Role of H Transfer in the Gas-Phase Sulfdation Process of MoO₃: A Quantum Molecular Dynamics Study

Chunyang Sheng,† Sungwook Hong,† Aravind Krishnamoorthy,† Rajiv K. Kalia,† Aiichiro Nakano,‡ Fuyuki Shimojo,‡ and Priya Vashishta*†

†Collaboratory for Advanced Computing and Simulations, Department of Chemical Engineering & Materials Science, Department of Physics & Astronomy, Department of Computer Science, and Department of Biological Sciences, University of Southern California, Los Angeles, California 90089-0242, United States
‡Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan

Supporting Information

ABSTRACT: Layered transition metal dichalcogenide (TMD) materials have received great attention because of their remarkable electronic, optical, and chemical properties. Among typical TMD family members, monolayer MoS₂ has been considered a next-generation semiconducting material, primarily due to a higher carrier mobility and larger band gap. The key enabler to bring such a promising MoS₂ layer into mass production is chemical vapor deposition (CVD). During CVD synthesis, gas-phase sulfdation of MoO₃ is a key elementary reaction, forming MoS₂ layers on a target substrate. Recent studies have proposed the use of gas-phase H₂S precursors instead of condensed-phase sulfur for the synthesis of higher-quality MoS₂ crystals. However, reaction mechanisms, including atomic-level reaction pathways, are unknown for MoO₃ sulfdation by H₂S. Here, we report first-principles quantum molecular dynamics (QMD) simulations to investigate gas-phase sulfdation of MoO₃ flake using a H₂S precursor. Our QMD results reveal that gas-phase H₂S molecules efficiently reduce and sulfdize MoO₃ through the following reaction steps: Initially, H transfer occurs from the H₂S molecule to low molecular weight MoO₄ clusters, sublimated from the MoO₃ flake, leading to the formation of molybdenum oxyhydride clusters as reaction intermediates. Next, two neighboring hydroxyl groups on the oxyhydride cluster preferentially react with each other, forming water molecules. The oxygen vacancy formed on the Mo−O−H cluster as a result of this dehydration reaction becomes the reaction site for subsequent sulfdation by H₂S that results in the formation of stable Mo−S bonds. The identification of this reaction pathway and Mo−O and Mo−O−H reaction intermediates from unbiased QMD simulations may be utilized to construct reactive force fields (ReaxFF) for multimillion-atom reactive MD simulations.

Two-dimensional materials like graphene and transition metal dichalcogenides (TMDs) have led to the exploration of novel nanostructures with remarkable functionality. In particular, monolayer molybdenum disulfide (MoS₂), an archetypal layered TMD material, has attracted great attention due to its large direct band gap, high carrier mobility, excellent current on/off ratio, and interesting photoluminescence features as well as exceptional mechanical properties. Monolayer MoS₂ is also considered an outstanding candidate for a wide range of nanoscale applications such as single-layer MoS₂ transistors, ultra-sensitive photodetectors, monolayered heterojunction solar cells, MoS₂-supported gold nanoparticles for methanol synthesis, and catalysts for the electrochemical hydrogen evolution reaction. Among different types of synthesis
The midstream, and a substrate for MoS2 growth placed either
CVD setup for synthesis of monolayer MoS2 includes a carrier
and the uniformity and stability of grown
gas
reduces MoO3 to volatile MoO3
such high temperatures, sulfur powder starts evaporating and
on top of MoO3 powder or next to it downstream. During
Inset images in (b) show the formation of water (the green rectangle)
Figure 2.
QMD snapshots of the gas-phase sul
numbers on Mo
fragments that are deposited on the substrate as a
monolayer. Extensive experimental studies have been
carried out to understand the sulfidation processes of MoO3
reactants with sulfur precursors. The basic steps of the
MoO3 sulfidation processes were proposed using X-ray
photoelectron and infrared emission spectroscopy experi-
ments, and it was inferred that the exchange of S atoms in
the sulfur precursor with O atoms in MoO3 reactants is the key
reaction step for the sulfidation process. Furthermore, recent
studies proposed that continuity and uniformity of MoS2 layers
could be improved by the proper selection of sulfur precursor.
Namely, gas-phase H2S precursor, instead of the conventional
sulfur powder, could lead to the synthesis of high-quality
monolayer MoS2.

However, atomic-level reaction pathways for the sulfidation
process of the MoO3 reactants have remained unclear because
of the short length and time scales involved, which are beyond
the spatial and temporal resolution of experimental techniques.
To provide a better understanding of the sulfidation process
of MoO3, the main scientific questions are (1) what are the
reaction pathways of the sulfidation process using MoO3,
reactants and H2S precursors and (2) what is the role of
hydrogen in these reaction pathways. To address these
questions, we perform first-principles quantum molecular
dynamics (QMD) simulations based on the density functional
theory (DFT) that provide unbiased information about the
detailed atomistic pathways for the sulfidation of MoO3 flake
by H2S. In the following, we provide computational details of
QMD simulations, followed by results and discussion and
conclusions of this study.

In this work, we used highly parallelized QMD simulation
software developed by the authors. During QMD simu-
lations, electronic states were calculated using the project-
ator-augmented wave (PAW) method. Projector functions were
generated for the 2s and 2p states of O atoms, the 1s state for
H, the 3s and 3p of S atoms, and the 3d, 4s, and 4p states of
Mo atoms. The generalized gradient approximation was used
for the exchange–correlation energy with nonlinear core
corrections. The DFT-D method was employed for semi-
empirical correction of the van der Waals interaction. In
order to assess the effects of spin polarization and on-site
Coulomb interaction between localized d-electrons, spin-
polarized DFT and DFT+U calculations were employed, but
they were found not to change key findings. The
momentum-space formalism was utilized, where the plane-
wave cutoff energies were set to be 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.
In these simulations, a pair of atoms is considered to be
bonded if their interatomic distances in the simulation cell are
less than the cutoff distance for the given pair of elements.
These cutoff distances are chosen from bond lengths available
in experimental literature. Further, these bonds are
considered to be stable if the lifetime of the bond is greater
than 10 fs. The initial configuration for our QMD simulations
consists of a full monolayered MoO3 flake (i.e., fully O-
terminated MoO3 surface) consisting of 16 MoO3 formula
units (representative of MoO3 powder used in CVD) and 25
H2S molecules in an orthogonal supercell (22.18 Å ×
14.302 Å × 19.120 Å) with periodic boundary conditions
along x-, y-, and z-directions. This initial configuration (Figure
1) is initially relaxed using the quasi-Newton method to

Figure 2. QMD snapshots of the gas-phase sulfidation processes at
(a) 1.3 and (b) 4.2 ps, respectively. The initial MoO3 flake ejects
MoO9 clusters at 2500 K (c). Changes in Mo coordination
numbers on MoO9 clusters during the sulfidation process (d,e).
Inset images in (b) show the formation of water (the green rectangle)
and the Mo–S bond (the blue rectangle), respectively.
remove residual forces and then used to perform QMD simulations.

QMD simulations are performed using the NVT ensemble (i.e., the average temperature, simulation cell dimensions, and number of particles are kept constant throughout the simulations), where a Nose–Hoover thermostat is used to maintain the temperature of the simulated system at 2500 K. Quantum-mechanically computed equations of motion for all atoms are integrated with a time step of 0.85 fs over an 8 ps long trajectory. QMD simulations are performed at an elevated temperature of 2500 K (compared to the experimental growth temperature of ∼1500 K) in order to increase collision rates and thus observe important pathways and reaction steps within the very brief time window (∼8 ps) that can be investigated in QMD simulations.

Figure 2a,b depicts snapshots of the simulation cell at 1.3 and 4.2 ps after the beginning of the QMD simulation. The MoO$_3$ flake ejects several Mo$_x$O$_y$($x=2,3$) fragments of varying molecular weights, including transient MoO$_4$ clusters, that are stable for only ∼0.2 ps. Such unstable clusters quickly agglomerate with other sublimated MoO$_x$ fragments to form larger Mo$_x$O$_y$($x=2,3$) clusters. These clusters, predominantly Mo$_2$O$_7$ (average lifetime of >10.4 ps), are the main reaction intermediates that undergo both reduction and sulfidation reactions with H$_2$S. This is accompanied by a change in the local coordination number of Mo ions from the six-fold...
coordination in the MoO₃ flake to four-fold tetrahedral coordination in transient MoO₄ clusters and Mo₂O₇ fragments. Subsequent reduction processes reduce this further to three-fold coordination (Figure 2c). Figure S1 and Table S1 depict a snapshot of the transient MoO₄ cluster and its structural characteristics, respectively, showing that one of the oxygen atoms (O₄) in the cluster is only weakly bonded to the remaining MoO₃ fragment. In addition, the migration of the Mo₂O₇ cluster is fully derived by unbiased QMD simulations (i.e., not because of high pressures), as confirmed in Figure S2.

We observe the following key reaction events: (1) H₂O formation (Figure 2d) and (2) Mo–S bond formation (Figure 2e). We track these reaction events and thus the overall rate of MoO₃ sulfidation by analyzing the time evolution of Mo–O and Mo–S bond populations in the system (Figure 3a). Similarly, the rate of hydrogen transfer can be tracked by plotting the number of H₂S and OH species in the simulation cell (Figure 3b).

The femtosecond time resolutions and atomistic spatial resolution of QMD simulations also allow us to monitor mechanisms for the two fundamental reaction steps, namely, hydrogen transfer from H₂S to Mo₂O₇ and formation of Mo–S bonds. Figure 4a shows the overall QMD snapshot at 1.970 ps, at the beginning of H transfer and the Mo–S bond that follow.

The H transfer reaction includes the following steps: (1) A H₂S molecule diffuses close to a Mo₂O₇(x=2,3) clusters (Figure 4b); (2) the cleavage of one of the H−S bonds in H₂S is accompanied by the simultaneous formation of O−H bonds between the cleaved H and the Mo₂O₇ cluster (Figure 4c); (3) the HS fragment is free to participate in a reaction with an oxygen-deficient (i.e., reduced) Mo₂O₆ cluster (such as Mo₂O₅) to form the Mo–S bond (Figure 4d). These two steps can be summarized in the following reaction.

\[
\text{MoO}\text{HS} + \text{MoO(OH)} → \text{MoO(OH)} + \text{HS}
\]

Movie S1 in the Supporting Information provides full dynamics of the first H transfer and Mo–S bond formation by the QMD simulations.

The formation of reduced Mo₂O₇ clusters required for the sulfidation reaction occurs by the self-reduction of oxygen-rich clusters like Mo₂O₇ (see Figure 5a−c). Specifically, the transfer of multiple H atoms to the same Mo₂O₇ clusters can lead to the formation of Mo oxohydride clusters with neighboring hydroxyl groups (Figure 5b). H atoms from one of the OH groups can preferentially react with the O atoms of the neighboring OH group to form an OH₂ group (Figure 5c,d). The strengthening of the O−H bond is accompanied by simultaneous weakening and lengthening of the Mo−O bond until the H₂O molecule is liberated (Figure 5e), leading to the formation of an effective O vacancy in the Mo₂O₇ cluster that serves as the site for nucleophilic attack by HS fragments and formation of Mo–S bonds, as described in eqs 1 and 2.

Equation 3 describes the reaction pathway for the subsequent H transfer and H₂O formation

\[
\text{MoO}_2\text{O}_7 + \text{H}_2\text{S} \rightarrow \text{MoO}_2\text{O}_6(\text{OH}) + \text{HS}
\]

Movie S2 in the Supporting Information provides full dynamics of the subsequent H transfer and water formation by the QMD simulations.
consistent with experimental reaction pathways such as (MoO3 in the simulation cell as a function of time (Figure S3). Over and kinetically favorable reaction. Lastly, we calculated the precursors at elevated temperatures is a thermodynamically

molecules make Mo

strong reduction (going from the nominal +6 charge state in Mo2O7 to the +4 charge state in MoS2, consistent with prior XPS studies by Niemantsverdriet48). Similarly, oxygen ions are sublimated Mo

Further, toward the end of our simulation trajectory, we also notice the evolution of an O2 molecule by the self-reduction of the MoO3 +H2S reaction, Mo ions undergo oxidation of the MoO 3 cluster, thus activating the sulfidation processes.

The reaction mechanisms in Figure 6a–c are qualitatively consistent with experimental reaction pathways such as (MoO3 + H2S → MoO2S + H2O).44 Our QMD results support experimental work that concluded that H2S precursors to the CVD process could result in high-quality MoS2 layers because we have confirmed that the H2S molecule acts as an effective reducing agent for the MoO3 flake. In addition to the sublimated MoO5 fragments and water molecules, the simulation cell also contains H atoms and HS fragments formed by thermal decomposition of the H2S precursor.

Figure 6a–c clearly summarizes the reaction pathways for H transfer and water formation as well as stable Mo–S bond formation, as shown in Figures 4 and 5. It is obvious that H transfer plays a major role in the reduction of the MoO3 cluster that leads to the formation of water and a stable Mo–S bond during the sulfidation process. Namely, the H2S molecules make MoO4 (n=2,3) clusters lower oxidation states, thus activating the sulfidation processes.

Figure 7a,b, H atom transfer from H2S molecules to the transient MoO4 cluster at elevated temperatures can preferably occur because of their exothermicity along with moderate reaction barriers (0.06 eV), suggesting that sulfidation of the MoO3 flake using H2S precursors at elevated temperatures is a thermodynamically and kinetically favorable reaction. Lastly, we calculated the Mulliken charge state of all atomic species (i.e., Mo, O, S, H) in the simulation cell as a function of time (Figure S3). Over the course of the MoO3 + H2S reaction, Mo ions undergo strong reduction (going from the nominal +6 charge state in MoO3 to the +4 charge state in MoS2, consistent with prior XPS studies by Niemantsverdriet48). Similarly, oxygen ions are reduced, and sulfur ions undergo oxidation. XPS techniques, which are very sensitive to such variations in charge state, can be used to validate this mechanism.

In summary, we have performed QMD simulations to identify reaction pathways for the gas-phase sulfidation process of the MoO3 flake using H2S. The sulfidation reaction proceeds via (1) H transfer from H2S to the MoO3 cluster leading to the formation of the Mo oxysalt; (2) subsequent H transfers between two hydroxyl groups on the oxysalt cluster resulting in self-reduction and the evolution of a water molecule, thus reducing the MoO3(OH)2 to Mo2O6; and (3) nucleophilic attack of the HS− ligand on the reduced MoO3 cluster forming a stable Mo−S bond. These mechanisms, fully derived by our QMD simulations, elucidate the detailed role of H transfer during the sulfidation process for CVD synthesis of MoS2 layers. Our work provides a fundamental understanding of the atomistic reaction pathways for the sulfidation of MoO3 assisted by H2S. We believe that these new chemical insights will help refine reactive force fields (ReaxFF) for multimillion-atom reactive MD simulations of these systems in the same temperature range as experimental synthesis.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcllett.8b02151.

Transient MoO3 cluster that forms a MoO2 cluster during QMD simulations, system pressures vs times during QMD simulations, and changes in atomic charges of elements during QMD simulations (PDF)

QMD trajectories describing the initial sulfidation process corresponding to Figure 4 (MP4)

QMD trajectories depicting the subsequent reaction pathway corresponding to Figure 5 (MP4).

**AUTHOR INFORMATION**

**Corresponding Author**

E-mail: priyav@usc.edu.

**ORCID**

Sungwook Hong: 0000-0003-3569-7701
Aravind Krishnamoorthy: 0000-0001-6778-2471
Aiichiro Nakano: 0000-0003-3228-3896
Priya Vashishta: 0000-0003-4683-429X

**Author Contributions**

C.S. and S.H. contributed equally to this work.

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