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# **Genesis of MoS<sub>2</sub> from model-Mo-oxide precursors supported on $\gamma$ -alumina**

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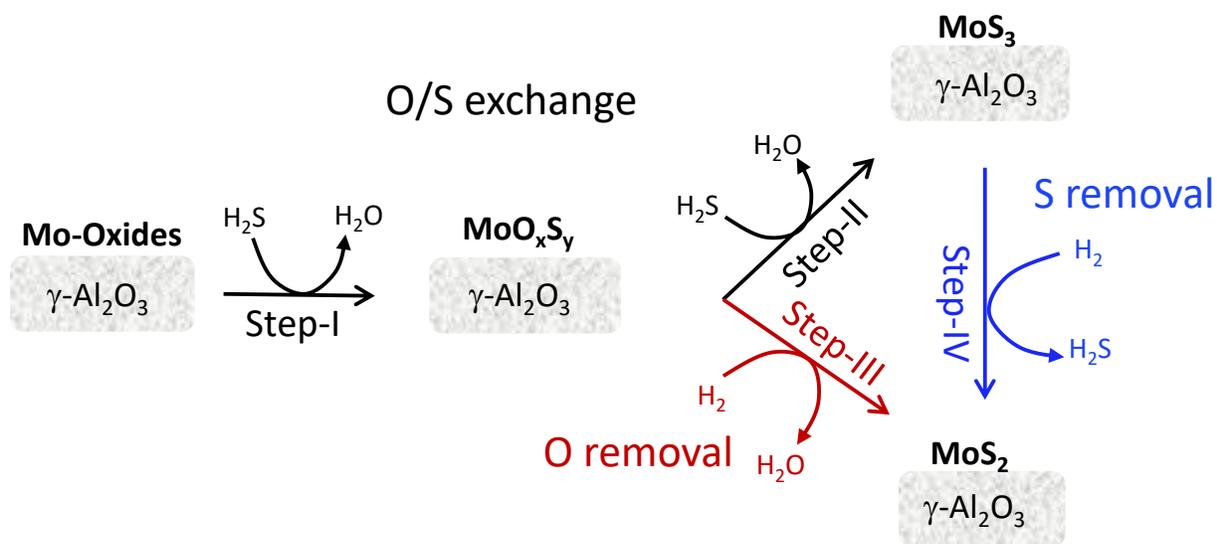
**ABSTRACT:** The molecular-scale understanding of the genesis of the MoS<sub>2</sub> phase from Mo-oxide precursors by sulfo-reduction supported on alumina is highly challenging with a strong impact on the activation process of heterogeneous industrial catalysts. By means of density functional theory (DFT), we quantify the activation free energies of the elementary steps involved in the sulfo-reduction mechanisms of Mo-trioxide oligomers and the stability of the corresponding Mo-oxysulfide intermediates supported on the  $\gamma$ -alumina (100) surface. The Gibbs free energy profiles highlight the characteristic chemical reactivity of various oxygen sites involved in the O/S exchange mechanism and reveal that that interfacial oxygen atoms (Mo-O-Al) are the most challenging sites to be exchanged with S. We quantitatively compare the two main paths proposed experimentally: the one involving Mo-oxysulfide and Mo-trisulfide intermediates and the second one involving only Mo-oxysulfide. While O/S exchange requires moderate activation energies, the rate-determining steps correspond to S- and O-removal on small Mo<sub>n</sub>O<sub>3n-x</sub>S<sub>x</sub> or Mo<sub>n</sub>S<sub>3n</sub> ( $n \leq 3$ ) oligomeric intermediates. To overcome these high energy steps, the small Mo-trisulfide (Mo<sub>n</sub>S<sub>3n</sub>) oligomers are proposed to be fast diffusing surface species and to promote the growth process towards the targeted MoS<sub>2</sub> phase. A reconstruction from chain to triangular Mo<sub>3</sub>S<sub>9</sub> conformer also facilitates this phase transformation.

**KEYWORDS:** MoS<sub>2</sub> catalyst,  $\gamma$ -alumina, activation, sulfidation, reduction, diffusion, growth, Mo-oxide, oxysulfide, MoS<sub>3</sub>, density functional theory, mechanism.

## 1. Introduction

MoS<sub>2</sub> based materials represent a wide interest for various catalytic and electrocatalytic applications such as hydrodesulfurization process, hydrogen evolution reaction, etc. However, the catalytic performances strongly depend on the sulfidation state of Mo resulting from the preparation steps.[1] More particularly, the final activation step is crucial for the genesis of the targeted disulfided Mo active phase from its Mo-oxide precursors deposited on a support (such as  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>),[2–4] anatase-TiO<sub>2</sub>,[5] amorphous silica (SiO<sub>2</sub>),[6] and amorphous silica-alumina)[5] after impregnation, drying, or calcination. This activation involves a sulfo-reduction process with either H<sub>2</sub>/H<sub>2</sub>S gas phase (laboratory scale) or organo-sulfur compounds in a liquid phase (industrial scale) at elevated temperature (350°C).[1,7–9] In the latter case, the sulfidation starts only after the liquid organo-sulfur compound decomposed into H<sub>2</sub>S.[8,10–12]

Therefore, to improve the resulting properties of these catalysts, it remains critical to better understand at a molecular scale how the MoS<sub>2</sub> active phase is engendered from its oxide precursors. Even though the activation step of  $\gamma$ -alumina supported molybdenum oxide precursor by sulfo-reductive treatment has been the subject of many spectroscopic studies,[13–18] several mechanistic questions remain open regarding the nature of the Mo-oxysulfides (MoO<sub>x</sub>S<sub>y</sub>) and Mo-trisulfide (MoS<sub>3</sub>) intermediates, the reaction pathways, and the kinetically limiting steps (**Figure 1**).



**Figure 1.** Schematic diagram of sulfidation of Mo-oxide precursors by  $\text{H}_2\text{S}$  into Mo oxysulfides ( $\text{MoO}_x\text{S}_y$ ), and from oxysulfides to  $\text{MoS}_2$  following two pathways: direct reduction to  $\text{MoS}_2$  by  $\text{H}_2$  (steps I and III) or sulfidation into  $\text{MoS}_3$  followed by transformation to  $\text{MoS}_2$  (steps I, II and IV).

The oxidation state of Mo changes from VI, to V and IV during the activation process, corresponding to widely invoked  $\text{MoO}_x\text{S}_y$ [7,15,16,19,20] and  $\text{MoS}_3$ [15,17,18,21–24] intermediates. These intermediates are complex amorphous compounds often well dispersed on  $\gamma$ -alumina. Identifying molecular structures for these amorphous compounds remains challenging. For instance, a wide structural diversity exists for the  $\text{MoS}_3$  polymorphs as a function of size even without support effects.[25] The structural insights for Mo oxysulfides is even more elusive, particularly in the presence of the alumina support.

Considering the respective role of  $\text{H}_2\text{S}$  and  $\text{H}_2$  as potential reactants during sulfo-reduction of alumina-supported Mo-oxide,  $\text{H}_2$  consumption was observed at high temperature only during temperature-programmed reduction (TPR). At the same time,  $\text{H}_2\text{S}$  uptake was seen at low

temperatures in temperature-programmed sulfidation (TPS).[7,19,20] Furthermore, it has been shown that H<sub>2</sub>S is the key reactant to allow the formation of the MoS<sub>2</sub> phase even without H<sub>2</sub> uptake at an early stage.[7,19,20,24,26] In a second stage, the observed release of a substantial quantity of H<sub>2</sub>S may feature the conversion of Mo-trisulfide intermediates into Mo-disulfide phase through H<sub>2</sub> reduction.[15–18,21,23] Therefore, if the MoS<sub>3</sub> intermediate is involved, the activation process is proposed to occur in two stages: O/S exchange with H<sub>2</sub>S[20,27] leading to the MoS<sub>3</sub>-phase[15,24,28] from MoO<sub>3</sub>-like species (steps I and II in **Figure 1**), followed by its transformation to MoS<sub>2</sub> phase thanks to H<sub>2</sub> reduction (step IV). However, at this stage, the possibility of direct reduction of oxysulfide to disulfide phase cannot be (step III) ruled out. For these reasons, our study will focus on the key role of H<sub>2</sub>S only as sulfiding agent in steps I, II, and by considering the possible role of H<sub>2</sub> at a latter stage in steps III and IV.

Thus, identifying and characterizing Mo-oxysulfides intermediate remains crucial but challenging from an experimental point of view. In particular, in situ EXAFS enabled to follow the evolution of bond lengths such as Mo-O, Mo-S, Mo-Mo[8,17,18] and to reveal some key intermediates such as MoO<sub>x</sub>S<sub>y</sub> and MoS<sub>3</sub>. Time-resolved XAS and Raman spectroscopy on Ni promoted MoS<sub>2</sub> catalyst supported on Al<sub>2</sub>O<sub>3</sub> provided critical insights on such intermediates by chemometric multivariate curve regression with altering least-squares (MCR-ALS) method.[29] Interestingly, the molecular models of MoO<sub>x</sub>S<sub>y</sub> intermediates proposed by EXAFS are constituted from dimeric or trimeric Mo clusters. The XAS analysis also enabled to distinguish specific Mo-oxysulfide intermediates depending on gas phase or liquid sulfidation protocol.[8] Another interesting trend revealed by in-situ XAS is that during liquid phase sulfidation, the delayed sulfidation temperature induces a depolymerization of the polyoxomolybdate precursor between 80 to 230°C.[8] Hence, small Mo-oxide oligomers (as small as dimers or trimers) highly

dispersed on the support are formed and will be the relevant oxide species involved in sulfidation. For that reason, as also explained in what follows, we will consider such small Mo-oxide oligomers as the starting species for the simulation of sulfo-reduction mechanisms.

Also, the disappearance of some characteristic top oxo-species  $\text{Mo-O}_t$  and the appearance of  $\text{S}_2^{2-}$  and  $\text{S}^{2-}$  species was analyzed as a function of temperature by in situ Laser Raman Spectroscopy for alumina supported Ni-promoted  $\text{MoS}_2$  catalyst.[18] Temperature-dependent infra-red (IR) emission spectrum of sulfidation of crystalline  $\text{MoO}_3$  showed that around 100-200 °C, the peak of bridging oxo-species  $\text{Mo-O-Mo}$  disappears, and a new peak assigned to top oxo-species  $\text{Mo=O}_t$  appears before  $\text{Mo-S}$  formation. Then, on Mo-oxysulfides, the  $\text{Mo=O}_t$  species disappear more rapidly than  $\text{Mo-O-Mo}$  species.[16] This analysis also seems to differentiate the behavior of bulk crystalline  $\text{MoO}_3$  from the one dispersed catalyst.

Lastly, transmission electron microscopy (TEM) highlighted that the sulfidation process occurs through a layer-by-layer growing process involving the diffusion of presumably small Mo-oxysulfides or sulfides species on the support.[30] The nature and role of such small Mo-entities remain to be elucidated.

Very few density functional theory (DFT) studies addressed the sulfidation process of Mo-oxide supported on alumina. Some DFT investigations analyzed the interactions of Mo, or W-oxide clusters of various sizes support by  $\text{Al}_2\text{O}_3$ ,[31,32]  $\text{TiO}_2$ ,[33–36] and  $\text{SiO}_2$ . [37] Several plausible mono-oxo and di-oxo Mo centers were proposed for  $\text{Mo}_1\text{O}_3$ , and  $\text{Mo}_2\text{O}_6$  species on  $\gamma$ -alumina (100) and (110) surfaces using DFT calculations.[31,32] DFT was also applied to investigate the stability and interaction mode of the final sulfided  $\text{MoS}_2$  clusters on  $\gamma$ -alumina and  $\text{TiO}_2$  surface, revealing  $\text{Mo-O-Al(Ti)}$  chemical bridges.[38,39] Also, the thermochemistry of sulfur-oxygen exchange at the edges of the  $\text{MoS}_2$  nano-crystallite to identify the possible residual

Mo-O chemical bonds after sulfidation using DFT suggested that the MoS<sub>2</sub> edge is the most difficult to sulfide and maybe the location of residual oxidized Mo sites.[40] Similarly, the sulfur/oxygen exchange was predicted to occur in the long-run on the MoS<sub>2</sub> edges under electrocatalytic conditions such as hydrogen evolution reaction (HER).[41]

The dissociative adsorption of H<sub>2</sub>S was investigated on multilayers of the  $\alpha$ -MoO<sub>3</sub> phase deposited on two different  $\gamma$ -alumina models by using DFT. The reactivity of the monolayer of MoO<sub>3</sub> deposited on the surface of non-spinel  $\gamma$ -alumina was shown to be highest due to charge transfer from alumina to the MoO<sub>3</sub> monolayer.[42] Other quantum simulation studies attempted to rationalize the O/S exchange thermodynamics of bulk,[43] monolayer or large clusters of MoO<sub>3</sub>. [44–46] In general, it was found that replacing the terminal oxo-site by sulfur is more feasible (through vacancy formation) and exothermic in nature than the O/S exchange for bridging (two fold) or tridentate oxygen sites. Moreover, O-vacancy creation increases the reactivity of sulfiding agents (H<sub>2</sub>S or S<sub>2</sub>), which means that the use of hydrogen would enhance the sulfidation rate. As more terminal oxygens are being replaced by sulfur, they can form S-dimers leading to a stabilization of the system.[45] Thermodynamic trends in thiolysis energies of Mo oxide precursors as a function of various supports (including alumina) analyzed by DFT calculations on small molecular clusters showed an appealing correlation between thiolysis energy descriptor and sulfidation degree and/or dispersion,[47] although no kinetic analysis was provided by this study and the realism of the small cluster models remains questionable.

However, to the best of our knowledge, no DFT study addressed the sulfo-reduction mechanisms of Mo-oxides dispersed on a support such as  $\gamma$ -alumina. Hence, numerous open questions remain about the molecular mechanisms and key oxysulfides intermediates involved in the elementary steps of **Figure 1**, such as O/S exchange, S-removal, O-removal involved during

activation. In particular, it would be crucial to identify the most refractory oxygen sites with respect to sulfidation, and the role of the Mo-trisulfide invoked by numerous experimental studies.

We have chosen to consider the sulfidation of small  $\text{Mo}_n\text{O}_{3n}$  oligomers ( $n=1, 2,$  and  $3$ ) deposited on the (100)  $\gamma$ -alumina surface since this surface have been suggested to have a higher degree of sulfidation than other planes of alumina.[48,49] The  $\text{Mo}_n\text{O}_{3n}$  oligomers have been suggested to be present on numerous oxide support (including alumina)[50–57] under various thermal conditions. Moreover, the Mo-oxysulfides intermediates formed in the course of sulfidation are also reported by EXAFS analysis to exhibit a very small Mo-Mo coordination number corresponding to such dimers or trimers.[19,29] As mentioned before, small Mo-oxides oligomers result from the depolymerization of polyoxomolybdates in high-temperature liquid phase sulfidation.[8] Finally, Mo-oxide trimers supported on alumina exhibit various types of O-species (top-oxo, bridging oxo, O-interfacial). These O-sites might feature characteristic reactivities towards  $\text{H}_2\text{S}$  and  $\text{H}_2$ , informing about the most O/S exchange-resisting sites encountered in the real experimental system.

We will thus investigate the interaction of small Mo-trioxide precursors with alumina and their sulfidation using  $\text{H}_2\text{S}$  and  $\text{H}_2$  as key reactants. We will address the kinetic and thermodynamic aspects of sulfo-reduction and corresponding Mo-oxysulfide or trisulfide intermediates along the main path depicted in **Figure 1**. Finally, we will also discuss the effect of size, diffusion, and growth during this whole process.

## 2. Computational details

For all total energy calculations, density functional theory (DFT) as implemented in VASP[58–60] has been used relying on the Perdew-Burke-Ernzerhof (PBE)[61] functional within the framework of generalized gradient approximation (GGA). The long-range London dispersion interactions were included through a density-dependent dispersion correction (dDsC).[62,63] The projector augmented-wave (PAW) method[64] was chosen to describe the electron-ion interaction. The kinetic energy cut-off for the plane-wave basis set has been fixed at 400 eV. For the minimization of the electronic energy, Gaussian smearing with a width of 0.2 eV was chosen.

A mixture of the blocked-Davidson scheme and residual minimization method direct inversion in the iterative subspace has been applied. Spin-polarized calculations were performed to obtain the ground state of the clusters. By scrupulously varying the difference of two spin components, we examined the spin effect, but the ground states remained nonmagnetic. Electronic convergence was assumed to be achieved at  $10^{-6}$  eV. For geometry optimization, the conjugate gradient algorithm was used. Geometric convergence cut-off has been set to 0.02 eV/Å.

For frequency calculations, the structures have been optimized with tighter convergence criteria:  $10^{-7}$  eV for electronic properties and maximum gradients below 0.01 eV/Å. The finite difference method has been used to calculate the frequencies and the density functional perturbation theory (DFPT) method to simulate the infra-red (IR) spectra within the framework of dipole approximation as implemented in VASP.[65–67] For systems where both methods have been applied, they are found to give consistent results. To avoid the peaks from alumina support, we have only simulated the modes concerning the cluster and bonded or weakly interacting part of underneath alumina.

For determining the reaction energy ( $\Delta E$ ) of various reaction steps on alumina at 0 K, the following formal equation was used:

$$\Delta G = G(\mathbf{P}_{\text{surface}}) + G(\mathbf{P}_{\text{gas}}) - G(\mathbf{R}_{\text{surface}}) - G(\mathbf{R}_{\text{gas}}) \quad (1)$$

where  $G(\mathbf{R}_{\text{surface}})$  (respectively  $G(\mathbf{P}_{\text{surface}})$ ) is the Gibbs free energy of the reactant (respectively product) adsorbed on the “catalytic surface”, and  $G(\mathbf{R}_{\text{gas}})$  (respectively  $G(\mathbf{P}_{\text{gas}})$ ) is the Gibbs free energy of the reactant (respectively product) in the gas phase. The detailed equations of each considered reaction are reported in **Supporting Information S1**.

This study focused on the (100) surface of  $\gamma$ -alumina (**Figure S1**). This slab has been constructed following the procedure by Digne et al.[68,69] according to the bulk alumina model defined by Krokidis et al.[70] Moreover, it has been shown that in sulfur-reduction conditions as encountered in this work, the surface remains dehydrated and is not sulfided.[71] We have relaxed the first two layers of the surface, and the bottom two layers have been kept fixed.

Once the most stable adsorption sites for the Mo-oxide clusters are identified on the surface, we assume that the adsorbed cluster will not move or diffuse on the surface in the course of the sulfo-reduction mechanism. This assumption is based on the strong Mo-oxide or Mo-oxysulfide support interaction shown later in the results. This does not exclude that locally the anchoring sites evolve as a function of sulfidation.

During these sulfo-reduction steps into the final disulfides, we identify the limiting steps and corresponding activation energies. To determine the activation energy, we computed the energy of the transition state (TS). We used the Nudged Elastic Band (NEB) method in conjunction with constrained force-based optimizers to determine the geometry of the transition states (TS).[72–75] To generate the intermediate images between reactant and product, we used the Opt’npth

open-source code.[76] We performed the frequency calculations to confirm TS as a first-order saddle point on the potential energy surface with only one imaginary frequency, and that the imaginary mode corresponds to the restoring force along the direction from the TS to the reactant or product. We have used an open-source code to trace the reaction energy plots.[77]

All aforementioned electronic energies were corrected by the contribution of zero-point energy, thermal corrections at T=623K (experimental temperature for sulfo-reduction), and entropy corrections in order to determine the vibrational free energy:

$$\Delta G = \Delta H - T\Delta S \quad 2$$

$$\Delta H = \Delta U + P\Delta V \quad 3$$

$$\Delta U(S) = \Delta U(S)_{ele} + \Delta U(S)_{vib} + \Delta U(S)_{rot} + \Delta U(S)_{trans} \quad 4$$

We assumed that the  $Mo_nO_{3n}$ ,  $Mo_nO_xS_{3n-x}$ , and  $Mo_nS_{3n}$  oligomers are immobile on the alumina surface due to their strong chemical anchorage. We included the translational and rotational  $U(S)$  contributions for the gas-phase molecules  $H_2O$ ,  $H_2S$ , and  $H_2$ .

All free energy diagrams are plotted for 1 bar partial pressure of  $H_2O$ ,  $H_2S$ , and  $H_2$ . It is possible to include a correction on the thermodynamic reference levels of these molecules in gas phase induced by pressure effects as described in **Supporting Information 1**.

### 3. Results

#### 3.1. Interaction of molybdenum oxides precursors with $\gamma$ -alumina

Based on the experimental insights described in the Introduction, we first explore the stability of monomeric ( $MoO_3$ ), dimeric ( $Mo_2O_6$ ), and trimeric ( $Mo_3O_9$ ) Mo-oxides dispersed on alumina. To determine the optimal interaction and the adsorption sites of  $\gamma$ -alumina, we systematically explored the energetic stability of these species on the (100)  $\gamma$ -alumina surface.

For Mo<sub>1</sub>O<sub>3</sub> and Mo<sub>2</sub>O<sub>6</sub>, our results (**Supporting Information 3.1**) are mainly consistent with previous theoretical works.[31,32] The Mo<sub>3</sub>O<sub>9</sub> oligomer may exhibit two conformers in the gas phase: either cyclic or chain-like (**Figure-S2 c and d**), similar to the Mo<sub>3</sub>S<sub>9</sub> (Mo-trisulfide) cluster where the chain and triangular conformers are competing.[14,21,25,78–83] The cyclic conformer is more stable than the chain by about 0.86 eV in the gas phase (**Figure S4**), similar to our previous finding for Mo<sub>3</sub>S<sub>9</sub> clusters.[25] However, the strong support effect induces an inversion of the relative stability of the two conformers: the chain conformer becomes more stable by -0.42 eV on the (100)  $\gamma$ -alumina surface (**Figure S6**). The same support effect is also observed for Mo<sub>3</sub>S<sub>9</sub> clusters, as discussed later. The support interaction enables the formation of new Mo-O-Al and Mo-O<sub>surf</sub> bonds, which cauterizes the under-coordination of Mo-atoms in the chain and leads to a square-pyramidal environment for each Mo-atom (**Supporting Information 3.2**), while in the absence of support, the Mo atoms are all stabilized in the tetrahedral environment by Mo-O-Mo cyclization (**Figure S2**). This interaction with support also impacts the nature of oxygen atoms which will be involved in the sulfur/oxygen exchange process, as described in the following.

**Figures 3** and **S6** highlight the four distinct types of oxygen atoms present in the supported Mo<sub>3</sub>O<sub>9</sub> (chain or cyclic): terminal oxo-species (O<sub>t</sub>), bridging (O<sub>br</sub>), interfacial-bidentate (O<sub>int(bi)</sub>), and interfacial-tridentate (O<sub>int(tri)</sub>). Terminal oxo-species (O<sub>t</sub>) are connected to one Mo center only, while bridging oxo- (O<sub>br</sub>) are bonded to two Mo-atoms (Mo-O-Mo). Interfacial-bidentate (O<sub>int(bi)</sub>) are initial (gas phase) terminal oxo- that also interact with the aluminum site of support, becoming bridging species (Mo-O<sub>int(bi)</sub>-Al). Interfacial tridentate (O<sub>int(tri)</sub>) are initial bridging oxo- that also becomes bonded to aluminum sites of support  $\begin{array}{c} \text{Mo}-\text{O}-\text{Mo} \\ | \\ \text{Al} \end{array}$ . We found two competing Mo<sub>3</sub>O<sub>9</sub> chain conformers (**Figure S6a** and **S6b**), but we will discuss in the main text only the

most relevant one (**Figure S6a**) based on the sulfidation thermodynamics and kinetics consideration. This chain conformer exhibits two-terminal oxo ( $O_t$ ) species, three bridgings ( $O_{br}$ ), three interfacial bidentates ( $O_{int(bi)}$ ), and one interfacial tridentate ( $O_{int(tri)}$ ). All three Mo-atoms are penta-coordinated but possess distinct geometrical orientations. The central Mo-atom has an octahedral vacancy site; however, the terminal Mo-atoms have distorted square-pyramidal conformation. The details of the second conformer are given in **Supporting Information 3.2**. The analysis of the local environment of Al and O sites on  $Mo_nO_{3n}$  oligomers ( $n=1, 2,$  and  $3$ ) is compatible with earlier experimental ones proposed for various catalytic systems (not only HDS), where molybdenum oxides are found in a highly dispersed form on various oxide surfaces and could even exist as isolated  $MoO_x$  species after thermal treatment.[19,50–57]

### **3.2. Oxygen/sulfur exchange for $Mo_3O_9$ on alumina**

#### **Thermodynamic considerations**

The supported oxide oligomers are expected to undergo a sulfo-reduction process to form Mo-oxyulfides or Mo-trisulfides intermediates, followed by their further transformation (reduction) to the final Mo-disulfide phase. The cyclic conformers remain more stable in the gas phase than the chain along the entire sulfidation path leading to the trisulfide phase (**Figure S3** and **S4**). By contrast, this trend is again reversed by the support. As explained in detail in Introduction, numerous published experimental works underlined the key role of  $H_2S$  during the early stage of sulfo-reduction of Mo-oxide, we will thus assume here that hydrogen will not react at the first steps (I and II). Instead, we consider first that O/S exchange by  $H_2S$  adsorption and  $H_2O$  removal is thermodynamically preferred (as illustrated in what follows), which is in line with the earlier proposal by Muijsers et al.[28] Moreover, using  $H_2S$  is also coherent with some experiments that

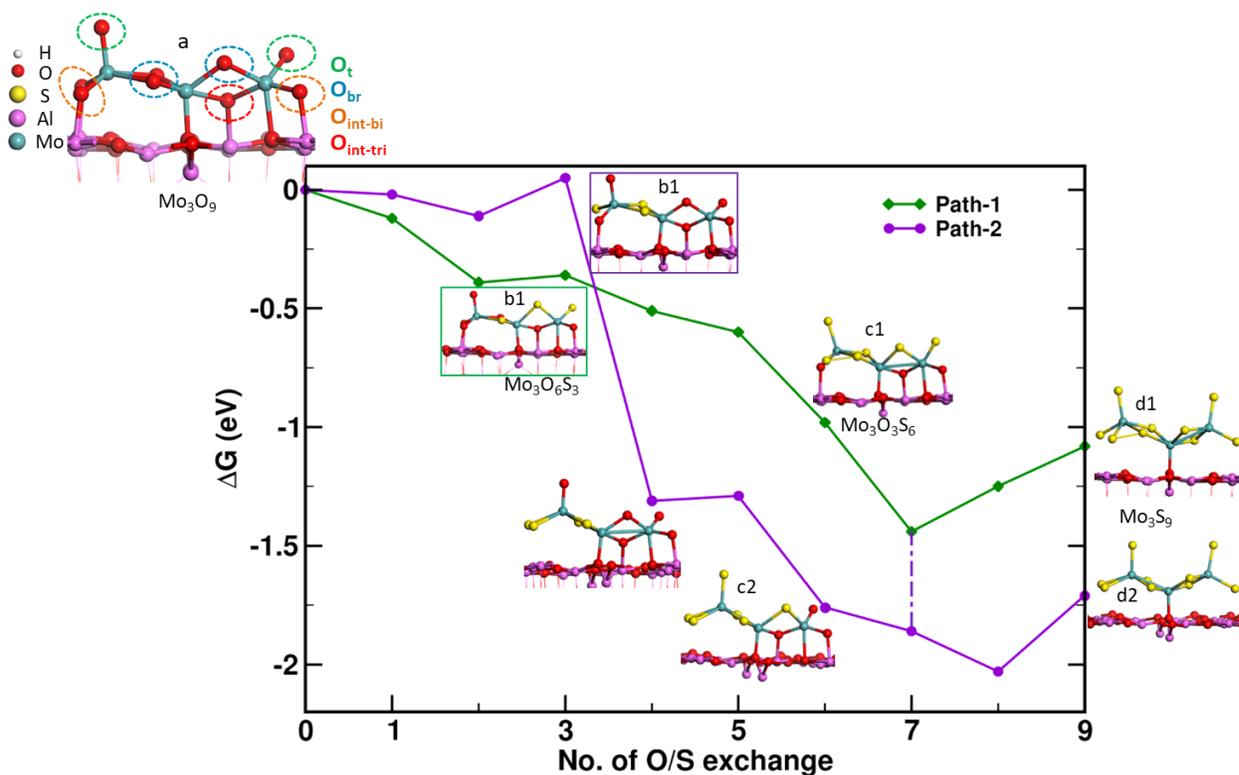
reported MoS<sub>2</sub> formation under pure H<sub>2</sub>S environment.[24,26] Note that we preliminary found that the direct reduction of Mo<sub>3</sub>O<sub>9</sub> by hydrogen is endothermic (0.2 eV – 1.76 eV for first oxygen removal (**Supporting Information 5.3**) and 0.51 eV – 1.89 eV for the second oxygen removal). Thus,

We systematically examined the O/S exchange for multiple models: monomer, dimer, trimer (chain and cyclic) according to the various types of oxygen sites identified. Detailed results are reported in **Supporting Information 4, 5, and 6**; we present in what follows two thermodynamically relevant paths (path-1 and -2) for the chain Mo<sub>3</sub>O<sub>9</sub> conformer. The O/S replacement on path-1 occurs more homogeneously than on path-2 (**Figure 2** and **Figure S8**). The first two steps of path-1 and path-2 are similar and involve bridging O-sites in O/S exchange. However, the main difference arises at the third and fourth steps where path-1 replaces the terminal oxygen, while path-2 replaces the interfacial (O<sub>int(bi)</sub>). On path-1, the three Mo-atoms become all partially sulfided (connected to one S-atom) at Mo<sub>3</sub>O<sub>6</sub>S<sub>3</sub>, whereas on path-2, only two Mo-atoms are sulfided at Mo<sub>3</sub>O<sub>6</sub>S<sub>3</sub>.

**Figure 2** reveals that the overall trend is exergonic. Even though step three is slightly less favored for path-2, the free energy gain at the 4<sup>th</sup> step for path-2 becomes more significant, about -0.8 eV (**Figure 2**). This enhanced stability comes from the formation of S<sub>2</sub>-dimer replacing two adjacent O<sub>int(bi)</sub> by S. Interestingly, such S<sub>2</sub> dimers are observed experimentally (see the forthcoming spectroscopic analysis). Path-1 favors the replacement O<sub>int(bi)</sub> and O<sub>int(tri)</sub> after the bridging and terminal oxygen. At the 7<sup>th</sup> step, path-1 can be linked to path-2 by dissociating the half-bridged dimer formed at step 6 and creating a new S<sub>2</sub> dimer at step 7. The formation of new terminal S<sub>2</sub> dimer results in -0.5 eV stabilization. This observation is consistent with an earlier

DFT study of MoO<sub>3</sub> O/S exchange, where the S<sub>2</sub>-dimer formation results in ~0.5 eV further stabilization.[45]

We thus propose that both paths co-exist or that a mixed solution combining path-1 until step 7 and a transition to path-2 after step 7 will lead to the formation of the most stable chain-Mo<sub>3</sub>S<sub>9</sub>. **Figure S12** highlights that the second chain conformer (**Figure S6b**) is actually slightly less stable on the sulfidation path, justifying our choice to focus on the chain conformer of **Figure S6a** only.



**Figure 2.** Gibbs free energy at 625 K for the O/S exchanges of chain-trimer Mo<sub>3</sub>O<sub>9</sub> according to path-1 and path-2 using the alumina adsorbed Mo<sub>3</sub>O<sub>9</sub> as reference. The possible transition between path-1 to path-2 is shown at step 7 by the vertical broken lines.

The O/S exchange energies of bridging and terminal oxygens are very similar from a thermodynamic aspect, whereas exchanging  $O_{\text{int}(\text{tri})}$  site costs  $\sim 0.65$  eV additional energy. Except for the last few steps, every O/S exchange is exergonic by about  $-0.2$  eV to  $-0.5$  eV. Interestingly, this observation remains valid across the size and models (**Figure-S12**). This trend suggests that the last few O/S exchanges involving  $O_{\text{int}(\text{tri})}$  or  $O_{\text{int}(\text{bi})}$  are thermodynamically more arduous than earlier ones.

### Structural and vibrational analysis of key intermediates

During the O/S exchanges, the local chemical and structural environment of  $\text{Mo}_3\text{O}_{9-x}\text{S}_x$  intermediates evolve, involving the disappearance of Mo-O bonds and the simultaneous formation of new Mo-S and S-S bonds as highlighted by the evolution of Mo-O(S) bond lengths and coordination number of the critical intermediates in **Figure S9** where a comparison with EXAFS data is also given.[16–19,84] As detailed in **Supporting Information 5.2**, the DFT optimized structural values are consistent with EXAFS ones, and the calculations recover the various Mo-O bond lengths as a function of the type of O site.

The homogeneous path-1 involves the replacement of terminal and bridging oxygen first and later the interfacial ones ( $O_{\text{int}(\text{tri})}$  and  $O_{\text{int}(\text{bi})}$ ), while the heterogeneous path-2 exchanges the two bridging species followed by two  $O_{\text{int}(\text{bi})}$  out of three, then terminal ones, and finally  $O_{\text{int}(\text{tri})}$  and  $O_{\text{int}(\text{bi})}$ , respectively (**Figure 2** and **Figure S8 b and c**). These oxysulfides contribute to the emerging Mo-S bonds as more oxygens are replaced by sulfur from  $\text{Mo}_3\text{O}_6\text{S}_3$  and  $\text{Mo}_3\text{O}_3\text{S}_6$  (**Figure S9 and S10**). For instance, new terminal Mo-S bonds of  $2.14 \text{ \AA}$  ( $2.24 \text{ \AA}$ )[18] and Mo-S-Mo bonds of  $2.41 \text{ \AA}$  ( $2.38 \text{ \AA}$ )[18] appear and are evidence of the presence of different S species such as  $\text{S}_2^{2-}$  and  $\text{S}^{2-}$  as also confirmed by IR/Raman,[16,18,21] while  $\text{Mo-O}_t$  vanishes as more S

replaced the oxygen (**Figure S9 and S10**). Moreover, since EXAFS revealed that a short Mo-O<sub>t</sub> bond is still present in late oxysulfides intermediates,[17,18] the path-2 where sulfidation occurs heterogeneously from one side, may explain that the remaining terminal oxo species until Mo<sub>3</sub>O<sub>3</sub>S<sub>6</sub>, as seen in EXAFS spectrum for short Mo-O bond. The Mo-Mo bond shrinks from 3.31 Å to 2.86 Å as more O/S exchanges take place.

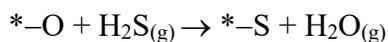
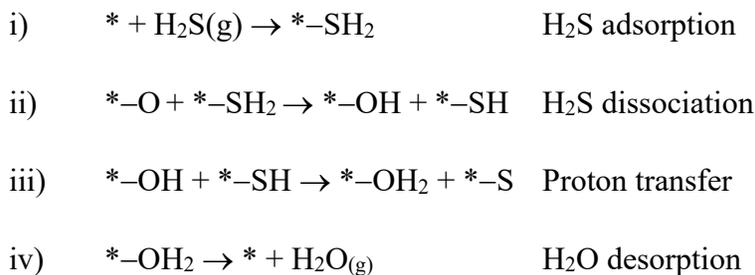
To further assess the reliability of our Mo-oxysulfide intermediates, we also undertook a similar analysis by simulating the IR spectrum of each intermediate and compared them with available experimental data (**Figure-S10**). Various Mo-O stretching modes were recovered between 700-1000 cm<sup>-1</sup>: Mo-O<sub>t</sub> : 980 cm<sup>-1</sup>, [16,52] Mo-O<sub>int(bi)</sub> : 800-900 cm<sup>-1</sup> and Mo-O<sub>surf</sub> : 700-750 cm<sup>-1</sup>. As the bridging oxygens are being replaced, several Mo-O, Mo-O-Al, and Al-O-Al peaks start diminishing while peaks of the newly formed Mo-S<sub>t</sub>, and Mo-S-Mo appear (around 550 cm<sup>-1</sup> and below).

### **Mechanism and kinetics of O/S exchange from Mo<sub>3</sub>O<sub>9</sub> to Mo<sub>3</sub>S<sub>9</sub> (step I and II)**

As explained in detail in Introduction, numerous published experimental works underlined the key role of H<sub>2</sub>S during the early stage of sulfo-reduction of Mo-oxide, we will thus assume here that hydrogen will not be involved in the sulfidation mechanisms at the first steps (I and II). Instead, we consider first that O/S exchange by H<sub>2</sub>S adsorption and H<sub>2</sub>O removal is thermodynamically preferred (as illustrated in what follows), which is in line with the earlier proposal by Muijsers et al.[28] Moreover, using H<sub>2</sub>S is also coherent with some experiments that reported MoS<sub>2</sub> formation under pure H<sub>2</sub>S environment.[24,26] Note that we preliminary found that the direct reduction of Mo<sub>3</sub>O<sub>9</sub> by hydrogen is endothermic (0.2 eV – 1.76 eV for first oxygen removal (**Supporting Information 5.3**) and 0.51 eV – 1.89 eV for the second oxygen removal).

Thus, we will first focus on the role of H<sub>2</sub>S and its reactivity on oxides/oxysulfides to trisulfides conversion (in line with steps I and II of **Figure 1**), and further, we will analyze the possible role of H<sub>2</sub> to allow the transformation either from trisulfide to disulfide (**Figure 1**, step IV), or from oxysulfide to disulfide (Figure 1, step-III).

Oxygen to sulfur exchange by H<sub>2</sub>S will involve four crucial steps as described in **Scheme 1**.

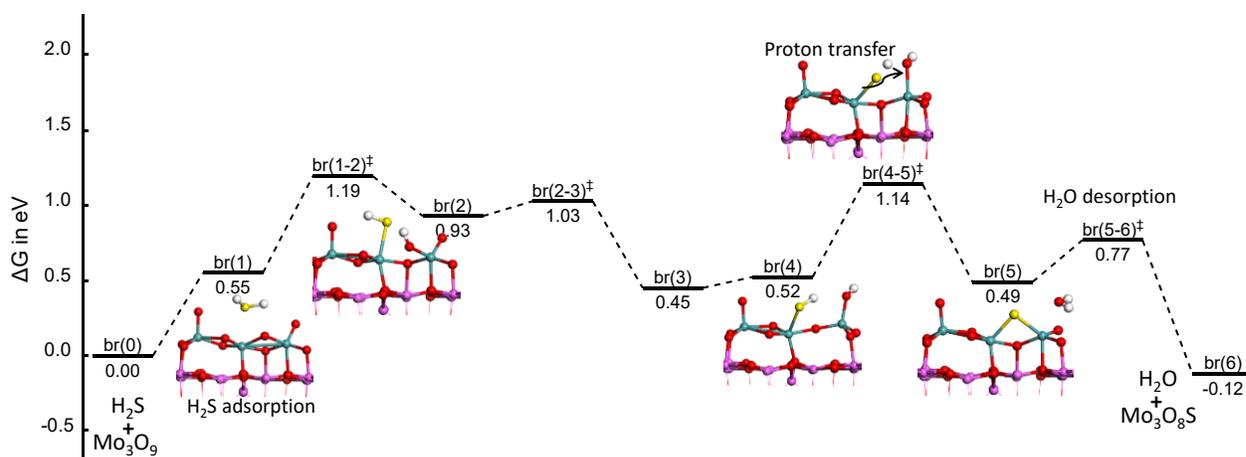


**Scheme 1.** Main elementary steps for the O/S exchange involving H<sub>2</sub>S/H<sub>2</sub>O. \* represent formally a Mo site of the Mo<sub>3</sub>O<sub>9-x</sub>S<sub>x</sub> intermediates (when O<sub>t</sub> and O<sub>b</sub> are involved), where an O site is removed or where H<sub>2</sub>S adsorbs. In some cases, it may also represent an Al site of the (100)  $\gamma$ -alumina surface where H<sub>2</sub>S adsorbs (when O<sub>int</sub> are involved).

Apart from these four main steps, there might be SH or OH reorientation and S migration steps. We have examined the reactivity of all four oxygen sites described before and their respective O/S replacement mechanism steps. According to the previous thermodynamic investigation, bridging/terminal oxygens are the easiest to replace, while interfacial ones are more challenging.

**Bridging-oxygen sites.** Adsorption and activation of H<sub>2</sub>S is the first step towards sulfidation of the starting Mo<sub>3</sub>O<sub>9</sub> oxide. Since the targeted replaceable oxygen atoms are the bridging ones, we

restrict the adsorption of H<sub>2</sub>S on the Mo central site close to the reactive site. Furthermore, this central Mo-atom was observed to have the strongest capacity to adsorb (confirmed by more exhaustive exploration not reported here) due to its square-pyramidal environment providing one empty site (\* in **Scheme 1**) available for H<sub>2</sub>S adsorption. While the adsorption energy of H<sub>2</sub>S (at 0 K) is exothermic (-0.48 eV, **Figure S15 a**), this step is actually endergonic at 625 K ( $\Delta G_{br_0 \rightarrow 1} = +0.55$  eV) when including entropy and thermal corrections.



**Figure 3.** Free energy profile of O/S exchange involving bridging oxygen and H<sub>2</sub>S. Color legend: red balls: O, blue balls: Mo, pink balls: Al, yellow balls: S, and white balls: H.

During the next step, the H<sub>2</sub>S dissociation with a proton transfer to the targeted oxygen occurs. The activation free energy for this H<sub>2</sub>S dissociation is  $\Delta G_{br_1 \rightarrow 2}^{\ddagger} = +0.64$  eV which is expected to be accessible in sulfo-reductive conditions (T = 625 K). Once H<sub>2</sub>S is dissociated, one of its protons is transferred to the bridging oxygen leading to the scission of one Mo-O bond and the simultaneous formation of one OH group. Consequently, the Mo-S bond shortens as H<sub>2</sub>S dissociates (from 2.79 Å with H<sub>2</sub>S to 2.42 Å with SH), which reveals the strengthening of the interaction of the SH group with the Mo-site with respect to the initial H<sub>2</sub>S molecule.

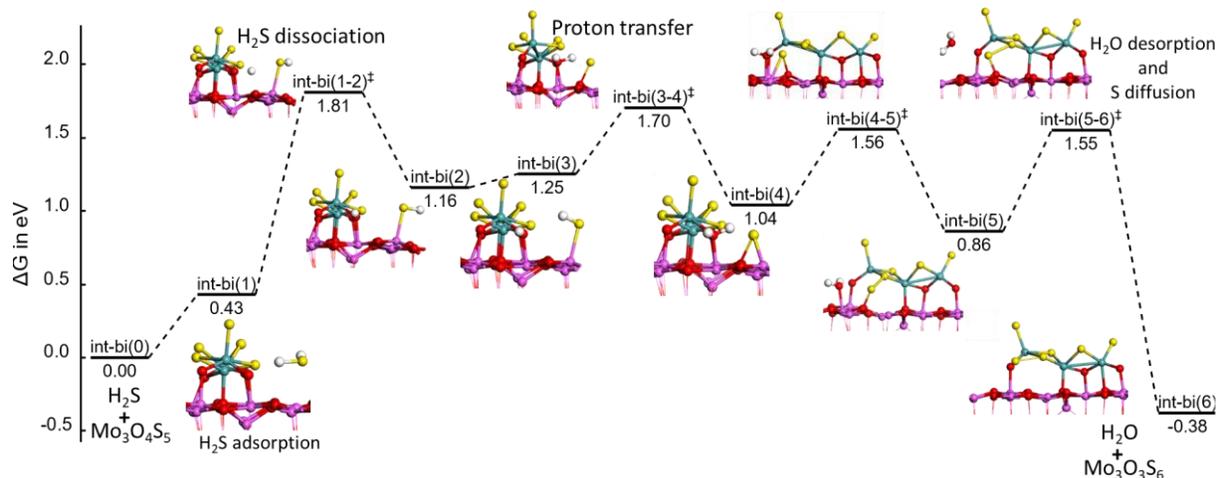
The energy level of the product is quite close to the TS level (br(2) and br(2-3)<sup>‡</sup>,  $\Delta G^{\ddagger}_{br_2 \rightarrow 3} = +0.10$  eV) due to their structural similarity. A slight internal arrangement, SH and OH rotations, occurs before the next proton transfer involving weak activation energy around +0.07/0.15 eV (activation for H-rotation not shown here), which is far lower than the barrier of other key steps. Therefore, it is reasonable to neglect these activation steps and assume that they will not significantly impact the overall processes.

After these rearrangements, the proton transfer occurs and is coupled with S migration from top to bridging site and water formation. The S bridging process promotes water formation and desorption by cauterizing the Mo-vacancy site where O is removed. This stabilizing effect also explains why the O/S exchange process is more favored than the direct O-removal by H<sub>2</sub> (**Supplementary Information 5.3**). The free energy of activation of this step is  $\Delta G^{\ddagger}_{br_4 \rightarrow 5} = +0.62$  eV which is also reasonable. The final step concerns the removal of water which exhibit about free energy of activation of  $\Delta G^{\ddagger}_{br_5 \rightarrow 6} = +0.28$  eV. The entropy of water makes the overall path slightly exergonic (-0.12 eV).

**Top-oxygen sites.** According to the thermodynamic study, terminal oxygen would not differ significantly from bridging oxygens. We explored the O/S exchange mechanism for terminal oxygen on a Mo<sub>3</sub>O<sub>7</sub>S<sub>2</sub> oxysulfide where the two bridging atoms have been substituted (**Figure S13**). The same central Mo-site exhibits a slightly weaker molecular adsorption of H<sub>2</sub>S with  $\Delta G_{t_0 \rightarrow 1} = +0.79$  eV in contrast with the previously discussed O/S exchange. With a slight activation free energy barrier of  $\Delta G^{\ddagger}_{t_1 \rightarrow 2} = +0.18$  eV H<sub>2</sub>S dissociates. After subsequent SH/OH rotation (t(2) → t(3)), the proton transfer takes place. This step is also coupled with S migration (from top to bridging site) similarly to the bridging O, which is much less energy-demanding

than the direct creation of O-vacancies on top of the Mo site upon H<sub>2</sub>/H<sub>2</sub>O exchange (**Supplementary Information 5.3**). The proton transfer associated with S migration is the rate-limiting step for this terminal O/S exchange and is higher ( $\Delta G^\ddagger_{t_3 \rightarrow 4} = +0.92$  eV) than the rate-limiting step for the bridging O/S one. After water formation, migration of S from bridging site to top site is easily leading to a precursor of the water desorption weakly activated ( $\Delta G^\ddagger_{t_5 \rightarrow 6} = +0.15$  eV). It must be underlined that the S/O exchange occurring on a top monomeric Mo<sub>1</sub>O<sub>3</sub> is located at a lower energy level than the trimeric one (**Supplementary Information 4**).

***Interfacial-bidentate oxygen sites.*** Interfacial oxygens remaining on Mo<sub>3</sub>O<sub>4</sub>S<sub>5</sub> can be considered as top/bridging O-sites are already replaced. O<sub>int(bi)</sub> interacts with Al through Mo-O-Al linkage. There are two intrinsic complexities for the O/S exchange on these sites: one, O accessibility to H<sub>2</sub>S is sterically hindered, and two, strong interaction with Al sites. The adsorption of H<sub>2</sub>S on the central Mo-atom is relatively weak compared to the previous cases, and the interfacial oxygen would not be accessible with such pre-adsorbed H<sub>2</sub>S on the Mo site. Consequently, we had to consider that H<sub>2</sub>S adsorbs on one of the Al sites of support located in the close vicinity of the interfacial oxygen to be exchanged. As support Al sites initiate the mechanism, some intermediate steps might differ from the two previous cases, but the four key steps described in **Scheme 1** remain the same, assuming that one Al site is involved as a free site (\*). H<sub>2</sub>S is adsorbed on support with a stronger interaction (also involving some H-bonding) than on Mo-site. At 625 K, the H<sub>2</sub>S adsorption step is thus slightly less endergonic ( $\Delta G_{int-bi_0 \rightarrow 1} = +0.43$  eV, **Figure 4**).



**Figure 4.** Free energy profile of O/S exchange involving interfacial bidentate oxygen and H<sub>2</sub>S. Color legend: red balls: O, blue balls: Mo, pink balls: Al, yellow balls: S, and white balls: H.

H<sub>2</sub>S then dissociates by migrating the hydrogen to the replaceable oxygen O<sub>int(bi)</sub> with an activation energy of  $\Delta G^{\ddagger}_{int-bi_1 \rightarrow 2} = +1.38$  eV. A relatively large distance between O to be protonated and S during proton transfer (S---H---O) could be the reason for the significantly higher activation free energy than in previous cases. This proton migration also weakens the associated Mo-O bond (2.03 Å vs. 1.81 Å). Furthermore, the instability of SH on the Al site keeps the intermediates at higher energy. This SH group and the subsequent S atom are more stable on the Mo-site of the cluster by 0.54 eV and 0.2 eV, respectively than on Al-site. The next proton transfer step involves a smaller activation energy  $\Delta G^{\ddagger}_{int-bi_3 \rightarrow 4} = +0.45$  eV (with a high energy level at +1.70 eV vs. 1.81 eV for the previous one) and leads to water formation. The H<sub>2</sub>O molecule remains bounded to the support's Al site and diffuses on the support before desorbing. In parallel, the S atom formed on the support migrates to the cluster and bonds with a bridging S atom. From a general point of view, the overall mechanism is much more complex than previous ones and involves four high-energy steps (above 1.55 eV).

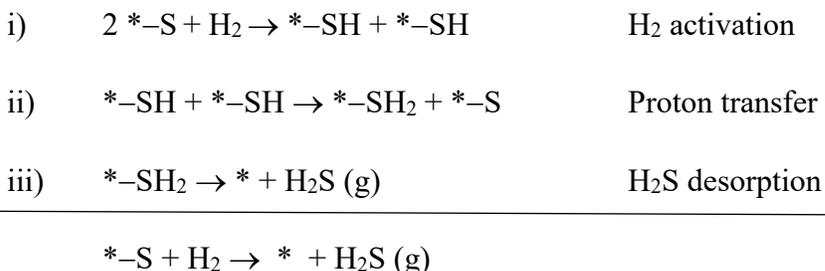
By contrast, if we consider the monomeric Mo<sub>1</sub>OS<sub>2</sub> precursor, S/O exchange occurring on an interfacial bidentate O site of Mo<sub>1</sub>OS<sub>2</sub> is located at a significantly lower energy level (+1.35 eV) than the trimeric one (**Supplementary Information 4**). This difference is due to the adsorption of H<sub>2</sub>S to the Mo site in the Mo<sub>1</sub>OS<sub>2</sub> site (and not on the Al site), which facilitates its activation/dissociation and H-transfer to the interfacial O-site of Mo<sub>1</sub>OS<sub>2</sub>. This size effect will be further discussed in **Section 4**.

**Interfacial-tridentate oxygen site.** We consider the MoO<sub>2</sub>S<sub>7</sub> oxysulfide intermediate containing one O<sub>int(bi)</sub> and one O<sub>int(tri)</sub> site for this step (**Figure S14**). After H<sub>2</sub>S adsorption on the support ( $\Delta G_{int-tri_{0 \rightarrow 1}} = +0.37$  eV), the hydrogen atoms of H<sub>2</sub>S cannot reach the targeted oxygen site. Hence, H<sub>2</sub>S dissociates first on a neighboring alumina  $\mu_3$ -oxygen and transforms it into  $\mu_2$ -OH with a weak activation energy of  $\Delta G^\ddagger_{int-tri_{1 \rightarrow 2}} = +0.43$  eV. Thereafter, it diffuses and is transferred to the O<sub>int(tri)</sub> (targeted oxygen) atom forming  $\mu_3$ -OH with a high activation free energy ( $\Delta G^\ddagger_{int-tri_{2 \rightarrow 3}} = +1.00$  eV). Since the proton of SH is too far from O<sub>int(tri)</sub> to react, the SH group must diffuse from alumina to an accessible terminal sulfide to form a Mo-S-S-H species with a low activation free energy ( $\Delta G^\ddagger_{int-tri_{4 \rightarrow 5}} = +0.42$  eV). The proton is more easily accessible to oxygen through this S-S-H species and can be transferred smoothly with a moderate activation free energy of  $\Delta G^\ddagger_{int-tri_{5 \rightarrow 6}} = +0.41$  eV. The newly formed water is still in strong interaction with alumina and Mo, which makes the water desorption step demanding with  $\Delta G^\ddagger_{int-tri_{6 \rightarrow 7}} = +0.73$  eV, similar to the O<sub>int(bi)</sub> site. In general, we observe that water desorption from support is kinetically more limited than from a Mo site of the cluster (~0.7 eV vs. ~0.2 eV). The water desorption on Mo-site is promoted by the exchanged S atom, but on the support, it occurs more or less independently. After the

desorption of water, the O-vacancy should be replaced by S, which currently exists as S-S dimer with terminal S. The splitting of the S-S bond requires an activation free energy of  $\Delta G^\ddagger_{int-tri_{7 \rightarrow 8}} = +0.92$  eV. As in the previous case, many energy levels involved are high, and the elementary steps are more numerous, making the overall mechanism much more complex.

### 3.2 Transformation of Mo<sub>3</sub>S<sub>9</sub> trisulfides into Mo<sub>3</sub>S<sub>6</sub> disulfides (step IV)

The Mo-trisulfide into disulfide conversion (step IV in **Figure 1**) involves H<sub>2</sub> as a reactant and H<sub>2</sub>S as product. The three main elementary steps are described in **Scheme 2**.

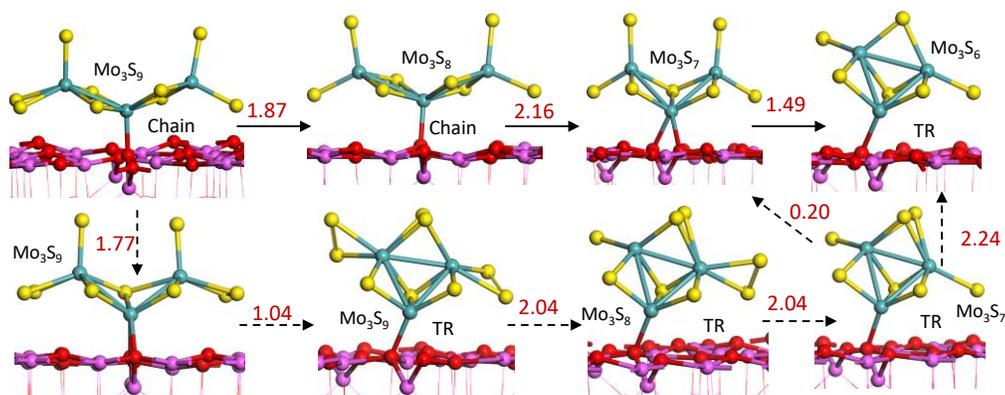


**Scheme 2.** Main elementary steps for the S removal H<sub>2</sub>/H<sub>2</sub>S. \* represents formally a Mo site of the Mo<sub>3</sub>S<sub>9-x</sub> intermediates. Note: instead of involving 2 Mo-sites, one single site bearing 2 S or one S<sub>2</sub> dimer may be concerned ( $* -S_2 + H_2 \rightarrow HS - * -SH_2$ ).

Like in previous cases, some intermediate SH reorientation and S diffusion or rearrangement are also involved. As they are not the limiting ones, we will not report their activation energies. The detailed kinetic pathways corresponding to the different S-species (terminal and bridging) are reported in **Supporting Information 7.2**. One preliminary remark is that we identified possible chain to triangular reconstructions during the Mo<sub>3</sub>S<sub>9</sub> to Mo<sub>3</sub>S<sub>6</sub> transformation (**Figure 5**). It is known that the targeted MoS<sub>2</sub> phase exhibits a triangular Mo<sub>3</sub> pattern where Mo-atoms

are connected by  $\mu_3$ -sulfur atoms. Several  $\text{Mo}_3\text{S}_9$  conformers have been proposed in the literature, such as triangular[21,82,85] or chain-like ones.[78–80,83,86] Hence, one key question for the genesis of the  $\text{MoS}_2$  phase could be linked to the kinetics of formation of this triangular pattern. **Figure 5** illustrates the structures of the most relevant  $\text{Mo}_3\text{S}_{9-x}$  intermediates found along the  $\text{Mo}_3\text{S}_9$  to  $\text{Mo}_3\text{S}_6$  transformation activated by  $\text{H}_2$ . As shown in **Figure S18a**, the S-removal steps are almost all isergonic. The chain-like  $\text{Mo}_3\text{S}_9$  is more stable than triangular- $\text{Mo}_3\text{S}_9$  by  $\sim 0.5$  eV on the alumina support in contrast with their gas-phase structures.[25] As it was already confirmed for the  $\text{Mo}_3\text{O}_9$  tri-oxide and for  $\text{Mo}_3\text{O}_x\text{S}_y$  ( $x+y = 9$ ) oxysulfides presented before. However, the trend is inverted for the  $\text{Mo}_3\text{S}_6$  species that are stabilized with a triangular shape due to the undercoordination of Mo in the chain conformer. For 1:3 stoichiometry of Mo:S/O, the interaction with the alumina site is a strong stabilizing factor for the chain conformer over triangular, which involves significant reconstruction of the chain and triangular with respect to their gas-phase ground-state structures. Nevertheless, the support can no longer stabilize chain shapes for Mo:S/O ratio of 1:2 due to the undercoordination of Mo atoms.

Several elementary steps are thus suspected of inducing the chain to the triangular reconstruction of  $\text{Mo}_3\text{S}_y$  intermediates in the course of S removal. This chain to triangular reconstruction may occur at the initial  $\text{Mo}_3\text{S}_9$  stage (**Figure 5**, bottom path) or while removing sulfur atoms from  $\text{Mo}_3\text{S}_9$  into  $\text{Mo}_3\text{S}_6$  (**Figure 5**, top path). The direct  $\text{Mo}_3\text{S}_9$  chain to triangle reconstruction requires a competing activation free energy of +1.77 eV (**Figure S23**). The complete structural description of this reconstruction is reported in **Supporting Information 8.4**. The triangular- $\text{Mo}_3\text{S}_9$  will then further transform into triangular- $\text{Mo}_3\text{S}_6$ . Even though the triangular- $\text{Mo}_3\text{S}_9$  is slightly less stable, the reconstruction may compete with the S-removal on chain conformers involving higher activation energies.



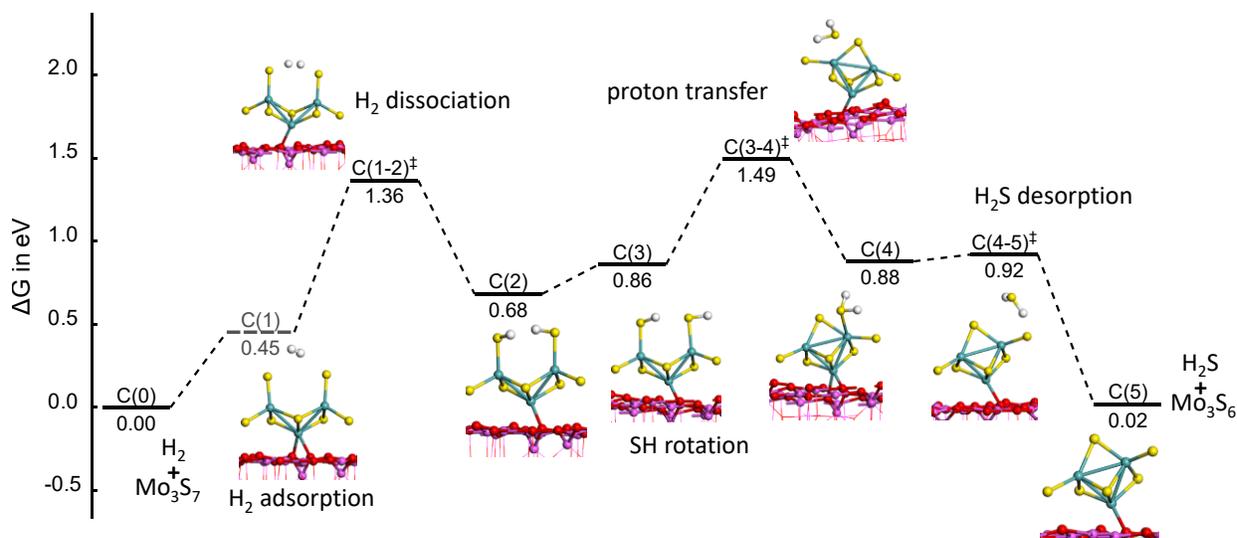
**Figure 5.** Two possible pathways for the chain- $\text{Mo}_3\text{S}_9$  to triangular- $\text{Mo}_3\text{S}_6$  transformation: keeping the chain conformation as long as possible (top path), or through triangular- $\text{Mo}_3\text{S}_9$  (bottom path). Red numbers are free energies of activation calculated for each given step (referring the highest TS to its lowest energy precursor of the given step, see **Supporting Information 8.1** for the detailed free energy profiles).

To explore how the S-removal occurs, we screened the various possible sites for S removal on-chain and triangular  $\text{Mo}_3\text{S}_9$  and observed that the terminal- $\text{S}_2$  dimer is kinetically the most prominent to be removed (**Figure S19a** and **S24**). In chain- $\text{Mo}_3\text{S}_9$ , it leads to a symmetrical structure, and in triangular both terminal- $\text{S}_2$  dimers can be disintegrated likewise. Since the activation free energy of breaking the  $\text{S}_2$  dimer along with dissociative adsorption of  $\text{H}_2$  is relatively high  $\Delta G_{\text{Chain}_{A_0 \rightarrow 2}}^\ddagger = +1.87$  eV (**Figure S19a**) vs.  $\Delta G_{\text{TR}_{t-\text{S}_2 \rightarrow 2}}^\ddagger = +2.04$  eV (**Figure S24**), this step would be a rate-limiting step. It is followed by SH rotation, and the third step is a proton transfer from one SH to the neighboring SH leading to the formation of  $\text{H}_2\text{S}$  with activation energy  $\Delta G_{\text{Chain}_{A_0 \rightarrow 4}}^\ddagger$  of +1.74 eV. This proton transfer is relatively more accessible for triangular case ( $\Delta G_{\text{TR}_{t-\text{S}_2 \rightarrow 4}}^\ddagger = +0.86$  eV). The proton transfer and  $\text{H}_2\text{S}$  desorption are a

concerted process for chain and separate for triangular but with no additional cost. From  $\text{Mo}_3\text{S}_9$  to  $\text{Mo}_3\text{S}_8$ , the conformation of the cluster remains unchanged.

From  $\text{Mo}_3\text{S}_8$  to  $\text{Mo}_3\text{S}_7$ , the bridging sulfur is thermodynamically more advantageous than the terminal ones to be removed in the chain conformer. Pulling out, the bridging S creates a vacancy initiating the chain to triangular reconstruction illustrated in **Figure S19b**. As mentioned earlier, the first step would be  $\text{H}_2$  dissociation that requires about +1.83 eV ( $\Delta G^\ddagger_{B_0 \rightarrow 2}$ ) as activation energy. The proton transfer and the formation of  $\text{H}_2\text{S}$  involves high overall activation energy of +2.16 eV ( $\Delta G^\ddagger_{B_0 \rightarrow 4}$ ) which asserts to be the rate-limiting step. The desorption of  $\text{H}_2\text{S}$  creates S vacancy and induces the bending of the  $\text{Mo}_3$ -chain leading to the initiation of a triangular conformer converting bridging sulfur ( $\mu_2$ -S) into apical sulfur ( $\mu_3$ -S) with a negligible barrier. The reconstruction results in the stabilization and S-removal process from  $\text{Mo}_3\text{S}_8$  into  $\text{Mo}_3\text{S}_7$ , which becomes exergonic, contrasting with the previous endergonic S removal. In the case of a triangular conformer, the second S removal from terminal- $\text{S}_2$  dimer is assumed to occur in a similar fashion as the first one.

The remaining excessive sulfur of  $\text{Mo}_3\text{S}_7$  is removed identically (**Figure 6**) with a rate-limiting step of proton transfer ( $\Delta G^\ddagger_{C_0 \rightarrow 4} = 1.49$  eV). As in the previous case, the  $\text{H}_2\text{S}$  removal is associated with a further reconstruction, and terminal  $\mu_1$ -S converted into bridging  $\mu_2$ -S, which closes the triangular pattern of the  $\text{Mo}_3\text{S}_6$  disulfide. This structure is reminiscent of the triangular pattern observed in  $\text{MoS}_2$  phases. In the triangular case, the bridging  $\text{S}_2$ -dimer dissociates and converts into the triangular  $\text{Mo}_3\text{S}_7$  observed from the chain conformer, and S-excess is removed in the same way (**Figure 5**).



**Figure 6.** Free energy profile of S removal using H<sub>2</sub> and formation of the triangular Mo<sub>3</sub> pattern: Mo<sub>3</sub>S<sub>7</sub> + H<sub>2</sub> → Mo<sub>3</sub>S<sub>6</sub> + H<sub>2</sub>S. C(1) corresponding to H<sub>2</sub> physisorbed precursor state is subject to higher uncertainty on its entropic contribution so its free energy level is represented with a dashed line. Color legend: red balls: O, blue balls: Mo, pink balls: Al, yellow balls: S, and white balls: H.

It could be noticed that the various calculated free energies for H<sub>2</sub> activation through homolytic dissociation leading to two Mo-SH groups on Mo<sub>3</sub>S<sub>x</sub> trimer, such as reported in **Figure 6** or in **Supplementary Information 7.2** are very consistent with those previously found on MoS<sub>2</sub> edges.[87] Even if we cannot fully rule out that this activation step might occur through a heterolytic dissociation (Mo-H and Mo-SH) such as found on monomeric Mo<sub>1</sub>S<sub>3</sub> (**Figure S31**), the calculated values reported in Ref.[87] indicate that the heterolytic dissociations are in the same range of the homolytic ones. Hence, the trend reported in our work might not be strongly affected.

### 3.3 Transformation of $\text{Mo}_3\text{O}_3\text{S}_6$ oxysulfides into $\text{Mo}_3\text{S}_6$ disulfides (step III)

As explained in the Introduction,  $\text{Mo}_3\text{S}_6$  formation may occur through the direct reduction of  $\text{Mo}_3\text{O}_3\text{S}_6$  by  $\text{H}_2$  (so-called oxysulfide pathway: step III in **Figure 1**) without further use of  $\text{H}_2\text{S}$ . The mechanism involves O-removal and water as a product, and it can be written in a similar way as in **Scheme 2**). After every O removal step, cluster reconstruction occurs and eventually leads to the formation of TR- $\text{Mo}_3\text{S}_6$ , whereas the initial state of  $\text{Mo}_3\text{O}_3\text{S}_6$  oxysulfide is chain-like. Activation energies are comparable to those involved in the trisulfide pathway except for the last O-removal, which is highly unfavored. For the sake of clarity, the detailed results are reported in **Supporting Information 7.3** and discussed in the next section.

## 4. Discussion

### 4.1. O/S exchanges from $\text{Mo}_3\text{O}_9$ to $\text{Mo}_3\text{O}_3\text{S}_6$ (step I)

Considering Step I of **Figure 1**, our study confirms that the sulfidation of highly dispersed Mo-oxide oligomers involves an O/S exchange mechanism, as previously proposed in the literature.[16,24,28] This mechanism involves four successive elementary steps: i) adsorption of  $\text{H}_2\text{S}$  on Mo site, ii) dissociation of  $\text{H}_2\text{S}$  by migrating the proton to neighboring O, iii) proton transfer from SH to OH resulting in water formation, and d) water desorption. Simultaneously, we identify the nature of oxy-sulfide species and quantify their interaction with alumina support from thermodynamic and kinetic aspects. Though the thermodynamic energy favors the  $\text{O}_{\text{int}(\text{bi})}$  replacement to form S-S dimer according to a heterogenous path, these oxygens involve the highest activation energies, which might kinetically prohibit the sulfidation of these oxygens before bridging or terminal ones. Similarly,  $\text{O}_{\text{int}(\text{tri})}$  would be one of the last oxygens to be replaced due their even lower accessibility.

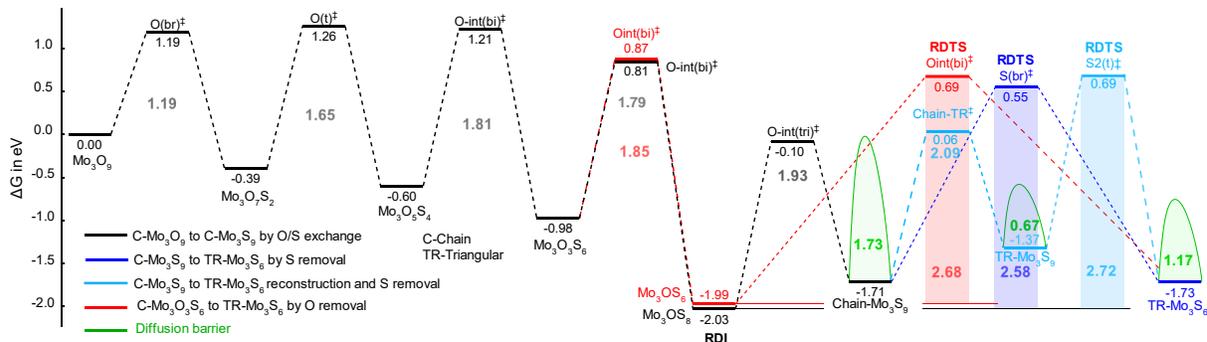
If we consider the thermodynamic diagram (homogeneous path-1 vs. heterogeneous path-2 in **Figure 2**), O/S exchange will follow path-1 at the early stage of sulfidation since bridging and terminal oxygens are easily replaceable kinetically. Some earlier DFT studies on unsupported bulk MoO<sub>3</sub> found that the top oxo species are thermodynamically preferred,[44–46] which difference can be explained by the distorted Mo<sub>3</sub>O<sub>9</sub> chain structure which enhance the reactivity of bridging oxo site. Once the second interfacial oxygen is replaced (Mo<sub>3</sub>O<sub>3</sub>S<sub>6</sub>→Mo<sub>3</sub>O<sub>2</sub>S<sub>7</sub>), a transition from the homogeneous path-1 to the heterogenous path-2 should occur. If heterogeneous path-2 occurs preferentially, the oxysulfide intermediate such as Mo<sub>3</sub>O<sub>3</sub>S<sub>6</sub> will retain the oxo (terminal) species for a longer sulfidation degree, which is compatible with EXAFS observations showing the presence of the smallest Mo-O bonds also for Mo<sub>3</sub>O<sub>3</sub>S<sub>6</sub>. [17,18]

#### 4.2. Competition between oxysulfide pathway and trisulfide pathway

The summarized free energy profile shown in **Figure 7**, is based on the dominating kinetics showing that the O/S exchange occurs in the following order: O<sub>br</sub> > O<sub>t</sub> > O<sub>int-bi</sub> > O<sub>int-tri</sub>. Based on several tests, we assume that the same types of oxygen (or sulfur) sites exhibit similar kinetic barriers (although some of them have not been calculated explicitly). We compare in what follows the free energies of activation of the Rate Determining Transition States (RDTS) and Determining Intermediates (RDI) and propose an overall discussion on kinetic effects.

In **Figure 7**, until the formation of Mo<sub>3</sub>O<sub>3</sub>S<sub>6</sub>, the rate-limiting step is exchanging the O<sub>int-bi</sub> ( $\Delta G_{int-bi}^\ddagger = 1.81$  eV). The next O/S exchange is competing with O removal by a direct reduction pathway (steps III in **Figure 1**): from Mo-oxysulfide (Mo<sub>3</sub>O<sub>3</sub>S<sub>6</sub>), removing interfacial oxygen with H<sub>2</sub> requires comparable free activation energies as replacing the same oxygen sites by S

(+1.85 eV vs. +1.79 eV). Moreover, thermodynamically the O/S exchange also competes with reduction accompanied by oxygen removal. Indeed, the RDI of the trisulfide pathway obtained for the  $\text{Mo}_3\text{OS}_8$  intermediate, exhibits a very similar free energy ( $\sim -2$  eV) as for the RDI  $\text{Mo}_3\text{OS}_6$  in the O-removal of the oxysulfide path. Therefore, it seems challenging to discriminate between O/S exchange leading to  $\text{Mo}_3\text{OS}_8$  (step II) and oxygen removal (step III) leading to  $\text{Mo}_3\text{OS}_6$  starting from the common  $\text{Mo}_3\text{O}_3\text{S}_6$  intermediate. Exchanging the final oxygen by sulfur ( $\text{Mo}_3\text{OS}_8 \rightarrow \text{Mo}_3\text{S}_9$ ) is endergonic ( $\Delta G = +0.32$  eV) and requires the maximum activation energy among all O/S exchanges ( $\Delta G_{int-tri}^\ddagger = +1.93$  eV). By contrast, the last O-removal on  $\text{Mo}_3\text{OS}_6$  reveals a kinetic limitation due to the high-energy intermediate generated (+2.68 eV of  $\text{Mo}_3\text{S}_6$ ) before its reconstruction towards the most stable one. Instead of removing the last oxygen in  $\text{Mo}_3\text{OS}_6$  alternatively, it can be replaced by the O/S exchange leading to  $\text{Mo}_3\text{S}_7$ . This alternative step reveals a free activation energy of  $\Delta G_{F(4-5)}^\ddagger + 1.96$  eV (**Figure S21c**), which is the highest value among all the individual activation energies found for the mechanisms studied in this work. After replacing this O with S, it will transform into  $\text{Mo}_3\text{S}_7$ , and the last S removal step, to eventually transform into  $\text{Mo}_3\text{S}_6$ , will be the same as the trisulfide path (**Figure 6**). Considering the limitation for the last interfacial oxygen removal, the trisulfide pathway involving  $\text{Mo}_3\text{S}_9$  seems to be more favorable than the direct reduction from  $\text{Mo}_3\text{O}_3\text{S}_6$  (oxysulfide) to  $\text{Mo}_3\text{S}_6$  (disulfide). Nonetheless,  $\text{Mo}_3\text{S}_9$  eventually has also to transform into disulfide  $\text{Mo}_3\text{S}_6$ .



**Figure 7.** Free energy comparison of entire sulfo-reduction pathways from chain- $\text{Mo}_3\text{O}_9$  to TR- $\text{Mo}_3\text{S}_6$  formation: O/S exchange (black: step III), chain to triangular reconstruction and S-removal to disulfide (light blue: step-III), chain-trisulfide to triangular disulfide by S-removal (dark blue: step-III) and oxysulfide to disulfide by O-removal (red: step IV) with respective rate-limiting step and involved oxygen or sulfur species. The corresponding RDI and RDTs are also mentioned for the concerned pathways. The green curve shows the barrier for translatory diffusion of sulfide on (100) surfaces of  $\gamma$ -alumina. The entire energy profile is reported in **Figure S30**.

Regarding the transformation of chain  $\text{Mo}_3\text{S}_9$  into triangular  $\text{Mo}_3\text{S}_6$ , the sulfur removal steps are clearly kinetically unfavored since relatively high free activation energies are required for the S-removals (+2.58 eV with respect to RDI, **Figure 7**). Hence, after the formation of chain- $\text{Mo}_3\text{S}_9$ , we must consider an alternate path where the reconstruction to a triangular conformer may take place before S-removal on chain  $\text{Mo}_3\text{S}_9$ . The exploration of this alternate path (**Supporting Information 8.1**) is also justified by the fact that the trisulfide  $\text{Mo}_3\text{S}_9$  phase has a much weaker interaction with the support than all other chain-like oxysulfide intermediates (see also next section), suggesting that this transformation should be more accessible at the trisulfide stage than at the oxysulfide stage. The activation energy of this  $\text{Mo}_3\text{S}_9$  chain to triangle

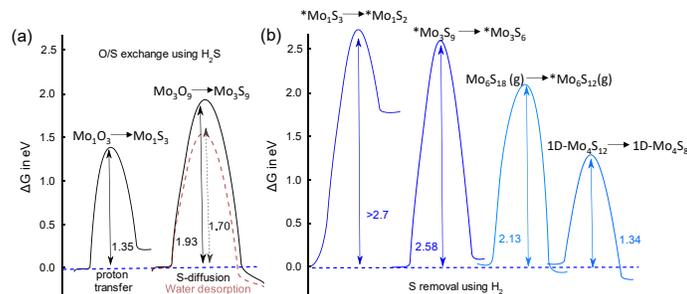
reconstruction is about +2.09 eV (related to RDI, **Figure 7**) which is preferred to the direct formation of  $\text{Mo}_3\text{S}_6$  intermediate through S- or O-removal. However, the subsequent removals of S-atoms from TR- $\text{Mo}_3\text{S}_9$  to TR- $\text{Mo}_3\text{S}_6$  are again kinetically limited (+2.72 eV, **Figure S24** and **Figure 7**). Chain and triangular  $\text{Mo}_3\text{S}_9$  are thus kinetically accessible, but the subsequent steps of S-removals are kinetically prohibited. So, the unique alternative for the  $\text{Mo}_3\text{S}_9$  intermediates to evolve could be to diffuse on the alumina surface and grow before giving rise to the  $\text{MoS}_2$  phase as discussed in the following.

### 4.3. Mobility, growth, and size effects

As quantified in **Supporting Information 9.1**, the interaction energy of Mo-oxysulfides and Mo-sulfides with alumina reveals that the Mo-sulfides oligomers are the less strongly bonded species, as expected from chemical intuition. Based on this preliminary interaction energy analysis, we have quantified the translational diffusion of 4 key Mo-sulfide species (chain- $\text{Mo}_3\text{S}_9$ , triangular- $\text{Mo}_3\text{S}_9$  and triangular- $\text{Mo}_3\text{S}_6$ , and  $\text{Mo}_1\text{S}_3$ ) on the alumina (100) surface following some main principal orientations of the surface, which allow the migration of the oligomers from one O site to another (**Supporting Information 9.2**). The translational diffusion barrier is significantly higher for chain- $\text{Mo}_3\text{S}_9$  than for triangular conformers (1.73 eV vs. 0.67 eV). Therefore, the mobility of  $\text{Mo}_3\text{S}_9$  triangular intermediates is favored with respect to chain- $\text{Mo}_3\text{S}_9$ . We thus expect that the growth of  $\text{MoS}_3$ -polymorphs should be predominant through  $\text{Mo}_3\text{S}_9$  triangular species before their ultimate transformation into the  $\text{MoS}_2$  active phase, as suggested by the observed sizes of sulfides evaluated by EXAFS studies.[8,17,18] The diffusion

barrier of triangular-Mo<sub>3</sub>S<sub>9</sub> is also lower than Mo<sub>3</sub>S<sub>6</sub> (0.67 eV vs. 1.17 eV). Therefore, if Mo<sub>3</sub>S<sub>6</sub> species are formed, their mobility could also allow the formation of the MoS<sub>2</sub> phase. Since the S-removals on chain-Mo<sub>3</sub>S<sub>9</sub> are kinetically limited as aforementioned, the chain to triangle reconstruction followed by diffusion of triangular-Mo<sub>3</sub>S<sub>9</sub> will preferentially occur. This diffusion process will allow their subsequent condensation into larger trisulfide Mo<sub>3n</sub>S<sub>9n</sub> 2D patches of finite size, so called 1T'-MoS<sub>3</sub> phase in our previous study.[25] Molecular dynamics simulation revealed that the condensation of triangular-(Mo<sub>3</sub>S<sub>9</sub>)<sub>n</sub> (n=2,3) oligomers into Mo<sub>3n</sub>S<sub>9n</sub> 2D patches is indeed possible in gas phase.[25] Moreover, According to Ref.[25], the energy gain by the condensation of isolated triangular-Mo<sub>3</sub>S<sub>9</sub> into Mo<sub>3n</sub>S<sub>9n</sub> 2D patches is substantial (around -2 eV to -2.5 eV/Mo<sub>3</sub>S<sub>9</sub> depending on n). Since the interaction energy of triangular-Mo<sub>3</sub>S<sub>9</sub> on  $\gamma$ -alumina is about -1.5 eV (**Figure S25**), this implies that the formation of such 2D patches from triangular-Mo<sub>3</sub>S<sub>9</sub> dispersed on alumina is an exothermic process. If so, the S-removal steps would occur on such larger size Mo<sub>3n</sub>S<sub>9n</sub> 2D patches rather than on the Mo<sub>3</sub>S<sub>9</sub> for which the S-removal is energetically too demanding. **Supporting Information SI.11** and **Figure 8** show that the estimated barriers for the S-removal step decrease by increasing the Mo trisulfides cluster size. This S-removal results in the transformation of Mo<sub>3n</sub>S<sub>9n</sub> 2D patches into Mo<sub>3n</sub>S<sub>6n</sub> 2D patches which could diffuse and further grow to form the crystalline MoS<sub>2</sub> phase.

We also expect that even smaller Mo trisulfides entities (Mo<sub>2</sub>S<sub>6</sub> or Mo<sub>1</sub>S<sub>3</sub>, **Figure S29**) diffuse easily to enable the growth of the MoS<sub>3</sub> phase. Such fast diffusing trisulfide surface monomers, dimers or trimers might be at the origin of the layer-by-layer growing process of the MoS<sub>2</sub> phase supported on MgAl<sub>2</sub>O<sub>4</sub> observed by in situ TEM.[30]



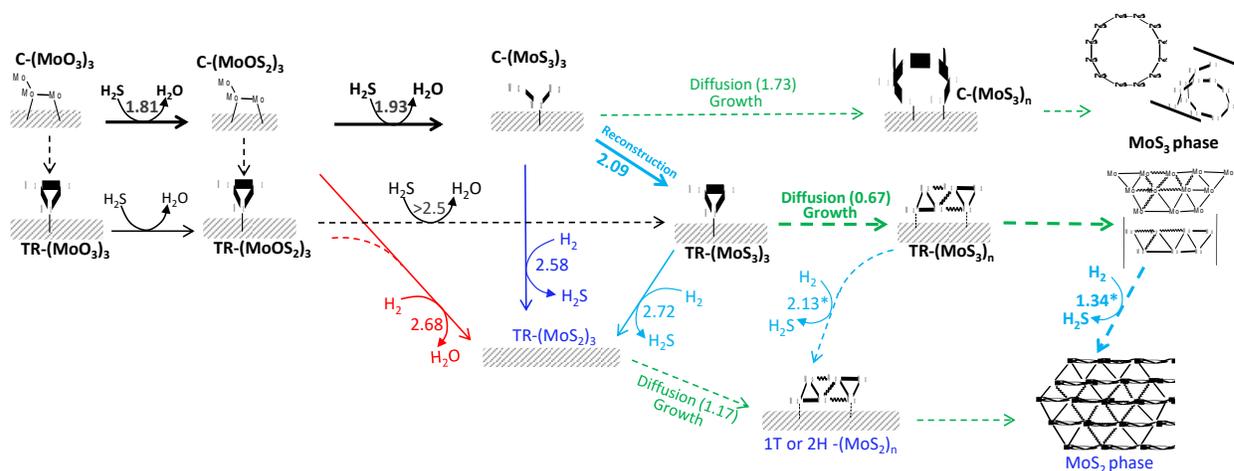
**Figure 8.** Comparison of Gibbs free energies of activation for O/S exchange and S-removal for diverse sizes. \* denotes the supported species, g: gas phase, and 1D: 1 dimensional periodic.

Moreover, the O/S exchange step is also influenced by the effect of size, and the monomeric  $\text{Mo}_1\text{O}_3$  cluster exhibits a significantly smaller activation free energy of +1.35 eV (**Supporting Information SI.4**) than  $\text{Mo}_3\text{O}_9$ . This implies that the trisulfide pathway (steps I and II in **Figure 1**) should be predominant for small  $\text{MoO}_3$  oligomers, including monomeric ones. Therefore, once these small Mo oxide clusters are trisulfided, they rapidly diffuse on the alumina surface (**Figure S29**) and grow to form larger  $\text{Mo}_{3n}\text{S}_{9n}$  2D patches before transforming into  $\text{MoS}_2$  phase by S-removals.

## 5. Conclusions

Using DFT calculations, we examined the sulfo-reduction mechanisms of Mo-oxide oligomers on the (100) surface of  $\gamma$ -alumina support. Mo-oxysulfides model intermediates have been validated by comparison with available structural data and IR spectra. As first perspective, we propose that the numerous Mo-oxysulfide structures identified in this work could be used for the simulation of in situ X-ray Absorption Spectra (EXAFS or XANES) in order to help for a refined identification of the key intermediates involved in the sulfo-reduction pathway.

We compared the two competing pathways of the genesis of the active phase: the first one involving Mo-oxysulfide intermediate only and the second one involving Mo-oxysulfide/Mo-trisulfide. A complete free energy analysis has been performed, accounting for various effects: the oligomer size, the chain to triangular shape reconstruction, and the diffusion of the Mo clusters on the alumina surface. Based on the gained understanding, we propose a comprehensive reaction network for the sulfidation/reduction process from  $\text{Mo}_3\text{O}_9$  oxide to  $\text{MoS}_3$  and  $\text{MoS}_2$  active phase, as summarized in **Figure 9**.



**Figure 9.** Schematic representation of the entire reaction network during activation, starting from Mo-oxide precursors to final  $\text{MoS}_2$  active phase. (C-Chain; TR-Triangular, \* values are estimated on unsupported clusters and periodic structures)

As shown in **Figure 9**, a sulfo-reduction pathway of Mo-oxides on alumina (100) surface, leading to the  $\text{MoS}_2$  phases, should proceed as follows.

- The sulfidation of  $\text{Mo}_n\text{O}_{3n}$  into  $\text{Mo}_n\text{S}_{3n}$  becomes progressively harder from  $x=1$  to  $x=3$  and occurs via a S/O exchange mechanism (dark arrows in **Figure 9**), whereas the O-removal is extremely demanding (red arrows). The kinetic order of O/S exchange in  $\text{Mo}_3\text{O}_9$  follows:  $O_{\text{br}} > O_{\text{t}} > O_{\text{int-bi}} > O_{\text{int-tri}}$ .

- The chain-like  $\text{Mo}_3\text{S}_9$  cluster should reconstruct into a triangular one to be able to transform further (plain light blue arrows in **Figure 9**).
- The small size  $\text{Mo}_n\text{S}_{3n}$  oligomers ( $x \leq 3$ , including triangular  $\text{Mo}_3\text{S}_9$ ) are fast diffusing species and oligomerize into larger species (dashed green arrows in **Figure 9**), last but not least into  $(\text{Mo}_3\text{S}_9)_n$  2D patches.
- For  $\text{Mo}_3\text{S}_9$ , the S-removal occurs preferentially on terminal- $\text{S}_2$  and terminal-S while bridging S requires the highest activation energy. However, the S-removal is expected to take place at a lower cost on larger  $(\text{Mo}_3\text{S}_9)_n$  2D patches (dashed blue arrows in **Figure 9**).
- As discussed in Ref.,[25] these  $(\text{Mo}_3\text{S}_9)_n$  2D patches may be the precursor of the 1T- $\text{MoS}_2$  phase, subsequently leading to 2H- $\text{MoS}_2$ .

Since we analyzed the role of  $\text{H}_2\text{S}$  and  $\text{H}_2$  as individual reactant leading to sulfidation and/or reduction, we propose as a second perspective to investigate if an interplay could exist between both reactants being simultaneously involved in the elementary steps.

We found that the support shows a substantial impact on energetics and structures (with respect to isolated species): cyclic- $\text{Mo}_3\text{O}_9$  and triangular  $\text{Mo}_3\text{S}_9$  are more stable in the gas phase, while the alumina (100) surface stabilizes the linear conformers through single or multiple Mo-O-Al bonds. Nevertheless, we expect that the specific alumina facet may impact the mobility of the species that we have quantified in the present work. In the future, it would thus be relevant to extend the study to other  $\gamma$ -alumina surfaces which were proposed to influence the sulfidation

degree of the MoS<sub>2</sub> phase,[48,49] and which features OH groups under sulfo-reduction conditions together with other Al sites as compared to the (100) surface.

**Supporting Information.** The gas phase sulfidation, and complementary data on thermodynamics, kinetics and frequency analyses of various pathways (including diffusion and reconstruction) for monomers and trimers, EXAFS and IR comparison for intermediates, have been reported in supporting information. The structural data for all intermediates and transition states are available from the corresponding author upon reasonable request. [32]

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