Crater structures on a molybdenite basal plane observed by ultra-high vacuum scanning tunneling microscopy and its implication to hydrotreating

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Abstract

Atomic structure of a natural molybdenite (MoS_2) single crystal basal plane was examined by ultra-high vacuum scanning tunneling microscopy (UHV-STM). Numbers of crater structures with diameters ranging from 5 to 9 nm were observed on pristine as well as on high-temperature (473 K) resulfided surfaces. Atomic structures within these craters were continuous from the surrounding terrace, with no step structures at the rims of the craters. Atoms in the bottom of the craters showed higher corrugations compared to the terrace atoms, indicating higher electronic density of states in the craters. Its implication on hydrotreating activity over curved MoS_2 nanoparticles is discussed.
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1. Introduction

Hydrodesulfurization (HDS) catalysts have been receiving increasing attentions because of severer legislative movements toward cleaner fuels [1,2]. Supported Mo or W sulfide promoted by Co or Ni has been and is the main component of industrial HDS catalysts [3].

It is well recognized that the morphology of MoS_2 particles, in particular the stacking structure of MoS_2 basal layers, determines the catalytic selectivity for hydrogenation and HDS of Mo-based HDS catalysts. Daage and Chianelli [4] suggested, with their "rim-edge" model, that the rim sites (edges of the outermost layers) of MoS_2 particles are active for both hydrogenation and direct HDS, while the edge sites (edges of interior layers) are responsible only for direct HDS. Nishijima et al. [5] also proposed a similar

structure-reactivity relation for supported MoS_2 nanoparticles.

Another fine structure of MoS_2 nanoparticles that may be relevant to their catalysis is their curved structures often observed by transmission electron microscopy (TEM) [3,6]. Those MoS_2 nanoparticles often show worm-like TEM images, which are considered to be a stack of MoS_2 basal layers viewed parallel to the basal plane. Topsфe et al. [3] proposed their structural model as a stack of atomically smooth curved basal planes. On the other hand, Iwata et al. [6] suggested, in their 1-methylnaphthalene hydrogenation study over unsupported MoS_2 particles, that such a curved structure introduces "inflection" to the otherwise flat basal surface, which then functions as a "rim-edge" proposed by Daage and Chianelli. Thus, two types of models have been proposed for the curved structure of supported or unsupported MoS_2 nanoparticles, while no further study has been done because of difficulties in its characterization using conventional techniques.

Recently, a new approach to HDS catalyst study has emerged, i.e. a surface science approach using model catalysts. By means of scanning tunneling microscopy (STM), Besenbacher and coworkers have succeeded in observing

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atomic scale structures of single-layer MoS$_2$ triangular nanoclusters fabricated on a herringbone-reconstructed Au(1 1 1) surface [7–10]. They showed that the edges of the triangular clusters are composed of reconstructed S edges [7]. They further found that there exist one-dimensional metallic states close and parallel to the edges of these triangular clusters, manifested as higher atomic corrugations [8]. Thiophene adsorption was examined on the H$_2$-adsorbed clusters, and the results were analyzed with the aid of density functional (DFT) calculations [10]. Kushmerick and Weiss [11] studied, also by means of STM, the mobility of Ni atoms on the basal plane of MoS$_2$. These model catalyst approaches promise more detailed understanding of hydrotreating catalysts through atomic level characterization.

In the present study, we report an ultra-high vacuum (UHV) STM observation of unusual "crater" structure on the basal plane of natural MoS$_2$ crystals (molybdenite) heretofore unreported. The structure is compared with a curved structure of supported MoS$_2$ nanoparticle hydrotreating catalysts observed by high resolution TEM, and its relation to the catalytic HDS reaction is discussed.

2. Experimental

A natural MoS$_2$ crystal (molybdenite) obtained from Climax Molybdenum Development Co. was employed in the present study. The sample was mounted on a heatable sample holder, cleaved under ambient conditions in order to expose a clean basal plane, and immediately placed in the loading dock of a UHV-STM. After the loading chamber is evacuated to 5.0×10^{-6} Pa, a mixture of H$_2$ and H$_2$S (95:5) is admitted at a level of $(1.3-2.7) \times 10^4$ Pa. Sample is then heated at a rate of 5.5 K/min to 473 K, kept at the temperature for 1 h in order to resulfide the crystal, and then the chamber is evacuated back to 5.0×10^{-6} Pa. After cooling down to room temperature, the sample is transferred to the analysis chamber that is kept at a base pressure of 1.0×10^{-8} Pa for STM examinations.

The above-described resulfidation procedure was taken here as a precautionary measure, since some part of the crystal may be oxidized due to a prolonged exposure to ambient atmosphere. A pronounced difference due to resulfidation, however, was found at step edges [12], and the crater structures discussed here showed no apparent differences between the pristine and the resulfided surface, and the resulfidation process may be considered irrelevant as far as the present paper is concerned.

Scanning tunneling microscopy observations were made using UNISOKU UHV-STM, with vertical and lateral resolutions of 0.02 and 0.1 nm, respectively. Surface scanning was performed in constant current mode, with mechanically formed Pt–Ir tip.

In order to compare the single crystal structure with that of supported catalysts, MoS$_2$ supported on γ-Al$_2$O$_3$ at a level of 9.1 wt.% Mo was prepared through a conventional method,

and its structure was examined by TEM. The MoS$_2$/γ-Al$_2$O$_3$ powder sample was evacuated, sealed in a glass tube, and then in a glove-bag filled with N$_2$ gas to avoid the contact with air, was suspended in acetone and placed on a TEM specimen grid. The sample grid was transferred in a stream of N$_2$ to a sample holder attached to the microscope. Images of supported MoS$_2$ particles were taken with a JEM-2010 electron microscope at an accelerating voltage of 200 keV. Further details of TEM measurements were found elsewhere [13,14].

3. Results

Scanning tunneling microscopy observations revealed that the present molybdenite surface mostly consists of flat (0 0 0 1) basal planes, as commonly observed with STM. The present investigation, however, found an interesting feature that has not been reported on MoS$_2$ surface: the surface showed numbers of apparent craters of the size of 5–9 nm. An example is given in Fig. 1(a) which shows an STM image of an area of 100 nm × 100 nm with high population of those apparent craters. A line scan shown in Fig. 1(b) along the dotted line in the center region of (a) indicates that these apparent craters have depth of 0.4 to 0.5 nm, less than the MoS$_2$ layer stacking height of 0.615 nm.

A striking feature of these crater structures is that they are not holes in the top basal plane of the sample, as may be
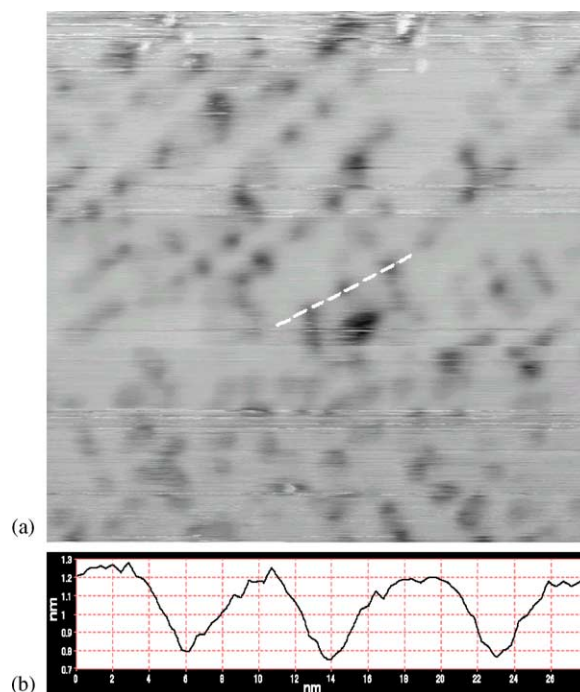

(a)

(b)

Fig. 1. (a) A 100 nm × 100 nm STM image of a resulfided MoS$_2$ basal plane showing high population of crater structures; (b) line scan along the dotted line in the center region of (a). The apparent craters have depth of 0.4–0.5 nm, which is less than the MoS$_2$ layer stacking height of 0.615 nm: $V_t = -0.55$ V; $I_t = 0.45$ nA.
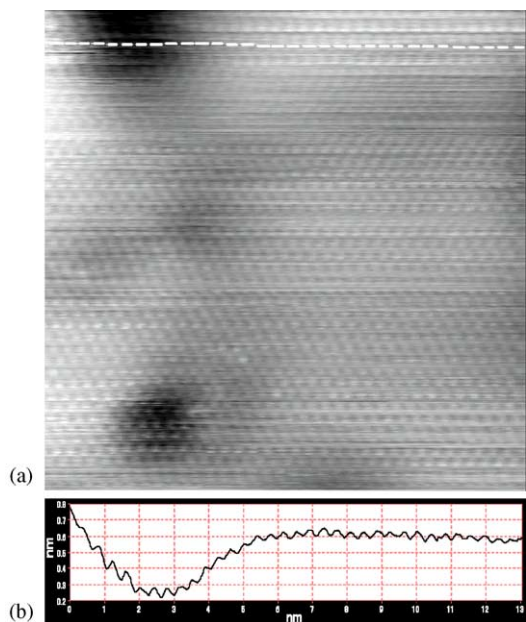
Fig. 2. (a) A 13 nm × 13 nm STM image of a resulfided MoS$_2$ basal plane, showing a hexagonal arrangement of S atoms; (b) line profile across the apparent crater area along the dotted line. The atomic array appears to be continuous from the terrace area into the crater with no disruptions nor apparent steps. Atomic corrugation in the crater appears to be larger than that on the terraces: $V_t = +0.1$ V; $I_t = 0.75$ nA.

Table 1
Atomic corrugations on the terraces and at the bottom of the craters

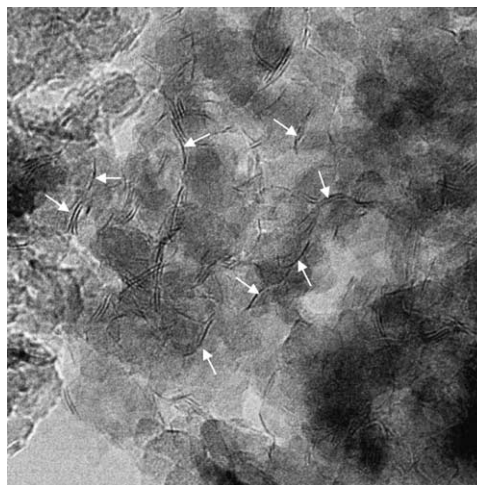| Position	Atomic corrugation (nm)
Terraces	0.042 ± 0.014
Crater bottoms	0.056 ± 0.025

Fig. 3. An 84 nm × 84 nm TEM image of γ-Al$_2$O$_3$-supported MoS$_2$, showing numbers of curved structures of MoS$_2$ nanoclusters as indicated by arrows.

conceived at the first glance, but are actually a continuous member of the top layer, only being concave at the crater positions. This is evidenced in a detailed STM scan of the structure shown in Fig. 2(a). This 13 nm × 13 nm STM image shows a hexagonal arrangement of atoms with the average atom–atom distance of about 0.33 nm, which corresponds to the expected S atom–atom distance of 0.316 nm on a MoS$_2$ basal plane. When a line profile across the apparent crater area is taken, as shown in Fig. 2(b), it is found that the atomic array continues from the terrace area into the crater, with no disruptions nor apparent steps at its rim, keeping regular atomic distance from the terrace area into the crater and back. This indicates that the apparent crater observed here is a curved concave structure of the top MoS$_2$ basal plane.

It is noted here that similar but distinctly different "ring" structures have been observed on natural MoS$_2$ by STM [15,16]. The reported "ring" structures are 1.5–4 nm in diameter, with the rings convex from the basal plane while their centers concave. Atomic arrangements are continuous from the basal plane through convex ring to concave center without disruptions [15].

Another striking feature of the apparent craters observed here is that the atomic corrugation in the craters is larger than that on the terraces. This is evident in Fig. 2(b) and also in Table 1 which compares average atomic corrugation on the terraces and in the craters observed in the present study.

Such a difference of atomic corrugation is obviously a reflection of electronic modification on the crater atoms, and will be discussed later in more detail.

Similar curved structures have been reported in an electron microscopic study of supported and unsupported MoS$_2$ catalysts [3,6]. We also obtained TEM images of γ-Al$_2$O$_3$-supported MoS$_2$, and an example is shown in Fig. 3. In the figure numbers of curved structures of MoS$_2$ nanoclusters, some of which are highlighted with arrows in the figure, are obvious.

In order to examine the similarities and/or dissimilarities between the STM-observed craters in resulfided natural molybdenite and the TEM-observed curved structures in Al$_2$O$_3$-supported MoS$_2$, the size and the curvature of the observed structures were measured in each image, and compared in Table 2. As may be apparent in the table, for a similar diameter d of a crater or a curved cluster, STM-observed craters show 1.3 to 2 times larger curvature values, R_c, than TEM-observed curved clusters, meaning that the crater structures on the present MoS$_2$ single crystals are less curved than the Al$_2$O$_3$-supported MoS$_2$ nanocluster particles.

Table 2
Curvature of STM-observed craters and TEM-observed curved structures

STM		TEM	
d (nm)	R_c	d (nm)	R_c
5.0	9.8	5.1	7.3
6.0	11.4	6.2	7.6
7.0	14.3	7.0	10.9
9.0	22.7	8.9	11.74

d: diameter of a curved structure or a crater; R_c: curvature.

4. Discussion

The first question that might arise regarding the present STM-observed crater structures on the molybdenite surface is that what might be the cause of these structures. In this regard, it is interesting to note that in the STM image shown in Fig. 1, those apparent craters are located on the surface in a fairly regular manner, lining up along certain directions. Two directions are obvious: on the upper left section of the image the direction is from upper right to lower left, and on the lower right section it is from upper left to lower right. This observation leads to a speculation that these apparent craters observed in the present study may be related to some crystal defect of the natural MoS_2 crystal.

There are no clues at this moment as to the origin and the nature of this possible defect. In the present natural molybdenite sample similar crater structures were observed on pristine (not resulfided) surfaces, indicating that the structures are inherent characteristics of the present sample. Heckl et al. [15] found a ring structure on a basal plane of a natural MoS_2, which showed continuous atomic structure from the terrace to throughout the ring structure. They suggested two possible causes for the structure: morphological one due to inclusion of organic or biological molecules when the mineral was formed, and electronic one due to substitutional point defects. The present crater structure reported here may be considered morphological, since the size range of the present structure is 2 to 6 times larger than the ring structures previously observed [15,16], and it is difficult to envision any electronic perturbation due to impurity point defects to effect such a large area.

On the assumption that the present crater structure is morphological, the detailed atomic structure of the crater seems to shed some light in the discussion of the curved structures of supported or unsupported MoS_2 particle [3,6]. For those curved nanoparticles which were also observed by TEM in the present study and shown in Fig. 3, Topsфe et al. proposed a model of a stack of atomically smooth curved basal planes [3], whereas Iwata et al. suggested that the a stack of basal planes are bent to make a hemispherical structure consisting of small flat sheets [6]. Apparently, the present STM data found in Fig. 2 side with the model by Topsфe et al., since our STM image also shows continuous curved atomic structure from the terrace region into the crater bottom.

If this is the case, then, how the enhanced hydrogenation activity over curved MoS_2 structures reported by Iwata et al. [6] be explained? For this we would like to point out the enhanced atomic corrugation within a crater area compared to that on terraces (cf. Table 1). Constant current STM images reflect isosurface of the local density of states (LDOS) on the surface. Thus higher corrugations in STM images mean higher LDOS on those atoms.

Although the reason for this increased LDOS is not apparent, it is highly likely that the crater structure introduces neighboring atomic environment different from that on the terraces, and this structural change such as dihedral angles

and nearest-neighbor distances inevitably brings about the associated changes in Mardelung potential which will alter the electronic band structures in the crater region.

Lauritsen et al. [10] found, in their STM and DFT investigation of thiophene adsorption on H_2-adsorbed MoS_2 clusters, that thiophene preferentially adsorbs on the high LDOS region of their MoS_2 model clusters. Their high LDOS region exists next to the rim of the clusters, consisting a one-dimensional metallic state [8]. While our high LDOS exist at the bottom of the crater structure, similar effects due to the increased electronic density on hydrogenation reaction may be expected.

At this point it is further noted that the present crater structure gives much larger curvature compared to supported MoS_2 clusters (cf. Table 2). Assuming that the curvature of the basal plane is the main cause of the observed LDOS increase, this electronic modulation due to curved structure may be even higher for the supported MoS_2 nanoclusters observed by TEM.

5. Conclusions

A UHV-STM study of a single-crystal MoS_2 basal plane found crater structures on its pristine and resulfided surfaces. The atomic structure in the crater is continuous from the surrounding terrace. Similarities of this structure with the TEM-observed curved structures of supported MoS_2 nanoclusters are noted. Atomic corrugation at the bottom of the crater was larger than those on the surrounding terrace, indicating the electronic perturbation on the atoms in the craters. Catalytic activity associated with the curved structures may be related to this electronic modulation.

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