

In situ observation and reaction modeling of hydrodesulfurization over single-layer Co-promoted MoS₂ model catalysts: A combined STM and DFT study



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REVIEWER COMMENTS

Reviewer #2 (Remarks to the Author):

This is an interesting continuation on the work this group has done on studying hydrodesulfurization (HDS) reactions using CoMoS as a catalyst. The authors used scanning tunneling microscopy using a ReactorSTM to observe the HDS reaction *in situ* under conditions that are close to what industries would use. The authors also used density functional theory calculations to model the reaction pathways that can occur during the HDS reaction of methanethiol. From their DFT calculations they found that the Co promoter in the catalysts improves the HDS reactions.

Their work explains why it is important to have Co as a promoter in catalyst and why it is important to study these reactions *in situ* to later on design better catalyst.

After revisions this work would be a significant addition to the study of HDS reactions. This is relevant work to what the authors have done in the past and it seems they are working on expanding this work in the future, which I appreciate.

The methodology was well explained and easy to follow in the paper. The amount of detail provided should be enough for others to reproduce the results. My only concern with the data is that it was difficult to understand some of the terms and few figures could use some tweaks to make them easier to understand as well.

Comments that could be revised:

- 1) Is there a reason to switch between methanethiol and CH₂SH as frequently? Some consistency would make the paper easier to read.
- 2) Line 93 italic font on *in situ*.
- 3) It would be a good addition to add more information of the ReactorSTM used in the project as supplemental information. Not needed necessarily for this to be published, but would be beneficial for others who are new to this field to distinguish it from a regular STM.
- 4) Line 198 [SI, Figure S1.] in red. Should it just be black text?
- 5) Line 206 a citation would be better to lead people to the code used to generate the simulated STM images.
- 6) Lines 203 to 206: Could you elaborate what is meant by the experimental bias value of the corresponding STM image. There are no images near this section, nor do I see a simulated image that corresponds to an experimental image.
- 7) Line 228 to 229: Why are there variations in the intensity of the BRIM edges? Could you explain in more detail what you mean when attributing this to the different amounts of residual polarizations?

8) When explaining Figure 1 the term in registry and out of registry are used a lot. This to me is unclear exactly what you mean when some edges are in registry. Figure 1c) did not make it clear either. Do you mean that these edges align with a specific atomic terminated edge? Could you elaborate on this?

Side note: Could you split Figure 1 into two separate ones where one is the experimental work and the other the DFT models? Explaining them individually could add some clarity to each one and can help explain the results you want to present in that section.

10) Line 307 cite Figure 2.

11) Lines 313 to 316: Is there a before and after image to show no changes?

12) Figure 2: a-d seem to be different sizes. Also it is hard to read the red numbers on the orange spots of the STM images. For slide g where you explain the colors did you forget Carbon? Or is the carbon not imaged there?

Side note: Inconsistency when mentioning sulfur. Only element that is not just written by its symbol.

13) Figure 3: The caption labels a-h then labels h. This is also reflected in the text. Do you mean to describe a-g in the text? and then separately describe 3h? This is also another figure where it is hard to see the color red on the image. The small red circles are hard to visualize.

14) Line 476 PVD is a new acronym not introduced.

15) Line 483 should it be Figure 4a-j instead of Figure 4a-k?

16) Line 492 and Figure 5: The frames in Figures 4i and 4j do not seem to match the zoomed in shots in Figures 5a and 5b. Were other frames used?

Side note: Could a smoother graph be used to represent the line scans in Figure 5? The line scans seem messy although it is clear there is a difference.

The methods and results sections were for the most part well written. To me the main conclusions were explained in the Results sections and then summarized in the Conclusion section.

The references cited are well aligned to what is presented in the paper.

Reviewer #3 (Remarks to the Author):

The authors present an in-situ surface science study of Co-promoted MoS₂ nanoparticles (so called CoMoS) on a Au(111) support under hydrodesulphurization of methyl thiol, herein combining in-situ STM with DFT calculations. Mainly rationalized from the extensive DFT part, Co insertion into the C-S bond was identified as a relevant reaction step, while some of the apparent rate-determining intermediates seem to match the STM data for the transient edge structures of those in-situ experiments.

The topic of this paper is highly relevant for the field of catalytic hydrotreatments and the used ReactorSTM is an appropriate and novel experimental technique to investigate catalysts in their active state. The overall claim, that a model catalyst is observed in the active state, is relatively well supported by the analysis and DFT modelling. A weakness of the paper is that the interpretation of the STM data and the structural interpretation of edge structures and S terminations, which is then fed into the DFT work, is rather confusing and, in some places, weakly supported as the paper stands. Sufficient experimental details are given to ensure the reproducibility of the results. The scope is suitable for Nature Comm, but the paper needs some revision before a decision can be made about publication.

1. Some of the analyzed particles appear to be at least partially surrounded by cobalt sulfides (fig. 1c) or other matter (fig. 2c). Since this may affect the overall distribution of different edge types (considering a Wulff-construction based on the free edge energies), the authors may comment how this impacts their analysis. Why do the authors not focus on freely lying particles?
2. One new and one previously published model of the Co-edge structure is presented in fig 1d and the corresponding discussion, but in the end the authors state that both do not reflect their experimental results. I would encourage the authors to shorten this discussion or put it into the SI, since it appeared a bit confusing to me, and does not seem to add to the main message.
3. When calculating the MoS₂ on Au(111) it was not clear if the Au is stretched/compressed and how this might influence bonding energies of the proposed thiol intermediates. In general, it was not clear when the Au was used for the calculations or not, but it seems that it was only for the STM simulations. In other cases this may affect the bonding strength to the overlayer (e.g in oxide films) and also this system (Nanoscale, 2021, 13, 10167-10180), so was it checked if the same edge species are actually produced when the Au is there?
4. Figure 2a+b: Here the assignment of edges seems to be based on the appearance of the brims and the registry of atoms, referencing to literature. It seems the particles appear lower than the surrounding gold (especially in figure 2a) and in other images not, so what does that mean to the contrast assignment?
5. Figure 2c. An argument related to steric hindrance is used to explain why the thiols are spaced regularly two sites apart and all oriented in the same way. The molecule is rather small, so this might be a limited effect. Is there any result from DFT to support this claim?
6. It was not clear when Gibbs free energies or pure DFT energies were used throughout to calculate the configurations, which is particularly relevant in Figure 7.
7. The in-situ STM images shown in figure 4 appear to be of significantly better quality than the

images shown in fig. 3. The discussion related to Figure 3 is confusing. Clearly also the middle part changes contrast, so how much of the image is due to tip changes and how much is due to the process which is claimed to happen? Could you elaborate on how much was done to ensure that bias, speed etc was not influencing it? It also seems that there is a problem with the levelling of these images (when for example comparing c and e), which makes the edges appear brighter in one case.

8. Figure 4: Here it seems that the active edges are assigned to the Co terminated edge, but it is not clear how this assignment is done. What are the main assumptions here? In figure 2, the shorter edges are with Co, but for the particle here it is the opposite. I think this needs to be explained better, since it is crucial to the starting point of the DFT work and the link to experiment.

9. Figure 4: it is mentioned that the experiment took 44 hours. It would be useful with time stamps on the images. Is it realistic that the most relevant intermediates of these types are stable on the time scale between images?

10. The imaged transient states in Fig 5 appear of different height (between for example 3 and 5 Å for species I). Could the authors comment on this? Furthermore, the manuscript would need a statistical analysis of the appearance of these transient states to be convincing. It seems to be based only on imaging of one edge, but different changes are also evident from the other edges of the same type.

11. It is surprising to see a significant amount of post-HDS structures in the STM since these (i.e. the added S) would presumably be removed fast. Is there an argument that they can actually be seen on the relevant time scale, and be statically adsorbed (unlike the H)?

12. Sulphur vacancies are not considered in the manuscript. I understand that for adsorption in vacancies there is some similarity to the later HDS mechanism after H₂S removal ((4) in fig. 7b) however, can the authors comment on if S vacancies play a role in here and if they were imaged in-situ as well?

13. Most of the discussion of the DFT results contains information of the overall energetics of the processes, but in the figures only the activation barriers are displayed. I think it would be beneficial to include the total energetics of the transient states into the figures.

14. In connection with the discussion of pressure and ΔG values. It would be interesting to know if the calculated processes are more favored at 100bar, relevant to real conditions, and also if they would be observable at lower pressure, e.g. by other techniques such as IR or XPS.

15. The authors have reported mass spectroscopy data for processes before with the reactorSTM. Methane is the product here. Was an attempt done to detect this?

16. A general comment: The figures would benefit from a careful revision, for example to make sure they appear as one piece (fig. 6 and 7), have boxes of aligned sizes (fig. 2), or all have scale bars/scales (fig. 1c, fig. S2)

Other details

a. Frequently “et al.” comes with typos (for example: et. al. (ll216 and ll 250)), et. al (ll222), ...).

b. Ll 62 and 76: While single-layer MoS₂ is introduced first as the relevant catalysts, the authors later also consider multi-layer stacks as the industrial catalyst (which seems to be more precise). This should be consistent.

c. Ll. 320: The authors state, the even numbered edges in fig. 2b have “a much brighter BRIM compared to the ones marked with odd numbers”. This seems to be not the case, if not the other

way round. Finally, in ll344-346, it is then stated reversely (“... we identify the even numbered edges of fig. 2b with the darker brim as the Mo-terminated edge and the odd numbered edges with a very bright brim ...”). This should be revised to the correct version.

d. L1664: The structure that is shown in fig 8a in the DFT model is actually structure 5 of fig. 7b, not figure 4 (typo I guess). Why was structure 12 of figure 7b not chosen as a potential transient state, even if it is in front of an approx. 1.5eV barrier?

e. L1 686: The authors state the structure of fig 8b is identical to figure 2g. Indeed, they exhibit a very similar simulated STM image, but in figure 8b there is one adsorbed H on the S atom right of the thiolate, which is absent in fig. 2g. I suggest to revise to be precise here to not confuse the reader.

Reviewer #4 (Remarks to the Author):

The manuscript deals with the hydrodesulfurization (HDS) on a cobalt doped MoS₂ using scanning tunneling microscopy (STM) and density functional theory calculations (DFT). Such a combination of methods is indeed needed to interpret the experimental results and, on the other hand, to perform the calculations for relevant systems. The experiments have been performed in situ in a model reactor, which makes them more realistic from the applications point of view. The emphasis is on the reactions occurring on the cobalt doped edge of MoS₂, which has not been studied earlier in the same extent as the bare molybdenum edge. In their DFT based transition state search, the authors have found new pathways for the HDS reaction of methanethiol. The STM images calculated for the essential stages of the reaction agree well with the experimental ones, enabling a construction of the full reaction cycle. The results are sound, and the paper is well written. I recommend publication after the authors have addressed the following issues:

In the discussion about Fig 2 b it is stated that the set of edges marked with even numbers have a much brighter brim than the ones marked with odd numbers. However, 5 appears to be brighter than 4, or am I misinterpreting the labels?

It is hard to see the blue and especially the red dots in Figs. 1 and 2. Would there be a better way to indicate the positions?

C is not mentioned in the explanation of atom types in Fig. 2. Is it missing or just not visible in these configurations?

In Fig. 1 c the scale seems to be missing.

Why is ‘brim’ written with capital letters as if it were an acronym?

When discussing the different structures, e.g. in Fig. 6, would it be possible to address the structures by both number and a compact description of the structure in question? This would make it easier to identify the structure without always referring to the figure.

There is a reference to Fig. 9, which is missing; this should obviously be 8 d.

Reference 27 is the same as reference 28.

REVIEWER COMMENTS

Reviewer #1

The claim of this paper is to carry out In situ observation of hydrodesulfurization and modelling over Co-promoted MoS₂ by STM and DFT study. This could lead to exciting characterization of real catalyst under industrially relevant conditions, giving enormously new useful information.

However, I am unsure how much new information we can get from this work beyond the previous studies. Research groups, such as Grønberg and Mom have investigated the structures of the edges and the interactions with the Au substrate, especially, some recent works had employed the same catalysts under similar gases using the same ReactorSTM and carried out corresponding modelling studies as that of the present work.

Overall, I felt that this work looks preliminary in its current form, and the present evidence for some claims should be substantiated.

We thank the reviewer for the critical comment on our work. We would like to point out that our present work is a significant stride forward from the works done by Grønberg and Mom et al. (our previous work) in the following ways:

- a. We have directly observed a CoMoS model catalyst in action with both Mo and S edges under near-industrial HDS conditions. While the reaction conditions we use are very similar to that of Mom et al., this previous work concerned pristine MoS₂ with Mo terminated edges only.
- b. The work of Grønberg studies a CoMoS model catalyst at a pressure 6 orders of magnitude lower than our work, and at thermodynamic equilibrium conditions without an organosulfur reactant. They extrapolate the effects observed experimentally to higher pressures. We experimentally demonstrate that the active edges in our system are not at thermodynamic equilibrium because of significant reaction rates of CH₃SH desulfurization on the S edges. This is not the case in either of the works of Grønberg or Mom.
- c. We also detect the product formation of CH₄ and H₂S in the residual gas analyzer. This was not observed in the works of either Grønberg or Mom.
- d. Based on this experimentally observed dynamic edge structure on the S edge, we model a new DDS reaction pathway assisted by the edge Co atoms. The modeling in our work does not concern the S edges at thermodynamic equilibrium as in the previous works, but one that is active during the HDS reaction of CH₃SH. This approach is both new and radically different from the previous works.

Additionally, since the work of Mom et al. was carried in our group, we fully appreciate the significance of the steps forward in understanding hydrodesulfurization. These motivations behind our work are now presented in the Main manuscript at [line number 114-130 and 104](#).

1. While hydrodesulphurization of CH₃SH is interesting in this work, this molecule rather than using substituted thiophenes, the nature of model catalyst and conditions are still far from those of industrial hydrodesulfurization.

We thank the reviewer for this comment.

The reaction conditions used in our work are the highest possible that can be attained with the current state-of-art video rate in situ STMs for observing heterogeneous catalysis with organosulfur compounds. While this may be 1 or 2 orders of magnitudes away from the industrial pressures, we already bridge a pressure gap of 6 orders of magnitude to observe new effects on the CoMoS edges not observed in any experiment before. This is a significant experimental advancement for directly observing the complex chemistry of a catalytic reaction like HDS.

These arguments are mentioned at [line number 96-102](#) to strengthen the introduction.

On the usage of thiophene; Towards the broader goal of understanding the complex reaction mechanisms of HDS, we think that we show not a single but several significant steps involving decades of experimental challenges. This is because,

1. HDS of thiophenes can occur via both direct desulfurization (DDS) and hydrogenation (HYD) pathways simultaneously. To understand the multi-pathway HDS of a complex aromatic molecule like thiophene, separating the two reaction pathways is necessary. By using a simple C1 thiol, possible HYD pathways are irrelevant, and thus, we can gain insights into the C-S bond scission without other competing effects.
2. In order to gain complete understanding of thiophene HDS, the desulfurization of C1-C6 compounds must be understood first, as HDS of thiophenes will inevitably result in the ring opening. Up to now, no in situ observation of the HDS of the simple thiols on the CoMoS edges at elevated pressures had been carried out.
3. C2-C6 are liquid thiols and hence, much more difficult to dose into the system without causing irreversible contamination. In the current state, the ReactorSTM is not designed to handle liquid thiols but this is an experimental challenge that will be overcome in the future. C1 thiol, being a gas, is the best practical solution based on the existing state-of-the-art facilities.

We also have carried out modeling of a hydrogenated thiophene system (in the same spirit as the reviewer's comment) with an aim to experimentally study thiophene HDS in a future work.

The above arguments are now mentioned in the results section at [line number 330-343](#).

2. I appreciate the authors used higher pressure/temperature closer to industry conditions than that of Mom's work. However, the STEM image quality such as Figs. 3-5 is really poor under such the higher gas pressure, which can hardly support their DFT calculations. It is rather speculative to use unclear bright (dark) image analysis of STEM without invoking other evidence.

We thank the reviewer for this comment.

We would like to clarify that we do not use a Scanning Transmission Electron Microscope (STEM) in our experiments, but a Scanning Tunneling Microscope (STM) that directly probes the local density of states on the active sites.

We note that the quality of our STM images are a significant improvement of the quality of images shown in the previous work of Mom et al. Operating an STM under the very aggressive chemical conditions for heterogeneous catalysis and expecting atomic resolution of the quality observed in many low-temperature, ultrahigh vacuum STMs is not very realistic, as at catalysis conditions, there is a very high diffusion of molecules and emergent slower kinetic phenomena, such as the slow HDS chemical reaction itself. In this work, we aim to study the latter, as the former is too fast to be observed. The high pressure inevitably causes background noise, which is a direct result of 10^6 times

higher number of species present in our system in comparison to many UHV-based works on the topic.

Further on the quality of the STM images in our work, we refer to our response to comment #7 of reviewer 3.

Additionally, we would also like to clarify that the electronic structure of the MoS₂ and CoMoS edges is very sensitive to adsorption of the smallest molecules (even atomic H). Adsorption of CH₃SH, H₂, and H₂S, among other moieties, results in very drastic changes in the edge structure seen in the STM images. This is a well-known fact demonstrated in several STM-based molecular adsorption experiments carried out on MoS₂ and CoMoS edges in the past, rather than a speculation arising singularly out of our experiments alone.

Some of these arguments along with the references are now provided at line number 446-453 in the results section.

3. Any analysis of 1H or 2T structure under different pressures/temperatures?

We thank the reviewer for this question.

The aim of this work is to study the CH₃SH HDS reaction on the edges of purely 1H CoMoS slabs only. Under the synthesis conditions used here, 1T CoMoS is not expected to form(25) and synthesis of this metastable structure is outside the scope of this work.

This is now mentioned at line number 152-155.

4. I felt that the authors should at least use some characterization tools such IR/Raman and insitu product gas analysis, to substantiate their conclusions. For example, H on the edge S atoms should be experimentally confirmed instead of solely relying on the DFT calculations.

Again, Figure 2d cannot offer convincing STEM images for dissociative chemisorption of CH₃SH (any proof for adsorption of CH₃S by IR ?) or transfer of thiol on the Co edge, to that of simulated images as Figure 2g.

We thank the reviewer for this suggestion. The product analysis is now provided in Figure 5e. Additionally, we refer to our response comment #15, reviewer 3.

The experimental detection of adsorbed H on the edges has already been carried out using pyridine and NO adsorption experiments over CoMoS slabs supported on Au(111) in the work of Grønberg(17). The formation of CH₃S⁻ and adsorbed H upon the chemisorption of CH₃SH on unsupported and supported MoS₂ edges has already been well-documented through in situ IR spectroscopy in the past. (reference 54-57) The effect of other organosulfur adsorbates has also been studied in the past. (reference 58-61) The CH₃SH structures considered in our work are based on the findings of these works.

These clarifications and the references are now provided at line number 361 and 446-453.

5. The DFT calculations did not seem to correlate well with experimental parts.

What is the justification for 'activation energy 580 of 1.08 eV/atom, H₂S formation is certainly feasible' ?

We thank the reviewer for the comment. The statement is now changed to (line 708-711) –

H₂S formation is feasible at the reaction conditions used with low turn-over frequencies of ~10⁻², similar to the turn-over frequencies of the S edges seen in our experiments. Additionally, this finding also agrees well with the detection of H₂S formation in Figure 5e.

6. For the activation of CH₃-S by single Co atom, they claimed that the elementary step is the insertion of C-S bond by Co. In this part, experimental verification must be required to clarify whether it needs one or two or even multiple sites required.

We thank the reviewer for this comment.

The models presented in our work describe the simplest mechanism involving C-S bond scission with assistance of single Co sites. This is done to demonstrate the feasibility of this pathway in comparison to C-S bond breaking by hydrogen transfer, for example. There is no evidence in our work that suggests that multiple Co metal atoms are involved in this reaction. Furthermore, given the low hydrogen pressures used, the S edges have many different local structures. Therefore, it is highly unlikely that a process involving multiple metal atom sites occurs under the reaction conditions used in our work. Multiple-site reaction pathways may be more feasible at higher hydrogen pressures.

These clarifications are now mentioned at [line number 822](#).

7. The cleavage of 'X-Y' molecule by Co to form X-Co-Y is indeed a typical oxidative addition reaction in organometallic chemistry, however, Y requires unsaturated moieties such as CO, acetyl, aromatic to facilitate bonding alteration rather than over the rather non-polarised CH₃-S (the cited reference was for thiophene cleavage).

We thank the reviewer for this comment.

It is indeed true that oxidative addition is typical of cobalt addition across polar bonds as well as aromatic sulfides. In our case, what happens is a methyl transfer to the nearby Co site rather than a true metal addition as the metal atom is also in a bound state on the edge of MoS₂ rather than as a free metal atom. The example of thiophene is given, due to the relevance of HDS chemistry, given that thiophene-like molecules are commonly encountered in industrial feeds. To reflect this argument better, the statement in the main text is altered to – “where the methyl transfer occurs to the Co, followed by a H hop and hydrogenation on the Co site to form methane.”

Additionally, the process of Co addition has been renamed as ‘methyl transfer’ to better describe the mechanism and to avoid confusing the reader.

Furthermore, we would like to clarify that rather than CH₃SH, an adsorbed CH₃S⁻ bound to edge cobalt atoms is present in our case. In this situation, the charge transfer from the Co induces additional polarity in the, otherwise weakly, polar C-S bond. Fundamental experiments in the past using TPD, IR, and XPS on the adsorption of CH₃SH upon Mo and Co low coordination surfaces have shown that methyl radicals form at elevated temperatures strongly suggesting a methyl transfer to the metal atoms. We use these results of previous findings as an inspiration to explore the possibility of CH₃ transfer to edge Co. It turns out that this step is more favorable than the other mechanisms we have considered for both Mo and Co edges.

Finally, we agree that the proposed mechanism could not *a priori* be expected to be the dominant pathway. For that reason we have explored the pathways with start of the art DFT modeling.

These arguments along with the references (63-65) are now mentioned at [line number 728-737](#).

8. Some minor mistakes while I read the article:

Minor issues:

There is a typo in Fig. 1a: “Co sulfide sheets” is wrongly spelt.

Page 9, Lines 246 – 249: it is stated that the edge (1) in Fig. 1c has an out-of-registry structure, and the edge (2) has in-registry edge protrusions. However, in Fig. 1c, it is labelled the opposite. The authors need to check and correct these mistakes.

We thank the reviewer for pointing out the errors. We have corrected them in the revised manuscript.

Reviewer #2 (Remarks to the Author):

This is an interesting continuation on the work this group has done on studying hydrodesulfurization (HDS) reactions using CoMoS as a catalyst. The authors used scanning tunneling microscopy using a ReactorSTM to observe the HDS reaction in situ under conditions that are close to what industries would use. The authors also used density functional theory calculations to model the reaction pathways that can occur during the HDS reaction of methanethiol. From their DFT calculations they found that the Co promoter in the catalysts improves the HDS reactions.

Their work explains why it is important to have Co as a promoter in catalyst and why it is important to study these reactions in situ to later on design better catalyst.

After revisions this work would be a significant addition to the study of HDS reactions. This is relevant work to what the authors have done in the past and it seems they are working on expanding this work in the future, which I appreciate.

The methodology was well explained and easy to follow in the paper. The amount of detail provided should be enough for others to reproduce the results. My only concern with the data is that it was difficult to understand some of the terms and few figures could use some tweaks to make them easier to understand as well.

The methods and results sections were for the most part well written. To me the main conclusions were explained in the Results sections and then summarized in the Conclusion section.

The references cited are well aligned to what is presented in the paper.

We thank the reviewer for the words of encouragement, critical insights and comments to improve the quality of this work. The revisions made in the manuscript based on the suggestions of reviewer #2 are mentioned in green colored text.

Comments that could be revised:

1) Is there a reason to switch between methanethiol and CH₂SH as frequently? Some consistency would make the paper easier to read.

We thank the reviewer for this suggestion. All the references to methanethiol except the first one are now changed to "CH₃SH" throughout the manuscript.

2) Line 93 italic font on in situ.

We thank the reviewer for this comment. The line now reads:

... as *in situ* during the desulfurization of CH_3SH at 1 bar. ...

3) It would be a good addition to add more information of the ReactorSTM used in the project as supplemental information. Not needed necessarily for this to be published, but would be beneficial for others who are new to this field to distinguish it from a regular STM.

We thank the reviewer for this suggestion. Supporting information S0 now mentions some details about the ReactorSTM. The reference to S0 is also made in the experimental methods section.

4) Line 198 [SI, Figure S1.] in red. Should it just be black text?

We thank the reviewer for this comment. This is now changed to black font.

5) Line 206 a citation would be better to lead people to the code used to generate the simulated STM images.

We thank the reviewer for this comment. The reference is now provided as a citation (43).

6) Lines 203 to 206: Could you elaborate what is meant by the experimental bias value of the corresponding STM image. There are no images near this section, nor do I see a simulated image that corresponds to an experimental image.

We thank the reviewer for this suggestion.

The bias voltage is a term that refers to the potential difference between the tip and the sample. The term is now changed to sample voltage to be more specific. The statement now reads –

The STM images were simulated by the Tersoff-Hamann approach by plotting a plane of constant density of states, taking into account a sample voltage within 0.05 V of that used for imaging the surface. (line 244-246)

7) Line 228 to 229: Why are there variations in the intensity of the BRIM edges? Could you explain in more detail what you mean when attributing this to the different amounts of residual polarizations?

We thank the reviewer for the comment. The following text with the explanation is now added to the paragraph at line number 272-277:

The intensity of the brim sites varies between adjacent edges exposed to vacuum, as illustrated in Figure 1b and 1c. This variation arises from the diverse edge terminations—whether Mo or S termination—and their stability, along with their interactions with the Au substrate and gases. Different types of dangling bonds may exist on the edges as a result of these interactions. This leads to varying degrees of polarity at the Co- and Mo-terminated edges, resulting in differing levels of edge metallicity that contribute to the brightness of the brim sites.

8) When explaining Figure 1 the term in registry and out of registry are used a lot. This to me is unclear exactly what you mean when some edges are in registry. Figure 1c) did not make it clear

either. Do you mean that these edges align with a specific atomic terminated edge? Could you elaborate on this?

We thank the reviewer for pointing out the lack of clarity in the arguments. We have modified the paragraph to explain the concept of registry better for the reader (line number 280-289):

In Figure 1c the edges of a CoMoS slab are shown with atomic resolution. In studies of MoS₂ and Co-promoted MoS₂ slabs, the alignment of edge protrusions in STM images with respect to the line of atoms in the basal plane—referred to as edge registry—strongly correlates with the atomic structure of the edge.¹⁷ Past STM investigations have often revealed that the observed locations of bright features along the edges may not precisely correspond to the expected atomic positions. Instead, they might be slightly translated along one or more of the crystallographic directions, or along a line perpendicular to the line of atoms on the edge.⁴⁵ Moreover, recent STM research by Grønberg¹⁷ and Mom¹⁸ has highlighted that both the edge registry and the brim site contrasts are highly sensitive to the interaction of edge S atoms with the Au substrate. By considering all of these effects in the STM images, it becomes possible to deduce the atomic structure of the edge.

Side note: Could you split Figure 1 into two separate ones where one is the experimental work and the other the DFT models? Explaining them individually could add some clarity to each one and can help explain the results you want to present in that section.

We thank the reviewer for this suggestion. The DFT models in Figure 1 are moved to SI. This indeed has no consequence for the remainder of the work. (We also refer to the comment #2 of reviewer 3.)

10) Line 307 cite Figure 2.

We thank the reviewer for this comment. The citation is now provided.

11) Lines 313 to 316: Is there a before and after image to show no changes?

We thank the reviewer for this suggestion. The STM images for comparison are now shown in SI, S2 as Figures S2B and S2C.

12) Figure 2: a-d seem to be different sizes. Also it is hard to read the red numbers on the orange spots of the STM images. For slide g where you explain the colors did you forget Carbon? Or is the carbon not imaged there?

Side note: Inconsistency when mentioning sulfur. Only element that is not just written by its symbol.

We thank the reviewer for the suggestion. Sub-figures in Figure 2 have been resized to have the same dimensions. The color of the orange text is changed to green; the markings are made with thicker lines for the ease of viewing (we also refer to the response to comment #2 from Reviewer 4). The carbon atoms are now mentioned in the caption. (we also refer to the response to comment #3, Reviewer 4). Sulfur is now mentioned as S.

13) Figure 3: The caption labels a-h then labels h. This is also reflected in the text. Do you mean to describe a-g in the text? and then separately describe 3h? This is also another figure where it is hard to see the color red on the image. The small red circles are hard to visualize.

We thank the reviewer for the questions. The caption now has a-h) mentioned in the text. The orange text is now changed to green for the ease of viewing in all the figures. The small circles are drawn with thicker lines.

14) Line 476 PVD is a new acronym not introduced.

We thank the reviewer for this comment. The line (536) is now changed to - physical vapor deposition (PVD) process

15) Line 483 should it be Figure 4a-j instead of Figure 4a-k?

We thank the reviewer for this comment. Figure 4k is now included with the time stamp and the line (550-551) now reads – ... images in Figure 4a-k very clearly show that the Co edges of the Co-promoted MoS₂....

Additionally, the figure caption is updated accordingly. Other references to the figures have also been changed.

16) Line 492 and Figure 5: The frames in Figures 4i and 4j do not seem to match the zoomed in shots in Figures 5a and 5b. Were other frames used?

We thank the reviewer for pointing out this discrepancy. This is an oversight from the missing Figure 4k. The line (567-568) now reads - The measured height profiles along the Co edge for two successive frames in Figure 4k and 4h are shown in Figure 5a and 5b, respectively

Side note: Could a smoother graph be used to represent the line scans in Figure 5? The line scans seem messy although it is clear there is a difference.

We thank the reviewer for this suggestion. A smoother line scan is now shown with line-only representation.

Reviewer #3 (Remarks to the Author):

The authors present an in-situ surface science study of Co-promoted MoS₂ nanoparticles (so called CoMoS) on a Au(111) support under hydrodesulphurization of methyl thiol, herein combining in-situ STM with DFT calculations. Mainly rationalized from the extensive DFT part, Co insertion into the C-S bond was identified as a relevant reaction step, while some of the apparent rate-determining intermediates seem to match the STM data for the transient edge structures of those in-situ experiments.

The topic of this paper is highly relevant for the field of catalytic hydrotreatments and the used ReactorSTM is an appropriate and novel experimental technique to investigate catalysts in their active state. The overall claim, that a model catalyst is observed in the active state, is relatively well supported by the analysis and DFT modelling. A weakness of the paper is that the interpretation of the STM data and the structural interpretation of edge structures and S terminations, which is then fed into the DFT work, is rather confusing and, in some places, weakly supported as the paper stands. Sufficient experimental details are given to ensure the reproducibility of the results. The scope is suitable for Nature Comm, but the paper needs some revision before a decision can be made about publication.

We thank the reviewer for the encouragement, critical insights and the constructive comments provided. The relevant revisions made in the manuscript are denoted by red colored font.

1. Some of the analyzed particles appear to be at least partially surrounded by cobalt sulfides (fig. 1c) or other matter (fig. 2c). Since this may affects the overall distribution of different edge types

(considering a Wulff-construction based on the free edge energies), the authors may comment how this impacts their analysis. Why do the authors not focus on freely lying particles?

We thank the reviewer for this question.

The possibility of 2D CoS₂ sheets influencing the edges (both Mo and Co-substituted S) was also considered for the analysis presented in this work. We found that only those step edges of the Co-promoted MoS₂ nanoclusters which directly interact with 2D CoS₂ (or even Au step edges) have a different atomic structure, which is expected considering the chemical bonding between the two phases. Only very small nanoclusters (<1 nm) not considered in this work are strongly influenced by neighboring phases. In our study, most of the nanocluster edges are too long (7 to 15 sites) to be influenced by this effect. For Figure 1 (and later for Figure 2 in this work), only the edges exposed to the vacuum are considered for analysis. For atom-resolved STM images of Co-promoted MoS₂ nanoclusters not interacting with 2D CoS₂ slabs, we refer to the additional STM images provided in SI, Figure S2B.

These clarifications are now provided at line 303-313 of the revised manuscript.

2. One new and one previously published model of the Co-edge structure is presented in fig 1d and the corresponding discussion, but in the end the authors state that both do not reflect their experimental results. I would encourage the authors to shorten this discussion or put it into the SI, since it appeared a bit confusing to me, and does not seem to add to the main message.

We thank the reviewer for this comment. The section considering Figure 1d has been moved to SI, S3.

3. When calculating the MoS₂ on Au(111) it was not clear if the Au is stretched/compressed and how this might influence bonding energies of the proposed thiol intermediates. In general, it was not clear when the Au was used for the calculations or not, but it seems that it was only for the STM simulations. In other cases this may affect the bonding strength to the overlayer (e.g in oxide films) and also this system (Nanoscale, 2021, 13, 10167-10180), so was it checked if the same edge species are actually produced when the Au is there?

We thank the reviewer for this comment.

For the 1D gold slab, a stripe consisting of two layers, each comprised of 9 rows of 13 Au atoms (totaling 234 Au atoms), was created. Based on the experimental crystal structure of Au at room temperature (RT), it was observed that a row of 12 Au atoms measured 37.492 angstroms long. This measurement closely approximated the main axis length of 37.527 angstroms used in all calculations for the stripe model, accounting for 99.91% of it. A slight compression was found, likely attributed to the PBE Density Functional, which tends to provide lattice constants approximately 1% longer than experimental values. Additionally, thermal expansion at 510 K could also contribute to the minor deviation.

These points are mentioned in SI, S1 and referred at line number 251-255 in the main text.

One of the goals of the modeling carried out in this work is to investigate an alternative reaction pathways for the HDS of CH₃SH that works without an Au support, as the typical DDS pathway is not feasible on the S edge. This general model should then be adapted further to specific systems

involving complex model industrial supports in future studies. Therefore, the effect of the Au support on the structures was not considered. Geometry optimization showed that the effect of the Au slab on the intermediate structures was minor, mostly in terms of edge sulfur atoms interacting with the support.

The above arguments are now mentioned at line number 833-839.

4. Figure 2a+b: Here the assignment of edges seems to be based on the appearance of the brims and the registry of atoms, referencing to literature. It seems the particles appear lower than the surrounding gold (especially in figure 2a) and in other images not, so what does that mean to the contrast assignment?

We thank the reviewer for this critical and important question.

In prior literature work on HDS based on STM, the authors typically provide information from a single tip-state and do not mention any electronic effects. This is because their measurements are carried out in UHV or HV conditions. While scanning under the reaction gases (especially H_2 is present), the STM tip undergoes spontaneous tip state changes (reversible, but undesirable) every few 10^1 s because of the gas-tip interactions and likely chemical reactions on the tip, making the process of maintaining atomic resolution, scanning stability and tip stability at the same time extremely challenging. In one of the less likely of these states, the CoMoS nanoclusters appear darker. This electronic effect is also visible in some of the sub-figures in Figure 3, 4, and between Figure 5a and 5b. Additionally, the spontaneous switch in the tip states is also visible between Figures 4d to 4e and 4h to 4i. When imaged in this state, all of the edge states including BRIM contrasts, appear lower by about 1 Å, but their overall positions and registry with respect to the basal plane atomic rows largely remain unchanged. This effect is also visible in the height profiles of the Co edges in Figure 5a and 5b. For e.g., structure I in Figure 5a (slabs imaged bright) and Figure 5b (slab imaged dark) appear to be 4.2 Å and 3 Å high respectively, without any significant registry shift in the features. Additionally, the contrast difference between the BRIM sites on Mo and Co edges are not significantly influenced by this effect. For the sake of consistency and ease of comparison with previous works, whenever possible, we consider the STM images obtained with the tip states where the basal planes and edges are imaged bright and clear, for the edge identification.

Some of the above arguments are provided as an additional paragraph at line number 603-620 in the revised manuscript.

(The above arguments also answer the comment #10)

5. Figure 2c. An argument related to steric hindrance is used to explain why the thiols are spaced regularly two sites apart and all oriented in the same way. The molecule is rather small, so this might be a limited effect. Is there any result from DFT to support this claim?

We thank the reviewer for this query.

The argument provided is based on the observation from the structure (5) in Figure 7c that the $-SCH_3$ groups tend to stick out away from the edge whenever an $[SSH]^-$ ion and $-SH$ site are present next to it. A side view of this effect is now shown in Figure 7c as an inset. The directional ordering of the adsorbed $-SCH_3$ units at high edge coverage such as that seen in Figure 2c is attributed to this

nearest-neighbor interaction between the edge species. DFT calculations were not carried out to further optimize this structure, as it is only a special case that occurs when CH₃SH is abundant in the system, a condition not typically encountered during the HDS reaction.

These arguments are mentioned in the main text at line number 714-719 with a reference at line 467-468.

6. It was not clear when Gibbs free energies or pure DFT energies were used throughout to calculate the configurations, which is particularly relevant in Figure 7.

We thank the reviewer for this remark. All the energies mentioned in the paper are DFT energies. This is mentioned now at line number 251-255.

7. The in-situ STM images shown in figure 4 appear to be of significantly better quality than the images shown in fig. 3. The discussion related to Figure 3 is confusing. Clearly also the middle part changes contrast, so how much of the image is due to tip changes and how much is due to the process which is claimed to happen? Could you elaborate on how much was done to ensure that bias, speed etc was not influencing it? It also seems that there is a problem with the levelling of these images (when for example comparing c and e), which makes the edges appear brighter in one case.

We thank the reviewer for the critical comments.

On the point of STM image quality and effects of the tip, we refer to our earlier response to comment #4.

Additionally, the main difference between the structures in Figure 3 and 4 is the partial pressure of H₂. The lower H₂ partial pressure increases the lifetime of the tip states where the slab basal planes and edges are imaged clearly and also decreases the background noise, improving the imaging quality.

The STM images in Figure 4 are leveled better now, especially c and d. This decreases the brightness on the edge slightly along the fast scan direction (left to right), as the reviewer points out. The difference in the BRIM contrasts between the Mo and the Co edges are still visible.

When scanning under the aggressive chemical conditions during the HDS reaction studies, it is always possible that tip sample interactions and scanning conditions could create artifacts and other undesirable effects. To ensure that this does not happen, the scanning was always carried out below a tunneling current of 1 nA. At 1.2 nA (-0.3 V sample voltage) and above, the tip-sample interactions were found to be significant. Additionally, for every gas condition used, the scanning was also attempted at many sample voltages between -1 (filled state) to +1 V (empty state), for tunneling currents between 100 to 1000 pA, and at various scanning speeds to ensure that significant tip-sample interactions do not occur. This is quite expected as the CoMoS nanoclusters studied in this work are small enough to not show significant band-gap effects on the basal planes of the MoS₂ slabs.

These arguments are now presented in an additional paragraph in the experimental methods section at line number 204-213

8. Figure 4: Here it seems that the active edges are assigned to the Co terminated edge, but it is not clear how this assignment is done. What are the main assumptions here? In figure 2, the shorter edges are with Co, but for the particle here it is the opposite. I think this needs to be explained better, since it is crucial to the starting point of the DFT work and the link to experiment.

We thank the reviewer for this comment.

In Figure 4, the edge identification is carried out in a similar fashion to that for Figure 3 as we are still within HDS conditions. Figure 4e is modified to show the edge identification. We make an assumption that the slightly lower hydrogen partial pressure does not significantly affect the edge chemistries. The edges with bright BRIM sites (marked 1,3 and 5, Figure 4e) are observed to have an out-of-registry structure with respect to the basal plane atoms. These edges are designated as the Mo-terminated edges with a 38 %S -25% CH₃SH time-averaged structure. The adjacent edges (marked 2,4 and 6, Figure 4e) with the darker BRIM sites are identified as the Co-substituted S edges.

These arguments are mentioned at line 543-550 of the main text.

Additionally, for the sake of clarity, the section discussing the edge identification for Figure 3 (line 489-508) is modified to include the assumptions made and to comment on the edge length. The section now reads:

The STM images in Figure 3 show that one set of the edges (marked 2,4 and 6, Figure 3a) of the hexagonal slabs have the brim contrast quenched while the adjacent edges (marked 1,3 and 5, Figure 3a) have a relatively much higher brim contrast. The latter also shows a static out-of-registry structure with respect to the basal plane which is identified in Figure 3h. The features of this edge match well with those of Mo-terminated edges of pristine MoS₂ slabs from the work of Mom et al., (ref 18) where it was shown that a 38 % S-25 % CH₃SH edge structure over the Mo edge is most stable at the reaction conditions used. Blue circles indicate the expected positions of the protrusions and green circles mark the measured positions of their work, an assumption was made that the HDS reactions are too slow to disturb the equilibrium of the Mo edge with H₂ and CH₃SH. At an imaging temperature of 510 K, the structure undergoes time averaging, resulting in an out-of-registry edge structure concerning the basal plane atoms. This phenomenon is expected to occur for the Mo edge on a CoMoS slab as well. Additionally, we assume that any spillovers along the corner sites from the adjacent Co edge do not affect the chemistry of the Mo edge. Therefore, we designate the edges exhibiting the brightest brim sites and out-of-registry edge protrusions as the Mo-terminated edges of the CoMoS slab. Consistently, we observe that the adjacent set of edges of the CoMoS slabs exhibit high activity under the reaction conditions and display a darker brim compared to the Mo edges. Following the Wulff construction, we attribute this active edge as the Co-substituted sulfur edge. Furthermore, we observe significant variations in the lengths of the Mo and Co edges among the nanoclusters. The size of the edges of the slabs was not found to affect the assignment made here.

9. Figure 4: it is mentioned that the experiment took 44 hours. It would be useful with time stamps on the images. Is it realistic that the most relevant intermediates of these types are stable on the time scale between images?

We thank the reviewer for this comment.

Generally, we expect to see the intermediates from the slowest reaction steps only. The intermediate species on the Co edge have a turn-over frequency of $\sim 10^{-2} \text{ s}^{-1}$ as scanning at speeds slower than 30 seconds/image resulted in poor edge resolution. This kind of turn-over frequency, and hence, edge species stability is very much expected for the HDS reaction conditions used in our experiment. In fact, highly-optimized industrial catalysts working at similar conditions have reported turn-over frequencies of 10^{-2} to 10^0 per second. (29-30)

This argument and references are now mentioned at line number 515-518

The STM images in Figures 3 and 4 now have time stamps.

10. The imaged transient states in Fig 5 appear of different height (between for example 3 and 5 Å for species I). Could the authors comment on this? Furthermore, the manuscript would need a statistical analysis of the appearance of these transient states to be convincing. It seems to be based only on imaging of one edge, but different changes are also evident from the other edges of the same type.

We thank the reviewer for this critical comment.

The differences in height are due to a flipping of the tip state that also cause the slabs to appear lower. This point is explicitly covered in our response to comment #4.

We also thank the reviewer for the very interesting idea of providing a statistical analysis of the edge structure. This is now provided as Figure 5c and 5d. The following arguments are added to support the figures (line 578-590):

In order to gain more insights into the distribution of structures I, II and III, statistical analysis of the Co-substituted S edges of the CoMoS slabs is performed. For this purpose, the HDS experiments were also repeated for intermediate pressure ratios ($\text{H}_2:\text{CH}_3\text{SH}$) of 3:1 and 6:1 on identical prepared model catalyst, to gain additional insights into the effects of hydrogen partial pressure, while keeping the partial pressure of CH_3SH the same for all the experiments. STM images of several CoMoS slabs of sizes between 3-7 nm) were analyzed for the reaction gas mixtures containing $\text{H}_2:\text{CH}_3\text{SH}$ ratios of 1:1, 3:1, 6:1 and 9:1. Figure 5c shows the distribution of structures I, II and III among all of the occupied sites on the Co edge, and the total occupancy of the Co edges by I,II and III is shown in Figure 5d for slabs of various sizes. Generally, the slab sizes are found to not have a significant effect on the occupancies or the distribution of structures I, II and III. Figure 5c shows that upon increasing the hydrogen partial pressure, the occurrence of structures II and III decreases. Additionally, there is also a corresponding slight decrease in the number of occupied sites on the Co edges suggesting that hydrogen likely plays a role in the disappearance of II and III.

Furthermore, comparison is made between our DFT findings and experimental work, referring to the new figures at line number 886-892:

Additionally, Figure 8d also suggests that higher partial pressures of hydrogen could favor the removal of H_2S . This effect is observed in Figures 5c and 5d, where increasing the hydrogen content in the gas leads to a decrease in the number of observed structures II and III on the Co edges of the CoMoS slabs and also a slight decrease in the overall occupancy of all the structures on the Co edges. Thus, we find an excellent agreement between our rationalization of the HDS reaction of CH_3SH and

our experimental observations using the operando ReactorSTM at near-industrial HDS conditions.

11. It is surprising to see a significant amount of post-HDS structures in the STM since these (i.e. the added S) would presumably be removed fast. Is there an argument that they can actually be seen on the relevant time scale, and be statically adsorbed (unlike the H)?

We thank the reviewer for this comment.

We note that despite the significantly lower barrier for H₂S removal (1.08 eV, as shown in Figure 7b), we still observe a number of post-hydrodesulfurization (HDS) structures on the Co edges. This phenomenon is attributed to the rather crowded nature of the edges under the relatively mild HDS conditions employed. The statistical analysis presented in Figure 5c and 5d shows a lower occurrence of the post-HDS state (structure II) with increasing partial pressure of hydrogen to 0.9 bar, indicating the role of H₂ in its removal.

The above arguments are provided at line number 861-867

12. Sulphur vacancies are not considered in the manuscript. I understand that for adsorption in vacancies there is some similarity to the later HDS mechanism after H₂S removal ((4) in fig. 7b) however, can the authors comment on if S vacancies play a role in here and if they were imaged in-situ as well?

We thank the reviewer for this question.

In general, all the adsorption steps discussed in the reaction pathways so far for the Co edge, are considered for single sulfur vacancy sites on the edge corresponding to a 50% S saturation. In the study by Grønberg et al., they explore the stability of edges with varying degrees of sulfur vacancies. However, for the conditions utilized in our experiments, we do not anticipate the formation of double sulfur vacancies at thermodynamic equilibrium. Nevertheless, it is worth noting that the adsorption of CH₃SH may alter this outcome. In our previous work (Mom et al.), we observed that CH₃SH adsorption leads to the creation of additional sulfur vacancies on a Mo edge. While we have not explicitly investigated the possibility of structures with lower sulfur vacancies for the Co edges in this study, as we have not experimentally observed any such structures, it may be worthwhile to explore this reaction pathway in future investigations. It is conceivable that at very high partial pressures of H₂, such as those encountered in industrial settings, double sulfur vacancies may occur more frequently on the Co edge during the HDS reaction. This could be an effect of bridging another 2 orders of magnitude of the pressure gap.

The above arguments are now provided at line number 813-825.

13. Most of the discussion of the DFT results contains information of the overall energetics of the processes, but in the figures only the activation barriers are displayed. I think it would be beneficial to include the total energetics of the transient states into the figures.

We thank the reviewer for this suggestion. The total energies of the structures are tabulated in the SI, S7 for all the reaction pathways in Figures 6 and 7. The tables are referred to in the main text.

14. In connection with the discussion of pressure and delta_G values. It would be interesting to know if the calculated processes are more favored at 100bar, relevant to real conditions, and also if they would be observable at lower pressure, e.g. by other techniques such as IR or XPS.

We thank the reviewer for this suggestion.

If the partial pressure of H₂ is raised to 99.9 bar, keeping the CH₃SH partial pressure 0.1 bar, we expect the Co edge to have a slightly different thermodynamically stable edge structure with lower sulfur saturation, likely with double sulfur vacancies. We expect these types of sites to be more reactive and hence, resulting in lower barriers for the key steps.

In the current state, the ReactorSTM is not suitable for carrying out operando IR or XPS measurements due to the construction of the setup (the O-rings are not optically transparent, and there is no optical access to the reactor). We think that the reaction should be observable in a synchrotron NAP-XPS given that up to 100 mbar total pressures are achievable in some of the setups around the world. The current limitation is the lack of infrastructure for handling CH₃SH owing to its toxicity and difficulty of removal from large UHV systems, especially, the detectors. This endeavor will be a part of our future work.

The above arguments are mentioned at line number 870-874.

15. The authors have reported mass spectroscopy data for processes before with the reactorSTM. Methane is the product here. Was an attempt done to detect this?

We thank the reviewer for this suggestion. The mass spectroscopy data is presented in Figure 5e.

The mass spectrometer was used to analyze the gases leaving the reactor. Given that only the STM tip and the sample are exposed to the reaction gases, we expect that any observable activity can be attributed to the model catalyst surface as no other parts of the system have any catalytic activity. Figure 5e shows the product analysis for an H₂:CH₃SH ratio of 9:1 measured at room temperature where we do not expect significant HDS activity and at 510 K where the time-variant Co edge structures were observed in the STM images. The CH₄ (m/z = 16) and H₂S (m/z = 34) detected at room temperature are attributed to the trace contaminants present in the H₂ and CH₃SH gas bottles. In comparison to this baseline, the product streams at 510 K show the formation of additional CH₄ and H₂S by the same order of magnitude. Given the mild HDS conditions used, small amount of catalyst present, and the design of the ReactorSTM, we expect low yields of methane if any, such as in Figure 5e.

Above arguments are provided at line number 591-602 to support Figure 5e.

Additionally, the experimental methods section is modified at line 199-201 to reflect the additional HDS conditions.

16. A general comment: The figures would benefit from a careful revision, for example to make sure they appear as one piece (fig. 6 and 7), have boxes of aligned sizes (fig. 2), or all have scale bars/scales (fig. 1c, fig. S2)

We thank the reviewer for the corrections. All the figures have been revised now with scale bars, and same dimensions and fonts.

Other details

a. Frequently “et al.” comes with typos (for example: et. al. (lI216 and lI 250)), et. al (lI222), ...).

The typos are now corrected.

b. lI 62 and 76: While single-layer MoS₂ is introduced first as the relevant catalysts, the authors later also consider multi-layer stacks as the industrial catalyst (which seems to be more precise). This should be consistent.

The line now reads “islands of single-layer CoMoS slabs are known to be present”.

c. lI. 320: The authors state, the even numbered edges in fig. 2b have “a much brighter BRIM compared to the ones marked with odd numbers”. This seems to be not the case, if not the other way round. Finally, in lI344-346, it is then stated reversely (“... we identify the even numbered edges of fig. 2b with the darker brim as the Mo-terminated edge and the odd numbered edges with a very bright brim”). This should be revised to the correct version.

We thank the reviewer for pointing this out. We have corrected this error. We also refer to our responses to comment #12, reviewer 2; comment #4 of reviewer 4.

d. lI664: The structure that is shown in fig 8a in the DFT model is actually structure 5 of fig. 7b, not figure 4 (typo I guess). Why was structure 12 of figure 7b not chosen as a potential transient state, even if it is in front of an approx. 1.5eV barrier?

We thank the reviewer for pointing out the error. The structure is indeed structure (5), Figure 7b and all the references to this structure are corrected.

For modeling the STM images, we have only considered structures from the Co addition pathway in figure 7b. Because of the very low barriers, structure 12 and structure 5 are expected to be time-averaged in the STM images. Hence, structure 12 is not chosen.

e. lI 686: The authors state the structure of fig 8b is identical to figure 2g. Indeed, they exhibit a very similar simulated STM image, but in figure 8b there is one adsorbed H on the S atom right of the thiolate, which is absent in fig. 2g. I suggest to revise to be precise here to not confuse the reader

We thank the reviewer for pointing this out. This line is now removed for the reader's clarity.

Reviewer #4 (Remarks to the Author):

The manuscript deals with the hydrodesulfurization (HDS) on a cobalt doped MoS₂ using scanning tunneling microscopy (STM) and density functional theory calculations (DFT). Such a combination of methods is indeed needed to interpret the experimental results and, on the other hand, to perform the calculations for relevant systems. The experiments have been performed in situ in a model reactor, which makes them more realistic from the applications point of view. The emphasis

is on the reactions occurring on the cobalt doped edge of MoS₂, which has not been studied earlier in the same extent as the bare molybdenum edge. In their DFT based transition state search, the authors have found new pathways for the HDS reaction of methanethiol. The STM images calculated for the essential stages of the reaction agree well with the experimental ones, enabling a construction of the full reaction cycle. The results are sound, and the paper is well written. I recommend publication after the authors have addressed the following issues:

We thank the reviewer for the words of encouragement and the comments provided. The suggested corrections have been made and the changes are shown in yellow highlight.

1. In the discussion about Fig 2 b it is stated that the set of edges marked with even numbers have a much brighter brim than the ones marked with odd numbers. However, 5 appears to be brighter than 4, or am I misinterpreting the labels?

We thank the reviewer for pointing out this discrepancy. This is an error in the text and has now been corrected (line number 358, 359).

2. It is hard to see the blue and especially the red dots in Figs. 1 and 2. Would there be a better way to indicate the positions?

We thank the reviewer for this comment. The positions are now indicated with thicker lines to bring out the contrast for ease of viewing in both Figures 1 and 2.

3. C is not mentioned in the explanation of atom types in Fig. 2. Is it missing or just not visible in these configurations?

We thank the reviewer for pointing out this discrepancy. The atom C is shown in black, and the figure caption now carries this description.

4. In Fig. 1 c the scale seems to be missing.

We thank the reviewer for this comment. A scale has now been added to Figure 1c.

5. Why is 'brim' written with capital letters as if it were an acronym?

We thank the reviewer for this question. In the earlier STM works, the sites are referred to as brim. More recently, due to a trademark, the sites are sometimes referred to as BRIM. To avoid confusing the reader, BRIM is changed to brim throughout the manuscript.

6. When discussing the different structures, e.g. in Fig. 6, would it be possible to address the structures by both number and a compact description of the structure in question? This would make it easier to identify the structure without always referring to the figure.

We thank the reviewer for this comment. The paragraphs discussing Figures 6 and 7 now have compact descriptions of the structure in question whenever relevant.

7. There is a reference to Fig. 9, which is missing; this should obviously be 8 d.

We thank the reviewer for pointing this out. The revision now reads Figure 8d.

8.Reference 27 is the same as reference 28.

We thank the reviewer for pointing out this error. Reference 28 has been removed.

REVIEWERS' COMMENTS

Reviewer #2 (Remarks to the Author):

Again this is an interesting continuation to the group's previous work on studying hydrodesulfurization (HDS) reactions. They looked at the HDS of methanethiol gas over CoMoS catalysts at near industrial HDS conditions using a ReactorSTM. From their experimental work they modeled modeled the reaction pathways that this HDS reaction can occur on the step edges of the CoMoS catalyst.

This is a significant addition to the study of HDS reactions and shows the current limitations when studying these reactions close to industrial settings. This is relevant work to what the authors have done in the past and it seems they are working on expanding this work in the future, which I appreciate.

The authors have answered most of my previous comments, but there are still some minor revisions that can be addressed.

1)Line 120 DDS is a new acronym not introduced.

2)Figure 1: 1b seems out of place. It is a zoomed out version of 1c and shows the bright brim sites, but this could probably just be shown using 1a and 1c. 1c is missing a scale bar as well. Also the circles in 1c look more grey than blue as stated in the caption.

3)Figure 2: Can be cleaned up a bit. 2b and 2d have different colored borders. Is this to represent where the zoom in is coming from? Also in 2c the label for edge (4) is not legible. I still think this figure can be split up into two. One the STM results and the other the DFT work. Is the inset in 2c needed since you are showing the registry in 2d?

4) Both figures 2a and S2c are labeled as taken at 1 bar and 510K after 180 minutes of reductions. Is there a before image taken at the same 510K and 1 bar conditions? The figures S2a and S2b are in UHV, but would the imaging at those rougher conditions still show that the CoMoS slabs would remain unchanged?

5)Line 467 should say Figure 3a-h.

6)You mention that methane and hydrogen sulfide are contaminants at room temp, how do you distinguish the contaminant amount from the additionally formed methane and hydrogen sulfide from the Figure in 5e?

7)Figure S1B colors of H and C don't match in caption and figure.

Additional comments:

Imaging at higher pressures and temperatures using STM is complicated and the difference can be seen in the quality of STM images in S2 where the authors showed STM images under UHV/room temp and under 1 bar/510 K. In Figures 3 and 4 you see these transient features that you're attributing to the HDS of methanethiol. When imaging at high pressures and temperatures do you see any transient features on the edges at all? To rule out any other source for these features? Or do they only show up when in presence of the hydrogen-methanethiol mix?

There is plenty of detail explained to reproduce the work done in this paper. I appreciate the addition of the ReactorSTM information. I would say the figures could still be worked on as well to make them clearer and easier to visualize.

Reviewer #3 (Remarks to the Author):

The authors have improved the manuscript significantly and have replied and reacted appropriately to most of the comments. Especially the explanations about tip states and which features were considered for the data analysis and which features were not, are important to the reader. Also, the statistics in figure 5 help to convince about the transient states. The experiment is very interesting and will be a valuable contribution to the understanding of this type of catalyst.

The rather extensive revision includes several new or added sections/figures, and I found some minor comments that the author should consider.

- Given the issue with the two interchanging tip states, it could be helpful to mark which of the images are imaged with the “irregular” tip state.
- Figure 5c/d: What is the total number of analyzed edges? It took me a while to figure out the difference between c and d, maybe a label like “Edge occupancy” would help. Also, I think it is difficult to understand the little details in 5c (slab sizes and species) because the symbols are small and the colors blue and red have been priorly used to mark the height profiles in a and b, but here in c/d they represent the different species I, II and III. I would suggest to use a consistent color code for I, II and II throughout the paper.
- The figures have been significantly improved, but the STM images in figure 3 remain of lower quality compared to those in figure 4, but both bear a very similar message. I would still suggest moving figure 3 to the SI and base the discussion on figure 4 to ensure clarity and conciseness.

Reviewer #4 (Remarks to the Author):

The authors have provided a detailed response to the referees' comments. I recommend publication of the manuscript in its present form.

A side remark; it seems like the line numbers given in the response letter do not match the ones in

the manuscript. This is likely due to an addition of some text at the beginning of the paper in a late stage. This does not, of course, affect the quality of the manuscript, but please be careful with this issue in the future.

Referee #2

Again this is an interesting continuation to the group's previous work on studying hydrodesulfurization (HDS) reactions. They looked at the HDS of methanethiol gas over CoMoS catalysts at near industrial HDS conditions using a ReactorSTM. From their experimental work they modeled modeled the reaction pathways that this HDS reaction can occur on the step edges of the CoMoS catalyst.

This is a significant addition to the study of HDS reactions and shows the current limitations when studying these reactions close to industrial settings. This is relevant work to what the authors have done in the past and it seems they are working on expanding this work in the future, which I appreciate.

The authors have answered most of my previous comments, but there are still some minor revisions that can be addressed.

We thank the reviewer for the constructive critique and the support of our work. Our response to the reviewer is provided in the color blue in the manuscript

1) Line 120 DDS is a new acronym not introduced.

We thank the reviewer for pointing out this oversight. The acronym DDS has been expanded in the main text.

2) Figure 1: 1b seems out of place. It is a zoomed out version of 1c and shows the bright brim sites, but this could probably just be shown using 1a and 1c. 1c is missing a scale bar as well. Also the circles in 1c look more grey than blue as stated in the caption.

We thank the reviewer for this suggestion. Figure 1b has been removed. Figure 1c is now labelled as Figure 1b. Additional label for Brim site is added. The new Figure 1b now has a scale bar. The figure caption is modified to reflect the changes. The transparency of the blue circles is modified to highlight the blue color better.

3) Figure 2: Can be cleaned up a bit. 2b and 2d have different colored borders. Is this to represent where the zoom in is coming from? Also in 2c the label for edge (4) is not legible. I still think this figure can be split up into two. One the STM results and the other the DFT work. Is the inset in 2c needed since you are showing the registry in 2d?

We thank the reviewer for this suggestion. The borders of Figures 2c and 2d are now black. The colors were indeed used to represent the areas which are zoomed in. Edge (4) label is moved for better visibility. The inset in 2c is necessary as it shows the registry of an Mo-edge while the one in 2d shows a Co edge. An additional label of Co-edge is added in Figure 2d to highlight this difference. Figures 2e, f and g are split and now labelled as Figure 3a, b and c, respectively. The numbering of the remaining figures has been altered.

4) Both figures 2a and S2c are labeled as taken at 1 bar and 510K after 180 minutes of reductions. Is there a before image taken at the same 510K and 1 bar conditions? The figures S2a and S2b are in UHV, but would the imaging at those rougher conditions still show that the CoMoS slabs would remain unchanged?

We thank the reviewer for this question.

We would like to clarify that the STM images in figures S2A and S2B are of the model catalyst before the H₂ reduction. The in situ STM images in Figures 2a and S2C are of the same model catalyst after 180 minutes of H₂ reduction. Between the two images, clearly the truncated-hexagonal slab shapes are retained. An additional image with a zoomed inset acquired under 1 bar H₂ at 510 K after 90 minutes of reduction is provided as S2D.

Imaging the catalyst up to ~90 minutes of reaching the operating temperature is not possible due to large thermal drifts from the heating up of the sample, seals and STM components which leads to tip crashes. Any potential slab shape change is expected to occur within this window, as the shape-change kinetics are fast (Gronborg et al.). Furthermore, it also takes additional several tens of minutes for all the gas-solid and gas-tip interaction processes to reach steady state and better quality STM images can be acquired.

Some of the above arguments are now provided in S2.

5)Line 467 should say Figure 3a-h.

We thank the reviewer for this suggestion. The line has been changed.

6)You mention that methane and hydrogen sulfide are contaminants at room temp, how do you distinguish the contaminant amount from the additionally formed methane and hydrogen sulfide from the Figure in 5e?

We thank the reviewer for this question.

At room temperature, we do not expect HDS reaction to occur. The CH₄ and the H₂S background signatures detected in the gas stream at room temperature (Figure 5e) are due to the contaminants in the gas bottles. If there was no catalytic activity, we expect this background to remain unchanged irrespective of the model catalyst temperature. However, upon raising the temperature to 510 K, additional CH₄ and H₂S formation is detected against the background, while the H₂ and CH₃SH signatures remain unchanged. This additional amount of CH₄ and H₂S is attributed to the products of the HDS of CH₃SH.

For the clarity of the reader, the statement - "If there is no catalytic activity, we expect the background CH₄ and H₂S signals to remain unchanged irrespective of the model catalyst temperature." is now mentioned at line 478-479.

7)Figure S1B colors of H and C don't match in caption and figure.

The caption is now changed to – "brown atoms are those of C."

Additional comments:

Imaging at higher pressures and temperatures using STM is complicated and the difference can be seen in the quality of STM images in S2 where the authors showed STM images under UHV/room temp and under 1 bar/510 K. In Figures 3 and 4 you see these transient features that you're attributing to the HDS of methanethiol. When imaging at high pressures and temperatures do you see any transient

features on the edges at all? To rule out any other source for these features? Or do they only show up when in presence of the hydrogen-methanethiol mix?

We thank the reviewer for this question. We do not observe any transient features on the Co or Mo edges in either pure H₂ or CH₃SH at 510 K. The mixture of both components and a T>473 K is necessary to see them. In fact, the edge occupancies and distribution of the states I, II and III of the transients are found to be related to the H₂:CH₃SH ratios used (now Figures 6c and 6d).

There is plenty of detail explained to reproduce the work done in this paper. I appreciate the addition of the ReactorSTM information. I would say the figures could still be worked on as well to make them clearer and easier to visualize.

We thank the reviewer once again for their suggestions to improve the quality of this work. The changes made to the figures are mentioned in the author checklist.

Referee #3:

The authors have improved the manuscript significantly and have replied and reacted appropriately to most of the comments. Especially the explanations about tip states and which features were considered for the data analysis and which features were not, are important to the reader. Also, the statistics in figure 5 help to convince about the transient states. The experiment is very interesting and will be a valuable contribution to the understanding of this type of catalyst.

We thank the reviewer for the constructive critique and the support of our work. Our response to the reviewer is provided in the color green in the manuscript.

The rather extensive revision includes several new or added sections/figures, and I found some minor comments that the author should consider.

- Given the issue with the two interchanging tip states, it could be helpful to mark which of the images are imaged with the “irregular” tip state.

We thank the reviewer for this suggestion. The relevant STM images are marked with a * in the Figures 4 and 5 (now, 5 and 6).

- Figure 5c/d: What is the total number of analyzed edges? It took me a while to figure out the difference between c and d, maybe a label like “Edge occupancy” would help. Also, I think it is difficult to understand the little details in 5c (slab sizes and species) because the symbols are small and the colors blue and red have been priorly used to mark the height profiles in a and b, but here in c/d they represent the different species I, II and III. I would suggest to use a consistent color code for I, II and III throughout the paper.

We thank the reviewer for this suggestion.

The statistics in c) and d) are based on 2-3 minutes of in situ observation of 50-55 Co edges (18-20 slabs) each for H₂:CH₃SH up to 6:1 and 20 Co edges (6 slabs) for H₂:CH₃SH = 9:1. This statement is now mentioned in the caption of Figure 5 (now 6).

The Y axis labels are now changed to % Co edge state distribution and % Co edge occupancy. The symbols in 5c and 5d (now 6c, d) have been enlarged and the color scheme has been changed.

- The figures have been significantly improved, but the STM images in figure 3 remain of lower quality compared to those in figure 4, but both bear a very similar message. I would still suggest moving figure 3 to the SI and base the discussion on figure 4 to ensure clarity and conciseness.

We thank the reviewer for this suggestion. We had already considered this possibility at the previous stage of the revision very carefully. The reviewer's suggestion from an aesthetic standpoint is important. We think that Figure 3 (now 4) however, ought to be retained in the main text despite the lower quality for two reasons:

1. Most typical laboratory HDS experiments involving industrial catalysts are conducted at 9 times higher partial pressures of H₂ at least in comparison to the organosulfur compound to be desulfurized. Imaging a model catalyst at this condition is therefore, very relevant for the HDS catalysis research and the heterogeneous catalysis community at large.

2. The ability to obtain atomic resolution at the aggressive chemical conditions and a total pressure of 1 bar is a significant improvement over previous works and is very relevant for the scanning probe microscopy (SPM) community which aims to enhance the resolving capabilities of future microscopes at even higher pressures and in more complex chemical environments (e.g. P = 100 bar, T < 800 K). We think that retaining these results in the main text will greatly encourage more future work for improving the operando SPM instruments.

Referee #4:

The authors have provided a detailed response to the referees' comments. I recommend publication of the manuscript in its present form.

A side remark; it seems like the line numbers given in the response letter do not match the ones in the manuscript. This is likely due to an addition of some text at the beginning of the paper in a late stage. This does not, of course, affect the quality of the manuscript, but please be careful with this issue in the future.

We thank the reviewer for their critical comments and support for improving the quality of this work.