PRF#: *58350-UR10*
Project Title: *Understanding Synergistic Effects of Nano-confinement and Catalysis on Methane Gas and Syn-Gas Conversion to Liquid Fuels using Synchrotron X-ray and Neutron Characterization*
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Budget and Scope of the Project:
The project beginning date was January 1, 2018 and ending date is August 31, 2021. The grant is 73% expended (18,667 out of 70,000 remains).

Overview of the Project:
The project goal is to enhance the efficiency of PdS, MoS_2, RuS_2, and TiS_2 catalysts for converting methane into ethylene by nanoconfining those catalysts into metallorganic frameworks (MOFs), SBA-15, and anodic alumina.

In 2013, the sulfides were demonstrated in the laboratory of Tobin Marks (Northwestern University) to effect "soft" oxidation of methane with reasonable-to-good selectivity for ethylene. Selectivity was shown dependent on the catalyst—with PdS having highest selectivity (18% at 1325K) and MoS_2 having the lowest (1% at 1275K). MoS_2 had a very high methane conversion efficiency of 13% at 1275K (albeit not to ethylene product).

In unpublished work reported for their summer school 2015, the NIST Center for Neutron Research (NCNR) used MOFs to demonstrate a marked slowing of dynamics of methane gas.

The current project merges these two works in order to improve methane conversion efficiency and ethylene selectivity. By using nanoporous materials to slow methane dynamics and confining sulfide catalysts into those pores to increase interaction probability, efficiencies can be increased. Our work focuses on making and analyzing the nanoconfined sulfides (using synchrotron X-ray scattering and absorption spectroscopy).

Research Accomplishments:
January to December 2018 - What we learned?
At the outset of the project, we discovered that it was cost prohibitive to include RuS_2 in our experiments (the cost was nearly 700 USD for 5g of material). Instead, we moved forward with two other three sulfides.

Two students pursued separate methods for nanostructuring the sulfides, based on literature reports in exfoliation of MoS_2 and WS_2 2D materials. One student, Stephen Hickey, pursued a technique which required ultrasonication within organic solvents (ethanol and acetone) and water for periods up to 1 hour. These studies were performed on MoS_2, PdS and TiS_2. In this case, particle size reduction, but no nanostructuring, occurred. The other student, Nabil Jamhour, used salt-assisted milling, whereby NaCl and KCl intercalates the layers of the 2D materials during high energy ball milling. He milled for up to 3 hours. These studies were performed on MoS_2. Small-angle X-ray scattering results showed that 55nm MoS_2 were achieved, however yields were low since the process requires (1) copious amounts of salt added to the sulfide (in a 10:1 ratio by mass) and (2) dissolution of salt in water after ball milling (followed by centrifugation to isolate the remaining sulfide). For both approaches, EXAFS and XANES showed little or no changes in local atomic structures—indicated that single layer exfoliation as not achieved. Single layers are not important for our application, only nanosizing the materials in the lateral dimension for insertion into the porous templates. Students reported their results in poster presentation at Rowan University (in July 2018) (see posters in Figure 1). Each summer 2018 student also had a second project. As the purchase of 20, 50, 100, and 200nm porous alumina is deemed too costly, Stephen pursued the formation of anodic alumina in our laboratory—but with limited success. Nabil designed a 3D printed nozzle for the delivery of the methane and sulfur feed gases in the ratios (following the work of the Tobin Marks' group) of CH_4:S of 1, 3.6, and 6. The use of additive manufacturing and nozzle design for feed gases is novel to this work. Nabil's poster won 2nd prize in the end of summer research poster session (there were approximately 50 posters presented).

January to December 2019 - What we learned?
Three students performed studies by closely following the 2018 findings to enhance results achieved. One student, Joseph Jackson, performed ultrasonication in organic solvents and water for periods up to 12 hours. Synchrotron X-ray scattering results determined that nanostructuring had not occurred. We did not have access to EXAFS and XANES during the semester that Joseph worked on the project—and so Joseph followed up with Raman spectroscopy and learned that the MoS_2 still showed spectra most similar to bulk (rather than 2D exfoliated). We also learned that the TiS_2 had been oxidized in the process—and the Raman spectra collected from the ultrasonicated

samples matched well with that of the anatase phase of TiO_2. Joseph did not continue on the project in summer, instead opting to pursue an Engineer Without Borders opportunity. He did not present his findings.

Armed with the knowledge and small successes from summer 2018, salt-assisted milling was pursued by the two students who worked on the project in summer 2019, Denise Omoruyi and Theresa Slater. This time, the students milled for time up to 12 hours (more closely following the literature on the topic). These samples were fully characterized by electron microscopy, USAXS/SAXS/WAXS, and EXAFS/XANES at Brookhaven National Laboratory. Findings were that we achieved nanosizing (USAXS/SAXS). Additional oxide peaks were present in the treated MoS_2 sample—as identified by EXAFS—but not for the WS_2 samples. We expect to publish these results in 2020.

Impact of Research on my career: This research represented a pivot in my research programs from using nanostructured materials for photototthermal therapy to using them for catalysis. Although we have not added a major gas handling apparatus to my laboratory, I began using the Linkam hot-stage for handling gases—along with additive manufacturing to design the flow control systems.

Impact of Research on Students who participated in the project: Four students have been funded by this project and one additional student worked on this project as his Federal Work Study (FWS) position at the university. Two of the four students funded by this project were from groups underrepresented in STEM disciplines.

- All five students traveled to Argonne National Laboratory's Advanced Photon Source (APS) in order to collect ultrasmall-Angle X-ray scattering (USAXS), small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) data. There, students were also mentored by world-renown experts Jan Ilavsky and Ivan Kuzmenko.
    - The single instrument which measures USAXS/SAXS/WAXS collects in a four minute time window.
    - Students used experimental design principles to make comparative sets of samples.
    - Students learned to process and interpret results from the copious amount of data collected.
- Two students traveled to the synchrotron facility owned and operated by the Louisiana State University, Center for Advanced Microstructures and Devices (CAMD) in summer 2018. There, we performed X-ray absorption spectroscopy (techniques known as EXAFS and XANES).
- Two students traveled to Brookhaven National Laboratory for EXAFS and XANES measurements with a world-renown expert, Bruce Ravel.
- The two students who worked on the project in summer 2019 presented a poster at the National Society of Black Physicist (NSBP) Conference—national in scope with 600 participants—in Nov 2019.
- One student who worked on this project in the summer of 2019 will present our findings at the American Physical Society April Meeting in 2020.

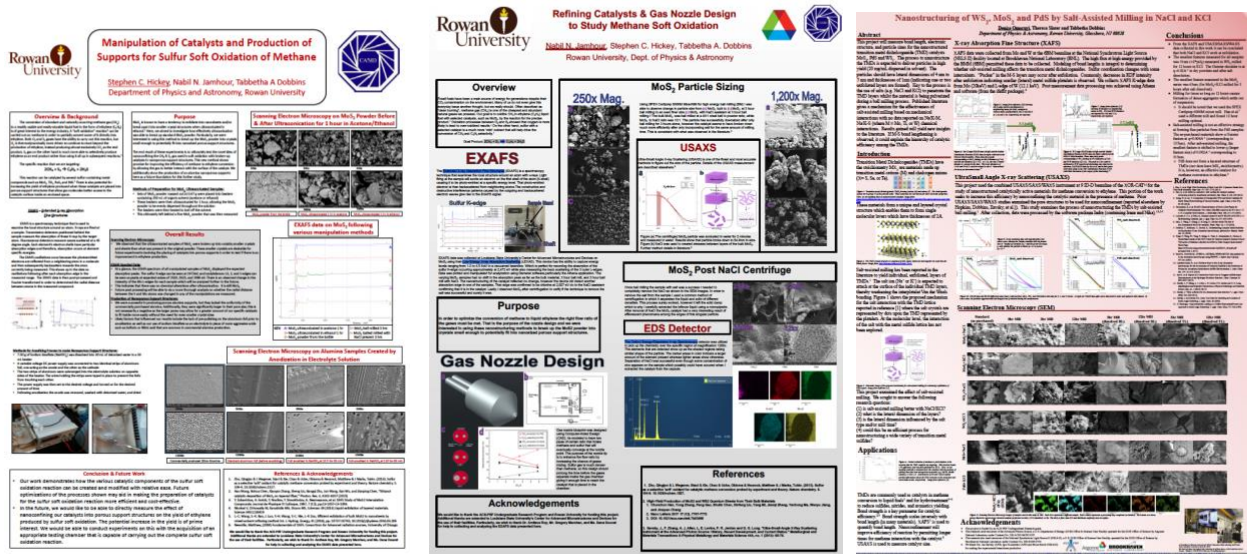

__Figure 1.__ Posters presented by (left to right), Stephen Hickey (research performed summer 2018), Nabil Jamhour (research performed summer 2018), and Denise Omoruyi and Theresa Slater (research performed summer 2019).