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 first year of the PI's two-year Doctoral New Investigator project. In this project period, one full-time Ph.D. student and part of the PI's summer salary were supported. 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_2 is commonly used for HDS catalysis, we lack knowledge of how to control the synthesis and growth of Ni-MoS_2 materials for the creation of materials with optimal structure and catalytic performance. During this project period, the project personnel made good progress towards these research goals. Specifically, procedures were developed to observe the sulfurization process *in situ* using transmission electron microscopy (TEM) heating techniques, and these experiments were conducted to gain unprecedented nanoscale understanding of the growth of Ni-MoS_2 catalyst materials under realistic conditions. These *in situ* experiments have also been complemented by a variety of other *ex situ* measurements to verify their accuracy and relevance.

To enable both *in situ* and *ex situ* characterization of sulfurization processes, we have focused on synthesizing Ni-MoS_2 materials through a solid-state thermolysis method. $(NH_4)_2MoS_4$ (ammonium thiomolybdate) is used as the solid-state precursor for the synthesis of MoS_2. Heating this precursor to temperatures >400 °C induces decomposition and crystallization of MoS_2. H_2S gas and sulfur vapor are released during this multi-step process. By introducing controlled amounts of Ni (either in metallic or ionic form), we have investigated the effects of Ni on the crystallization and growth of MoS_2 materials. Figure 1 shows scanning electron microscopy (SEM) images of thin-film samples fabricated by first spin coating $(NH_4)_2MoS_4$ precursor onto a Si wafer and then heating to 800 °C. The three different samples in Fig. 1 had different thicknesses of Ni metal evaporated onto the surface (0 nm, 5 nm, and 30 nm) before spin coating the ~50 nm thick $(NH_4)_2MoS_4$ precursor film. Figure 1d contains grazing incidence x-ray diffraction (XRD) data from these samples, which shows that the (002) MoS_2 peak is present with 0 nm or 5 nm of Ni, but it is not present with thicker Ni films. From these data, it is clear that the presence of Ni significantly influences both the morphology and structure of the MoS_2 material, but the data do not provide insight into the dynamics of this process.

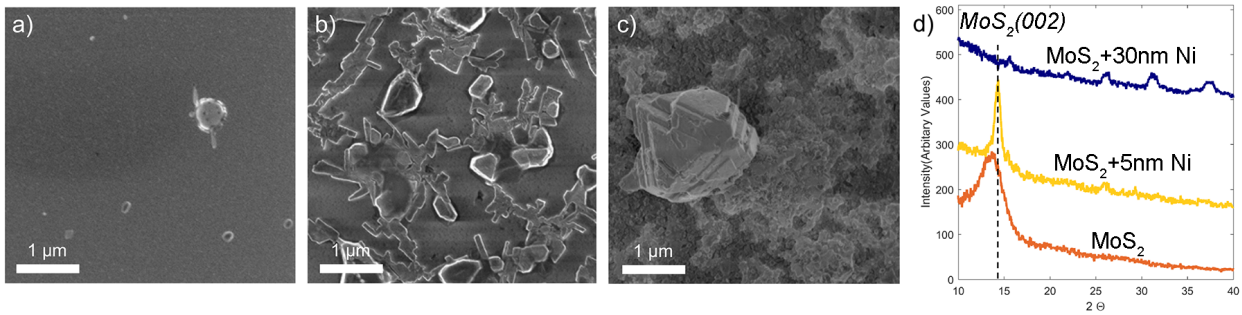

Figure 1. *SEM images of precursor thin films after the thermolysis process to grow MoS_2 with (a) no Ni, (b) 5 nm Ni, and (c) 30 nm Ni. A conformal MoS_2 thin film grows in (a), while a disrupted planar morphology is visible in (b). (d) XRD data showing the presence of MoS_2 after thermolysis only from the pure precursor and with 5 nm Ni. The differences in (002) peak width suggest different average particle sizes.*

To gain insight into these observed differences, *in situ* TEM with a specialized heating stage was used to probe the crystallization and growth behavior of MoS_2 with and without Ni. Fig. 2 shows the evolution of the pure precursor material (initially amorphous, Fig. 2a) during a heat ramp to 900 °C. MoS_2 crystallizes above ~400 °C to form a polycrystalline mass (Fig. 2b), and the crystals steadily grow until ~800 °C.

Heating above ~850 °C induces the decomposition of the MoS_2 to form Mo metal particles at the surface (Fig. 2d).

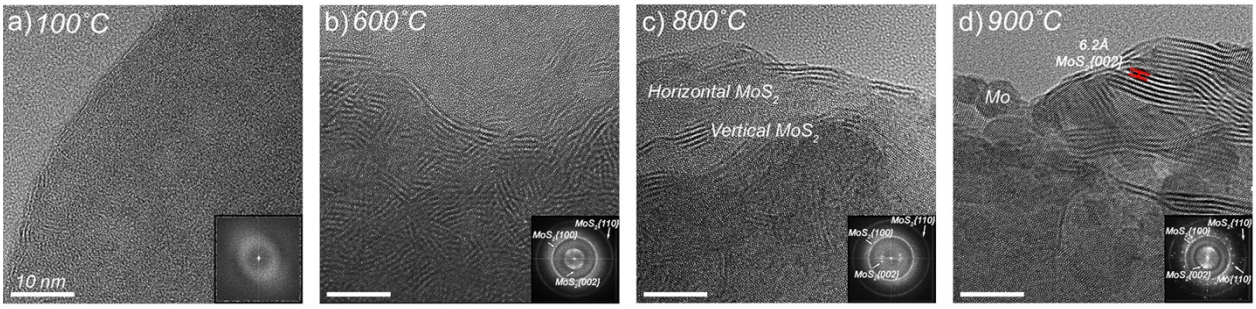

Figure 2. *In situ TEM showing the evolution of the pure precursor during a heat ramp to 900 ℃ over ~2 h.*

These observations are in contrast to the growth behavior of MoS_2 from a precursor layer coated onto ~5 nm of Ni, as shown in Fig. 3. The initial formation of polycrystalline MoS_2 at ~400 °C is similar (Fig. 3b), but upon heating to higher temperatures, the MoS_2 largely converts to a horizontal orientation with the basal planes aligned with the substrate. Ongoing work is focused on understanding the detailed dynamics of this process, as well as correlating these observations with other measurements to determine where the Ni species resides on the crystals (likely the edge sites based on previous reports). Upon heating to higher temperatures (~800 °C), large horizontally-oriented MoS_2 crystals were observed to form (Fig. 3d). Thus, the addition of Ni modifies the morphological evolution of MoS_2 during the synthesis process.

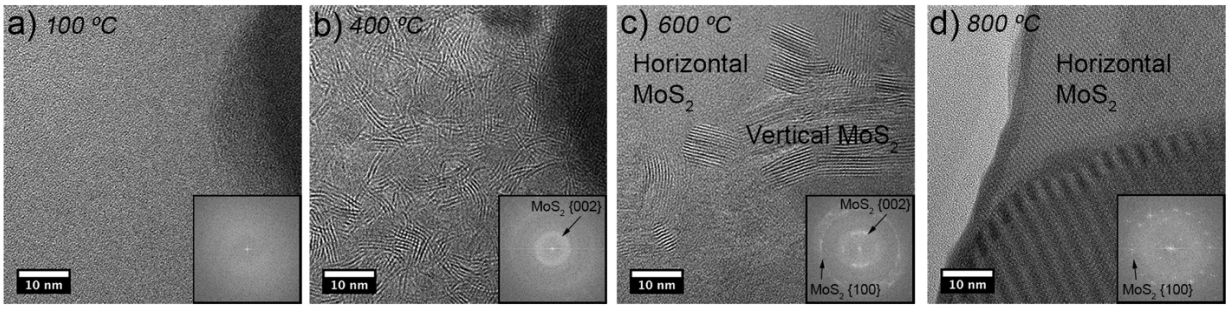

Figure 3. *In situ TEM showing heating of the $(NH_4)_2MoS_4$ precursor on top of 5 nm of Ni.*

These results are among the first to reveal the synthesis process of HDS catalyst materials at the nanoscale under realistic *in situ* conditions. While the thermolysis of the $(NH_4)_2MoS_4$ precursor is not the typical synthetic pathway for HDS catalysts, this process accurately mimics synthesis procedures because of the release of H_2S during thermolysis, which is similar to industrial sulfurization processes. These results are important since they demonstrate the key role of Ni in controlling the evolution of MoS_2 morphology during synthesis, which should be considered when designing and synthesizing HDS catalyst materials. A manuscript is currently being drafted about this work, and it will be submitted in the coming months. In addition, the PI presented this research in an invited talk at the August 2018 ACS National Meeting.

So far, 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, as other studies on dynamic processes within layered materials such as MoS_2 are also being undertaken by other group members. Thus, this funding has enabled us to work in a new area, and it will affect the trajectory of my group for years to come. The funding has also allowed the student supported by the project (Neha Kondekar) to pursue her interests in the area of layered catalytic materials.