Atomic force microscope observation of MoS₂ particles synthesized on mica, MoS₂, and graphite

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Nanometer-sized particles of molybdenum oxide were thermally deposited and then sulfided on mica, MoS₂, and highly oriented pyrolytic graphite (HOPG) to simulate MoS₂ catalysts for the hydrodesulfurization reaction of petroleum. The topography of the particles observed by AFM reflected the interaction force dominant at the particle-substrate interfaces. Oxide particles ionically interacted with mica which restricted the mobility of the deposit and led to particles smaller in lateral dimension, whereas aggregated oxide was observed on the other non-ionic substrates. Basal-bonded MoS₂ crystals were observed on the three substrates when sulfided at 673 K. [DOI: 10.1380/ejsnt.2003.80]

Keywords: Atomic force microscopy; Mica; MoS₂; HOPG

I. INTRODUCTION

Molybdenumdisulfide (MoS₂) has been widely used as an industrial catalyst for the hydrodesulfurization reaction of petroleum [1] and as solid lubricants [2, 3]. Nanometer-scale topography of MoS₂ particles deposited on a solid surface is of vital importance in those applications. The activity and selectivity of catalysts are thought to be sensitive to the morphology of MoS₂ clusters synthesized on various supports [4-11]. For example, MoS₂ clusters edge-bonded to substrate were synthesized on Al₂O₃ [7, 8] and TiO₂ [9] and exhibited an improved activity in the hydrogenation reaction of methylnaphthalene in comparison with basal-bonded clusters [10].

MoS₂ deposited on graphite [12, 13] and on gold [14-16] was observed by scanning tunneling microscopes (STM). In the present study, nano-sized particles of molybdenum oxide were thermally deposited and then sulfided on mica, MoS₂, and highly oriented pyrolytic graphite (HOPG) to simulate the catalysts. The cleaved surface of the lamellar substrates is atomically flat and thus provides an advantage for observation by atomic force microscopy (AFM). Mica represents oxide supports frequently employed in industrial catalysts, while HOPG simulates activated carbon as another catalyst support [17-19]. In addition to the purpose of modeling catalysts, it is interesting to compare the structure of the MoS₂ synthesized on MoS₂ and on HOPG. Deposited particles are captured via van der Waals force on the two substrate. When van der Waals interaction is dominant at the deposit-substrate linkage, the morphology of the deposits is thought to be sensi-

tive to a subtle mismatch in lattice constant of the deposit and substrate as seen in the heteroepitaxial growth of metal-dicalcogenides [20-22], III-V compound semiconductors [23, 24], and C₆₀ [25] on MoS₂.

II. EXPERIMENTAL

Single crystal substrates, mica (Furuuchi Chemical Corporation), MoS₂ (molybdenite from nature), and HOPG (Advanced Ceramics Corporation, STM-1) were cleaved in air. The substrates maintained at room temperature were exposed to molybdenum oxide vapor from a Knudsen cell at 783 K. The thickness of the oxide film was controlled to be 0.013 nm by referring to a quartz oscillator. The oxide was then sulfided with H₂-balanced 5%-H₂S gas (1.0×10^5 Pa) at 473 and 673 K for 30 min each. An atomic force microscope (Jeol, JSPM-4200) was operated in the contact mode. Constant force topography of the surface was observed in a vacuum (5×10^{-4} Pa) at room temperature. A SiN₄ cantilever with a small spring constant of 0.02 N/m (Olympus, OMCL-TR400PSA-1) was employed with a small load of 10^{-11} N to minimize tip-induced perturbation in the topography.

III. RESULTS AND DISCUSSIONS

Figure 1 shows the AFM topography (500×500 nm²) of mica at each stage of synthesis. On the cleaved surface atomistic corrugations consistent to the crystallographic periodicity were resolved (not shown). Very small particles appeared on the oxide-deposited surface in (a). The lateral diameter and vertical corrugation of the particles were less than 2 nm and 0.2 nm, respectively. By sulfidation at 473 K they sintered each other to yield particles of 0.4 nm in height, as seen in (b). The substrate uncovered with the sintered particles was still covered with residuals,

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FIG. 1: Constant force topography of a cleaved mica surface (a) exposed to molybdenum oxide vapor, then sulfided at (b) 473 K and (c) at 673 K. Image size: $500 \times 500 \text{ nm}^2$. Cross sections determined on the lines in (a), (b), and (c) are presented in (d), (e), and (f), respectively.

and the atomistic corrugations could not be resolved. Sulfidation at a higher temperature, 673 K, yielded particles of 0.7 nm in height in (c). This height of the particles is consistent with the thickness of one set of S-Mo-S layers of MoS_2 crystals. The thickness of one S-Mo-S layer of MoS_2 crystal is 0.615 nm. The regulated height hence suggests that the sulfidation at 673 K provides MoS_2 particles with their basal plane lying on the substrate.

Deposited oxide on the MoS_2 substrate shown in Fig. 2 (a) exhibited particles larger than those on the mica. The height of the oxide particles exceeded 2 nm. The large amount of noise seen in the image indicates that the scanning tip brought the particles weakly bound to the substrate. Sulfidation at 473 K affected little the topography of the particles as shown in (b). When sulfided at 673 K in (c), the particles were dispersed to a smaller area. A majority (more than 90 %) of the 673-K sulfided particles were 0.6 nm high and again assigned to MoS_2 crystals basal-bonded to the substrate. Small amount of the particles ($\sim 3\%$) was 1.2 nm in height from statistic analysis of 292 clusters.

Molybdenum oxide deposited on HOPG presented large particles as well as that on MoS_2 . The particles also show

FIG. 2: Constant force topography of a cleaved MoS_2 surface (a) exposed to molybdenum oxide vapor, then sulfided at (b) 473 K and (c) at 673 K. Image size: $500 \times 500 \text{ nm}^2$. Cross sections determined on the lines in (a), (b), and (c) are presented in (d), (e), and (f), respectively.

a dendritic aggregation in the AFM image of Fig. 3 (a). The dendritic aggregation of a deposited material indicates its mobility on the surface as known in antimony and gold clusters on HOPG [26]. Molybdenum oxide impinging from the gas phase should have migrated over the graphite surface until quenched, because our time-lapse AFM imaging revealed no mobility of oxide particles in the aggregated dendrites. The height of the particles ranged from 0.5 nm to 2 nm. A dendritic feature was reserved upon sulfidation at 473 and 673 K. The distribution of the particle height was narrowed to 1.5-2 nm at 473-K sulfidation and regulated at 1.2 nm at 673-K sulfidation. The regulated height of 1.2 nm agreed with the double thickness of the MoS_2 crystal.

On the basis of the above observations, the synthesis of MoS_2 particles is summarized in Fig. 4. Molybdenum oxide deposited and sulfided on rutile TiO_2 single crystals was investigated by Auger electron spectroscopy and transmission electron microscopy [27, 28]. Raising the sulfidation temperature promoted the exchange of oxygen by sulfur. Sulfidation at 673 K was required to completely break the Mo-O-Ti linkage at the $\text{MoO}_x/\text{TiO}_2$ interface and to crystallize MoS_2 particles. This result is consistent

FIG. 3: Constant force topography of a cleaved HOPG surface (a) exposed to molybdenum oxide vapor, then sulfided at (b) 473 K and (c) at 673 K. Image size: $500 \times 500 \text{ nm}^2$. Cross sections determined on the lines in (a), (b), and (c) are presented in (d), (e), and (f), respectively.

with the AFM observations mentioned above.

The size (height and width) of the MoO_x particles was smaller on mica than on MoS_2 and HOPG. Electrostatic force among the ionic atoms of mica and of MoO_x restricted the mobility of the oxide. Particles incompletely

sulfided at 473 K were still dispersed over the surface due to the ionic force. The complete sulfidation and sintering at 673 K resulted in one-layer-thick MoS_2 crystals basal-bonded to the substrate. On the other two substrates, oxide particles should have been adsorbed with the van der Waals force. The expected mobility of the oxide led to the aggregated particles. The aggregated oxide was dispersed along the sulfidation. A homoepitaxial relationship was expected on MoS_2 substrate, though atomistic corrugations on the 673-K sulfided MoS_2 particles were not observed. On HOPG, mismatch of the hexagonal lattice constant (0.316 nm of MoS_2 vs. 0.246 nm of HOPG) prohibited the homoepitaxial growth. It is of interest to note how the double-layer-thick MoS_2 crystals are created on this substrate.

These results demonstrate the feasibility of atomic force microscopy to visualize model catalysts containing nanometer-scale particles. The choice of the lamellar substrates caused a remarkable difference in the size and shape of MoO_x thermally deposited and then sulfided. These results can be utilized in designing hydrotreating catalysts of improved activity and in better understanding van der Waals epitaxy on the lamellar substrates.

FIG. 4: MoS_2 particles synthesized on (a) mica, (b) MoS_2 , and (c) HOPG.

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