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Atomic insights into hydrodesulfurization

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Citation

Prabhu, M. K. (2021, June 3). *Atomic insights into hydrodesulfurization*. Retrieved from <https://hdl.handle.net/1887/3182531>

Version: Publisher's Version

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Issue Date: 2021-06-03

Chapter 7

Outlook

In this thesis, the ReactorSTM set up has been used to gain atomic-level insights into the formation and working of a Co-promoted MoS₂ HDS model catalyst. The work presented in this thesis raises many questions and opens up several avenues for future research. Herein, some of these questions and possible experiments to answer them are mentioned as a scope for future work.

Is it possible to grow multilayer 2D CoS₂ sheets? If yes, can we synthesize a new layered bulk Co sulfide purely by a bottom-up approach?

In the work presented in Chapter 3, the total coverage of CoS₂ has been <1 monolayer (ML). It is currently not known if 2D CoS₂ can also form multilayers supported upon itself. The results of the DFT calculations indicate that the stabilizing interactions with Au(111) are necessary for the formation of a single-layer S-Co-S sheet. Attempts to grow multilayers will test this result of our DFT model. Multilayer CoS₂ could be grown with a recipe that involves repeated deposition of Co followed by annealing in H₂S in a cyclic manner.

Do the other earth-abundant metal sulfides such as those of Cu, Ni and Fe which do not have a layered structure in the bulk also form TMDC structures on Au(111)?

The work done by Kibsgaard et al.¹ reports the formation of the sulfides of Cu, Ni and Fe as byproducts while attempting to grow Ni- Fe- and Cu- promoted MoS₂ respectively. All of these sulfides have an atomically-flat surface, grow strictly as a 2D layer and also have a moiré structure that appears similar to 2D CoS₂, as is evident from their STM images. However, in their work, the metal sulfides are merely identified as a separate phase and not investigated as a possible new TMDC. It is very likely that these metal sulfide sheets are also TMDCs similar to 2D CoS₂. A methodology similar to the one presented in Chapter 3 could be used to grow TMDCs of metals such Ni, Cu and Fe on Au(111) and perform their structural characterization in combination with DFT calculations, thus opening up new avenues for their potential applications. Furthermore, these experiments can also give us valuable insights into the trends for forming supported TMDCs in the periodic table.

Do the results presented in Chapter 4 correlate well with catalysts supported on oxide substrates such as titania or alumina?

To take another major step to bridge the materials gap with the real HDS catalysts, the simultaneous Co and Mo oxide sulfidation experiment could be repeated on a model oxide substrate such as TiO₂(110). The work presented in Chapter 5 takes a step in this direction by sulfiding partially oxidized Mo nanoparticles. Oxide substrates like titania are known to have strong interactions with oxides of Mo and Co. Given the stronger substrate interaction, we can expect a greater barrier to sulfidation and formation of the CoMoS phase.^{2,3}

How does sulfidation with pure H₂S compare with using a mixture of H₂ and CH₃SH?

While controlled sulfidation in UHV can give us many structural insights, it is also necessary to perform the sulfidation under industrially-relevant conditions. Furthermore, organosulfur compounds like dimethyldisulfide are commonly used in the industry to sulfide the oxidic catalyst precursor, many a time, also in the presence of H_2 . An experiment to gain insights into the relation between the sulfiding agent and the morphology of the CoMoS model catalyst could involve preparing identical mixed Mo- and Co- oxide precursors supported on Au(111) and $TiO_2(110)$. The precursors could then be sulfided in the ReactorSTM using pure H_2S , CH_3SH , a mixture of H_2/H_2S and H_2/CH_3SH respectively. A similar experiment could also be performed with the help of synchrotron-based Near-Ambient Pressure XPS (NAP-XPS) to gain chemical insights into the sulfidation process in situ.

What is the atomic structure of the MoS_x stripes reported in Chapter 5?

To answer this question, diffraction techniques such as LEED, surface-XRD could be used to resolve the atomic structure and by combining these results with DFT calculations, a consistent atomic model can be constructed. A typical experiment could involve growing MoS_2 on the $TiO_2(110)$ substrate using the recipe used in Chapter 5 with an Mo coverage of <0.2 ML. Analysis of the LEED pattern of the $TiO_2(110)$ surface before and after the synthesis of MoS_2 can resolve the atomic structure of the MoS_x stripes. Additionally, the experiment could also be repeated with the addition of Co in the precursor prior to sulfidation. This could provide insights into the possibility of the incorporation of Co in the MoS_x phase. Furthermore, it is also possible that the formation of MoS_x striped phase is dependent on the sulfiding agent. The experiment to investigate this possibility has been discussed in the previous paragraph.

What are the key factors that contribute to the formation of curved CoMoS slabs with higher-index terminations?

In Chapter 6, we have observed the formation of CoMoS slabs with curved edges under HDS conditions. The effect of the partial pressure of methylthiol, the type of the organosulfur compound (aliphatic vs aromatic) and the reaction temperature could all play a key role in the formation of CoMoS slabs with high index edges. The CoMoS model catalyst used in Chapter 6 could be studied under higher partial pressure of CH_3SH , at higher HDS temperature and also with model aromatic thiols such as thiophene. The usage of aromatic thiol vapor will require minor modification of the gas dosing system of the ReactorSTM setup. These studies could be coupled with DFT calculations to investigate the stability of high index Co-substituted S edges such as the $(11\bar{2}0)$ termination.

What are the key factors that contribute to the mass transport along the Co-substituted edges of the CoMoS phase?

The ‘chemically blind’ nature of the STM makes it very difficult to identify the nature of the diffusing species. Some insights could be gained by studying the 2D- CoS_2 sheets separately under HDS conditions. Analysis of the step edges of these sheets as well as the XPS signatures of Co and S can give valuable insights into the mechanism of Co transport. Using synchrotron-based techniques such as the NAP-XPS, the transport of Co could potentially be tracked with some time resolution. The role of the support interactions could be investigated by using substrates such as $TiO_2(110)$ and highly-oriented pyrolytic graphite (HOPG). These studies could be supported with DFT calculations to understand if the support interactions play a key role in stabilizing the promoter atoms on the edges.

How do the effects observed on CoMoS slabs compare with those of NiMoS slabs?

Ni-substituted MoS₂ slabs have also been synthesized by the Aarhus recipe on Au(111).⁴ Such NiMoS model catalysts could be studied under the same HDS conditions as those of CoMoS slabs for a direct comparison of the behavior of Co-substituted and Ni-substituted edges. A follow-up experiment to compare NiMoS and CoMoS slabs could involve the usage of aromatic thiols such as thiophene and dihydrothiophene with isotopic markers, instead of CH₃SH. These experiments could give valuable insights into the relation between the atomic structure of the Co-substituted and Ni-substituted MoS₂ edges and the catalyst activity. Furthermore, theoretical modeling to calculate the barriers for organothiol sorption, C-S bond scission, H₂S desorption etc. can give more insights into the behavior and stability of the promoter-substituted edges.

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