Studies of the Molybdenum Catalysts. Part I. Changes in the State of the Hydrated Molybdenum Oxide Catalyst during a Reaction between Thiophene and Hydrogen

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(Received March 31, 1972)

The reaction between thiophene and hydrogen on hydrated molybdenum oxide was studied. Structural and compositional changes in the catalyst were found during the hydrodesulfurization of thiophene. The main products of the reaction were *n*-butane, butenes, and hydrogen sulfide. The conversion of thiophene increased with the progress of the reaction and reached a steady value after passing through a maximum. This reaction process was distinguished into two stages. One is the "aging stage," and the other is the "stationary stage." At the aging stage, three reactions, that is: i) dehydration, ii) reduction, and iii) sulfurization occur. The catalyst reacts with the reactants and changes in structure and composition. Hydrated molybdenum oxide was converted to MoO_3 by liberating the structural water, and MoO_3 was reduced to MoO_2. A part of the MoO_3 was also sulfurized directly with thiophene to MoS_2 during the aging stage, but MoO_2 could not easily be sulfurized. At the stationary stage, no further change in the catalyst was found, and only the catalytic hydrodesulfurization of thiophene occurred. The conversion at the stationary stage, when the aging temperature was low, was larger than the conversion at a high temperature. The difference between the conversions at different reaction temperatures was assumed to result from the structural and compositional changes in the catalyst caused by the different temperatures of the aging processes. In this reaction, the dehydration at the aging stage controls the activity of the catalyst.

The mechanism of the hydrodesulfurization of thiophene has been studied by a number of workers, and the findings up to 1957 have been reviewed by McKinley.[1] Recently, because of the industrial importance of the desulfurization of petroleum, very many workers have studied the hydrodesulfurization of thiophene on cobalt molybdate supported on alumina[2-4] as a model reaction for the desulfurization of petroleum, and several mechanisms have been proposed for the reaction.

In most of these works, catalysts have been activated and stabilized by pretreatment with hydrogen,[5] hydrogen sulfide,[3] or thiophene[2] before the kinetic measurements. However, only a little attention has been given to the structural changes in the catalyst during the reaction and to the relation between such structural changes and the activities.[4]

The purpose of this work is to obtain basic information about such structural and compositional chagnes in the hydrated molybdenum oxide catalyst during the hydrodesulfurization of thiophene and the relation between such changes and the activity of the catalyst.

As a catalyst, we used hydrated molybdenum oxide powder, without any promoter and supporter, in order to avoid the complexity introduced by the addition of these substances.

In this investigation, the structural and compositional changes in hydrated molybdenum oxide during the hydrodesulfurization of thiophene were investigated by means of chemical, X-ray diffraction, and thermal analyses. We also tried to learn how the structural and compositional changes influence the activity of the catalyst.

Experimental

A usual flow method was used for the reaction. The reactants and products were analyzed by means of gas chromatograph directly connected to the flow line. Hydrogen purified by passing through the platinum catalyst and molecular sieves flowed at a rate accurately controlled to 0.1 mol/hr by means of a needle valve and an auxiliary regulator. The flow rate was measured by means of a rotor meter and a soap film meter. Thiophene was fed as a liquid to the evaporator by means of a calibrated hypodermic pump. The feed rate of the thiophene, 1.4×10^{-2} mol/hr, was so small compared with that of hydrogen that the partial pressure had no effect on the reaction. A small amount of benzene, 1×10^{-3} mol/hr, was used as a marker, because benzene did not decompose under the reaction conditions.

Catalyst. (A) Hydrated molybdenum trioxide, $MoO_3 \cdot nH_2O$, was precipitated from a solution of ammonium molybdate by the addition of HNO_3. The precipitate was dried at 110°C for a day and was then calcined in air at 200°C for 6 hr. By differential thermal analysis (DTA) and thermogravimetric analysis (TGA), this oxide was found to be a hydrate of molybdenum trioxide. The water included in this oxide was kept at 400°C. This water was assumed to be a structural water. When this hydrated molybdenum oxide was left standing in a desicator, it absorbed about 0.26 mol of water, which was easily removed by heating at 200°C. This was physically-absorbed water.

(B) Anhydrous molybdenum trioxide, MoO_3, was prepared from hydrated molybdenum oxide by calcination in air at 600°C for 6 hr.

(C) Anhydrous molybdenum dioxide, MoO_2 was formed by reducing hydrated molybdenum oxide with hydrogen at 450°C for 5 hr.

(D) Molybdenum disulfide, MoS_2, was purchased from Wako Chemical Industries.

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[1] J. B. McKinley, "Catalysis," Vol 5, ed by P. H. Emmett, Reinhold Publishing Corporation, New York (1957), p. 405.

[2] P. J. Owens and C. H. Amberg, Advances in Chemistry Ser., No. 33, p. 182 (1961).

[3] Charles N. Satterfied and G. W. Roberts, *AIChE J.*, **14**, 159 (1968).

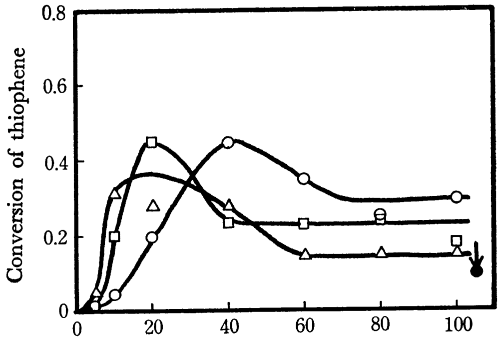
[4] J. M. J. G. Lipsh and G. C. A. Shuit, *J. Catal.*, **15**, 179 (1969).

[5] K. Toyoda and M. Kurita, *Shokubai*, **11**, 115P (1969).

The analysis of the sulfur content of the catalyst after the reaction was done gravimetrically by the $BaSO_4$ methods.[6]

Results

Conversion of Thiophene. Hydrated molybdenum oxide (1 gram) was used as the catalyst. To begin with, the catalyst was heated at a reaction temperature, of 350, 375, or 400°C. Then the reactants were introduced over the catalyst.

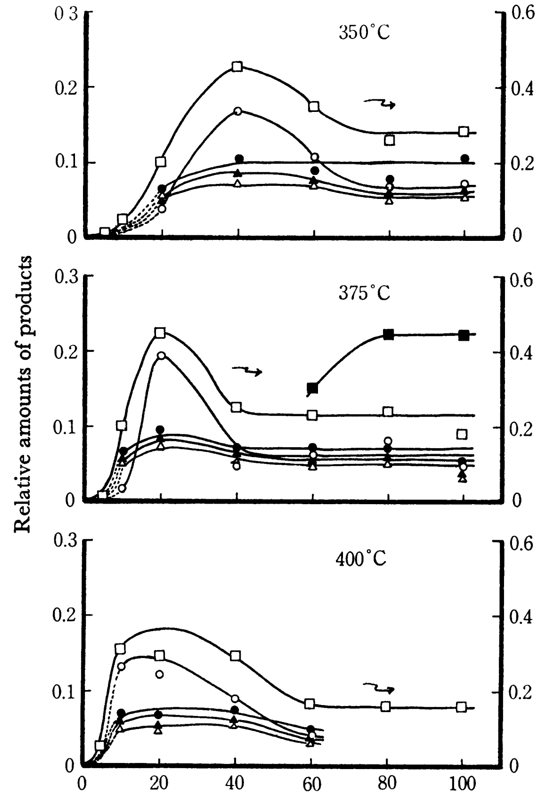


Time of run (min)

Fig. 1. The conversion of thiophene.
○: 350°C, □: 375°C, △: 400°C, ●: 350°C after 400°C

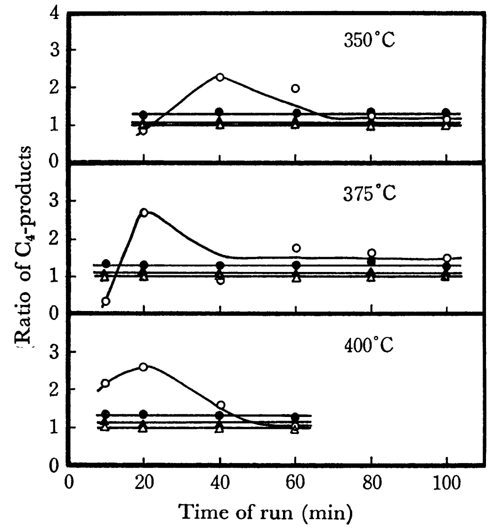
The conversion of thiophene, expressed in the ratio of the concentration decrease to the initial concentration, is shown in Fig. 1. The conversions at all the reaction temperatures have very similar curves with the reaction time. The conversion increased gradually and reached a steady value after reaching a maximum. We term the period when the conversion reached a steady value after the maximum, the "aging stage," and the period after the conversion reached the steady value, the "stationary stage."

The main products were *n*-butane, 1-butene, *cis*-2-butene, *trans*-2-butene, and hydrogen sulfide. Mercaptane, *tetra*-hydrothiophene and butadiene were not found, though they had been reported in previous works.[2,3] The products are also shown in Fig. 2a. The concentration of *n*-butane in the products was relatively large and reached a maximum when the conversion showed its maximum, at the aging stage. The ratio of C_4 products, calculated from the concentration of *cis*-2-butene as a standard, is shown in Fig. 2b. Only the ratio of *n*-butane shows its maximum at the aging stage, that of the butene shows a steady value. Hydrogen sulfide was not detected during the "aging stage." This suggests that most of the sulfur removed from thiophene by the reaction was consumed in the sulfurization of the catalyst. This shows that the reaction at the aging stage between thiophene and the catalyst is important in producing *n*-butane and molybdenum sulfide.



Time of run (min)

Fig. 2a. Reaction products.



Time of run (min)

Fig. 2b. The ratio of reaction products.
□: Total conversion, ○: *n*-butane, ▲: 1-butene,
●: *trans*-2-butene, △: *cis*-2-butene, ■: hydrogen sulfide

Reaction during the "Aging Stage." *(1) Sulfurization of the Catalyst*: sulfur content of the catalyst, determined by chemical analysis, is shown in Fig. 3 against the reaction time. This clearly shows that the catalyst was sulfurized by thiophene or by the hydrogen sulfide produced by the hydrodesulfurization of thiophene. The sulfurization proceeded during the aging process and stopped when the aging process was over. Only the hydrodesulfurization of thiophene occurred at the stationary stage. The sulfur content of the catalyst at the stationary stage was large when the aging temperature was low. It is interesting that the catalyst is sulfurized more in the bulk when the temperature is low.

(2) Reduction of the Catalyst: besides the sulfuriza-

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[6] "Bunsekikagaku Binran," Maruzen, Tokyo (1961), p. 495.

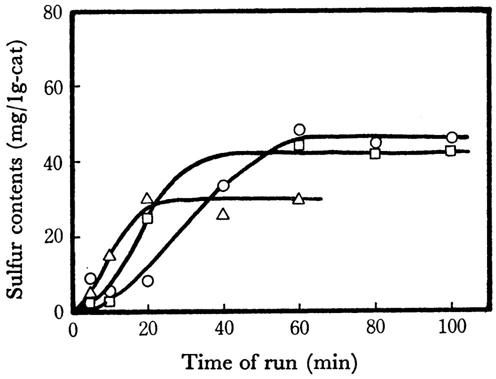

Fig. 3. Sulfur content of the catalyst.
○: 350°C, □: 375°C, △: 400°C

tion, the catalyst was reduced to MoO_2 during the aging stage. During the aging stage, the catalyst was transformed from $MoO_3 \cdot nH_2O$ to MoO_3 and then to MoO_2, as determined by the X-ray diffraction studies. The catalyst was found to be a mixture of these compounds in the course of the aging process. At the stationary stage, therefore, the catalyst was composed of MoO_2 and molybdenum sulfide.

Conversion during the "Stationary Stage." The lower the aging temperature, the larger the stationary value of the conversion at the stationary stage. The value of the conversion after the aging stage at 350°C was 0.3, about twice the value at 400°C.

The conversion was observed after the aging process at 400°C. The reaction temperature was subsequently lowered to 350°C, and then the conversion was determined. The conversion had decreased from 0.15 to 0.10, as is shown in Fig. 1 (the arrowed black point). We also observed the conversion at different reaction temperatures in order to obtain the temperature coefficient after the aging process at 350°C. The apparent activation energies calculated from these values were 3.2—4.4 kcal/mol. Therefore, the high stationary value of the conversion at a low temperature may be considered to be caused by chemical changes in the catalyst at the aging stage. Aging at low temperatures is more useful in obtaining a high activity for the hydrated molybdenum oxide catalyst.

Reactions on Other Samples. As has been described above, the catalyst in the course of the reaction consisted of a mixture of $MoO_3 \cdot nH_2O$, MoO_3, MoO_2, and MoS_2 at any reaction time and at any reaction temperature. Therefore, we also studied the conversion of thiophene, using each of these components as a catalyst. The results are shown in Fig. 4. In the case of MoO_3, the conversion changed in a manner similar to that in the case of $MoO_3 \cdot nH_2O$, but the stationary value of the conversion was somewhat smaller. In the case of MoO_2, the conversion was nearly constant throughout the reaction. On MoS_2, the conversion was not reproducible, so it was difficult to compare it with the conversion on other compounds. However, on MoS_2, the conversion was always high at first, rapidly decreased with the reaction time, and then reached a stationary value. We also studied partially-reduced MoO_3 at 350°C for 3 hr prior to the reaction. The conversion was very high at first, decreased, and then reached a stationary value.

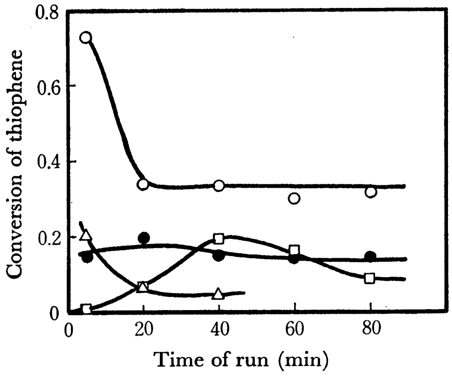

Fig. 4. The conversion of thiophene on various molybdenum compounds.
□: MoO_3, ●: MoO_2, ○: MoO_3+MoO_2, △: MoS_2

Discussion

As has been described above, the hydrated molybdenum oxide catalyst reacts with reactants at an early stage of the hydrodesulfurization of thiophene. The changes in the structure and composition caused by the reaction influence the final activity of the catalyst. That is, the aging temperatures dominate the activities of the hydrated molybdenum oxide catalyst.

Change in the Surface Area. The differences in the activities may be explained by the changes in the surface area of the catalyst. The BET surface area of hydrated molybdenum oxide before use was 3.4 m^2/g. The area increased to 8.6 m^2/g when the catalyst was used for 100 min at 350°C and to 8.0 m^2/g at 400°C. Thus, the difference in the surface area between the two reaction temperatures is not so large that we can not explain the difference in the conversion. That is, the activity does not depend on the surface area. Therefore, it is reasonable to conclude that the difference in the activity is attributable to the structural and compositional changes in the catalyst caused during the aging process.

Process of Structural Changes in the Catalyst. During the aging stage, three reactions occurred on the catalyst: i) dehydration, ii) reduction, and iii) sulfurization.

i) Dehydration: The catalyst removed the structural water during the aging process. The presence of the structural water seems to affect the reduction and the sulfurization. The process of the dehydration will be reported on in detail later.

ii) Reduction: The hydrated oxide was reduced to MoO_2 through an intermediate mixture of MoO_3 and MoO_2. At the stationary stage, a large portion of the catalyst consisted of MoO_2 at either reaction temperature.

iii) Sulfurization: At the same time, a small portion of the dehydrated MoO_3 was sulfurized. On the other hand, MoO_2 was not sulfurized easily.

To summarize the processes discussed above, we may conclude that the catalyst changes during the aging process as follows;

$$MoO_3\cdot nH_2O \longrightarrow MoO_3 \begin{array}{l} \nearrow MoO_2 \\ \searrow MoS_2 \end{array}$$

The catalyst is mainly composed of MoO_2 and MoS_2 at the stationary stage. The aging temperature has effects on the relative rate of the reduction and the sulfurization of MoO_3. In other words, the dehydration plays an important role in determining the rates of the reduction and the sulfurization.

Mechanism of the Sulfurization. The catalyst is considered to be sulfurized by two possible processes. One is direct sulfurization by thiophene (I). The other is sulfurized by hydrogen sulfide produced by the hydrodesulfurization of thiophene (II). That is:

$$\text{(I)}\quad MoO_3(MoO_2) + C_4H_4S + H_2 \longrightarrow MoS_2 + C_4\text{-Products} + H_2O$$

$$\text{(II) a)}\quad C_4H_4S + H_2 \xrightarrow{\text{Catalyst}} H_2S + C_4\text{-Products}$$

$$\text{b)}\quad H_2S + MoO_3(MoO_2) \longrightarrow MoS_2 + H_2O$$

Biltz and Kochen proposed that MoS_3 is labilized at a high temperature.[7] Nanba and Aonuma[8] reported that the final state of molybdenum sulfide is MoS_2 in the hydrodesulfurization of thiophene. By a hydrogenation reaction, MoS_3 is easily reduced at a high temperature; $MoS_3+H_2 \rightleftharpoons MoS_2+H_2O$.[9] It is reasonable to suppose that MoS_2 is formed under these reaction conditions, even though the formation of MoS_2 has not been confirmed by X-ray diffraction analysis. It can be assumed that MoS_2 does not have a perfect hexagonal crystal structure, but an amorphous mosaic-like structure.

As is shown in Figs. 1 and 3, the sulfurization of the catalyst stops and only the (IIa) reaction proceeds at the stationary stage. During the aging stage, the sulfurization by two processes (I) and (IIb), is possible. However, for the following reasons, the (I) process may be concluded to be the main reaction process.

(1) When hydrated molybdenum oxide was sulfurized for 60 min at 350°C by a mixture of H_2+H_2S, there was only a trace of sulfur content of the catalyst. The catalyst was partially reduced to MoO_2, but a large portion of the hydrated molybdenum oxide was maintained unchanged. This shows that the sulfurization by thiophene (I) is easier than that by hydrogen sulfide (IIb). This is inconsistent with the results of Tarama *et al.*[10] on vanadium molybdate. They reported that molybdenum in vanadium molybdate supported on alumina was more easily sulfurized by hydrogen sulfide than by thiophene.

(2) Figure 2b shows the ratio of C_4 products. Only the ratio of *n*-butane shows a maximum, that of butenes shows a constant value from the beginning. This suggests that, at the aging stage, the (I) process occurs much more than the (IIa) process. The sulfurization by the I process occurs more than that by the (IIb) process.

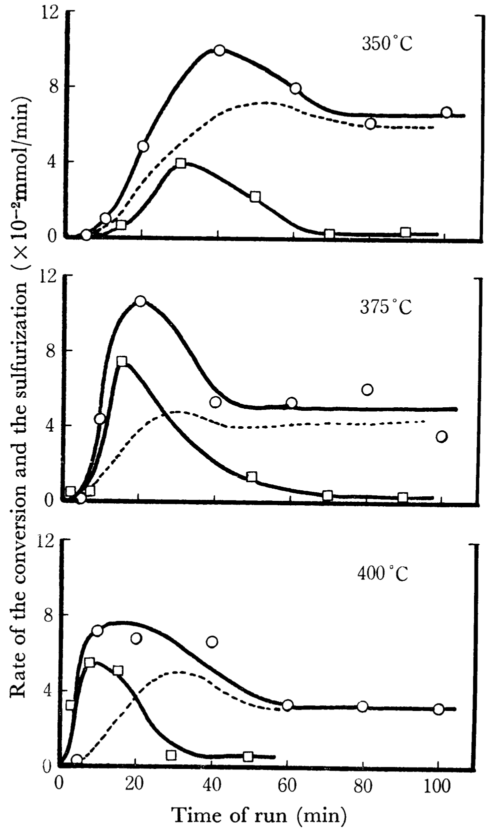

Fig. 5. The rate of the conversion of thiophene and the sulfurization of the catalyst.
○: conversion, □: sulfurization

(3) Figure 5 shows the rate of the sulfurization calculated from the sulfur analysis in Fig. 3 and the rate of the conversion of thiophene. A comparison of the two curves gives interesting information about the aging process. The rate of the conversion represents the rate of the total consumption of thiophene (I+IIa), which corresponds to the sum of the rate of the sulfurization of the catalyst (I+IIb) and the hydrodesulfurization (IIa). From these two reasons (I) and (2), the (IIb) process can be neglected more safely than the (I) process. Therefore, the difference between the rate of the conversion and the rate of the sulfurization represents the rate of hydrodesulfurization (IIa). The peaks of both curves agree at the aging stage. The dotted line in Fig. 5, which is the difference between the rate of the conversion and that of the sulfurization, shows the rate of net hydrodesulfurization (IIa). As it is relatively difficult for the (IIb) process to occur ,this suggests that the maximum of the conversion results from the overlapping of the sulfurization (I) with the hydrodesulfurization reaction (IIa).

When anhydrous MoO_2 was used as a catalyst, the sulfur content was 1.3 wt% after a reaction for 100 min at 350°C. This shows that MoO_2 is not easily sulfurized. On the other hand, the sulfur content of anhydrous MoO_3 after a reaction for 100 min at 350°C was 9.0 wt%. The conversion of neither anhydrous MoO_3 nor MoO_2 was very high compared with that

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[7] W. Biltz und A. Köchen, *Z. Anorg. Allgem. Chem.*, **248**, 172 (1941).

[8] S. Nanba and T. Aonuma, *Kogyo Kagaku Zasshi*, **74**, 1324 (1971).

[9] S. Shono, K. Itabashi, M. Yamada, and M. Kikuchi, *ibid*, **64**, 1357 (1961).

[10] K. Tarama, S. Teranishi, Hattori, and Azuma, *Nenryo Kyokaishi*, **42**, 99 (1965).

of hydrated molybdenum oxide at the stationary stage. Richardson[11] has reported that MoO_2 itself has a mild activity in the hydrodesulfurization of thiophene.

From the results presented above, it may be concluded that the dehydration at the aging stage controls the rates of the reduction and the sulfurization and, consequently, influences the activity of the catalyst.

The nature of the structural water in hydrated molybdenum oxide and the process of the dehydration of the catalyst will be reported on later.

We are indebted to Dr. I. Motooka for measuring the DTA and TGA and to Mr. Y. Sasaki for measuring the BET surface area. We also wish to thank Dr. S. Kishimoto for his helpful discussions.

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[11] J. T. Richardson, *Ind. Eng. Chem. Fundamentals*, **3**, 154 (1964).