

## KINETIC STUDY ON THE HYDRODESULFURIZATION REACTION OF THIOPHENE BY WATER GAS SHIFT REACTION

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**Abstract**—The in-situ hydrodesulfurization (HDS) reaction of thiophene was performed by using hydrogen which was generated by a water gas shift reaction (WGSR) in a same catalyst bed. The catalyst used was commercial CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and it was used after presulfiding. The activity in the conversion of thiophene by using hydrogen generated in-situ from a WGSR was inferior to that by the pure hydrogen. The lower efficiency in the in-situ HDS with WGSR was attributed to water, carbon monoxide and carbon dioxide which were mixed after WGSR. The following rate equation, which was revised from that of Satterfield, was proposed for this in-situ HDS reaction of thiophene with WGSR to explain the observed phenomena.

$$-r_{\text{HDS}} = \frac{kK_H K_T P_H P_T}{(1 + K_H P_H + K_T P_T + K_{\text{H}_2\text{O}} P_{\text{H}_2\text{O}} + K_{\text{CO}} P_{\text{CO}} + K_{\text{CO}_2} P_{\text{CO}_2} + K_S P_S)^2}$$

The experimental results were in good accordance with this equation. The active sites for both WGSR and HDS were ascribed to the prohibition of competitive adsorptions.

### INTRODUCTION

It is necessary to open new aspects on the utilization of the heavy petroleum fraction containing sulfur and nitrogen compounds as an energy source because of the depletion of petroleum. The hydrodesulfurization (HDS) of petroleum become more important. Hydrogenation of heavy petroleum demands lots of hydrogen and consequently cheap hydrogen source is required. The water gas shift reaction (WGSR) can be satisfied with this purpose. Thus, we decide to study HDS of thiophene, as a model reaction, by in-situ WGSR without isolating the hydrogen.

The in situ reductions by WGSR have been studied by several authors. Takemura et al. [1, 2] reported that the activity of hydrogen from an in-situ WGSR was superior to that of pure hydrogen in the HDS reaction of petroleum and cracking of diphenylmethane. Satterfield et al. [3] observed that the hydrodenitrogenation (HDN) reaction of quinoline with hydrogen was accelerated by the addition of water. However, there have been no reports concerning the effects of carbon monoxide and carbon dioxide on the HDS reaction.

Hence, kinetic study was carried out to examine

the factors responsible for this in-situ HDS reaction by WGSR. The HDS reaction by hydrogen generated from WGSR was compared with that of pure hydrogen. And the revised rate equation in the in-situ HDS reaction by WGSR was proposed and examined whether it was matched with experimental results or not.

### EXPERIMENTAL

The in situ HDS reaction of thiophene by using hydrogen generated from WGSR was examined in a continuous fixed bed reactor as shown in Figure 1. The reactor was made of stainless steel tube with a half inch inside diameter and twelve inch in length.

The catalyst used for this reaction was the HR-306 CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with 188 m<sup>2</sup>/g of surface area and 14-18 mesh of particle size. The catalyst was presulfided with the 25% H<sub>2</sub>S/H<sub>2</sub> mixed gas (flow rate 40 ml/min) at 400°C and 1 atm for 2 hours and reduced with pure hydrogen. Carbon monoxide and H<sub>2</sub>O were directly fed in the reactor while regulating the pressure of gas by a metering valve.

The mixture of thiophene and heptane containing 5 wt.% sulfur was injected by metering pump and vaporized into the flow of carbon monoxide. Both the

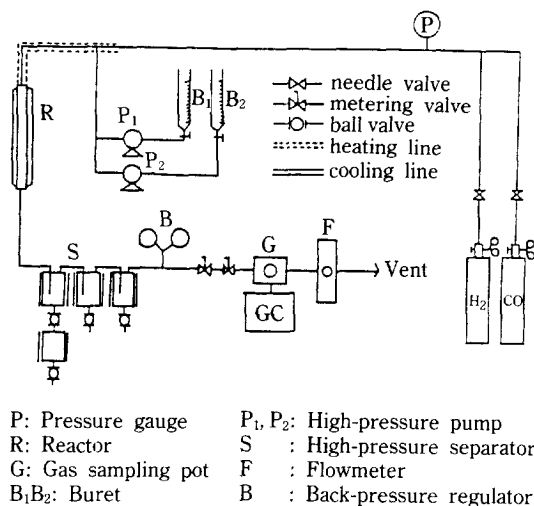


Fig. 1. Schematic diagram of HDS apparatus.

unreacted reactants and products were condensed in the high pressure separators. Liquid products trapped in a water cooled condenser were analyzed by the HP 5710 gas chromatograph. A Shimadzu model GC-8A TCD gas chromatograph was applied to perform the analysis of carbon monoxide and carbon dioxide using the carbosieve-s (100/120 mesh)  $1/8" \times 10'$ , stainless steel column and the porapak-Q (80/100 mesh)  $1/8" \times 6'$ , stainless steel column respectively.

Chemisorption experiments of  $H_2O$ , thiophene, carbon monoxide and carbon dioxide on the  $CoMo/\gamma-Al_2O_3$  catalyst were performed by BET adsorption apparatus (Accusorb 2100E Micrometrics) at various temperatures.

## RESULTS AND DISCUSSION

### 1. HDS Reaction of Thiophene by an in-situ WGS

HDS reaction of thiophene was investigated under the optimum condition of WGS; 1.5 mole ratio of  $H_2O/CO$  and  $390^\circ C$ . The effect of reaction temperature on the conversion rate of thiophene to butane or 1,3-butadiene is shown in Fig. 2. The conversion here was defined as a ratio of the weight of reacted thiophene to the weight of fed thiophene. Above  $390^\circ C$ , thiophene is almost completely transformed into butane or butadiene. Amberg et al. [4] studied that butadiene was formed as intermediate in the HDS reaction of thiophene.

Also, the HDS activity in the reaction of thiophene is dependent on hydrogen pressure. The reaction pressure were varied at  $390^\circ C$  of reaction temperature

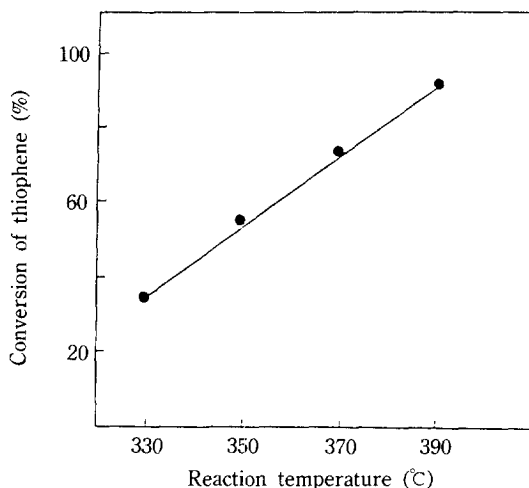


Fig. 2. Effect of reaction temperature on HDS reaction of thiophene.

and with the constant contact time (LHSV,  $6 \text{ hr}^{-1}$ ). Fig. 3 shows that the conversion of thiophene was enhanced with an increase of reaction pressure and the conversion became 100% at higher pressure than  $30 \text{ kg/cm}^2$ .

### 2. The Comparison of Activities between Pure Hydrogen and Hydrogen Generated from WGS in the HDS Reaction of Thiophene

The HDS reaction of thiophene with pure hydrogen which was externally supplied was compared with the HDS reaction by an in situ WGS, at the same hydrogen pressure of  $15 \text{ kg/cm}^2$ . Fig. 4 shows that the activity of pure hydrogen was superior to that of the hydrogen generated from WGS. The lower conversion of thiophene in the case of using hydrogen generated from WGS was ascribed to the contaminants such as carbon monoxide, water and carbon dioxide, which were simultaneously produced during WGS. So, the effects of water, carbon monoxide and carbon dioxide on this HDS reaction of thiophene were investigated to understand this phenomenon.

### 3. Effect of Water on the HDS Reaction

The effect of water on the HDS reaction was investigated by the addition of water to the HDS reaction system with pure hydrogen. Fig. 5 shows that the conversion of thiophene is diminished with the increment of water pressures at the hydrogen pressure of  $15 \text{ kg/cm}^2$  and temperature of  $280^\circ C$ .

This result is quite different from those reported by Satterfield et al. [3] and Glötekin et al. [5] on HDN reaction of quinoline which is enhanced by an increase of water partial pressure. To comprehend the negative effect of water on the HDS reaction, kinetic

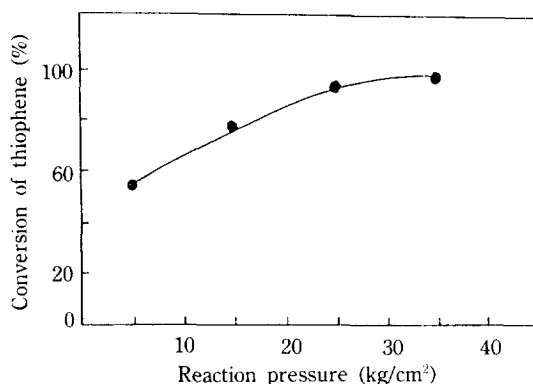


Fig. 3. Effect of reaction pressures in the HDS reaction of thiophene (Rx. temp.: 390°C, LHSV: 6 hr<sup>-1</sup>).

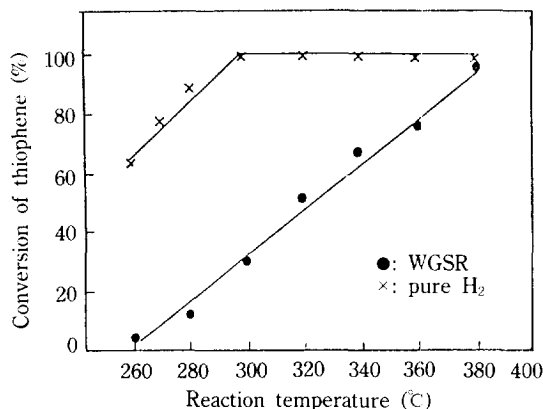


Fig. 4. Comparison of activities between pure hydrogen and hydrogen from in-situ WGSR in the HDS reaction of thiophene (H<sub>2</sub> pressure: 15 kg/cm<sup>2</sup>, LHSV: 6 hr<sup>-1</sup>).

study of the in situ HDS reaction with WGSR was undertaken.

#### 4. Kinetic Model

Kinetic studies of the HDS reaction of thiophene by pure hydrogen have been carried out by several research groups [6-8]. But the kinetic studies on the in situ HDS reaction with WGSR was not performed. The rate of HDS reaction with pure hydrogen was represented as equation (1) by Satterfield [6].

$$-r_{\text{HDS}} = \frac{kK_{\text{H}}P_{\text{H}}K_{\text{T}}P_{\text{T}}}{(1 + K_{\text{H}}P_{\text{H}} + K_{\text{T}}P_{\text{T}} + K_{\text{S}}P_{\text{S}})^2} \quad (1)$$

where  $k$ ; rate constant,  $P_{\text{H}}$ ,  $P_{\text{T}}$  and  $P_{\text{S}}$ ; partial pressure of hydrogen, thiophene and hydrogen sulfide, respectively and  $K_{\text{H}}$ ,  $K_{\text{T}}$  and  $K_{\text{S}}$ ; adsorption equilibrium constant of hydrogen, thiophene and hydrogen sulfide on the catalyst, respectively.

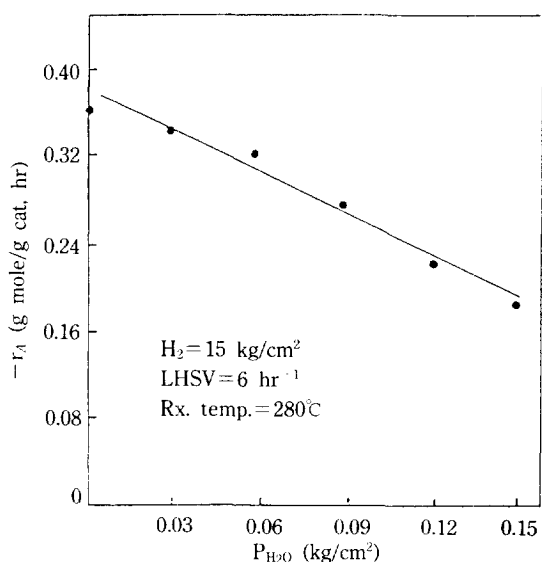


Fig. 5. The effect of water in the HDS reaction of thiophene.

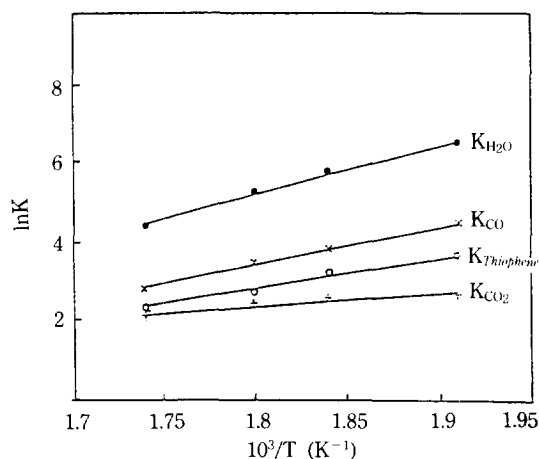
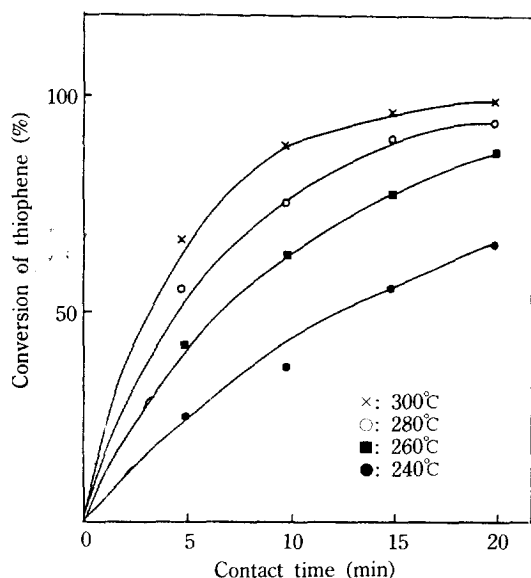


Fig. 6. Temperature dependency of adsorption constants.

As shown in equation (1), the rate depends directly on adsorption of reactants on catalyst. Hence, the adsorption equilibria of carbon monoxide, carbon dioxide, thiophene and water were tested at various temperatures. The adsorption equilibrium constants were in the sequence of water>carbon monoxide>thiophene>carbon dioxide. The enthalpies of adsorption were calculated from the Arrhenius plot displayed in Fig. 6. The equilibrium constants and enthalpies of adsorptions of water, carbon monoxide, carbon dioxide and thiophene on catalyst are summarized in Table 1. However, for the in situ HDS with WGSR, the rate

**Table 1.** The equilibrium constants and enthalpies for the adsorption of each reactant on the CoMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst

| Rx. temp.        | Adsorption equilibrium constant<br>(cc/min, g. cat) |            |            |            | Enthalpy<br>(kcal/mole) |
|------------------|---|------------|------------|------------|-------------------------|
|                  | 523<br>(K)  | 543<br>(K) | 553<br>(K) | 573<br>(K) |                         |
| H <sub>2</sub> O | 665   | 330        | 201        | 82         | -25                     |
| CO               | 67  | 45         | 35         | 16         | -18                     |
| Thiophene        | 40  | 25         | 15         | 10         | -16                     |
| CO <sub>2</sub>  | 14  | 13         | 11         | 9          | -4                      |



**Fig. 7.** The conversion of thiophene depending on contact times at various temperatures in HDS reaction with pure hydrogen (H<sub>2</sub> pressure, 15 kg/cm<sup>2</sup>).

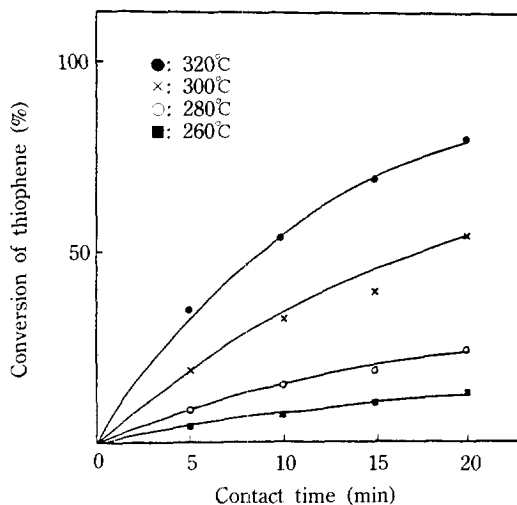
**Table 2.** The reaction rate constants of HDS reaction with pure hydrogen depending on temperature

| Rx. temp.<br>(°C) | Reaction rate constants (hr <sup>-1</sup> )<br>$k \times 10^{-2}$ |
|-------------------|---|
| 240               | 1.21  |
| 260               | 1.89  |
| 280               | 5.94  |
| 300               | 13.62   |

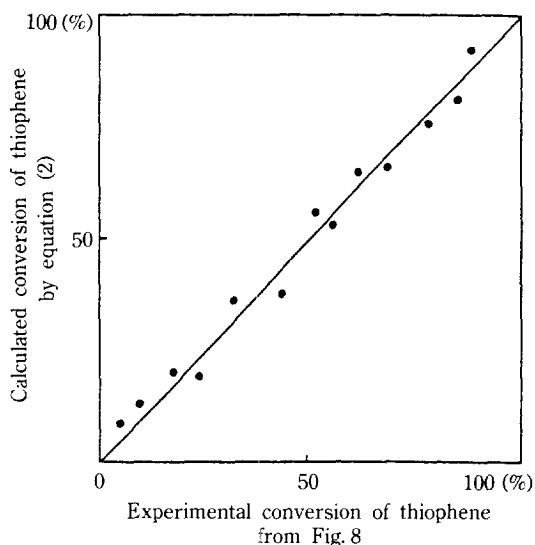
equation was revised as equation (2)

$$-r_{\text{HDS}} = kK_{\text{H}}K_{\text{T}}P_{\text{H}}P_{\text{T}} / (1 + K_{\text{H}}P_{\text{H}} + K_{\text{T}}P_{\text{T}} + K_{\text{H}_2\text{O}}P_{\text{H}_2\text{O}} + K_{\text{CO}}P_{\text{CO}} + K_{\text{CO}_2}P_{\text{CO}_2} + K_{\text{S}}P_{\text{S}})^2 \quad (2)$$

where  $k$ ; rate constant,  $K_{\text{H}}$ ,  $K_{\text{T}}$ ,  $K_{\text{H}_2\text{O}}$ ,  $K_{\text{CO}}$ ,  $K_{\text{CO}_2}$  and  $K_{\text{S}}$ ; adsorption equilibrium constant of hydrogen, thio-

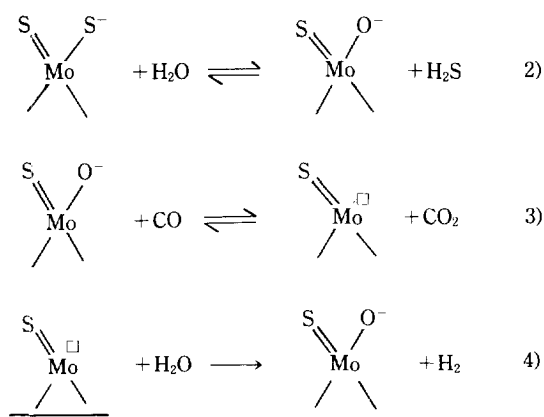


**Fig. 8.** The conversion of thiophene depending on contact times at various temperatures in in-situ HDS reaction with WGSR (H<sub>2</sub> pressure, 15 kg/cm<sup>2</sup>).

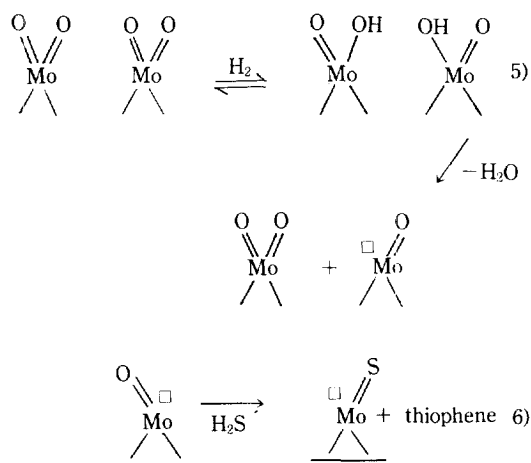


**Fig. 9.** Parity plots of the independent conversions of thiophene (%).

phene, water, carbon monoxide, carbon dioxide and hydrogen sulfide, respectively,  $P_{\text{H}}$ ,  $P_{\text{T}}$ ,  $P_{\text{H}_2\text{O}}$ ,  $P_{\text{CO}}$ ,  $P_{\text{CO}_2}$  and  $P_{\text{S}}$ ; partial pressures of hydrogen, thiophene, water, carbon monoxide, carbon dioxide and hydrogen sulfide, respectively. To test the equation (2), the rate constants ( $k$ ) obtained from the Fig. 7 were shown in Table 2. Fig. 7 and 8 show the changes in the conversion of thiophene depending on contact time at various temperatures in the case of using pure hydrogen and in-situ HDS reaction with WGSR, respectively.



Scheme 1. The mechanism WGSR proposed by Hou [8].



Scheme 2. The mechanism of HDS reaction presented by Massoth [9].

As shown in Fig. 9, equation (2) was confirmed by the assimilation of the experimental conversions of thiophene (Fig. 8) with those calculated from equation (2) using adsorption constants (Table 1) and rate constants (Table 2).

We speculated on the mechanism which was fitted for the equation (2). Hou [9] and Massoth [10] presented the reaction mechanism of WGSR and HDS, respectively,

as shown in Scheme 1 and 2. The proposed active site of catalyst were  $\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{Mo} \\ \diagdown \quad \diagup \\ \square \end{array}$  for both reactions. As shown in Table 1, the adsorption of water on the catalyst is the strongest among the reactants, thus water decrease dramatically the HDS reaction. Carbon monoxide and carbon dioxide also retard the HDS activity due to the competitive adsorption with thiophene on the same sites over the catalyst. Consequently, the poor efficiency of in-situ HDS reaction with WGSR seemed to be originated from these factors.

## CONCLUSION

Because the active sites in both HDS and WGSR were considered to be same, the poor efficiency of in-situ HDS reaction with WGSR was resulted from the competitive adsorptions of water, carbon monoxide and carbon dioxide with thiophene. The proposed rate equation (2), which was revised from that of Satterfield, was nicely coincided with this phenomenon.

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