the Mo atoms. We used the momentum-space formalism and set the plane-wave cutoff energies as 40 and 250 Ry for the electronic pseudowave functions and the pseudocharge density, respectively. The energy functional was minimized iteratively using a preconditioned conjugate-gradient method. The configuration of our system included a monolayered MoO₃ flake in the middle of the simulation domain (7.92 Å × 14.78 Å × 25.0 Å, in the *x*-, *y*-, and *z*-directions, respectively). The MoO₃ flake was fully periodic in the *x*- and *y*-directions while the flake was exposed to the vacuum layers of 20 Å. To investigate the effects of the addition of H₂ on the reduction/sulfurization process, we constructed two different systems: (1) the MoO₃ flake with 48 H₂S molecules (denoted as an MoO₃ + H₂S system) and (2) the MoO₃ flake with a mixture of 48 H₂S molecules and 24 H₂ molecules (denoted as an MoO₃ + H₂S + H₂ system). We assume that the addition of H₂ molecules in the same simulation domain does not significantly increase the average system pressures. This expectation was confirmed by our additional pressure calculations in the Supporting Information (Figure S1). To control system temperatures, we used the NVT ensemble with a Nosé–Hoover thermostat.^{38,39} Quantum mechanically computed equations of motion for all atoms were integrated with a time step of 0.97 fs up to 11 000 iterations. Note that our QMD simulations were performed at the elevated temperature of 2500 K while the experimental synthesis of MoS₂ is typically achieved at mild temperatures (e.g., below 1000 K)^{6,40} to increase the rates of atomic collisions and thus observe important reaction pathways within a very short period of time (~10.7 ps).

Panels a and b of Figure 1 show the initial configurations for the QMD simulations of the MoO₃ + H₂S and the MoO₃ +

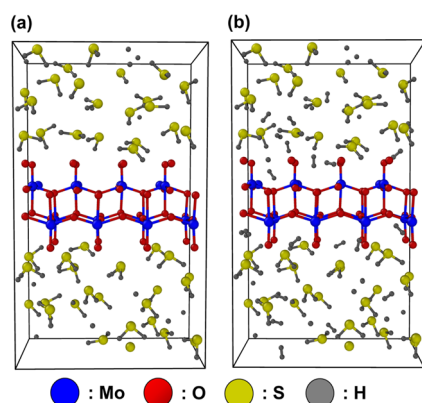


Figure 1. Initial configurations for QMD simulations: (a) the MoO₃ + H₂S system and (b) the MoO₃ + H₂S + H₂ system.

H₂S + H₂ systems, respectively. Two systems were then exposed to the temperature at 2500 K for 10.7 ps. To investigate the different reaction kinetics that may be caused by the introduction of H₂, time evolutions of two reactive systems were monitored (panels a and b of Figure 2). In both cases, the formation of H₂O gaseous species was observed at the early stage (~2.9 ps) because of the reactions of the MoO₃ flake and H₂S and/or the MoO₃ flake and the H₂ molecules. Interestingly, we found that a relatively large number of H₂O gaseous species was observed at 10.7 ps in the MoO₃ + H₂S + H₂ system, compared with the MoO₃ + H₂S system, indicating that the MoO₃ flake could be further reduced when

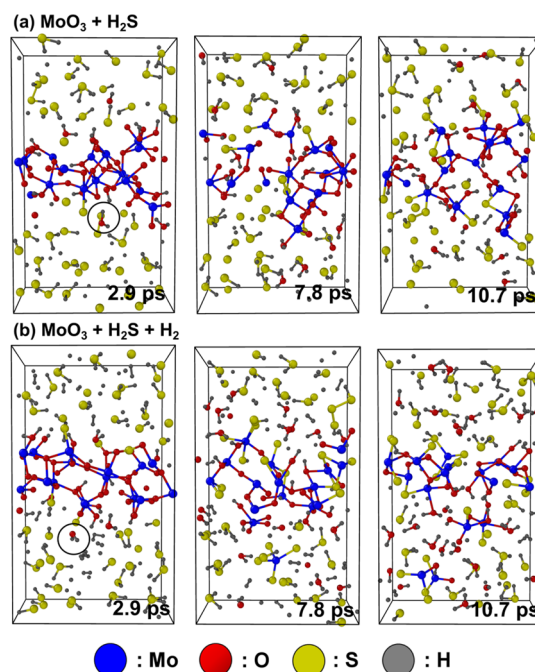


Figure 2. Time evolution of two different reactive systems for the sulfurization of the MoO₃ flake: (a) the MoO₃ + H₂S system at 2.9, 7.8, and 10.7 ps and (b) the MoO₃ + H₂S + H₂ system at 2.9, 7.8, and 10.7 ps. Note that the black circles at 2.9 ps highlight the formation of H₂O gaseous species during the reaction process, and an increased number of H₂O gaseous species were observed in the MoO₃ + H₂S + H₂ system, compared with the MoO₃ + H₂S system at 10.7 ps.

introducing H₂ molecules in the system. As discussed, our simulated temperatures (~2500 K) were somewhat elevated when compared to experimental CVD synthesis (below 1000 K). However, our simulation time scale is very short when compared to the experimental time scale. As such, after trial-and-error simulations, we found that the temperature of 2500 K reasonably described the key reaction steps for the sulfurization of the MoO₃ flake with a reasonable computing cost. In other words, at lower temperatures, the reduction and sulfurization reactions could be observed with relatively low reaction rates. This can be also justified by our previous QMD work.^{41,42}

To further clarify this observation, the numbers of the three gaseous species (H₂S, H₂, and H₂O) were counted for two different systems (panels a and b of Figure 3). For the entire QMD simulations, both systems consumed very similar numbers of H₂S molecules (the dark yellow curves), while the number of H₂O gaseous species (the blue curves) was almost doubled in the MoO₃ + H₂S + H₂ system; this could be attributed to the additional consumption of H₂ (the red curves), i.e., extra H transfers from the H₂ molecules to the MoO₃ flake. In other words, reactions of H₂ and MoO₃ are responsible for the formation of extra H₂O gaseous products. Consequently, in the MoO₃ + H₂S + H₂ system, both the reduction rate (i.e., a decrease in Mo–O bonds) and the sulfurization rate (i.e., an increase in Mo–S bonds) increased further compared with the MoO₃ + H₂S system (panels c and d of Figures 3). These results suggest that the MoO₃ flake could be reduced effectively by the new mechanism resulting from H₂ and MoO₃ reactions, rather than a very minor change in the system pressures (Figure S1).

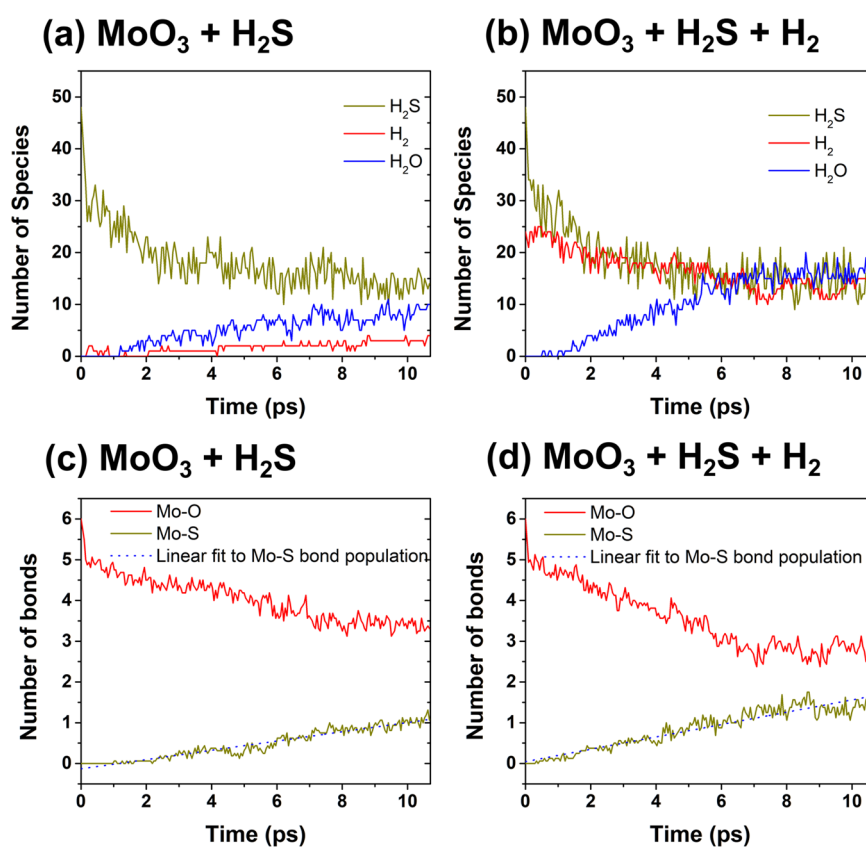
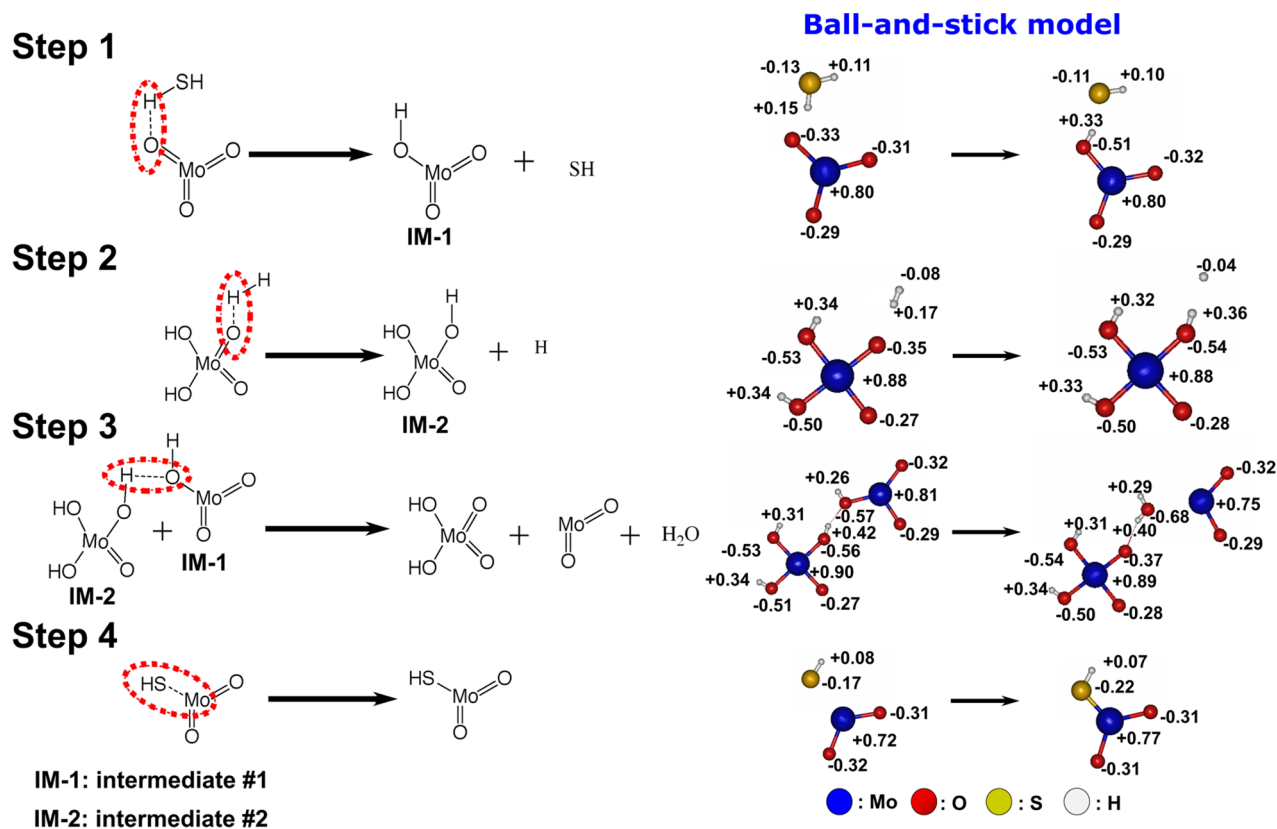


Figure 3. Time evolutions of species populations (H_2S , H_2 , H_2O) during the QMD simulations: (a) the $\text{MoO}_3 + \text{H}_2\text{S}$ system and (b) the $\text{MoO}_3 + \text{H}_2\text{S} + \text{H}_2$ system. Time evolutions of bond populations of Mo–O and Mo–S bonds (c) in the $\text{MoO}_3 + \text{H}_2\text{S}$ system and (d) in the $\text{MoO}_3 + \text{H}_2\text{S} + \text{H}_2$ system. Note that based on the linear fit to the Mo–S bond population in (c) and (d), we estimated the slopes of the sulfurization rates for the $\text{MoO}_3 + \text{H}_2\text{S}$ system and $\text{MoO}_3 + \text{H}_2\text{S} + \text{H}_2$ systems, which are 0.11 and 0.15, respectively, indicating that the sulfurization rate increased when adding H_2 molecules in the system.

We then investigated our QMD trajectories to understand the reaction mechanism for the reduction/sulfurization of the MoO_3 flake by the $\text{H}_2\text{S}/\text{H}_2$ mixture. Scheme 1 summarizes the reaction pathways for the interactions of the MoO_3 flake and the $\text{H}_2\text{S}/\text{H}_2$ mixture. During the first step, H transfers from the H_2S molecule to the MoO_3 cluster that was sublimated from the MoO_3 flake at elevated temperatures, which led to a hydroxide site on the MoO_3 cluster, i.e., it became an $\text{MoO}_2(\text{OH})$ cluster; during the second step, another H transfers from an H_2 molecule to a molybdenum oxyhydroxide cluster, resulting in the formation of an $\text{MoO}(\text{OH})_3$ cluster. The two hydroxide sites on the $\text{MoO}_2(\text{OH})_2$ cluster were obtained by the H transfers from H_2S molecules. These essential reaction steps are explicitly described and discussed in Scheme S1 in the Supporting Information; then H transfers from the $\text{MoO}_2(\text{OH})$ cluster (from Step 1, labeled as IM-1) to the $\text{MoO}(\text{OH})_3$ cluster (from Step 2, labeled as IM-2), liberating H_2O gaseous species and reducing the $\text{MoO}_2(\text{OH})$ cluster to an MoO_2 cluster. Note that another product of $\text{MoO}_2(\text{OH})_2$ may undergo further reduction by additional H transfers similar to the step 1; finally, the available SH radical is bound chemically to the reduced MoO_2 cluster, leading to a stable Mo–S bond. As such, our QMD results indicated that H_2 gas provides more possibilities to form additional hydroxide sites on the ejected MoO_x cluster, thus increasing the number of H_2O gaseous products, as confirmed in panel b of Figure 3. That is, the additional hydroxides on the $\text{MoO}_x(\text{OH})_y$ clusters reacted with each other, which led to additional H transfers

between two neighboring $\text{MoO}_x(\text{OH})_y$ clusters, thereby releasing extra H_2O products and reducing the $\text{MoO}_x(\text{OH})_y$ clusters to the lower oxidation state. To further investigate the thermodynamic drive for the reaction steps in Scheme 1, we calculated the reaction energies of all steps. Table S1 in the Supporting Information shows reaction energies of four reaction steps in Scheme 1. Based on the reaction energy information, we suggest that reaction steps 1 and 2 (i.e., the reduction) are thermodynamically favorable whereas step 3 could be achieved at high temperatures. After the reduction steps, the sulfurization (step 4) could preferably occur. It should be noted that reaction products in steps 1 and 2 (i.e., bisulfide and hydrogen ion) were bound to the available MoO_2 cluster and available oxyhydroxide cluster, respectively, based on the QMD trajectories. Ball-and-stick models in Scheme 1 provide reasonable charge balancing information. Further discussion confirming a neutral charge on each reactant/product can be found in Tables S2–S5 in the Supporting Information. Reaction steps in Scheme 1 are based on the primary reaction pathway observed during our QMD simulations, whereas different reaction pathways may exist depending on the system temperatures, system pressure, and initial precursors used. According to our previous work, MoS_2 can be formed with different pathways when using MoO_3 and H_2S reactants.⁴³ However, the reaction pathways, derived by unbiased QMD simulations in this work, provide a new physical insight into the accelerated reduction and sulfurization steps (Figure 3) with the level of quantum mechanical

Scheme 1. Summary of Reaction Pathways for the Sulfurization of the MoO₃ Flake with the H₂S/H₂ Mixture Fully Derived by Our QMD Simulations (Left) and the Corresponding Ball-and-Stick Models along with Atomic Charge Distributions (Right)⁴⁴



⁴⁴Step 1. H transfers from the H₂S molecule to the MoO₃ species, sublimated from the initial MoO₃ flake. Step 2. Another H transfers from the H₂ molecule to MoO₂(OH)₂. Note that the two “OH” groups on MoO₂(OH)₂ were obtained by multiple H transfers from the H₂S molecules. Step 3. H transfers from MoO₂(OH) (IM-1) to MoO(OH)₃ (IM-2), liberating H₂O gaseous species and reducing MoO₂(OH) to MoO₂. Step 4. A neighboring SH radical is chemically bound to the MoO₂ species, which are the product of Step 3, leading to a stable Mo–S bond. Note that the red dotted ellipses highlight the key reaction during each step.

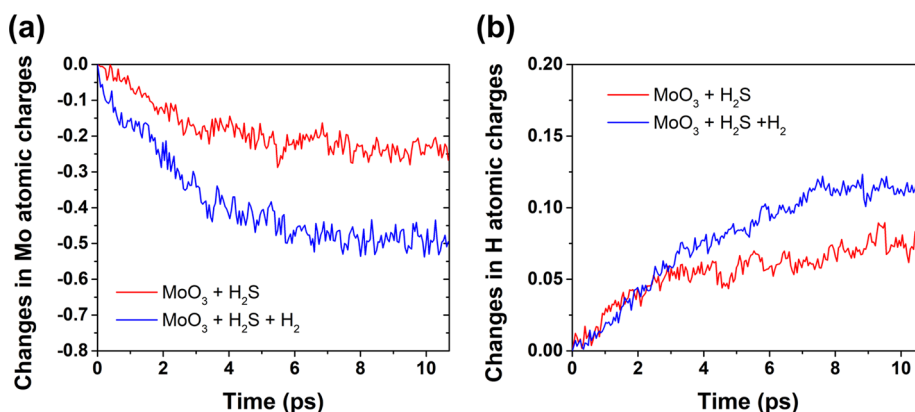


Figure 4. Changes in atomic charges during QMD simulations as analyzed by the Mulliken charge populations: (a) changes in average Mo atomic charges in the MoO₃ + H₂S and the MoO₃ + H₂S + H₂ systems and (b) changes in average H atomic charges in the MoO₃ + H₂S and the MoO₃ + H₂S + H₂ systems. Note decreases or increases in the charge values are evaluated with respect to the initial charge values.

accuracy, which may support the observation in the experimental synthesis of MoS₂ layers using the MoO₃ reactants and H₂S/H₂ mixture.

To demonstrate the reduction of the MoO₃ flake enhanced by the H₂S/H₂ mixture, we calculated the Mulliken⁴⁴ charge state of the Mo and H atomic species as a function of time for both in the MoO₃ + H₂S and the MoO₃ + H₂S + H₂ systems. Our QMD results indicated that average Mo ions underwent a

stronger reduction (i.e., the charge values decreased further) in the MoO₃ + H₂S + H₂ system (panel a of Figure 4). Similarly, H ions underwent further oxidation (i.e., the charge values increased further) when H₂ molecules were introduced into the system (panel b of Figure 4). Note that changes in the atomic charges of the S ions can be found in the Supporting Information (Figure S2). While this work shows the key reaction mechanisms for sulfurization of the MoO₃ flake,

transferring to MoO_xS_y clusters, structural transformation from MoO₃ to MoS₂ slab with the formation of defects may be simulated and investigated by quantum mechanically informed and validated reactive molecular dynamics (RMD) simulations.⁴⁵

In conclusion, we performed QMD simulations of the sulfurization of an MoO₃ flake using pure H₂S molecules and the H₂S/H₂ mixture. Our QMD simulations revealed that H₂ molecules can lead to the formation of extra hydroxide sites on the ejected MoO_x clusters during CVD synthesis, and thus an increased amount of the H atoms' transfer can occur between the MoO_x(OH)_y clusters, leading to the formation of the H₂O gaseous species. We also suggest that the H₂ carrier gas could act as an effective reducing agent for the MoO₃ flake, thereby accelerating the reduction and sulfurization reaction rates during CVD synthesis of MoS₂ crystals. More importantly, the identification of the reaction pathways and the Mo–O–S–H reaction intermediates from unbiased QMD simulations may help refine the reactive force fields (ReaxFF) for multimillion-atom RMD simulations in the same temperature range as experimental synthesis.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.jpcllett.0c03280>.

S1, comparison of the system pressures between the MoO₃ + H₂S and MoO₃ + H₂S + H₂ systems during QMD simulations (Figure S1); S2, reaction energies of the reduction and sulfurization steps (Table S1); S3, atomic charges of reactants and products during QMD simulations (Tables S2–S5); S4, formation of the molybdenum oxyhydride cluster, MoO₂(OH)₂ (Scheme S1); and S5, changes in the atomic charges of the elements during QMD simulations (Figure S2) (PDF)

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Notes

The authors declare no competing financial interest.

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