

**PRF # 57263-DNI10**

**Project Title:** “Understanding and Controlling Reactive Transformations in Hydrodesulfurization Catalyst Materials”

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**Co-PI:** None

This report provides information on the second year of the PI’s Doctoral New Investigator project. In this project period, one full-time Ph.D. student was supported. While the project was scheduled to end on Aug. 31, 2019, we have been granted a no-cost extension to enable support for 3-4 extra months to finish the project. The goals of this project are focused on i) understanding the dynamic changes that take place during the sulfurization of Mo-Ni-based hydrodesulfurization (HDS) catalysts, and ii) tailoring catalyst structure based on this knowledge. While Ni-doped MoS<sub>2</sub> is commonly used for HDS catalysis, we lack knowledge of how to control the synthesis and growth of Ni-MoS<sub>2</sub> materials for the creation of materials with optimal structure and catalytic performance. During this project period, the project personnel expanded upon the work completed during our first year, which involved using *in situ* transmission electron microscopy (TEM) to investigate how Ni-MoS<sub>2</sub> crystals grow from the precursor phase. Our efforts in project period 2 revealed further information about the significant effects of Ni on MoS<sub>2</sub> growth. The results were published in *ACS Nano* (N. Kondekar, *et al.* *ACS Nano* (2019) 13, 6, 7117-7126), the PI gave an invited talk on this work at the 2018 ACS National Meeting, and the graduate student gave a talk on the work at the 61<sup>st</sup> EMC conference sponsored by the Materials Research Society.

In the previous annual report, our initial results on the effect of Ni on MoS<sub>2</sub> growth were presented. Our findings showed that the addition of small amounts of Ni (<15 wt%) to an amorphous (NH<sub>4</sub>)<sub>2</sub>MoS<sub>4</sub> precursor caused much larger MoS<sub>2</sub> crystals to grow compared to samples without Ni. In the current project period, we have investigated this effect further and have made conclusions regarding its origin. In particular, we gained improved understanding of where Ni resides and how it affects growth. Figure 1 shows a high-resolution scanning TEM (STEM) image of a Ni-MoS<sub>2</sub> sample, along with energy dispersive spectroscopy (EDS) analysis of the elements within. The image in (a) shows a single MoS<sub>2</sub> crystal with a thinner region towards the top of the image. The EDS data of a different portion of the sample in Fig. 1c-f show that Mo and S elements are detected throughout, while Ni is primarily detected from the bright clusters visible in (c). It is known that Ni also decorates and substitutes at the edge sites of MoS<sub>2</sub> crystals. Thus, it is clear that MoS<sub>2</sub> is the primary crystalline product, with Ni present as clusters on the surface and also likely at edge sites.

Additional investigation into the crystallization process with and without Ni was carried out using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Figure 2a and b show data from heating three different Mo-S precursor samples: 0 wt% Ni (blue), 13 wt% Ni (black), and 50 wt% Ni (red). The endothermic peak at ~230 °C occurs in all three samples due to the thermolysis of the precursor

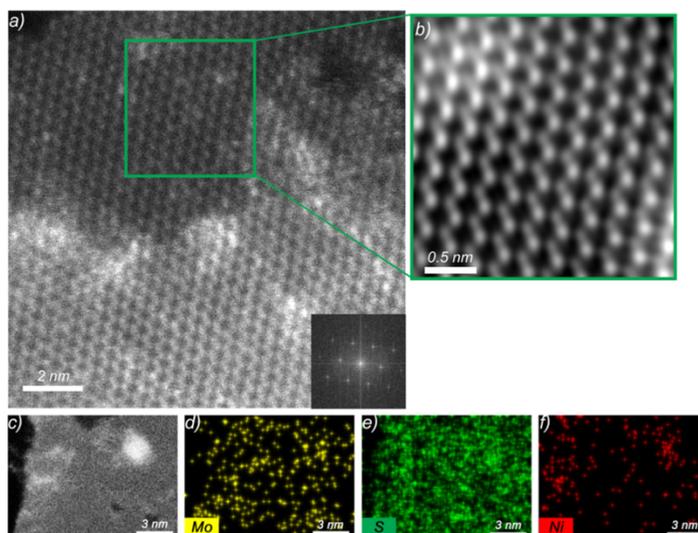


Figure 1. a) STEM image of a MoS<sub>2</sub> crystal grown from a sample with a small amount of Ni. b) Magnified section with Fourier filtering. c) Another section of the material at lower magnification. d-f) EDS data showing Mo (d), S (e), and Ni (f) signals.

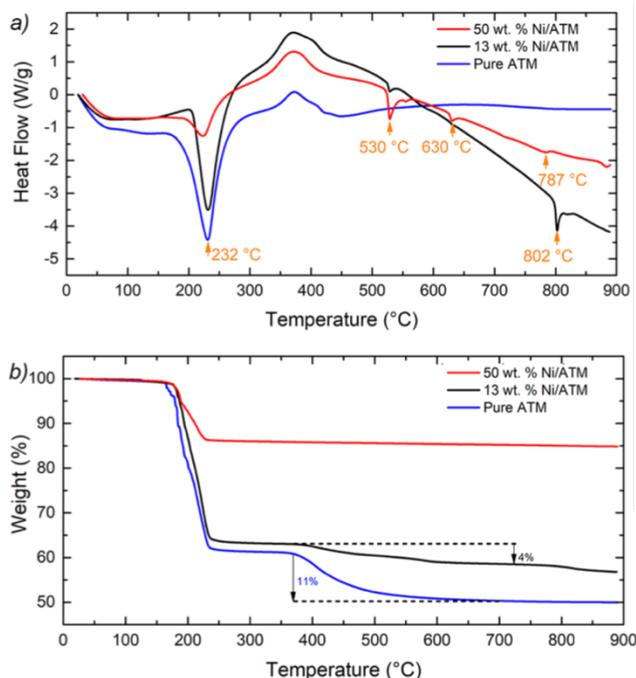


Figure 2. a) DSC heat flow across three samples: pure precursor (blue), 13 wt % Ni in the precursor (black), and 50 wt % Ni in the precursor (red). b) TGA analysis for the same samples.

spacing than MoS<sub>2</sub> and is somewhat disordered, and it is possible that Ni is intercalated between two-dimensional Mo-S layers. Regardless, it is clear that maintaining small concentrations of Ni is necessary to promote the growth of MoS<sub>2</sub> crystals.

These results comprehensively show the impacts of the addition of Ni to MoS<sub>2</sub> growth. They are important because Ni is often added to MoS<sub>2</sub> hydrodesulfurization catalysts, but the effect of Ni on growth processes were previously unclear. To explain these results, we postulate that the modification of MoS<sub>2</sub> edge planes by Ni atoms alters their mobility during the crystallization and growth process. Ni-substituted MoS<sub>2</sub> edge planes (or Ni-sulfides on the surface) could enable easier motion of these planes during crystal growth due to increased disorder, greater free volume, or different bonding characteristics. This would allow Mo and S atoms to be transported across these interfaces more readily to be added to a growing crystal or removed from a shrinking one. For design of MoS<sub>2</sub>-based HDS catalysts with controlled size and crystallographic characteristics, it is therefore necessary to control the amount of Ni within the precursor mixtures.

This PRF DNI grant has been a key aspect of the scientific development of the PI's research group. The PRF funding has launched an entire research area within the PI's group focused on understanding growth, interfacial reactions, and intercalation in layered chalcogenide materials. This has led to newly acquired funding in this topical area, as well as continued growth of related projects in the PI's lab. The funding has also allowed the student supported by the project (Neha Kondekar) to pursue her interests in the area of layered materials for catalysis and electronics applications.

to yield amorphous MoS<sub>3</sub>, which releases H<sub>2</sub>S and NH<sub>3</sub>. The exothermic peak at ~370 °C corresponds to the crystallization of MoS<sub>2</sub> from MoS<sub>3</sub>, along with further loss of sulfur. While weight loss is seen at the lower temperature in all three samples (Fig. 2b), the crystallization of MoS<sub>2</sub> is accompanied by significant weight loss only without Ni present. We hypothesize that the lower weight loss when Ni is added is due to the excess Ni reacting with the sulfur to form various nickel sulfides. Thus, the Ni species observed in Fig. 1 is likely Ni sulfide.

Experiments were also performed to examine the structure of MoS<sub>2</sub> samples with >15 wt% Ni. The previous annual report (and Fig. 1) shows that MoS<sub>2</sub> crystals were the primary product when smaller amounts of Ni were used. *In situ* TEM experiments with greater amounts of Ni added to the Mo-S precursor resulted in the formation of large metallic Ni particles, with no evidence for the formation of crystalline MoS<sub>2</sub>. However, in certain sections of the sample, MoS<sub>2</sub>-like layered structures were observed to coat the Ni particles (Fig. 3). This phase exhibits a different interplanar

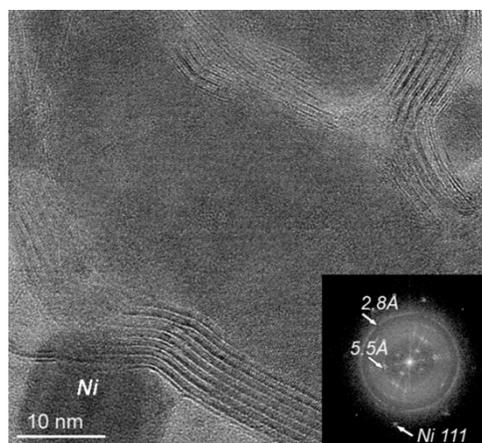


Figure 3. TEM image after an *in situ* heating experiment with >15 wt% Ni that shows a Ni particle (darker region in center of image) surrounded by a disordered layered structure that is likely disordered Mo-S.