The *in-situ* TEM Study of Microstructure Alteration of MoS$_2$ under Carburization

Jian Chen[1], Qiang Wei[2], Jinwen Chen[2]

[1.] National Institute for Nanotechnology (NINT), National Research Council Canada, 11421 Saskatchewan Drive, Edmonton, Alberta T6G 2M9, Canada.
[2.] CanmetENERGY-Devon, Natural Resources Canada, 1 Oil Patch, Devon, Alberta T9G 1A8, Canada.

Conversional hydrotreating catalysts mostly use Ni-promoted MoS$_2$ as active sites. Modifying conventional hydrotreating catalyst surface of MoS$_2$ by selectively introducing carbon atom into catalyst crystal structure can lead to an improved electronic property, increased capability of hydrogen adsorption and dissociation. Such process will effectively increase catalyst hydrogenation activity and selectivity [1].

Various hydrocarbon agents are available to introduce carbon into MoS$_2$. It has been shown that the choice of hydrocarbon has an important effect on the catalytic performance of the catalyst [2,3]. To date, most of the work has been focused on the use of mixtures of hydrogen and methane or hydrogen and a small molecule hydrocarbon as carburizing agents.These gas mixtures are unreactive and carburization requires high temperature. The resulting carbides are limited to high-temperature phases. Herein, we report the microstructure evolution of MoS$_2$ when heating up to 900°C under H$_2$/C$_2$H$_2$ in a Hitachi H-9500, a 300 kV environmental transmission electron microscope (ETEM).

A large MoS$_2$ region with its [0001] zone axis parallel to incident electron beam was chosen for microstructure characterization. The sample was heated *in-situ* up to 900°C first, and then delivering H$_2$ and C$_2$H$_2$ in sequence. Comparing to room temperature experiments, there are no obvious microstructural changes in MoS$_2$ at 900°C (middle image in Figure 1(A)). However,after exposure to H$_2$/C$_2$H$_2$, changes are observed. Figure 1(C) and (D) display an enlarged view of the region marked by a cubic square in Figure 1(A). It can be seen that MoS$_2$ flake stack breaks into small particle clusters in H$_2$/C$_2$H$_2$. The EELS spectrum suggests that part of MoS$_2$ turns into molybdenum carbides. We randomly picked formed molybdenum carbide nano particles (NP) for Nano-beam Diffraction (NBD). The simulation of the NBD pattern reveals that this molybdenum carbide NP is cubic α-MoC$_{1-x}$ with face-centered cubic (fcc) structure (seeFigure 2 (A), (B) and (C)). The α-MoC$_{1-x}$ is metastable and will be further transformed to β-Mo$_2$C in H$_2$ above 873K. The α-MoC$_{1-x}$ NP exhibits better catalytic performance for the hydrolysis of thiophene than [4]. Figure 2(D) shows HRTEM image of another α-MoC$_{1-x}$ NP formed in MoS$_2$ matrix. Twinning structure was found within the particle. This is typical (111)/[11-2] coherent twin plane in *fcc* structure. Usually, twin planes occur with a constant spacing and have a long-range order, resulting in twinning superlattice in a specific direction, as schematically shown in inset of Figure 2(D). In the inset, the thicker black lines represent twin planes (111). Red circles and solid black solid are lattice configurations before and after twinning, respectively. The existing of twin structure is beneficial for the catalytic performance of the corresponding carbides. Since α-MoC$_{1-x}$ is a metastable phase and should further transform to stable β-Mo$_2$C, the role of twinning structure in such transformation is an interesting aspect in the *in-situ* TEM study.

References:
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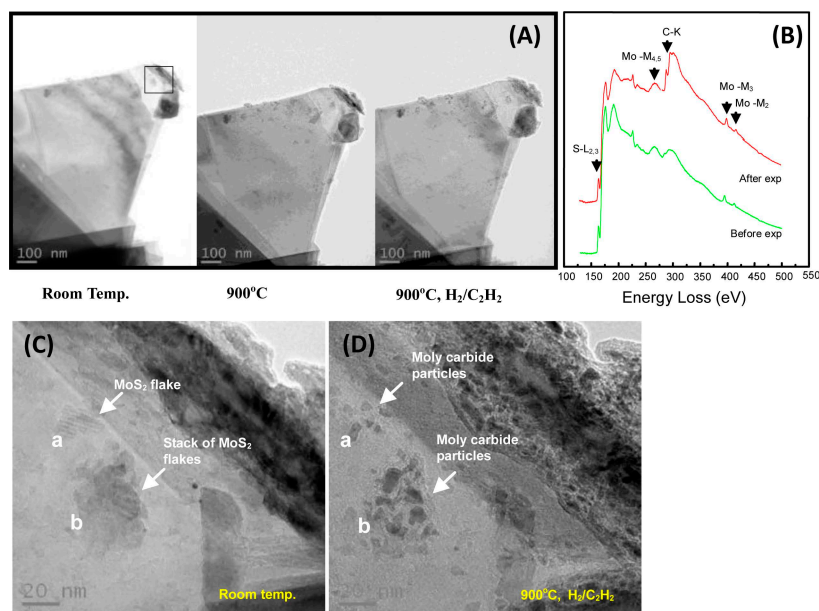[4] S D Yuang, S B D A Hamid et al, J. Mole. Catal. A 184 (2002) 257.

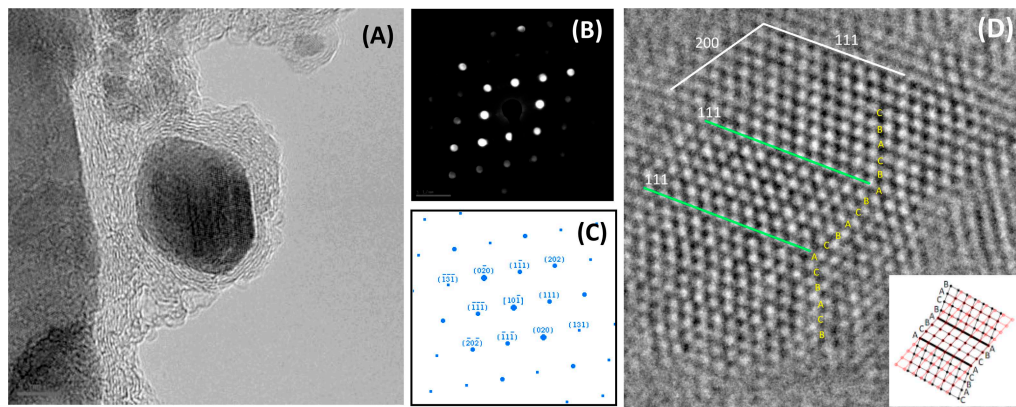Figure 1 Microstructure evolution of MoS$_2$ under *in-situ* TEM observation.

Figure 2 (A). HRTEM image of a MoC$_{1-x}$ NP, its NBD pattern (B) and simulation (C). (D) another α- MoC$_{1-x}$. Seven-layer deformation twin is shown between two (111) twin planes.