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THE REACTION BETWEEN THIOPHENE AND HYDROGEN ON
THE HEXAGONAL HYDRATE OF MOLYBDENUM OXIDE

BY NORIYUKI SOTANI

In the catalytic reaction between thiophene and hydrogen on the hexagonal hydrate of molybdenum trioxide, the catalyst reacted with the reactant gas and the change of the state took place at the early stage of the reaction ('aging stage'). To study the mechanism of the catalytic reaction, the changes in the conversion of thiophene and the composition of the reaction products were studied by the flow method at the reaction temperatures of 350°, 375° and 400°C. The main products of the hydrodesulfurization of thiophene were n-butane, 1-butene, trans-2-butene, cis-2-butene and hydrogen sulfide. At the early stage of the reaction, the conversion of thiophene and the concentration of n-butane rapidly increased to maxima and decreased to steady values, while the concentration of butenes simply increased to steady values. The catalyst used for the hydrodesulfurization was studied by ESR spectroscopy and the signal due to Mo(V) was observed. The intensity due to Mo(V) increased at first, decreased through a maximum, and increased again to a steady value. At the first half of the aging stage, Mo(V) was formed by the reduction of MoO₃, while, at the steady stage, Mo(V) was produced by the sulfidation of the catalyst. From the results obtained by ESR studies, in addition to the results of the conversion and the changes of the state of the catalyst, the author concluded that the reaction was composed of two independent processes. One is the process in which thiophene is adsorbed on Mo atom by the coordination of sulfur atom and is hydrogenated to give n-butane and higher sulfide of the catalyst. The other is the process that thiophene adsorbed parallel to the surface of the catalyst with four carbon atoms is catalytically hydrogenated to C₄-products through butadiene. The catalytic activity of the catalyst for the hydrodesulfurization of thiophene depends on the Mo(V) in the sulfide.

Introduction

Recently, because of the industrial importance of the desulfurization of petroleum, very many workers have studied on the hydrodesulfurization of thiophene on cobalt-molybdate supported on alumina as a model reaction for the desulfurization of petroleum, and several mechanisms have been proposed for the reaction. Toyoda and Namba reported that the sulfide formed in the molybdenum catalyst by the reaction with the reactant gases affected on the catalytic activity for the hydrodesulfurization of thiophene. On the other hand, Ueda also reported that Mo(V) in the molybdenum

(Received January 27, 1976)
2) C. M. Satterfield and G. W. Roberts, AIChE J., 14, 159 (1968)
5) S. Namba and T. Aonuma, Kagyo Kagaku Zashi, 74, 1324 (1971)
catalyst acted as an active center for the desulfurization of organic sulfur compounds.

Previously, the author studied on various forms of molybdic acid and found a new type of molybdic acid, the hexagonal hydrate of molybdenum trioxide. To investigate the natures of the hexagonal hydrate and its change of the state, the hydrate was treated in air, in hydrogen and in a hydrogen-thiophene mixture and studied by X-ray diffraction analysis, DTA-TGA, IR and NMR spectroscopies and other methods. Also the author studied on the catalytic hydrodesulfurization of thiophene when the hexagonal hydrate was used as a catalyst. He found that the conversion changed at first with time for several of ten minutes (the aging stage) and reached a steady value (the steady stage), and the catalytic activity at the steady stage depended on the changes of the state of the catalyst during the aging stage.

In the present paper, the reaction mechanism of the hydrodesulfurization of thiophene and the active center of the catalyst will be discussed synthetically from the results of ESR measurements of the catalyst, together with the results of the previous works on the conversion and the analysis of the reaction products.

Experimental

Catalyst sample

The hexagonal hydrate of molybdenum trioxide was prepared from the solution of ammonium paramolybdate by the method described in the previous paper.

Catalytic reaction

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 flowed at a rate accurately controlled to 0.1 mol/hr. Thiophene was fed to a stream of hydrogen with a rate of \(1.4 \times 10^{-5}\) mol/hr.

ESR and X-ray studies

The precise methods were described previously. After the hydrodesulfurization of thiophene, the catalyst was subjected to ESR and X-ray diffraction analyses.

Results

Conversion and reaction products

9) N. Sotani and M. Hasegawa, ibid., 46, 25 (1973)
10) N. Sotani, This Journal, 46, 1 (1976)
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Fig. 1 shows the change in conversion of thiophene, when the reaction was performed at 350°, 375° and 400°C. At all reaction temperatures, the conversion increases gradually with the time of reaction, reaches a maximum, and decreases to a steady value. The author terms the period until the conversion reached the steady value, the 'aging stage'; and the period after the conversion reached the steady state value, the 'steady stage'. As shown in Fig. 1, the steady state conversion is higher when the aging temperature is lower. The value of the conversion at 350°C is about twice of that at 400°C.

The products were $n$-butane, 1-butene, $trans$-2-butene, $cis$-2-butene and hydrogen sulfide. The change in the concentration of each product is also shown in Fig. 1. The concentration of $n$-butane shows a maximum at the aging stage, and reaches a steady state value. On the other hand, the concentrations of butenes simply increase to the steady state values. Hydrogen sulfide was not detected at first, but observed at the steady stage, showing that sulfur was taken up by the catalyst at the aging stage.

Fig. 2 shows the sulfur content of the catalyst determined by chemical analysis as a function of the time of reaction. The sulfur content gradually increases at the aging stage and reaches a constant value at the steady stage. As shown in Fig. 2, the lower the reaction temperature, the larger the sulfur content at the steady stage.

During the reaction, the reduction of the catalyst also took place as known from the X-ray studies and $H_2O$ was also expected to be produced by the reduction, but was not separated from hydrogen.
ESR signal of the sample used for catalytic reaction

The hydrate sample used as a catalyst for hydrodesulfurization of thiophene was studied by ESR spectroscopy. A signal appeared in the 5 min reaction at 350°C. Fig. 3a shows the spectra of the sample. The line shapes are asymmetric and complicated, but, as a whole, similar to those of the reduced sample. The line shape and the g-value change with the reaction time up to about 40 min, but is kept unchanged by further reaction. Similar changes are also observed at 375°C and 400°C (Figs. 3b and 3c).

Fig. 3 The ESR spectra of the catalyst

The g-value of the main signals increases with the reaction time from 1.927 to 1.932 at the end of the aging stage, and, during the steady stage, the g-value is kept at 1.932 independent of the reaction temperature. The main signal corresponds to that assigned to Mo(V) in the previous
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The g-values are collected in Fig. 4, together with other workers.

Fig. 4 The change in the g-value of the catalyst (●: 350°C, ■: 375°C, ▲: 400°C)

A fairly symmetric signal with $g = 2.003$ also appeared at the end of the aging stage and was maintained during the steady stage. The intensity of the main signal is easily reduced on the adsorption of oxygen, but the small signal with $g = 2.003$ is not affected by oxygen. The signal with the same g-value was also observed in the reduced sample and was attributed to the F-center in MoO$_3$. But, it disappeared on adsorption of oxygen or water. The above signal with $g = 2.003$ is attributed to another species, probably to carbon assigned by many workers.

Fig. 2 shows the change in the signal intensity due to Mo(V) of the catalyst against the time used for hydrodesulfurization of thiophene, together with the composition of oxides of the catalyst by X-ray diffraction analysis. During the aging stage, the intensity increases at first, decreases through a maximum, and increases again to a steady value. The intensity is kept at the value throughout the steady stage.

Discussion

As reported in the previous work by X-ray diffraction analysis. DTA-TGA and IR spectroscopy.

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12) K. S. Seshadri, F. E. Massoth and L. Petrakis, ibid., 19, 95 (1970)
the hydrate was easily dehydrated on heating and transformed to anhydrous hexagonal MoO₃ (denoted as (H)), having the same lattice structure with the hydrate, and (H) further transformed to rhombic MoO₃ (denoted as (R)). In hydrogen, the reduction to MoO₂ (denoted as (D)) took place successively to the above transformation. In the reaction atmosphere of the hydrodesulfurization of thiophene, the sulfurization also took place in addition to the reduction. The whole changes of the catalyst were summarized as follows:

\[(H)\cdot n\text{H}_2\text{O} \rightarrow (H) \rightarrow (R) \rightarrow (D)\]

These changes of the state took place at the aging stage, and a constant ratio between (D) and MoS₂ (denoted as (S)) was maintained during the steady stage.

**Mechanism of the formation of Mo(V) during the hydrodesulfurization of thiophene**

As shown in Fig. 2, the intensity due to Mo(V) shows a maximum at the first half of the aging stage at which the catalyst was partly reduced to (D) and increases again to a steady state value. As reported previously, in the reduction by hydrogen, the intensity due to Mo(V) showed a maximum at several percent of (D) and decreased to a very small value at over 60% of (D). The composition of the results in Fig. 2 with the relation between the signal intensity and the fraction of (D) in the catalyst by hydrogen reduction leads to the conclusion that the maximum of Mo(V) concentration, at the first half of the aging stage, is due to Mo(V) produced in (R) by the reduction of MoO₃. On the other hand, in spite of the fact that (D) is predominant at the latter half of the aging stage, (R) disappeared completely at the end of the aging stage and the signal intensity due to Mo(V) increases to a certain value.
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in contrast with the change in intensity by hydrogen reduction. This means that the gradual increase in intensity due to Mo(V) results from the other species. The increase in intensity is parallel to that in sulfur content of the catalyst. This suggests that the increase in Mo(V) at the latter half of the aging stage is attributed to the sulfurization of the catalyst. In Fig. 5, the average value of the signal intensities at the steady stage is plotted against the sulfur contents. This shows that the amount of the sulfide in the catalyst correlates with the concentration of Mo(V).

Mechanism of catalytic hyrodesulfurization reaction

Two independent processes for the hyrodesulfurization reaction are possible. One is the process containing sulfurization of the catalyst as an intermediate. That is,

(I) \[ C_{4}H_{5}S + H_{2} + \text{Catal} \rightarrow \text{Catal} - S + C_{4}\text{-products} + H_{2}O \]

or (I') \[ C_{4}H_{5}S + H_{2} + \text{MoS}_{2} \rightarrow \text{MoS}_{3} + C_{4}\text{-products} \]

and (II) \[ \text{Catal} - S + H_{2} \rightarrow \text{Catal} + H_{2}S. \]

The other is the catalytic reaction of reactant gases, that is:

(III) \[ C_{4}H_{5}S + H_{2} \rightarrow C_{4}\text{-products} + H_{2}S. \]

For the sulfurization of the catalyst at the aging stage, two similar processes are also considered to be possible, that is, (i) the sulfurization by thiophene (I or I') and (ii) the sulfurization by hydrogen sulfide, the reverse reaction of the II process, which was produced by the hyrodesulfurization of thiophene (the III process).

The catalyst was easily reduced by the mixture of H$_{2}$-H$_{2}$S to (D), but was sulfurized only slightly$^{9}$. On the other hand, the sulfurization of the catalyst occurred easily in the hydrogen-thiophene mixture. These facts show that, for the sulfurization of the catalyst, thiophene is more favorable than H$_{2}$S.

Fig. 6 shows an example of the plot of the total amount of thiophene consumed for the reaction and the sulfur content of the catalyst against the time of reaction (373°C). This figure clearly shows that, at the early stage of the reaction, most of thiophene is consumed for the sulfurization of the catalyst.

The rate of the net hyrodesulfurization of thiophene is obtained from the total conversion of thiophene by subtracting the portion consumed for the sulfurization of the catalyst. Fig. 7 shows the rate of the sulfurization of the catalyst, obtained from differentiation of the curve of the sulfur content together with the rate of the conversion of thiophene. The difference between the two curves (the dotted line) shows the rate of the net hyrodesulfurization. The former two curves have maxima at the aging stage, but the maxima are nearly compensated and the rate of the net reaction simply increases at the aging stage and reaches a steady rate. As described above, the hyrodesulfurization reaction is considered to proceed in two processes, but these curves seem to suggest that the maximum of the total conversion results from the overlapping of the sulfurization by the I (or I') process with hyrodesulfurization reaction by the III process. This means that the main reaction process of the net hyrodesulfurization is the III process, and the I (or I') process plays only a small part as a side reaction.
The composition of the product gases also supports the above mechanism. The concentration of n-butane in the product gases shows similar change with the total conversion of thiophene, having a maximum at the aging stage, while the concentration curves of butenes are similar in manner to that of the rate of the net hydrodesulfurization. It is reasonable, therefore, to consider that n-butane is a predominant product of the I process, while the composition of the products by the III process is nearly the same to that at the steady stage.

On the hydrodesulfurization of thiophene, Amberg proposed the reaction mechanism by one point adsorption model that the hydrodesulfurization proceeded through adsorbed mercaptane as a surface intermediate. On the other hand, Nicholson proposed, in his IR studies of adsorption of thiophene, one point form, in which sulfur atom directly coordinated on Mo atom, and two or four point form, in which the thiophene molecule is adsorbed with the two or four neighbouring carbons on two or four Mo atoms. Four point adsorption is favorable on MoS$_2$. The I process, the main process of sulfurization of the catalyst, is reasonably interpreted as the one point: adsorption form. The fact that thiolane is easily desulfurized to butane through butanethiol supports the selective formation of butane in the I process. The reaction is as follows:

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\[
\begin{align*}
\text{Equation 1:} & \\
\text{Equation 2:} &
\end{align*}
\]

On the other hand, the four point adsorption of thiophene easily explains the III process, the main process of the hydrodesulfurization of thiophene. In the four point model, the reaction is likely to give adsorbed butadiene and H₂S by cracking of two C-S bonds, giving various isomers of butenes and butane as final products\(^{21,22}\). The mechanism is represented by

Catalytic activity for the hydrodesulfurization

The net hydrodesulfurization of thiophene is small at the early stage of the reaction and increases gradually with the reaction time. The change in the reaction rate is nearly parallel to the sulfur content of the catalyst. This suggests that the sulfide contributes to the activity. The steady conversion at all reaction temperatures also have a correlation with the sulfur content as shown in Fig. 8. When the temperature is higher, the sulfur content of the catalyst is smaller and the rate of the reaction at the steady stage is smaller, showing the negative apparent temperature coefficient. To estimate the real temperature coefficient of the reaction rate, the following experiments were performed. After the steady value of the conversion was obtained at 400°C, the reaction temperature was lowered to 350°C. The conversion decreased from 0.16 to 0.11. An activation energy of the reaction is a small positive value (3.2-4.4 kcal/mol). Therefore, the steady state activity depends on the structural and compositional changes of the catalyst at the aging stage.

As mentioned above, the concentration of Mo(V) correlates with the sulfur content. This result readily leads to the conclusion that the activity of the catalyst for the hydrodesulfurization by the III process depends on the Mo(V) in the sulfide. In hydrodesulfurization, a certain amount of higher sulfide is produced in (S) by the I' (or I) and II processes. In these processes, the author expressed the higher sulfide as Mo₅S₆. However, exactly speaking, the sulfurization of (S) will produce Mo(V) and cation vacancies in (S) instead of the higher sulfide as Mo₅S₆, as (S) is known to be a p-type semi-

\(^{22}\) S. Kolboe and C. H. Amberg, ibid., 44, 2623 (1966)
conductor$^{20}$). The concentration of these defects in (S) will be determined by the relative rates of the competitive reactions of the sulfurization by thiophene (the $I'$ (or 1) process) and the reduction by hydrogen (the II process).

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