Chapter 3
3D Catalysts of Mo(W) Carbide, Nitride, Oxide, Phosphide, and Boride

In last two chapters, we have shown the exciting catalytic potential of the 2D Mo(W) dichalcogenides. Other Mo(W) based materials, such as Mo(W) nitride, carbide, oxide and phosphide, are usually in some 3D structures, catalytic performance depends on their morphology, size and exposed crystal facet. In this chapter, we focus on the preparation, characterization and novel catalytic applications of these 3D Mo(W) materials.

1. THE SYNTHESIS AND CHARACTERIZATION OF Mo(W) CARBIDE

Mo(W) carbide with a list of desired properties makes it very attractive for catalysis from both fundamental and industrial standpoints. Mo(W)-based carbides have been found to show special catalytic properties similar to noble metals. This has resulted in surging investigation on synthesis of various Mo₂C
structures, from nanoparticles to nanorods (Vrubel and Hu 2012, Chen et al. 2013a and 2013b, Youn et al. 2014 and Xiao et al. 2015). The methodologies and conditions used for molybdenum (tungsten) carbide preparation determine the chemical and catalytic nature of the obtained materials (Wan et al. 2014 and Wu et al. 2015).

Traditionally, the Mo(W) carbide material is usually synthesized by temperature-programmed reaction (TPR) where a given amount of the oxide precursor (for instance, MoO$_3$ or WO$_3$) is heated gradually under a mixture of hydrogen and hydrocarbon. The oxide firstly is reduced from high valence to lower valence oxide states and then carburized at high temperature. Normally the formed molybdenum carbide is stable hexagonal phase. The formed carbide is passivated using 0.5-1% O$_2$ before exposing to air owing to its pyrophoric property. Using the TPR procedure, many parameters are necessary to consider such as carburizing agent, C/Mo ratio, heating rate, isothermal treatment, and H$_2$ concentration.

MoO$_2$ is deemed the common intermediate in carburization process. Guzmán et al. (2013 and 2015) synthesized small MoO$_2$ nanoparticles using EG as reducing agent to fabricate high-dispersed Mo carbide. In-situ time resolved X-ray diffraction shows that the most intense peak of the monoclinic MoO$_2$ phase (011) became broad suggesting the presence of small crystalline domains (Figure 1).

Xiao et al. (2001) compared various molybdenum carbides prepared by the temperature programmed reaction method using mixtures of hydrogen and methane, hydrogen and ethane, or hydrogen and butane. The results show that the choice of hydrocarbon used to synthesize molybdenum carbide significantly affects the structure and texture of the resultant materials. Increasing the chain length of the carburizing agent reduces the particle size and the temperature for phase transformation. Carburizing with hydrogen/methane gives rise to hexagonal closed packed (hcp) carbide (β-Mo$_2$C), while using butane as the carbon source, molybdenum oxide is mainly reduced to face centered cubic (fcc) carbide (α-Mo$_2$C). When using ethane as the carbon source, the resultant carbide has a mixed phase composition with the hcp phase dominant. With modified TPR procedure, it is possible to synthesize nanocrystalline of molybdenum carbide in either cubic or hexagonal phase (Frauwallner et al. 2011).

However, using the typical TPR method, the transformation from oxide to carbide is usually incomplete since the reactions occur only on the gas-solid interface. Moreover, the bulky products generated are often covered by carbon species originated from the pyrolysis of excessive carbon-containing gases, which suppresses the surface activity. Furthermore, the complex and
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