Microscope Observation of MoS₂ Nanoparticles Synthesized on Rutile TiO₂ Single Crystals

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Nanometer-sized particles of MoS₂ were synthesized on (100), (001), and (110) surfaces of rutile TiO₂. Molybdenum oxide was deposited on the TiO₂ substrates and then sulfided to simulate the preparation of industrial catalysts. The nanoparticles which appeared on the sulfided surfaces were assigned to MoS₂ particles. The topography of the nanoparticles was observed by atomic force microscopy (AFM) and by transmission electron microscopy (TEM). The number density of the nanoparticles was related to the surface energy of the substrates through the population of nucleation centers. On the TiO₂(110) surface, AFM and TEM images assignable to MoS₂ crystals edge-bonded to the substrate were observed. The coincidental lattice spacings of MoS₂ and this particular surface were related to the observed edge-bonded growth. [DOI: 10.1380/ejsnt.2004.32]

Keywords: Atomic force microscopy; Transmission electron microscopy; MoS₂; TiO₂; Nano structure chemistry, processing and fabrication

I. INTRODUCTION

MoS₂-based catalysts have been intensely investigated for the hydrodesulfurization (HDS) reaction of petroleum [1]. It has been claimed that the aspect ratio (height vs. width) of MoS₂ nanoparticles supported on a substrate controls the selectivity of the reaction, *i.e.*, the HDS or hydrogenation [2,3]. MoS₂/Al₂O₃ catalysts promoted with cobalt additives present more advanced catalytic performances. It also has been pointed out that on Co-promoted catalysts, the CoMoS-II phase cluster of a multilayered structure is more active than the CoMoS-I phase of a single-layer structure [4,5]. In addition, the role of MoS₂ crystals edge-bonded to the substrates has been debated [6-8]. Recently, edge-bonded particles have been found on γ -Al₂O₃ [9,10] and anatase TiO₂ [11,12] substrates by transmission electron microscopy (TEM). These edge-bonded particles showed improved activity for hydrogenation [12]. Therefore, a method for making various figures of MoS₂ clusters is needed to control catalytic reactions. It is important to understand the 3-D topography of supported MoS₂ nanoparticles. Handling real catalysts is one of the advantages of TEM, while information on the cluster height is limited. Scanning probe microscopy (SPM) is a powerful method to deduce the 3-D topography of nanoparticles supported on a flat substrate. Macroscopic crystals of MoS₂ have been frequently observed by scanning tunneling microscopy (STM) as a substrate of compound semiconductors [13-17], as a conductive support of metal clusters [18], and as a model

catalyst for the HDS reaction [19,20]. MoS₂ nanoparticles have been observed by STM on graphite [21,22] and on gold [23-25] substrates. Atomic-scale topography of triangular-shaped MoS₂ was resolved on the latter substrate. In the present study, we chose rutile TiO₂ as the substrate to construct a more realistic model of industrial MoS₂ catalysts supported on metal oxides. Nanoparticles of MoS₂ were synthesized on (100), (001), and (110) single-crystalline surfaces of rutile TiO₂ and observed by atomic force microscopy (AFM) and by TEM, as an extension of our earlier works [9,26]. Molybdenum oxide was deposited on the TiO₂ substrates and then sulfided to simulate the preparation of industrial catalysts.

II. EXPERIMENTAL

One-side polished single-crystalline substrates of rutile TiO₂ (Shinkosha, 10 × 10 × 0.5 mm³) were used as substrates. The preparation method of the MoS₂ model catalyst on these substrates was described elsewhere [9,26]. Molybdenum oxide was vacuum evaporated from a Knudsen cell at 783 K to the substrate which was maintained at room temperature. The thickness of the deposited film was controlled to be 0.3 nm by referring to a quartz oscillator. The deposited samples were oxidized with O₂ gas (1.3 × 10⁻³ Pa) at 673 K for 30 min and then sulfided with H₂-balanced 5%-H₂S gas (1.0 × 10⁵ Pa) at 673 K for 30 min.

The topography of the sulfided samples was observed with an AFM (Jeol, JSPM-4200) under a vacuum (5 × 10⁻⁴ Pa) at room temperature using a SiN₄ cantilever (Olympus, OMCL-TR400PSA-1). The 3-D scale of the microscope was calibrated on HOPG (Advanced Ceramics, STM-1) and MoS₂ wafers. Constant force topography determined in a contact mode is presented in a gray scale.

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FIG. 1: Constant force topography of the model catalyst prepared on a $\text{TiO}_2(100)$ surface. (a): a surface before the MoO_x -deposition, (b): the surface of (a) following the MoO_x -deposition and oxidation at 673 K, (c) the surface of (b) sulfided at 673 K. Image size: $500 \times 500 \text{ nm}^2$. The cross sections determined on the lines in (a), (b), and (c) are presented in (d), (e), and (f).

TEM (Topcon EM-002B) observation was performed at 200 kV with a point resolution of 0.19 nm on the substrates, which were prepared by using a combination of punching, grinding, and ion-milling techniques [27].

III. RESULTS AND DISCUSSION

A. AFM observation

Figure 1 shows 500-nm-square AFM images of the $\text{TiO}_2(100)$ sample following the fabrication steps. The surface as received (washed by supersonic wave in acetone before use) (a) was flat with vertical corrugations less than 0.6 nm as shown in cross section (d). Molybdenum oxide was thermally deposited on the surface of (a) and oxidized at 673 K. The topography (b) and cross section (e) of the oxidized surface remained flat, indicating the TiO_2 substrate was homogeneously coated with molybdenum oxide. Similarly, a flat topography of the MoO_x layers was observed on $\text{TiO}_2(001)$ and (110) substrates

FIG. 2: Constant force topography of the sulfided model catalysts prepared on (a) (100), (b) (001), and (c) (110) surfaces of rutile. Image size: $1 \times 1 \mu\text{m}^2$. The cross sections determined on the lines in (a), (b), and (c) are presented in (d), (e), and (f).

(not shown). This is consistent with the epitaxial growth of MoO_2 found on these TiO_2 substrates [26]. The O/Mo atom ratio of the oxide-covered samples was determined to be 2 by Auger electron spectroscopy (AES). MoO_2 of a distorted rutile structure was proposed to epitaxially crystallize with Mo-O-Ti linkages along the following orientations,

on the basis of reflection high-energy electron diffraction (RHEED) [26]. Nanometer-sized particles appeared when the oxide-covered (100), (001), and (110) surfaces were sulfided. The topography of the sulfided (100) surface is shown in (c). These particles should have been assigned to the MoS_2 nanoparticles of composition, because the S/Mo atom ratio was determined at 1.9 on a similarly treated $\text{TiO}_2(100)$ substrate [26]. The size and number density of the MoS_2 nanoparticles were examined on wide-area scans and are described in the next paragraph. Corrugations on the flat plane other than the nanoparticles remained less than 0.6 nm. The amount of deposited

FIG. 3: The distribution of the topographic height of the MoS₂ nanoparticles on the (100) (white bar), (001) (gray bar), and (110) (dark bar) surface of rutile.

Mo (equivalent to an oxide thickness of 0.3-nm) was involved much more in the clusters as excess MoS₂ than the nanoparticles of MoS₂ composition. We thus assumed that the excess MoS₂ yielded clusters of sub-nanometer sizes and were spread over the plane among the nanoparticles. Those sub-nanometer clusters which directly interfaced with the TiO₂ substrate may have been incompletely sulfided [26]. Incompletely sulfided clusters which were anchored to TiO₂ substrates via Mo-O-Ti linkages were also observed by EXAFS [28] and XPS [29].

Figures 2(a), (b), and (c) show 1- μm -square AFM images of the MoS₂ nanoparticles which were synthesized on the (100), (001), and (110) substrates. The population and topographic height of the particles were sensitive to the orientation of the substrates. The number density of the MoS₂ nanoparticles was statistically determined based on a number of observations with values of 2.8×10^{-5} , 6.8×10^{-6} and $1.4 \times 10^{-6} \text{ nm}^{-2}$, respectively (Table 1). The height of the particles was measured on cross sections, a fraction of which are presented in (d)-(f). The distribution of the particle height is summarized in the bar-graph of Fig. 3. On the (001) substrate more than 80% of the particles fall in the 2-nm segment. The average height is listed in Table 1.

The number density of the nanoparticles is related to the surface energy of the substrates. A substrate with a larger surface energy yields more particles. The particles should be nucleated on singularities (steps, vacancies, etc.) of the single crystalline substrates. It is expected that the creation of those singularities is enhanced on a surface of large surface energy. When the total MoS₂ quantity available for the particle formation is the same on the three substrates, the maximum particle size should be found on the surface with the least number of particles. This was the case on the (110) substrate in Table 1.

On the other hand, the sub-nanometer clusters assumed in the interpretation of Fig. 1 may remain as Mo-O-Ti linkages to the substrates and may be restricted in surface

FIG. 4: Zoomed-up AFM topography of MoS₂ nanoparticles synthesized on the rutile (110) substrate. Image size: $1 \times 1 \mu\text{m}^2$.

mobility. The S/Mo ratio determined by our AES analysis [26] exhibits the lowest number, 1.5, on the (110) substrate. This suggests the Mo-O-Ti linkages on TiO₂(110) in particular resist being sulfided. The stability of the MoO₂/TiO₂ interface is possibly sensitive to the atomistic structure of the linkages rather than to the surface energy of the uncovered surface.

Indeed a characteristic feature of the nanoparticles synthesized on the (110) substrate was observed; oval and elongated shapes as shown in the zoomed-up topography of Fig. 4. The elongated axis of each nanoparticle was parallel to the [001], $[1\bar{1}0]$, or $[\bar{1}12]$ direction of the substrate. How the nanoparticles were aligned on the (110) substrates was examined by TEM.

B. TEM observation

Figure 5 shows the TEM image of model catalysts prepared on (110) and (100) substrates sulfided at 773 K. Short, dark rows were observed on the (110) substrate in (a), whereas only a few were recognized on the (100) substrate in (b). Most particles were fully sulfided on TiO₂(100) surface (Table 1). Basal-bonded MoS₂ clusters should be grown on TiO₂(100) during the sulfidation. However, it is difficult to image basal-bonded clusters by TEM [8]. Typical examples of the rows are pointed by white arrows in (a). Similar dark rows have been observed on MoS₂ supported on γ -Al₂O₃ [7-9, 27] and anatase TiO₂ powders [11] and assigned to the side-viewed Mo planes of MoS₂ crystals edge-bonded to the substrates. As shown in the zoomed images of (c), (d), and (e), the crystal plane of the edge-bonded clusters was oriented parallel to the [001], $[1\bar{1}0]$, and $[\bar{1}12]$ directions. The preferred directions observed by AFM (Fig. 4) and TEM (Fig. 5) were consistent. The length and layer-thickness of the edge-bonded cluster ranged from 1-3 nm and 1-3 layers in the TEM images, whereas its height ranged from 4-6 nm as shown in the AFM results.

On the basis of the atomically resolved TEM images of Fig. 5, Fig. 6 illustrates possible alignments of the edge-bonded MoS₂ cluster with its crystal planes parallel to the (a) [001], (b) $[1\bar{1}0]$, or (c) $[\bar{1}12]$ direction. Since the S/Mo atom ratio was lower (1.5) as shown in Table 1, some Mo atoms in the cluster were assumed to replace Ti atoms at the surface to make stable Mo-O-Ti linkages. The analysis has been successfully applied to the MoS₂/ γ -Al₂O₃ single crystal thin film [9,27] and

TABLE I: Statistics of MoS₂ nanoparticles synthesized on rutile surfaces. ^a: from [30]. ^b: determined by AES [26].

Orientation	TiO ₂ (100)	TiO ₂ (001)	TiO ₂ (110)
Number density (nm ⁻²)	2.8×10^{-5}	6.8×10^{-6}	1.4×10^{-6}
Topographic height (nm)	3.0	2.3	5.2
Surface energy (Jm ⁻²) ^a	2.08	2.40	1.78
S/Mo atom ratio ^b	1.9	1.8	1.5

FIG. 5: TEM image of the model catalysts sulfided on the (a) TiO₂(110) (41×41 nm²) and (b) TiO₂(100) (34×34 nm²) substrates. (c)-(e): Magnified image of individual MoS₂ particles edge-bonded to the (110) substrate.

MoS₂/anatase TiO₂ nano-crystal [11] systems. The distance between the two Mo planes was fixed at 615 pm. A MoS₂ crystal truncated normal to its [10 $\bar{1}$ 0] direction (316 pm of inline Mo-Mo distance) was interfaced to the TiO₂ surface. These structures contained lattice mismatches less than 9%, which are summarized in Table 2. The mismatches likely induced some edge-bonded crystals in Fig. 5 which caused them to bend. The results suggest that the edge-bonded MoS₂ cluster can be synthesized using lattice matching of the interface where the incomplete sulfided Mo-O-Ti bond is situated. We have reported evidence of an edge-bonded MoS₂ cluster on γ -Al₂O₃ and anatase TiO₂ by a TEM study. The present study of the rutile TiO₂ surfaces suggests that the edge-bonded MoS₂ generally grew as the result of the lattice matching be-

tween a cluster and a substrate.

IV. CONCLUSIONS

MoS₂ nanoparticles were synthesized on rutile (100), (001), and (110) surfaces via the deposition of molybdenum oxide and subsequent sulfidation to simulate the preparation of industrial catalysts. The number density of the sulfide nanoparticles was related to the surface energy of the substrates through the population of nucleation centers. Edge-bonded MoS₂ crystals were yielded on the (110) surface. The coincident lattice spacings of the deposit and the particular substrate allows effective linkage of Mo-O-Ti at the interface and results in the edge-

FIG. 6: Possible arrangements of MoS₂ crystals edge-bonded to the TiO₂(110) substrate. MoS₂ crystals were placed on the TiO₂(110) surface as a mismatch of period between Mo and Ti atoms was made into the minimum. The Mo planes are parallel to the (a) [001], (b) [110], and (c) [112] direction of the substrate.

TABLE II: Comparison of lattice mismatches between MoS ₂ crystal and rutile TiO ₂ (110) surface			
Alignments of MoS ₂	[001]	[110]	[112]
Inline Mo-Mo (316 pm)	+6.8%	-2.8%	+8.5%
Mo planes (615 pm)	-5.4%	+3.9%	-6.3%

bonded growth.

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