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EM, ED AND EMX STUDIES ON MOLYBDENUM OXIDE USED AS A CATALYST

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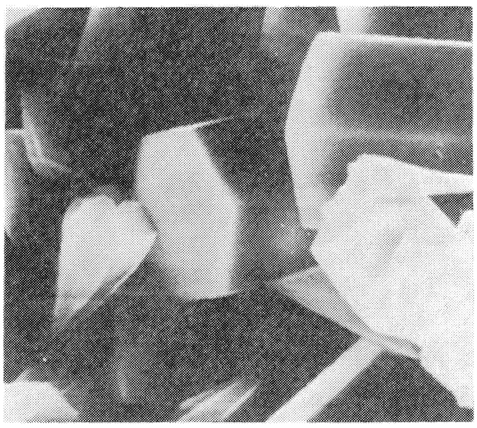
The needles appeared at the end of the crystal of molybdenum oxide used as a catalyst for hydrodesulfurization for 10 min at 350°C. They gradually grew and apparently stopped to grow after the 40 min reaction. The needles were produced in the presence of thiophene. They gave the ED pattern due to MoO_2. Also the catalyst was sulfurized uniformly all over the surface.

The hexagonal hydrate of molybdenum trioxide was used as a starting material. According to the X-ray studies, it has a hexagonal crystal structure with a lattice constant of a=6.09 Å and c=9.14 Å.1) Photograph 1 shows a scanning electron microgram.

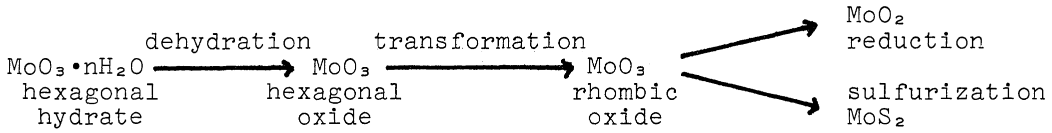
Time(min)	5	10	20	40
350°C	I+II	I+II	II+III	III
375°C	I+II	II+III	III	III
400°C	II+III	III	III	III

Table. The X-ray results of the catalyst after the reaction. I;hexagonal MoO_3(or hexagonal hydrate), II ;rhombic MoO_3, III; MoO_2.



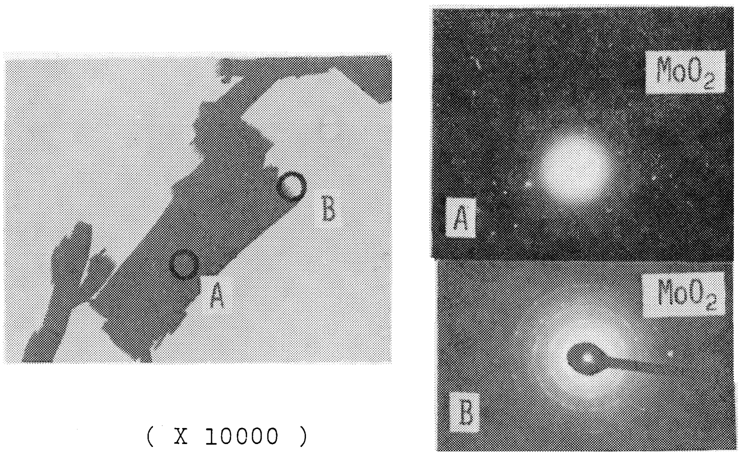
(X 6000)
Photo. 1. SEM image of the hydrate of molybdenum trioxide.

The hydrate was used as a catalyst for the hydrodesulfurization of thiophene at 350°, 375° and 400°C. The structural and compositional changes of the catalyst took place at the early stage of the reaction. In the previous papers,1,2) the authors studied the changes of the catalyst by X-ray diffraction analysis, DTA and other methods as shown in Table.1) The main reaction of the catalyst were the dehydration, transformation and reduction. While, accroding to chemical analysis, the catalyst was sulfurized and the sulfide was assumed to be MoS_2 under this reaction condition.2) Sulfur contents of the catalyst were about 5% and MoS_2 was possible to be detected by X-ray diffraction analysis. However, MoS_2 was not detected and assumed to be amorphous. The changes of the catalyst are as follows;



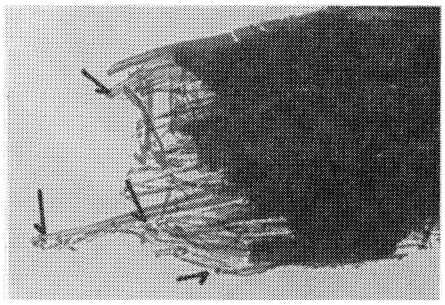
Photograph 2 shows a series of electron micrograms of the catalyst after used for the reaction at 350°C. The needles appeared at the end of the crystal by the 10 min reaction, gradually grew, and apparently stopped to grow after the 40 min reaction. Each needle grew up bigger at 400°C. The BET surface area of the hydrate before use was 3.4 m^2/g. The area increased to 8.6 m^2/g when the catalyst was used for 60 min at 350°C and to 8.0 m^2/g at 400°C. The increase in the surface area is attributable to the needles produced.

Photograph 3 shows ED pattern of the sample. The bulk of the crystal shows the ED pattern attributable to MoO_2 for the 60 min reaction at 350°C (Photo. 3A). On the other hand, the needles of the catalyst shows only the pattern due to MoO_2(Photo. 3B). Photograph 3B shows the ring pattern. However,



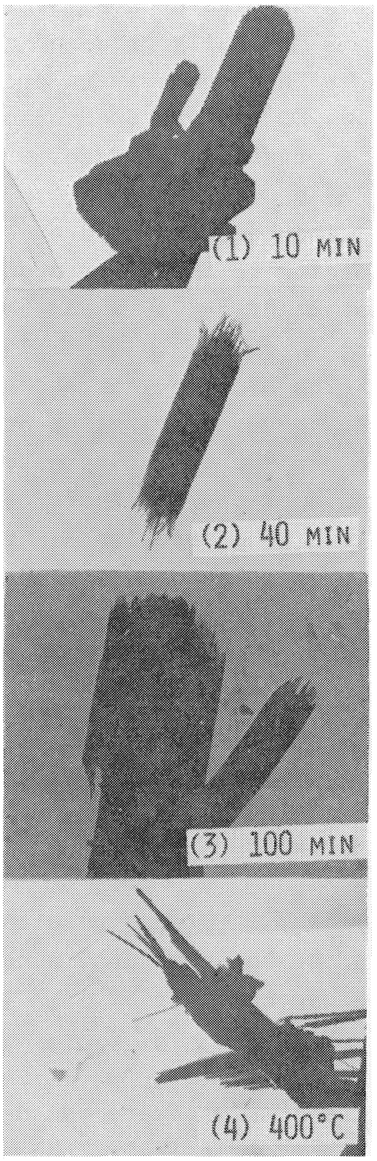
(X 10000)

Photo. 3. EM and ED images of the catalyst after the 60 min reaction at 350°C.



(X 40000)

Photo. 4. EM image of the needles.



(X 10000)

Photo. 2. EM images of the catalyst after the reaction at 350°C.

as the electron beam was not focussed on one of the needles, it is not clear whether the needle is the single crystal or the polycrystal.

There are two possible processes for the growth of the needles. One is the surface migration process, and the other, the evaporation-condensation process. Hashimoto3) reported that the ribons of molybdenum oxide were produced by the surface migration. According to Hashimoto, the drops of molybdenum oxide were produced on the surface, migrated and the ribons grew, when $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was decomposed at 700°C. Photograph 4 shows the magnification of the needles. Having observed the picture in detail, the drop like substances(arrowed) are recognized in the needles. This seems to show that the drop like substances migrated on the surface. The further investigation is in progress.

The hydrate was also reduced to MoO_2 by hydrogen. In this case, the needles were not observed by electron microscopy. While, the needles were produced in the presence of thiophene, as has been mentioned above. In addition to the above fact, the rate of sulfurization of the catalyst at 350°C slowed down at the 40 min reaction and was nearly zero at the 60 min reaction.2) On the other hand, the growth of the needles also stopped after the 40 min reaction, as described above. Therefore, this suggests that the presence of thiophene plays an important role for the growth of the needles. The mechanism of the formation of the needles in the presence of

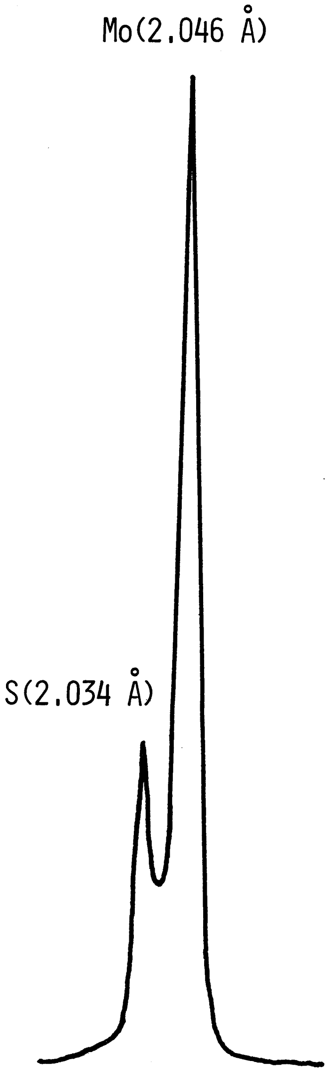


Fig. Spot analysis of the catalyst.

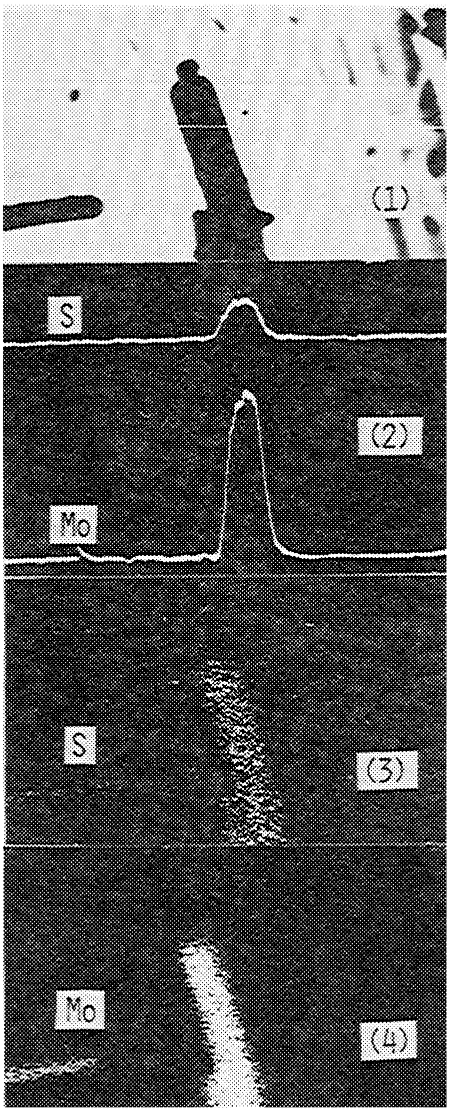


Photo. 5. EMX images of the catalyst after the 60 min reaction at 350°C. (1) SC image(X 5000), (2) X-line analysis, (3) Sulfur distribution, (4) Molybdenum distribution.

thiophene is not clear. However, it is considered that the presence of thiophene may easily produce moderately small drops of molybdenum oxide which can move on the surface.

During the hydrodesulfurization, sulfur content of the catalyst increased with the time of reaction and reached a steady value for 60 min at 350°C, as described previously.[2)] Sulfur content of the catalyst after the 60 min reaction at 350°C, when the needles apparently stopped to grow, was analyzed by the electron microprobe X-ray analysis(EMX). The wave lengthes of S $K\alpha_1$(2.034 Å) and Mo $L\alpha_1$(2.046 Å) were used to detect sulfur and molybdenum. They are very close to each other, but, from the result of spot analysis, two peaks of S $K\alpha_1$ and Mo $L\alpha_1$ were separated well as shown in Fig. The distributions of sulfur and molybdenum were studied by X-line analysis using S $K\alpha_1$ and Mo $L\alpha_1$ of X-ray radiation as shown in Photo. 5. The X-line for analysis was marked by a straight line on the SC image in Photo. 5. Also the surface distribution of sulfur was studied as shown in Photo. 5. These two pictures show that , for hydrodesulfurization of thiophene, the catalyst is not locally sulfurized as expected, but sulfurized uniformly all over the surface of the catalyst. Judging from the above pictures, it is considered that the needles were also sulfurized as well as the bulks were.

The sulfur contents of the catalyst for the 60 min reaction were 48 mg/g-catal at 350°C and 29 mg/g-catal at 400°C,[2)] respectively. Considering that the catalyst was uniformly covered with the sulfide, the average thickness of the sulfide was calculated from the values of the surface area of the catalyst and the density of bulk MoS_2 to be 11.7 Å at 350°C and 7.6 Å at 400°C.

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