Studies of Catalytic Cracking of Organic Sulfur Compounds over Solid Acid Catalysts (Part 8)*

—The Mechanism of Cracking Reaction of Aliphatic Mercaptans and Aliphatic Sulfides on Silica-Alumina Catalyst—

by Masatoshi Sugioka** and Kazuo Aomura**

Summary: The catalytic cracking of aliphatic mercaptans and sulfides on the silica-alumina catalyst were investigated by the use of a pulse reactor.

The cracking reactivities of aliphatic mercaptans and sulfides increase in the following order:

$$\begin{align*}
C_2H_5SH &< n-C_3H_7SH < i-C_3H_7SH < sec-C_4H_9SH \\
(CH_3)_2S &< (C_2H_5)_2S < (n-C_3H_7)_2S < (n-C_4H_9)_2S
\end{align*}$$

This order is also consistent with the order of the stability of alkyl carbonium ions produced from the corresponding alkyl groups. The linear relationship was observed between the logarithms of the apparent rate constants of the cracking reaction of aliphatic mercaptans and sulfides and the enthalpy change of formation of carbonium ion from the corresponding paraffins.

From these results, a hypothesis was proposed that the catalytic cracking of aliphatic mercaptans and sulfides on the silica-alumina catalyst takes place with the carbonium ion mechanism.

1 Introduction

In the petroleum refining industrial process such as catalytic cracking or reforming, very limited information is available on the behaviors of the organic sulfur compounds. The thermal cracking of the organic sulfur compounds was previously reported by Faragher, Malisoff and Thompson1)~3) in connection with the thermal cracking process of the petroleum. However, the catalytic cracking of organic sulfur compounds on the solid acid catalyst, which is used in the catalytic cracking of the petroleum, had not been reported. Recently, Imnadze4) and Shelemina et al.5) investigated on the catalytic cracking of aliphatic mercaptans with the silica-alumina catalyst, and qualitatively showed the relations between the molecular structure and the ease of cracking. However, they did not report the kinetics and mechanism of the cracking of aliphatic mercaptans. The effect of solvent in the catalytic cracking of aliphatic sulfides on the silica-alumina catalyst was investigated by Obolentsev et al.6), but the cracking mechanism of aliphatic sulfides was not reported.

Therefore, it will be worthwhile to make the detailed systematical studies on the cracking reactivity and cracking mechanism of these sulfur compounds with the silica-alumina catalyst.

2 Experimental

2.1 Materials

The silica-alumina catalyst used in this work was cracking catalyst produced by Shokubai Kasei Co.. The catalyst was sieved (150~200 mesh) and calcined at 500°C for 4 hours in the atmosphere. Prior to experiment, the catalyst was treated again at 500°C for 0.5~1.0 hour in the reactor with a hydrogen stream.

The aliphatic mercaptans and sulfides used in this work are listed in Table 1. Commercial grade of reactants were used without any purifications, since no impurity was detected by

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Reactants</th>
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<tbody>
<tr>
<td>EM</td>
<td>Ethylmercaptan</td>
</tr>
<tr>
<td>n-PM</td>
<td>n-Propylmercaptan</td>
</tr>
<tr>
<td>i-PM</td>
<td>i-Propylmercaptan</td>
</tr>
<tr>
<td>n-BM</td>
<td>n-Butylmercaptan</td>
</tr>
<tr>
<td>sec-BM</td>
<td>sec-Butylmercaptan</td>
</tr>
<tr>
<td>DMS</td>
<td>di-Methylsulfide</td>
</tr>
<tr>
<td>DES</td>
<td>di-Ethylsulfide</td>
</tr>
<tr>
<td>D-n-PS</td>
<td>di-n-Propylsulfide</td>
</tr>
<tr>
<td>D-n-BS</td>
<td>di-n-Butylsulfide</td>
</tr>
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the gaschromatograph.

2.2 Apparatus

A conventional pulse reactor connected to the gaschromatograph was used with 5-m of tricresylphosphate as an analytical column and with hydrogen as a carrier gas.

The reactor was a U type pyrex glass tube of 4-mmID, which was heated with an electric furnace. The temperature of the catalyst bed was controlled within ±1.0°C.

2.3 Measurement of Conversion \( x \)

The conversion \( x \) was determined from the peak areas of the reactant before and after catalytic cracking, because of the difficulty for the clear separation of the cracking products, hydrogen sulfide and olefins. Thus, the conversion \( x \) was calculated from the following equation:

\[
x = 1 - \left( \frac{A}{A_0} \right)
\]

where, \( A_0 \) and \( A \) are the peak areas of reactant before and after the cracking, respectively. The peak area, \( A_0 \), is equal to that obtained without the catalyst. The catalytic activity decreased gradually as the pulse number increased and had attained constant value after the pulse number of about ten. This constant activity was adopted as the conversion.

3 Results and Discussion

3.1 Kinetic Analysis of Cracking Reaction

The main reactions in the cracking of aliphatic mercaptan and sulfide were expressed in Eq. (2)-(4). In this paper, the term “Cracking” was defined by the breaking of C-S bond.

\[
\begin{align*}
\text{RSH} & \rightarrow \text{R'} + \text{H}_2\text{S} \quad (2) \\
\text{RSR} & \rightarrow \text{R'} + \text{RSH} \quad (3) \\
& \rightarrow 2\text{R'} + \text{H}_2\text{S} \quad (4)
\end{align*}
\]

where R is alkyl group and R' is the corresponding olefin. No other products were detected by the gaschromatograph. The original color of the catalyst was white, however, it turned black after use, due to the carbon deposit on the surface.

Echigoya et al. investigated the cracking of cumene on the silica-alumina catalyst by the use of a pulse reactor, and showed that the cracking reaction of cumene followed an irreversible first order kinetics. Thus, it was expected that the cracking reaction of aliphatic mercaptans and sulfides also may follow an irreversible first order kinetics on the silica-alumina catalyst. The equation of the first order approximation has commonly been used in the pulse reaction system

\[
k = -\frac{F}{W}\ln(1-x) \quad (5)
\]

In this equation, \( k \), \( F \), and \( W \) are the apparent rate constant (ml/g-min), flow rate of a carrier gas (ml/min at S.T.P.) and the weight of catalyst(g), respectively. The conversion \( x \) was measured at various weights of catalysts to test the first order kinetics. Then, \(-\ln(1-x)\) was plotted against \( W/F \) at various reaction temperatures. As being expected from Eq. (5), the linear relationship through the origin were observed between \( W/F \) and \(-\ln(1-x)\) for the cracking reaction of both of various aliphatic mercaptans and sulfides.

The typical examples, in the case of ethylmercaptan and diethylsulfide at 380°C, were shown in Fig. 1.

3.2 Arrhenius Plots

The apparent rate constants, \( k \), in the cracking of various aliphatic mercaptans and sulfides were listed in Table 2. From the Arrhenius plots of log \( k \) vs. 1/T shown in Fig. 2, the apparent rate constants, \( k \), can be expressed by the following equations.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Apparent Rate Constant</th>
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<tbody>
<tr>
<td>EM</td>
<td>( k = 7.02 \times 10^{10} \exp(-27.500/RT) )</td>
</tr>
<tr>
<td>n-PM</td>
<td>( k = 1.01 \times 10^{10} \exp(-27.500/RT) )</td>
</tr>
<tr>
<td>i-PM</td>
<td>( k = 9.82 \times 10^{10} \exp(-21.500/RT) )</td>
</tr>
<tr>
<td>n-BM</td>
<td>( k = 2.92 \times 10^{10} \exp(-27.900/RT) )</td>
</tr>
<tr>
<td>sec-BM</td>
<td>( k = 9.40 \times 10^{10} \exp(-25.000/RT) )</td>
</tr>
<tr>
<td>DMS</td>
<td>( k = 3.63 \times 10^{10} \exp(-45.400/RT) )</td>
</tr>
<tr>
<td>DES</td>
<td>( k = 2.04 \times 10^{10} \exp(-18.000/RT) )</td>
</tr>
<tr>
<td>D-n-PS</td>
<td>( k = 1.78 \times 10^{10} \exp(-14.900/RT) )</td>
</tr>
<tr>
<td>D-n-BS</td>
<td>( k = 1.95 \times 10^{10} \exp(-8.800/RT) )</td>
</tr>
</tbody>
</table>

Fig. 1 Relationship between W/F and -ln(1-x) in the Cracking of Ethylmercaptan and Diethylsulfide on the Silica-Alumina Catalyst at 380°C.
The similar value of the activation energy was obtained in the cracking of aliphatic mercaptans. The explanation of such phenomena, however, is difficult because of the complexity of this system at present.

3.3 The Order of Cracking Reactivity

The cracking reactivities of various aliphatic mercaptans and sulfides at 200°C, 250°C and 300°C were calculated from the equation of apparent rate constants and the results are listed in Table 3. In this paper, the cracking reactivity will be expressed by the logarithms of apparent rate constant.

As was evidenced from Table 3, the cracking reactivities of various aliphatic mercaptans and sulfides at the temperature range of 200°C to 300°C increase in the following order.

For aliphatic mercaptans:

- EM \(<n-PM<sec-BM<sec-PM<\text{DMS}<D-n-PS<D-n-BS

For aliphatic sulfides:

- DMS \(<D-n-PS<\text{D-n-BS}<n-BM<i-PM<sec-BM

The cracking reactivities of both of aliphatic mercaptans and sulfides increase with the increase of the molecular weight. For aliphatic mercaptans having the same carbon numbers, the cracking reactivity of branched-chain molecule is higher than the straight-chain one. Furthermore, the order of the cracking reactivities is also consistent with the stability of alkyl carbonium ions.

3.4 Cracking Mechanism

In the dealkylation of alkylbenzenes on the solid acid catalysts, Mochida and Yoneda reported to hold the linear relationship between the logarithms of apparent rate constants and the enthalpy change, \( \Delta H^*_c \), in the reaction of...
the hydride abstraction from the corresponding paraffins as described by Eq. (6).

\[ \text{RH} \rightarrow \text{R}^+ + \text{H}^+ + \text{H}^+_c^+ \]  

(6)

They concluded from this result that the dealkylation of alkylbenzenes on the solid acid catalysts occurs via an alkyl carbonium ion intermediate. In the cracking of aliphatic mercaptans and sulfides on the silica-alumina catalyst, the linear relationships between the logarithms of apparent rate constants and \( \Delta H^+ \), proposed by Mochida and Yoneda\(^{11}\), were also observed at various reaction temperatures as shown in Fig. 3 and Fig. 4. These results suggest that the catalytic cracking of aliphatic mercaptans and sulfides on the silica-alumina catalyst advances via an alkyl carbonium ion intermediate, as observed in the dealkylation of alkylbenzenes.

On the other hand, the catalytic activity of the silica-alumina in the cracking of aliphatic mercaptanes and sulfides decreased when the catalyst was treated by alkali solution. Furthermore, the solid phosphoric acid catalyst and NH\(_4\)Y-zeolite catalyst which have predominantly the Brönsted acid site also showed the catalytic activity in the cracking of aliphatic mercaptans and sulfides\(^{12-14}\). And the catalytic activity of NH\(_4\)Y-zeolite catalyst for the cracking of ethylmecaptan decreased with the increase of the calcination temperature of the catalyst. This change of the activity of NH\(_4\)Y-zeolite catalyst was in good accord with the changes of the amounts of the Brönsted acid sites, but was not in accord with that of the Lewis acid sites of the catalyst\(^{14}\).

Judging from these results, it was concluded that the effective active site of the silica-alumina catalyst in the cracking of aliphatic mercaptans and sulfides was the Brönsted acid site.

Thus, the cracking mechanism on the silica-alumina catalyst will be expressed as follows:

I. Cracking mechanism of aliphatic mercaptan

\[ \begin{align*}
\text{Step 1} & : \text{H}^+\text{A}^- & \xrightarrow{K_1} & \text{H}^+ + \text{A}^- \\
\text{Step 2} & : \text{RSH} + \text{H}^+ & \xrightarrow{K_2} & \text{R-SH}_2 \\
\text{Step 3} & : \text{R-SH}_2 & \xrightarrow{k_3} & \text{R}^+ + \text{H}_2\text{S} \\
\text{Step 4} & : \text{R}^+ + \text{A}^- & \xrightarrow{K_4} & \text{R}^+ + \text{H}_2\text{A}^- 
\end{align*} \]  

II. Cracking mechanism of aliphatic sulfide

\[ \begin{align*}
\text{Step 1'} & : \text{H}^+\text{A}^- & \xrightarrow{K_1'} & \text{H}^+ + \text{A}^- \\
\text{Step 2'} & : \text{RSR} + \text{H}^+ & \xrightarrow{k_5'} & \text{R-S-R}^+ 
\end{align*} \]  

The cracking mechanisms described above was very similar to that of dehydration reaction of alcohol and ether which is catalyzed with a proton on the solid acid catalysts\(^{15}\). Such similarity can be easily expected from the similarity in the molecular structures of these compounds.

In the cracking mechanism of aliphatic sulfide, a part of the aliphatic mercaptan being formed in step 3' will be cracked according to subsequent reaction step which is the same as that of the aliphatic mercaptan described above. Kinetic analysis, similar to that used by Mochida and Yoneda in the study of dealkylation of alkylbenzenes.

\[ \begin{align*}
\text{Step 3'} & : \text{R-S-R} & \xrightarrow{k_3'} & \text{R}^+ + \text{RSH} \\
\text{Step 4'} & : \text{R}^+ + \text{A}^- & \xrightarrow{k_4'} & \text{R}^+ + \text{H}_2\text{A}^- 
\end{align*} \]  

where \( \text{H}^+\text{A}^-, \text{R}^+ \) and \( \text{R}' \) represent the silica-alumina, alkyl carbonium ion and olefin, respectively.
zenes\textsuperscript{11}), was applied to our systems in order to make sure the validity of the cracking mechanism described above. Since the cracking mechanism of aliphatic sulfide is similar to that of aliphatic mercaptan, only the cracking mechanism of aliphatic mercaptan will hereinafter be discussed.

Assuming that the adsorption of aliphatic mercaptane to the silica-alumina catalyst is weak and the rate-determining step is Step 3, then the rate constant will be represented by:

$$k = k_0 K_1 K_a a_3$$  \hspace{1cm} (16)

where $k$ is the rate constant of the overall reaction, $k_0$ is that of the rate-determining step, $K_1$ is the average acid dissociation constant of the silica-alumina, $K_a$ is the equilibrium constant of adsorption of Step 2 and $a_3$ is the amount of total acid on the silica-alumina. When only enthalpy factor is considered, Eq. (16) will be converted into Eq. (17).

$$\log k = \text{const.} - \frac{(E_o + \Delta H_a)}{2.303RT}$$  \hspace{1cm} (17)

where $E_o$ is the activation energy of Step 3, $\Delta H_a$ is the heat of adsorption of Step 2.

As the reaction of Step 3 resembles reaction (6), the enthalpy change of Step 3, $\Delta H_a$, can be assumed to be linear to the enthalpy change of reaction (6).

$$\Delta H_a = \alpha_1 \Delta H_c^+ + \text{const.}$$  \hspace{1cm} (18)

If the Horiuti-Polanyi rule assume to hold between $E_o$ and $\Delta H_a$, then

$E_o = \alpha_2 \Delta H_c^+ + \text{const.}$

$= \alpha_3 \Delta H_a^+ + \text{const.}$

$= \alpha \Delta H_a^+ + \text{const.}$  \hspace{1cm} (19)

where $\alpha_1$, $\alpha_2$ and $\alpha$ are constants.

On the other hand, the heat of adsorption of Step 2, $\Delta H_a$, will depend mainly upon the basicity of mercaptan molecule. It is also expected that the aliphatic mercaptan will adsorb on the Brönsted acid site of silica-alumina by the sulfur atom which has the largest electron density in the mercaptan molecule. The electron density, i.e., basicity, of the sulfur atom in the mercaptan molecule could be correlated with the electron donating ability of alkyl group adjacent to the sulfur atom. When the Taft’s substitution constant, $\sigma^*$, is employed as a measure of the electron donating ability of alkyl group, the linear relationship will be expected between $\Delta H_a$ and $\sigma^*$,

$$\Delta H_a = \beta \sigma^* + \text{const.}$$  \hspace{1cm} (20)

Furthermore, the linear relationship is observed between $\sigma^*$ and $\Delta H_c^+$ as shown in Fig. 5.

$$\sigma^* = \beta_1 \Delta H_c^+ + \text{const.}$$  \hspace{1cm} (21)

From Eq. (20) and Eq. (21),

$$\Delta H_a = \beta \beta_1 \Delta H_c^+ + \text{const.}$$

$$= \beta \Delta H_c^+ + \text{const.}$$  \hspace{1cm} (22)

where $\beta_1$, $\beta_2$ and $\beta$ are constants.

Therefore, from Eq. (17), Eq. (19) and Eq. (22),

$$\log k = \text{const.} - (\alpha + \beta) \Delta H_c^+/2.303RT$$  \hspace{1cm} (23)

It is, thus, theoretically proved that the cracking reactivity, $\log k$, is proportional to $\Delta H_c^+$ as shown in Fig. 3 and Fig. 4. And it is also well explained that the catalytic cracking of aliphatic mercaptans and sulfides on the silica-alumina catalyst takes place with the carbonium ion mechanism which is concerned with the proton of silica-alumina.

4 Conclusion

The order of cracking reactivities of aliphatic mercaptans and sulfides on the silica-alumina catalyst was consistent with the order of the stability of alkyl carbonium ions. A linear relationship was observed between the logarithms of apparent rate constants of the cracking and the enthalpy change in the reaction of hydride abstraction from the corresponding paraffins.

Based on these results, it was concluded that the catalytic cracking of aliphatic mercaptans and sulfides on the silica-alumina catalyst takes place with the carbonium ion mechanism which is concerned with the proton of silica-alumina.
place with the carbonium ion mechanism, as reported in the dehydration of alcohol and ether.

Acknowledgement

The authors are indebted to Dr. Takao Yotsuyanagi of the University of Hokkaido for his valuable discussions.

References

2) Malisoff, W. M., Marks, E. M., ibid., 23, 114 (1931).
7) Sugioka, M., Hirano, T., Yotsuyanagi, T., Aomura, K., Bull. of the Faculty of Engineering, Hokkaido University, 57, 201 (1970).
8) Mashkina, A. V., Kinetis and Catalysis, 12, 95 (1971).