

1. PRF #: 58406-DNI5

2. **Project Title:** Development of Atomically-Planar, Well-Ordered Molybdenum-Nitride Thin-Films for Phase-Specific Hydrogenation Surface-science Model-Catalysis Studies

3. **PI Name, Affiliation:** William E. Kaden, University of Central Florida

The clearly defined objectives for year 1 of this project consisted of developing and characterizing suitable well-defined models for delta- and gamma-phase molybdenum-nitrides amenable for conventional surface-science investigations of hydrodenitrogenation (HDN) reaction processes. These objectives involved both experiment and theory, and a secondary thrust was to begin fabricating a new differentially pumped housing for our mass-spectrometer amenable to more refined TPD and isothermal surface reaction investigations. This report will highlight our progress along these thrusts during the first year of funding.

(1) Experimental development of a δ -MoN thin-film analogue

Using Ru(0001) as a template for epitaxial growth, we have successfully demonstrated a means for growing wetted MoN thin-films spanning 1-2 monolayers in thickness. The procedure involves the iterative sequential use of nitrogen ions produced via electron impact ($E_i = 100$ eV) incident at the sample surface with ~ 0 eV kinetic energy and gas-phase Mo produced via physical vapor deposition. Annealing films produced in this manner to ~ 700 K within a background of N_2/N^+ ions was found to result in optimal film wetting and crystallization to result in a fully wetted monolayer with a lattice parameter and hexagonal symmetry consistent with values obtained from bulk δ -MoN samples. Results from this work have been published in the journal *Topics in Catalysis* (Volume 62, Issue 12-16, pp 1035-1043), which is included in our ACS PRF-catalogued listing of supported publications. Key results from that work are provided in Figures 1-4. This portion of the work has been led by a graduate student partially supported through this grant. Continuing work on this task includes local structure analysis by STM and use of TPD as a chemical probe to investigate interactions with pyridine and related N-containing organics.

(2) γ -Mo₂N and theory developments

Work has begun to grow γ -Mo₂N on Ag(100) using an approach analogous to that used to grow δ -MoN on Ru(0001). To-date, the student involved in this portion of the project has succeeded only in mounting, cleaning and characterizing the pristine Ag(100) substrate (experimentally). The same student has simultaneously worked to develop DFT-optimized structural models compatible with our δ -phase results and predictive of our γ -phase thin-films. Results include film structure, formation energies, and simulated vibrational spectra and STM images. Ongoing work includes

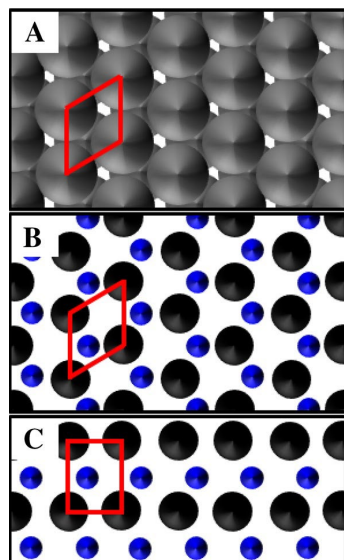


Figure 1. Model depicting the envisioned structure of the MoN thin-film grown via our approach. (A) top-view of the Ru-support. (B) Top-view of the MoN film. (C) Side view of the MoN film.

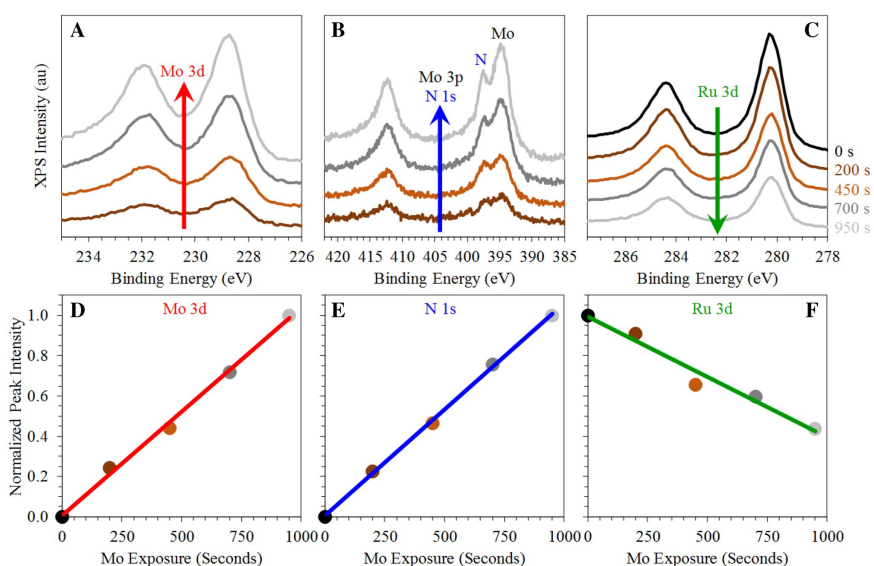


Figure 2. XPS spectra obtained from the Ru(0001) sample as a function of exposure to Mo (and N_2/N^+ ions). (A & B) track the growth of Mo and N signals, which are quantified in (D & E), while (C & F) provide the concomitant attenuation of the Ru 3d peak as a function of film growth.

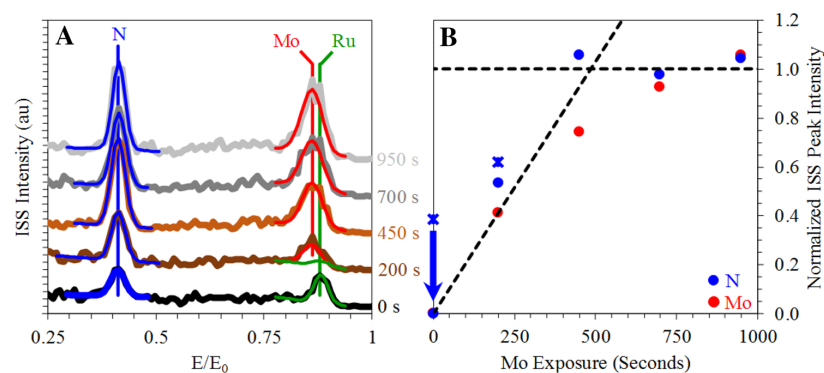


Figure 3. (A) ISS spectra of the molybdenum nitride films and (B) variation in associated peak-intensities as a function of total Mo exposure. The break-point near 500 seconds is consistent with a single monolayer coverage based on XPS quantitative analysis.

characterizing new films grown on Ag(100) via the approaches used on Ru(0001), probing surface chemistry, and establishing empirically constrained mechanistic understandings informed by theory

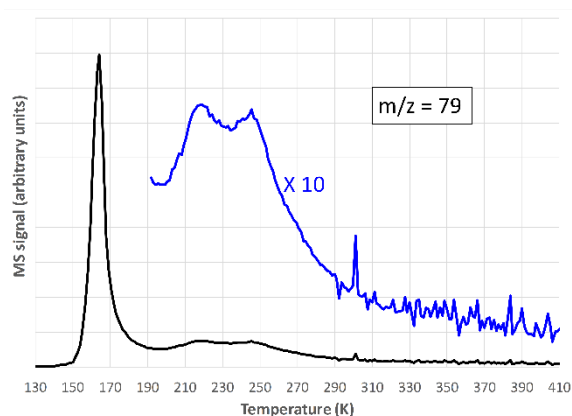


Figure 5. TPD showing bimodal molecular desorption of pyridine from a single-crystalline SiO₂ thin-film grown on Ru(0001) for the sake of comparison to forthcoming data from molybdenum-nitride.

(4) General trends in HDS activity as a platform for expansion of materials investigated for HDN

Related to the collaborative work used to provide theoretical models of molybdenum nitride thin-films suitable to model HDN surface-science studies, Dr. Kaden has closely examined DFT data sets provided by his computational collaborator to elucidate a unique 3-dimensional correlation between empirically measured activity and theoretically derived adsorption energy and charge-transfer for thiophene interacting with transition metals. Outcomes from this work have been included in a publication in the journal *Catalysis Letters* (Volume 149, Issue 11, pp 2953-2960), which is summarized in Figure 6. A main takeaway from this work, is that different groups of metals shared two different scaling relationships between C₄H₄S adsorption energy and charge transfer, and that the systematic differences between the groups separated them into two conventional volcano plots relative to either variable.

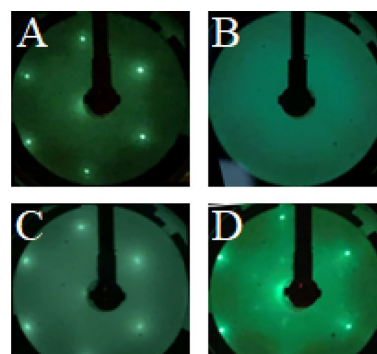


Figure 4. LEED patterns obtained from (A) Ru(0001), (B) sample (A) following exposure to ~2ML equivalents of Mo and N (but without annealing to 700K), (C) after annealing sample (B) to 700K, and (D) after annealing sample (C) to 1100K.

(3) Mass Spectrometer Housing Fabrication

To allow for improved chemical interrogation of HDN-related surface reactions, we have begun fabrication of a new differentially pumped mass-spectrometer housing. To-date all parts associated with our designed hardware have been purchased, and most pre-weld machining has been completed. In the meantime, a stop-gap housing has been fabricated and installed, which has allowed for improved TPD measurements before completion of our more robustly designed permanent replacement housing. Early TPD work has focused on exploring interactions of pyridine thin-films (including molybdenum-nitride analogues developed through this grant and specifically targeted for HDN). Results from this work are expected to be published this Fall.

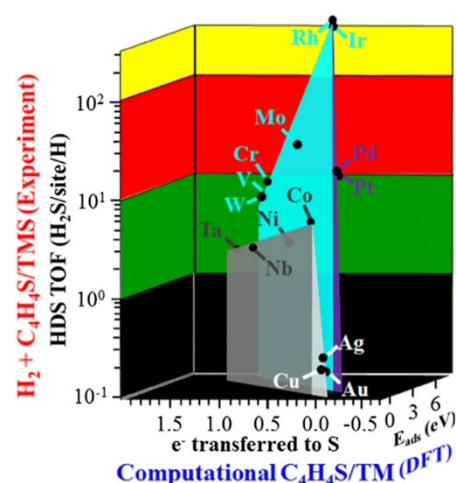


Figure 6. Volcano surface for transition-metal-sulfide activity towards thiophene HDS based on two distinct elemental metal-thiophene interactions predicted by theory.