

***In Situ* S/TEM Reduction Reaction of Ni-Mo₂C Catalyst for Biomass Conversion**

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Increasing interest exists in renewable energy sources to replace fossil fuels. Biomass has a great potential for chemical and fuel production, for example, via fast pyrolysis integrated with hydrotreating [1]. Due to the poor quality of the raw fast pyrolysis bio-oil and lack of effective hydrotreating catalysts for raw pyrolysis oil, it is important to understand and develop hydrotreating (e.g., hydrodeoxygenation) catalysts whose performance (e.g. selectivity, activity, stability) is optimized for biomass conversion processes. Molybdenum based carbides are promising catalysts for biomass conversion processes. Further, modifying the catalysts via metal doping (e.g., Ni) can not only increase metal/acid site ratios on the carbide surface but can also enhance stability against oxidation. The aim of this research is to better understand the roles of Ni species that are incorporated into molybdenum carbides using advanced characterization techniques including X-ray absorption spectroscopy (XAS), high-resolution and *in situ* scanning transmission electron microscopy (S/TEM).

In situ closed gas cell microscopy can be utilized to study a range of material systems in response to temperatures up to 1000°C and pressures up to 1 atm within a reactive gas environment, which was used here to study the structural and chemical changes of Ni-Mo₂C catalysts. The Ni-Mo₂C catalyst was prepared via carburization of Ni-MoO₃ beads with carburizing gas (15% CH₄/H₂). The beads were heated to 700°C and held for 1 hour under 15% CH₄/H₂ [2]. The low-resolution dark field S/TEM image (Figure 1a) shows the porous structure of the fresh, passivated NiMo₂C catalyst and the high-resolution image in Figure 1b indicates that the material is highly crystalline without any significant amorphous surface layer. For the *in situ* STEM experiments, the fresh Ni-Mo₂C catalysts were crushed in ethanol to decrease the size scale such that it will fit within the 5 μm gap within the gas-cell [3]. A droplet of the suspension was placed on the silicon nitride window of a Protochips™ E-chip heater chip. The Protochips Atmosphere™ gas reaction system was then used for the *in situ* STEM experiments, which were conducted using an aberration-corrected JEOL 2200FS operated at 200kV. The gas-cell was flushed three times with nitrogen from 300 to 0.5 Torr to ensure there was no O₂ present in the system. The pressure was then set to 300 Torr and the gas-cell was filled with 100% H₂. Temperature was brought from room temperature to 500°C under flowing 100% H₂ at 5°C/min. No significant change in the morphology of the catalyst particles was observed while the temperature was increasing up to 500°C. The Ni-Mo₂C was stable under reducing conditions at 500°C (Figure 2), which is consistent with other measurements (XRD, surface area measurement, surface reduction with gas analysis). Energy dispersive X-ray spectroscopy (EDS) elemental analysis after reaching 500°C confirmed that the catalyst was primarily associated with Mo and uniform distribution of Ni (Figure 3). There was no visible change in the composition distribution of both elements before and after reaction, thereby indicating this catalyst is stable under reacting conditions. These results show validation of *in situ* S/TEM capabilities that enable future identification of active sites and catalyst regeneration procedures [4].

References:

- [1] H Wang, J Male, Y Wang. *ACS Catal.* **3** (2013) p. 1047.
 [2] J S Lee, S T Oyama, M Boudart, *J. Catalysis.* **106** (1987), p. 125.
 [3] K A Unocic *et al*, *Oxid. Metals* **88** (2017), p. 495.
 [4] This work was performed in collaboration with ChemCatBio, a member of the Energy Materials Network (EMN), and supported by the U.S. DOE Bioenergy Technology Office under Contract no DE-AC05-00OR22725 (ORNL), Contract no. DE-AC36-08-GO28308 (NREL), and Contract no. DE-AC02-06CH11357 (ANL). Microscopy performed as part of a user project at the Center for Nanophase Materials Sciences (CNMS), which is a U.S. DOE Office of Science User Facility.

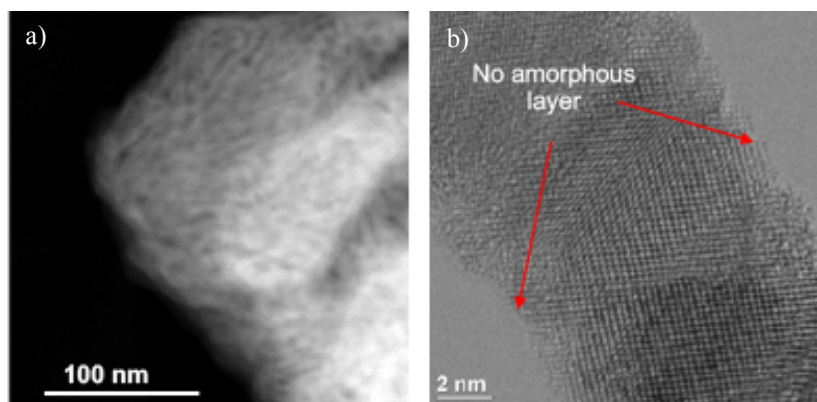


Figure 1. a) HAADF-STEM and b) high resolution BF-STEM images showing the structure of fresh Ni-Mo₂C.

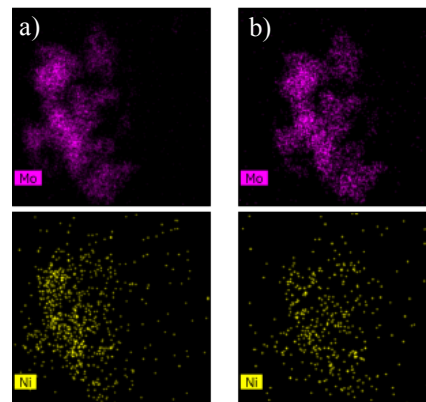


Figure 3. Mo and Ni elemental maps for the fresh passivated Ni-Mo₂C catalyst shown in Figure 2 at a) room temperature in vacuum and b) at 500°C in flowing 100% H₂ and 300 Torr using *in situ* S/TEM.

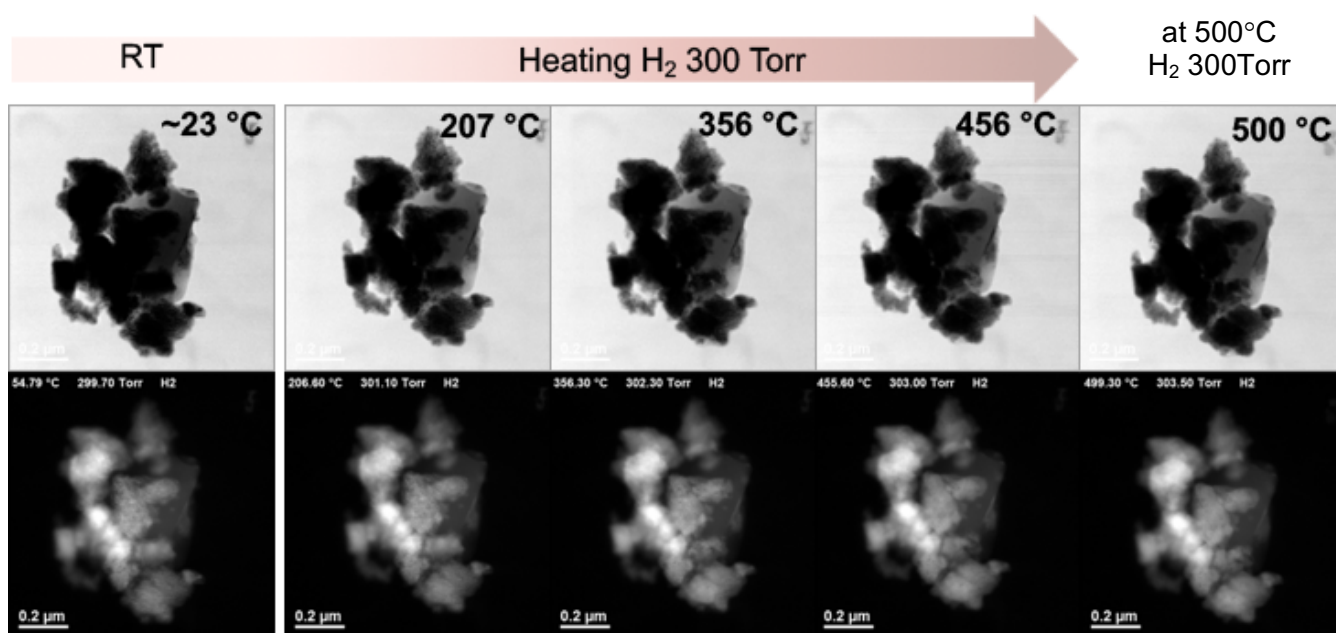


Figure 2. Time-lapsed HAADF-STEM and simultaneously acquired BF-STEM images showing behavior of fresh Ni-Mo₂C under heating to 500°C in flowing 100% H₂ at 300 Torr.