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## Atomic insights into hydrodesulfurization

Prabhu, M.K.

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**Author:** Prabhu, M.K.

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## Summary

The desire to understand the world for what it is, is the basis for fundamental experimental research. Typically, this understanding helps us in designing better technology to improve our life profoundly. Experimental research in the field of catalysis over the last hundred years has led to the advances in chemical technology that have drastically changed our lifestyle from one of survival to that of comfort. This, however, has damaged the environment so much that we are in need of better chemical technology that also preserves the planet for our future generations and the species after us. In order to develop such chemical processes, we first need to understand how the existing processes work using experiments at a very fundamental level, that being, at the atomic scale, so that we can use this information to design, for instance, better catalysts.

In this thesis, we address this challenge for a specific chemical process called Hydrodesulfurization (HDS) which is used for producing clean fuels and petroleum products that meet the stringent emission standards set by the local governments. Despite being a well-established process, we still do not completely understand how it works. In this work, we make an attempt to approach this problem systematically, first, by trying to understand the atomic structure of the hydrodesulfurization catalyst formed by various synthesis procedures and second, by observing the catalyst as the HDS reaction occurs. For this purpose, we make use of a state-of-the-art experimental setup called the ReactorSTM which is a self-contained machine specially designed to resolve the atomic structure of catalysts during the chemical reactions. In the following paragraphs, the findings of the four scientific chapters of this thesis are summarized.

Transition metal dichalcogenides (TMDCs) are a type of two-dimensional (2D) materials widely investigated by both experimentalists and theoreticians, because of their unique properties. In the case of cobalt sulfide, density functional theory (DFT) calculations on freestanding S-Co-S sheets suggest there are no stable 2D forms of cobalt sulfide, whereas experimental observations clearly show TMDC-like structures on Au(111). In chapter 3, we resolve this disagreement by using a combination of experimental techniques and DFT calculations, considering the gold surface explicitly. We find a 2D CoS(0001)-like sheet on Au(111) that delivers excellent agreement between theory and experiment. Uniquely this sheet exhibits a metallic character, contrary to most TMDCs, and exists due to the stabilizing interactions with the Au(111) substrate.

In chapter 4, we present the results of a study carried out to investigate the simultaneous sulfidation of Co and Mo oxide nanoparticles on Au(111) as a synthesis strategy to prepare a model catalyst for hydrodesulfurization (HDS). We make use of scanning tunneling microscope (STM) and X-ray photoelectron spectroscopy (XPS) to track the changes in chemistry and morphology through the synthesis of a mixed Mo and Co oxide precursor and the sulfidation to the respective sulfides. We investigate the effects of temperature and the duration of sulfidation on the completeness of the sulfidation process. Our study shows that the recipe can be used to make a CoMoS model catalyst. However, the yield of the Co-promoted MoS<sub>2</sub> slabs is low because of the kinetically hindered sulfidation of the Mo oxide phase.

MoS<sub>2</sub> supported on oxides like TiO<sub>2</sub> has a broad range of applications. The atomic structure of this system is therefore, very useful to study. Previous research work in this area has made use of high-temperature synthesis methods while the preparation of an MoS<sub>2</sub>/TiO<sub>2</sub> in very important applications such as catalysis makes use of a low-temperature synthesis method. In chapter 5, we investigate a low-temperature synthesis strategy for MoS<sub>2</sub> slabs supported on rutile TiO<sub>2</sub>(110). Using STM and XPS, we demonstrate that not only flat MoS<sub>2</sub> slabs with irregular shapes but also MoS<sub>x</sub> stripes with coordinatively unsaturated Mo atoms are formed. In particular, it becomes evident that for atomic structural characterization of MoS<sub>2</sub>/TiO<sub>2</sub> and similar oxide-supported systems grown by low-temperature synthesis methods, the surface structure of the support becomes highly relevant.

In chapter 6, the first direct observations of a Co-promoted MoS<sub>2</sub> slab (CoMoS) under industrially-relevant HDS conditions using the ReactorSTM are presented. A model catalyst containing the Co-promoted MoS<sub>2</sub> slabs supported on an Au(111) substrate has been used. Initially, we image the CoMoS slabs under 100% H<sub>2</sub> and 100% CH<sub>3</sub>SH atmospheres separately. We report a variety of new edge structures for the Co-substituted edges of the CoMoS slabs. Additionally, during the desulfurization of CH<sub>3</sub>SH, we observe a dynamic edge structure on the Co-substituted edge. The HDS reaction gasses transform hexagonal CoMoS slabs into curved CoMoS slabs with high index edge terminations. Additionally, we also observe mass transport from the larger CoMoS slabs along the Co-substituted edges which causes the edges to appear highly irregular. XPS results show that this mass transport could likely be due to the loss of the Co promoter atoms. Our experimental observations emphasize the importance of studying a complex catalyst such as Co-promoted MoS<sub>2</sub> during the catalysis process. The results presented in this work open up avenues for more fundamental research on HDS and theoretical modeling with DFT calculations.