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Phase Transformation of Molybdenum Carbide in Carburization of MoS_2 Studied by *in-situ* Environmental TEM

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The catalytic behaviour similarity of molybdenum carbides to the noble metals has brought great interest in academia and in industry. However, most molybdenum carbides are produced via high temperature reaction between molybdenum oxide and a carburizing gas. This leads to low surface area, which brings negative impact on ultimate catalytic performance of molybdenum carbides. To date, techniques for synthesizing MoS_2 with high surface area are well developed [1]. This provides a possibility to synthesize molybdenum carbides with high surface area through carburization of MoS_2.

In the current study, the in-situ carburization of MoS_2 was performed in the Hitachi H-9500 environmental TEM. Acetylene/H_2 mixture was employed in the experiment. MoS_2 sample was first heated up to 900^{o}C, and then H_2 and acetylene was delivered in sequence to the microscope column part which is separated from the rest part of column by differential pumping apertures. As shown in Figure 1, nano particles (NPs) emerged at the surfaces of MoS_2 slabs after exposure to acetylene for five minutes. Three NPs marked by a square are displayed in Figure 1(A). Their enlarged image is shown as an inset in the figure as well. Figure 1(B) shows another region where a particle with well-developed crystalline lattice (see inset in the figure) and its difractrogram. The simulation for the diffractrogram suggests a cubic α-MoC_{1-x} with face-centered cubic (fcc) structure form. The similarity between diffractrogram in Figure 1(A) and (B) suggests the NPs studied are all α-MoC_{1-x}. Judging from their sizes, we postulate that α-MoC_{1-x} is the first phase nucleates and grows under the experimental condition.

Studies suggest that there is a relationship between the formed type of molybdenum carbide and carburizing gas. For example, α-MoC_{1-x} usually forms when carburising with a mixture of butane and hydrogen while hexagonal closed packed (hcp) β-Mo_2C comes out when changing the carburizing agent to a mixture of methane and hydrogen [2]. Molybdenum carbide can occur in a variety of crystal structure, but is commonly seen in two types, fcc α-MoC_{1-x} and hcp β-Mo_2C, which possess different catalytic property [3]. Therefore studying the phase transformation mechanism between α-MoC_{1-x} and β-Mo_2C is beneficial for tailoring catalytic properties. α-MoC_{1-x} has an ABCABC packing of molybdenum atoms, whereas β-Mo_2C exhibits ABAB stacking sequence. The phase transformation from fcc to hcp structure can be realized by the passage of 1/6 <112> Shockley partial dislocation along alternate (111) plane in fcc structure. Figure 2 shows a HRTEM image of such a region. The indexation of the diffractrograms for

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regions A, B and C reveals α-MoC_{1-x} forms in A and B while β-Mo_2C develops in C. α-MoC_{1-x} in A and B forms a twin structure. The twinning plane is marked by Line 1. A Burgers circuit around the plane marked by Line 2 reveals closure failure in the <112> direction, which indicates the existence of Shockley partial dislocation (**b**=1/6 <112>) at the position indicated by arrow. This implies that Shockley partial dislocation induces fcc to hcp transformation in molybdenum atoms. A prominent structural feature of carbon in molybdenum carbide with fcc structure is to occupy octahedral sites sharing common edges. When fcc structure transfers to hcp structure, the connection of octahedral site changes from edge-sharing to face-sharing. A strongly repulsive interaction between carbon atoms would happen if carbon atoms occupy simultaneously two octahedral sites sharing a common face. Therefore, vacancies need to be introduced to carbon sublattice to accommodate such repulsive interaction. Obviously, large deviation from the stoichiometric composition in α-MoC_{1-x} provides such accommodation for the arrangement of carbon atoms in octahedral sites when phase transformation from fcc to hcp occurs in molybdenum atom arrangement.

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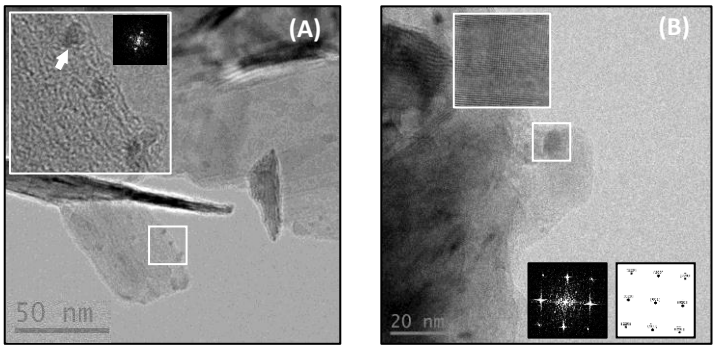

Figure 1 Bright field images of formed α-MoC_{1-x} NPs on MoS_2 slabs.

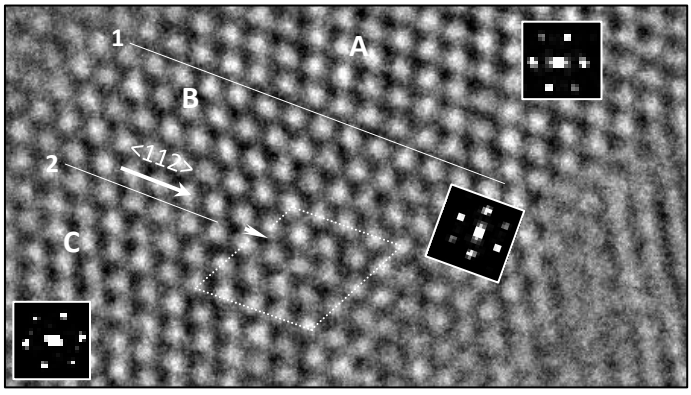

Figure 2 HRTEM image of a region where α-MoC_{1-x} and β-Mo_2C form. A Burgers circuit around the plane marked by line 2 reveals closure failures in the <112> direction.

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