

Production of Cyclohexene and Reactive Sulfur Species in Vapor-Phase Catalytic Oxidative Dehydrogenation of Cyclohexane with Carbonyl Sulfide

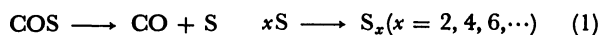
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The vapor-phase catalytic oxidative dehydrogenation of cyclohexane with COS over SiO₂ and Al₂O₃ catalysts (e.g., C₆H₁₂+COS→C₆H₁₀+CO+H₂S) has been investigated with respect to the production of cyclohexene and cyclohexadiene as well as the mechanism of the dehydrogenation reaction. The representative value of the combined yield of cyclohexene+cyclohexadiene is 8.0% and the combined selectivity to these two products at this yield obtained is 34.0%. These values are comparable to the values 8.0 and 30.8% reported in a recent Japanese patent. The comparison of the catalytic performance between two types of flow fixed-bed reactors demonstrates that the role of solid catalysts is to decompose COS into CO and sulfur, which then dehydrogenates hydrocarbons through a homogeneous mechanism. The results of the kinetic analysis of these reactions, together with the simulation of the overall catalytic reaction system, suggest a contribution of atomic sulfur to the oxidative dehydrogenation of cyclohexane in a conventional flow fixed-bed reactor.

The vapor-phase catalytic oxidative dehydrogenation of cyclohexane (C₆H₁₂) to cyclohexene (C₆H₁₀) is of industrial importance for the production of adipic acid and ε-caprolactam. A number of challenging works have been reported on the production of C₆H₁₀ through the oxidative dehydrogenation with gaseous oxygen: Cr₂O₃–CeO₂–K₂O/Al₂O₃,¹⁾ SiO₂–TiO₂–CeO₂,²⁾ native zeolites,³⁾ metal ion-exchanged zeolites,^{4,5)} group 2 metal silicates,⁶⁾ and polyquinones⁷⁾ have been employed as catalysts. A recent Japanese patent⁸⁾ also proposed the production of C₆H₁₀ through a similar catalytic oxidative dehydrogenation, but the yield and selectivity to C₆H₁₀ reported are as low as 8.0 and 30.8%, respectively, although a noble bimetallic catalyst Ru–Rh/SiO₂ is employed at 773K.

We have investigated the vapor-phase catalytic oxidative dehydrogenation of lower paraffinic hydrocarbons and arylalkyl compounds with COS.^{9,10)} In this oxidative dehydrogenation, COS is catalytically decomposed to CO and sulfur, which then abstracts hydrogen atoms from these hydrocarbons to give unsaturated hydrocarbons and H₂S.¹⁰⁾



One of the characteristic features of this dehydrogenation, compared with the conventional oxidative dehydrogenation with gaseous oxygen, is that the difference in reactivity of hydrocarbons is small between paraffinic and olefinic hydrocarbons, as shown by the reaction of butane and *trans*-2-butene over SiO₂ at 873K (e.g., conversion: butane 30% and *trans*-2-butene 48%).⁹⁾ Hence we expected to produce C₆H₁₀ with high yield and selectivity by the vapor-phase catalytic oxidative dehydrogenation of C₆H₁₂ with COS. In the present work, we have tried to find the best reaction conditions for the selective production of C₆H₁₀ and have then elucidated the nature of sulfur species responsible for the oxidative dehydrogenation through kinetic analysis of the reactions involved, and

by simulation of the overall catalytic reaction system.

Experimental

Reaction and Catalysts. Vapor-phase oxidative dehydrogenation of C₆H₁₂ was carried out with a conventional flow fixed-bed reactor at atmospheric pressure (1 Torr=133.322 Pa). The reactor system comprised a 15-mm-i.d. quartz tube, 470-mm long, and a concentric thermowell. The reactor was heated with a cylindrical electric furnace. Raschig rings (2×2 mm) were added above and below the catalyst bed. Guaranteed reagent grade C₆H₁₂ and commercially available COS of greater than 97.5 vol% purity (Matheson Co., CO₂ 1.4 vol%, N₂+CO 0.6 vol%, CS₂ 0.19 vol%, O₂ 0.10 vol% and H₂O 0.01 vol%) were used without further purification. Nitrogen (purity>99.99 vol%) was used as the diluent. The standard total feed rate was held constant at 150 (NTP) cm³ min⁻¹; the standard feed composition was 10 vol% each of C₆H₁₂ and COS. The catalysts employed are SiO₂ (20–40 mesh) and the referenced Al₂O₃ catalysts of the Catalysis Society of Japan (JRC-ALO-1 and -4). SiO₂ catalyst was prepared by the calcination of hydrated silica gel at 1073K in air for 5 h. Silica sol (Snowtex-O, Nissan Chemical Industries Ltd.) was used as the catalyst source. The BET surface area is 182 m² g⁻¹ (SiO₂), 176 m² g⁻¹ (JRC-ALO-1),¹¹⁾ and 174 m² g⁻¹ (JRC-ALO-4),¹¹⁾ respectively.

Analysis. The reaction products were analyzed by gas chromatography with helium as the carrier gas. Two columns in series, 2.0 m of Porapak R (50–80 mesh, 358K) and 2.0 m of molecular sieve 13X (60–80 mesh, room temperature), were used for the analysis of the gaseous reaction products (N₂, COS, CO₂, CO, CS₂, and H₂S). The liquid products (C₆H₁₂, C₆H₁₀, cyclohexadienes, and benzene) were analyzed with 6.0 m of PEG 6000 (20 wt% on Celite 545, 60–80 mesh, 338K). The yield of H₂S was always calculated on the basis of COS fed.

Results

Production of Cyclohexene. Table 1 summarizes the results of catalytic oxidative dehydrogenation of C₆H₁₂ with COS over SiO₂ at different reaction temperatures. Preliminary studies indicated that the yields of C₆H₁₀ and benzene (C₆H₆) are not restricted by the equilibrium of these reactions (e.g., K_p=661 and 2.61×

Table 1. Results of the Catalytic Oxidative Dehydrogenation of Cyclohexane with COS over SiO₂

Reaction temperature	Conversion of C ₆ H ₁₂	Yield/%			Selectivity to C ₆ H ₁₀ +C ₆ H ₈	Conversion of COS ^{a)}	Conversion to CO+S	Yield of H ₂ S
K	%	C ₆ H ₁₀	C ₆ H ₈	C ₆ H ₆	%	%	%	%
673	Neg ^{b)}	Neg	Neg	Neg	—	17.6	Neg	Neg
723	0.4	0.4	Neg	Neg	100	27.9	0.2	0.2
773	1.1	0.7	Neg	0.4	63.6	36.2	2.3	2.1
823	2.4	1.5	Neg	0.9	62.5	39.8	4.8	4.3
873	6.0	3.3	0.1 ^{c)}	2.6	56.7	45.2	11.6	11.0

Catalyst: 2.0 g. Total feed rate: 150 (NTP) cm³ min⁻¹ (C₆H₁₂ 10 vol%, COS 10 vol%, N₂ 80 vol%). a) The conversion to the side reaction (2COS→CO₂+CS₂) is included. b) Negligible. c) 1,3-Cyclohexadiene.

Table 2. Effect of the COS/C₆H₁₂ Feed Ratio on the Catalytic Oxidative Dehydrogenation of Cyclohexane

COS/C ₆ H ₁₂ feed ratio	Conversion of C ₆ H ₁₂	Yield/%			Selectivity to C ₆ H ₁₀ +C ₆ H ₈	Conversion of COS ^{a)}	Conversion to CO+S	Yield of H ₂ S
v/v	%	C ₆ H ₁₀	C ₆ H ₈	C ₆ H ₆	%	%	%	%
5/10	20.7	5.4	0.3	15.0	27.5	82.3	69.7	62.8 (102.0) ^{b)}
10/10	38.0 ^{c)}	8.2	0.2	29.3	22.1	78.8	59.3	57.9 (96.5) ^{b)}
15/10	34.0 ^{c)}	5.1	Neg ^{d)}	28.4	15.0	72.1	52.8	51.3 (60.2) ^{b)}

Catalyst: JRC-ALO-4 Al₂O₃ 1.0 g. Total feed rate: 150 (NTP) cm³ min⁻¹ (C₆H₁₂ 10 vol% fixed). a) The conversion to the side reaction (2COS→CO₂+CS₂) is included. b) Yield of H₂S calculated from the yields of C₆H₁₀, C₆H₈, and C₆H₆. c) A small amount of CH₄ (yield=0.3—0.5%) was formed.

10¹² for C₆H₁₀ and C₆H₆ formations, respectively, at 900K¹²⁾). Preliminary experiments showed that no significant change with time in the catalytic activity or selectivity took place during the reaction over SiO₂ and Al₂O₃ catalysts at 723—923K. The conversion of C₆H₁₂ was negligibly small at 673K: the conversion of COS to CO+S was nearly 0%, but the oxidative dehydrogenation took place at 723K, at which temperature the catalytic conversion of COS to CO+S was initiated (Table 1). The olefinic product in the oxidative dehydrogenation at 723K was only C₆H₁₀, but the formation of C₆H₆ was seen at 773K and the yields of these two products increased with further rise in reaction temperature. The formation of 1,3-cyclohexadiene (C₆H₈) was seen only at 873K, but its yield was as low as 0.1%.

Figure 1 shows the variation of the conversion of C₆H₁₂, the yields of C₆H₁₀+C₆H₈ and C₆H₆ and the combined selectivity to C₆H₁₀+C₆H₈ as a function of the conversion of COS to CO+S at 873K. The conversion of C₆H₁₂ and the yield of C₆H₆ were 4.4 and 1.7% at a conversion to CO+S of 7.4%, but they increased markedly at higher conversions and reached 44.5 and 38.5%, respectively, at 80.8%. In contrast, the combined selectivity to C₆H₁₀+C₆H₈ decreased from 61.4% to 12.1% with such an increase in the conversion to CO+S. The combined yield of C₆H₁₀+C₆H₈ showed a maximum at ca. 50% (Fig. 1). The combined yield and selectivity to C₆H₁₀+C₆H₈ at the conversions to CO+S of 40.0 and 59.3% were 8.0 and 34.0% and 8.4 and 22.1%, respectively (Fig. 1). It should be noted that the conversion of C₆H₁₂, the yields of C₆H₁₀+C₆H₈ and C₆H₆ and the combined selectivity to C₆H₁₀+C₆H₈

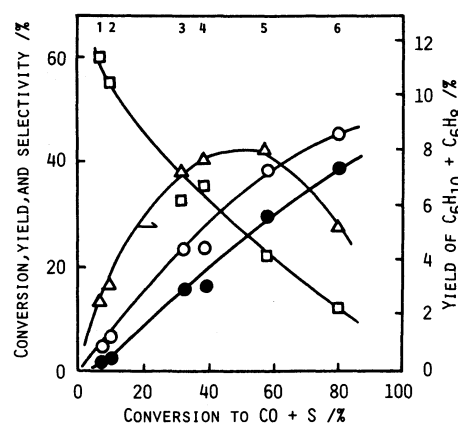


Fig. 1. Variation of the conversion of cyclohexane, the yields of cyclohexene+cyclohexadiene and benzene, and the selectivity to cyclohexene+cyclohexadiene as a function of the conversion of COS to CO+S.

Reaction temperature: 873 K. Total feed rate: 150 (NTP) cm³ min⁻¹ (C₆H₁₂ 10 vol%, COS 10 vol%, N₂ 80 vol%).

○: Conversion of C₆H₁₂, △: Yield of C₆H₁₀+C₆H₈, ●: Yield of C₆H₆, □: Selectivity to C₆H₁₀+C₆H₈.
1: SiO₂ 1.0 g, 2: SiO₂ 2.0 g, 3: JRC-ALO-4 Al₂O₃ 0.5 g, 4: JRC-ALO-1 Al₂O₃ 1.0 g, 5: JRC-ALO-4 Al₂O₃ 1.0 g, 6: JRC-ALO-4 Al₂O₃ 2.0 g. The yield of C₆H₈ is 0.1—0.5%.

are determined by the conversion of COS to CO+S, regardless of the catalysts employed (Fig. 1).

The catalytic oxidative dehydrogenation of C₆H₁₂ was carried out at 873K with JRC-ALO-4 Al₂O₃ at various COS/C₆H₁₂ feed ratios (Table 2). When the COS/C₆H₁₂ volumetric feed ratio was 5/10, the con-

Table 3. Results of the Vapor-Phase Homogeneous Reaction of Sulfur with Cyclohexane^{a)}

Reaction temperature K	Conversion of C ₆ H ₁₂ %	Yield/%			Selectivity to C ₆ H ₁₀ +C ₆ H ₈ %	Conversion of COS ^{b)} %	Conversion to CO+S %	Yield of H ₂ S %
		C ₆ H ₁₀	C ₆ H ₈	C ₆ H ₆				
823	4.7	3.0	Neg ^{c)}	1.7	63.8	39.1	9.5	8.4 (8.1) ^{d)}
873	8.1 ^{e)}	3.9	0.3	3.7	51.9	44.2	14.3	13.4 (15.6) ^{d)}

a) The reactor shown in Fig. 2 was employed. Catalyst: JRC-ALO-4 Al₂O₃ 2.0 g. Feed-1: COS 15 (NTP) cm³ min⁻¹ + N₂ 80 (NTP) cm³ min⁻¹. Feed-2: C₆H₁₂ 15 (NTP) cm³ min⁻¹ + N₂ 40 (NTP) cm³ min⁻¹. b) The conversion to the side reaction (2COS → CO₂ + CS₂) is included. c) Negligible. d) Yield of H₂S calculated from the yields of C₆H₁₀, C₆H₈, and C₆H₆. e) Yield of CH₄ is 0.2%.

version of C₆H₁₂ was 20.7% and the combined yield of C₆H₁₀+C₆H₈ was 5.7%. But, they increased to 38.0 and 8.4% at a COS/C₆H₁₂ feed ratio of 10/10 and then decreased to 34.0 and 5.1%, respectively, at 15/10. The yield of C₆H₆ showed a similar behavior. In contrast, the combined selectivity to C₆H₁₀+C₆H₈ decreased from 27.5% to 15.0% with such a change in the COS/C₆H₁₂ feed ratio (Table 2). For the selective production of C₆H₁₀, the COS/C₆H₁₂ volumetric feed ratio of 10/10 seems to be optimum at 873K. The observed values of the yields of H₂S (Table 2) give us some information about the mechanism of the oxidative dehydrogenation of C₆H₁₂. That is, the yields of H₂S calculated from the yields of dehydrogenation products (C₆H₁₀, C₆H₈, and C₆H₆) are always greater than the experimentally observed yields of H₂S, although the latter yields of H₂S are always comparable to the values of the conversion of COS to CO+S (Table 2). Similar results were obtained over JRC-ALO-1 and -4 Al₂O₃ at 873K (Fig. 1), but not over SiO₂ at 723–873K (Table 1). These results indicate that a large portion of the C₆H₈ formed, but not C₆H₁₂ or C₆H₁₀, was thermally dehydrogenated to C₆H₆ when the amount of sulfur evolved was smaller than that of hydrocarbons.

Mechanistic Studies. In order to elucidate the role of solid catalysts and the mechanism of oxidative dehydrogenation, the catalytic oxidative dehydrogenation of C₆H₁₂ with COS was carried out with a special reactor shown in Fig. 2. In this reactor, only the mixture of COS and N₂ is allowed to come into contact with solid catalyst and the resulting gaseous product containing sulfur is then mixed with another gaseous mixture (C₆H₁₂+N₂) in the absence of catalyst. The temperature of the reactor in which the homogeneous reaction of sulfur with C₆H₁₂ takes place is always kept to nearly equal to that for the catalytic decomposition of COS. The results obtained at 823 and 873K over JRC-ALO-4 Al₂O₃ are summarized in Table 3. At these two reaction temperatures, the oxidative dehydrogenation of C₆H₁₂ always took place to produce C₆H₁₀, C₆H₈, and C₆H₆ with formation of H₂S. Moreover, the values of the conversion of C₆H₁₂, the yields of C₆H₁₀+C₆H₈ and C₆H₆, and the combined selectivity to C₆H₁₀+C₆H₈ at 873K (Table 3) are nearly equal to the values (8.3, 4.2, 4.1, and 50.6%, respectively) expected from the conversion of COS to CO+S (14.3%)

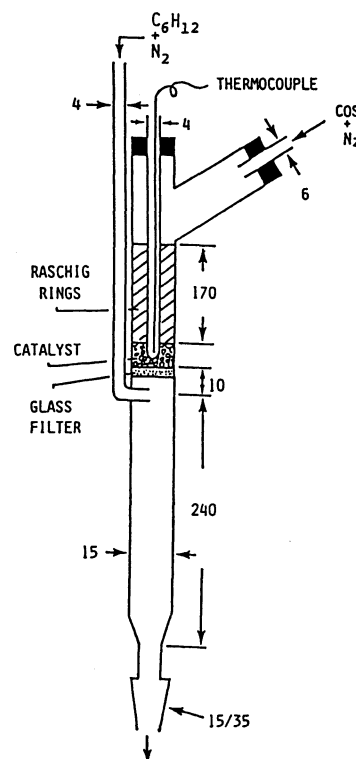
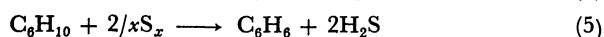
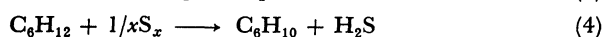
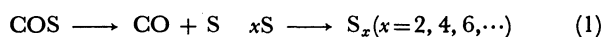


Fig. 2. A schematic figure of the reactor employed in the vapor-phase homogeneous reaction of sulfur with cyclohexane. The dimensions of the reactor are given in millimeters.

in Fig. 1. As discussed later, these results support the view that the role of solid catalyst is to decompose COS into CO and sulfur, which then dehydrogenates hydrocarbons through a homogeneous mechanism. The yield of H₂S at 823K (8.4%) is nearly the same as that calculated from the yields of C₆H₁₀, C₆H₈, and C₆H₆ (8.1%) (Table 3). This indicates that no thermal dehydrogenation of C₆H₈ to C₆H₆ took place during the oxidative dehydrogenation of C₆H₁₂ at 823K.

Kinetic Studies. We estimated the rate constants for the catalytic decomposition of COS to CO+S and for the dehydrogenation of C₆H₁₂ and C₆H₁₀ with S₂ and then predicted the nature of sulfur species responsible for the dehydrogenation by simulation of the overall catalytic reaction system. Based on the present mechanistic findings, we propose the following reactions for the catalytic oxidative dehydrogenation of

C₆H₁₂ with COS at 823K.



We use Reaction 5 instead of two consecutive reactions ($\text{C}_6\text{H}_{10} + 1/x\text{S}_x \rightarrow \text{C}_6\text{H}_8 + \text{H}_2\text{S}$, $\text{C}_6\text{H}_8 + 1/x\text{S}_x \rightarrow \text{C}_6\text{H}_6 + \text{H}_2\text{S}$) since the yield of C₆H₈ was always negligible at 823K (Tables 1 and 3). In a conventional fixed-bed reactor, Reactions 1 and 3 take place at the surface of solid catalysts, whereas Reactions 4 and 5 occur homogeneously. In these kinetic studies, we employed JRC-ALO-4 Al₂O₃ catalyst. The reaction order with respect to COS in Reaction 1 was approximately 0.8 at 823K and the chemical equilibrium was always established for Reaction 3, as shown later. Thus, the rate equations derived for these reaction steps are as follows:

$$d[\text{COS}]/d(W/F) = -k_{01}[\text{COS}] \quad (6)$$

$$K_{p1} = [\text{CO}_2][\text{CS}_2]/[\text{COS}]^2 \quad (7)$$

$$d[\text{C}_6\text{H}_{12}]/d(V/F) = -k_1[\text{C}_6\text{H}_{12}][\text{S}_x] \quad (8)$$

$$d[\text{C}_6\text{H}_{10}]/d(V/F) = k_1[\text{C}_6\text{H}_{12}][\text{S}_x] - k_2[\text{C}_6\text{H}_{10}][\text{S}_x] \quad (9)$$

$$d[\text{C}_6\text{H}_6]/d(V/F) = k_2[\text{C}_6\text{H}_{10}][\text{S}_x] \quad (10)$$

Here k_{01} , k_1 , and k_2 are rate constants for Reactions 1, 4, and 5, respectively, and K_{p1} , W , V , and F are equilibrium constant of Reaction 3, weight of catalyst, void volume in the catalyst bed, and total feed rate of reactant mixture. The parentheses in Equations 6, 7, 8, 9, and 10 denote the concentration of reactant species in mol fraction units. The density of JRC-ALO-4 Al₂O₃ was determined with liquid C₆H₁₂ and a measuring cylinder: the relation $V/F(\text{min}) = 8.03 \times 10^{-5} W/F(\text{g-catalyst} \cdot \text{min} \cdot \text{g-mol}^{-1})$ was obtained at 823K. Equation 10 shows that the rate-controlling step for the formation of C₆H₆ from C₆H₁₀ is the oxidative dehydrogenation of C₆H₁₀ to C₆H₈, not that of C₆H₈ to C₆H₆.

Estimation of k_{01} and K_{p1} . Figure 3 shows the effect of the contact time on the conversion of COS over JRC-ALO-4 Al₂O₃ at 823K. At a contact time of 15.0 g-catalyst·min·g-mol⁻¹, the conversion to CO+S was 5.8%, but it increased for longer contact times of the reaction and levelled off at 15.0% between 150 and 300 g-catalyst·min·g-mol⁻¹. In contrast, the conversion to CO₂+CS₂ was nearly constant at 30.3–30.8% between 15.0 and 300.0 g-catalyst·min·g-mol⁻¹. Hence one could say that the chemical equilibrium for the catalytic decomposition of COS to CO₂+CS₂ is readily established even at very short contact times of the reaction, whereas that for the decomposition to CO+S is established only above 150 g-catalyst·min·g-mol⁻¹. At these reaction conditions, the sulfur species formed at equilibrium is of S₂ type (Reaction 11).¹³ Using the composition of the gaseous product at 300 g-

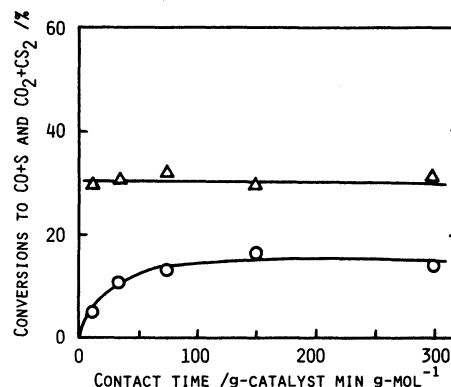
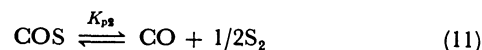


Fig. 3. Effect of contact time on the catalytic conversion of COS.

Catalyst: JRC-ALO-4 Al₂O₃. Reaction temperature: 823K. Total feed rate: 150 (NTP) cm³ min⁻¹ (COS 10 vol%, N₂ 90 vol%).

O: Conversion to CO+S, Δ: Conversion to CO₂+CS₂.

catalyst·min·g-mol⁻¹, the equilibrium constants for Reactions 3 and 11 were calculated to be 8.07×10^{-2}



and 2.40×10^{-2} , respectively. These values agree well with the thermodynamically calculated values ($K_{p1} = 2.29 \times 10^{-1}$, $K_{p2} = 2.21 \times 10^{-2}$).¹² At a contact time of 15.0 g-catalyst·min·g-mol⁻¹, the conversions to CO+S and CO₂+CS₂ and rate of the conversion to CO+S were 5.8 and 30.5% and 3.87×10^{-4} g-mol·g-catalyst⁻¹·min⁻¹, respectively. With these values and Equation 12, the rate constants k_{01} and k_{02} were

$$d[\text{CO}]/d(W/F) = k_{01}[\text{COS}] - k_{02}[\text{CO}][\text{S}_2] \quad (K_{p2} = k_{01}/k_{02}) \quad (12)$$

estimated to be 6.14×10^{-3} and 2.56×10^{-1} g-mol·g-catalyst⁻¹·min⁻¹ at 823K.

Estimation of k_1 and k_2 . The rate constants for the oxidative dehydrogenation of C₆H₁₂ and C₆H₁₀ with S₂ were estimated at 823K by the kinetic analysis of these reactions by using the reactor shown in Fig. 2. Here COS was decomposed at 467.3 g-catalyst·min·g-mol⁻¹ over JRC-ALO-4 Al₂O₃ at 823K and the evolved sulfur (S₂) was reacted with C₆H₁₂ at 823K (Table 4). From Equations 8 and 9, the following equation can be derived; here x , y , and k are the fractional conversion of C₆H₁₂, the fractional yield of C₆H₁₀, and k_2/k_1 , respectively:

$$y = \frac{1}{(k-1)} [(1-x) - (1-x)^k] \quad (13)$$

The averaged value of k was thus estimated to be 27.1 at 823K (Table 4).

The value of k_1 for the reaction of C₆H₁₂ with S₂ was estimated by the kinetic analysis of the reaction by using the same reactor (Fig. 2). By integration of Equation 8, the following equation is obtained:

Table 4. Determination of k

v/F^a /min	Conversion of C_6H_{12} /%	Yield/% ^b			k /—
		C_6H_{10}	C_6H_6	H_2S	
4.67×10^{-2}	5.1	2.8	2.3	9.2	26.0
2.32×10^{-2}	4.8	2.9	1.9	8.4	23.1
1.74×10^{-2}	3.3	2.1	1.2	4.9	29.1
0.83×10^{-2}	1.9	1.4	0.5	3.2	30.0

a) Reaction temperature: 823K. Catalyst: JRC-ALO-4 Al_2O_3 2.0 g. Feed-1: COS 15 (NTP) $cm^3 \cdot min^{-1} + N_2$ 80 (NTP) $cm^3 \cdot min^{-1}$ ($W/F=467.3$ g-catalyst $\cdot min \cdot g \cdot mol^{-1}$). Feed-2: C_6H_{12} 15 (NTP) $cm^3 \cdot min^{-1} + N_2$ 40 (NTP) $cm^3 \cdot min^{-1}$. The conversion of COS to $CO+S$ is 9.5%. a) v is the volume of reactor below the catalyst bed. This volume was changed by adding Rasching rings (2×2 mm). b) Yield of C_6H_8 is negligible.

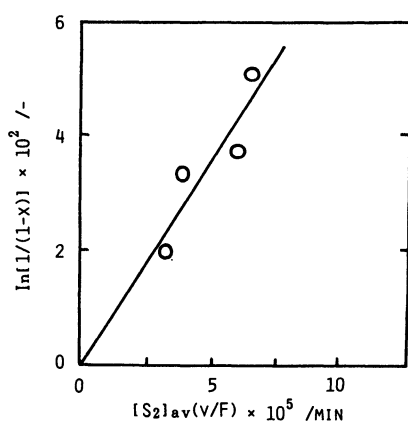


Fig. 4. Determination of k_1 based on Equation 14. Catalyst: JRC-ALO-4 Al_2O_3 2.0–10.0 g. Reaction temperature: 823K. Feed-1: 95–475 (NTP) $cm^3 \cdot min^{-1}$ ($COS/N_2=3/16$, fixed. $W/F=467.3$ g-catalyst $\cdot min \cdot g \cdot mol^{-1}$). Feed-2: 55–275 (NTP) $cm^3 \cdot min^{-1}$ ($C_6H_{12}/N_2=1/3$, fixed). v : 17.10–32.92 cm^3 .

$$k_1 = \frac{\ln[1/(1-x)]}{[S_2]_{av}(v/F)} \quad (14)$$

Here $[S_2]_{av}$ is the logarithmically averaged value of the concentration of diatomic sulfur throughout the homogeneous reaction zone and v is its volume. By changing the amount of catalyst, the volume of the homogeneous reaction zone, and the feed rates of the respective gaseous mixtures at the fixed concentration of C_6H_{12} at the inlet of the homogeneous reaction zone (10 vol%), the relation between $\ln[1/(1-x)]$ and $[S_2]_{av}(v/F)$ at 823K was determined (Fig. 4). From the slope of the straight line in Fig. 4, k_1 for the dehydrogenation of C_6H_{12} with S_2 was estimated to be $7.38 \times 10^2 \text{ min}^{-1}$ at 823K. With this value of k_1 and $k=27.1$, k_2 for the dehydrogenation of C_6H_{10} with S_2 was calculated to be $2.00 \times 10^4 \text{ min}^{-1}$ at 823K.

Simulation of Catalytic Reaction System. Assuming the participation of S_2 in the oxidative dehydrogenation and no gaseous volume change during the reaction, we simulated the catalytic oxidative dehydrogenation of C_6H_{12} with COS over JRC-ALO-4 Al_2O_3

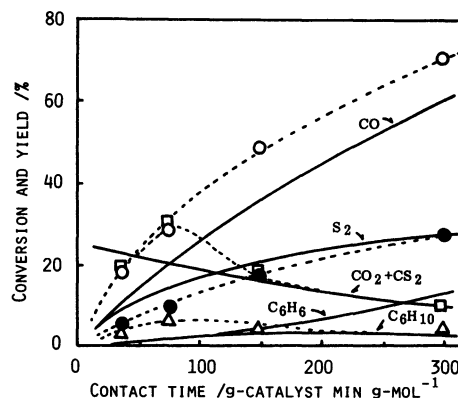


Fig. 5. Simulation of the catalytic oxidative dehydrogenation system.

Catalyst: JRC-ALO-4 Al_2O_3 . Reaction temperature: 823K. Feed composition: C_6H_{12} 10 vol%, COS 10 vol%, N_2 80 vol%.

Dotted lines—observed values. Solid lines—simulated values.

$k_0=6.14 \times 10^{-3} \text{ g} \cdot \text{mol} \cdot \text{g} \cdot \text{catalyst}^{-1} \cdot \text{min}^{-1}$, $K_{p1}=8.07 \times 10^{-2}$, $k_1=7.38 \times 10^2 \text{ min}^{-1}$, $k_2=2.00 \times 10^4 \text{ min}^{-1}$.

○: Conversion of COS to $CO+S$, □: Conversion of COS to CO_2+CS_2 , △: Yield of C_6H_{10} , ●: Yield of C_6H_6 .

at 823K in the conventional fixed-bed reactor using Equations 6, 7, 8, 9, and 10 and the values of k_{01} , K_{p1} , k_1 , and k_2 obtained above. The calculation was made by the Runge-Kutta Gill method. The calculated catalytic performance versus the contact time of the reaction is shown in Fig. 5. The calculated values of the conversion of COS to CO_2+CS_2 and the yield of C_6H_{10} are nearly equal to the experimentally observed values, especially at the contact time of 150–300 g-catalyst $\cdot min \cdot g \cdot mol^{-1}$. However, there is a big difference between the calculated and observed values of the conversion of COS to $CO+S$ and the yield of C_6H_6 although these two kinds of values similarly increase with increasing the contact time of the reaction. For example, the calculated (observed) values of the yield of C_6H_6 are 1.7 (9.1), 5.7 (17.0), and 14.2% (27.4%), respectively, at the contact time of 75, 150, and 300 g-catalyst $\cdot min \cdot g \cdot mol^{-1}$, and those of the conversion of COS to $CO+S$ at these contact times are 19.6 (28.4), 36.3 (48.3), and 60.1% (70.5%), respectively (Fig. 5). The most striking difference between the calculated and observed values is the much greater yields of sulfur (2.0–24.0% at $W/F=10$ –300 g-catalyst $\cdot min \cdot g \cdot mol^{-1}$) in the calculated result (Fig. 5). In this oxidative dehydrogenation, the yield of sulfur was always negligible, as shown by the nearly stoichiometric formation of H_2S (Tables 1, 2, and 3).

Assuming the participation of atomic sulfur in the oxidative dehydrogenation, we have again simulated the catalytic reaction system at 823K, in which, however, only the values of k_1 and k_2 are increased to nearly 36 times k_1 and k_2 values employed in Fig. 5. In agreement with the experimental observation, the

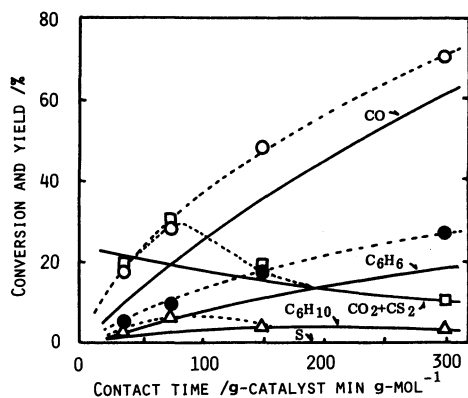


Fig. 6. Simulation of the catalytic oxidative dehydrogenation system.

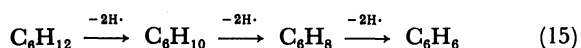
Reaction conditions and symbols used are the same as those in Fig. 5.

$k_0 = 6.14 \times 10^{-3} \text{ g-mol} \cdot \text{g-catalyst}^{-1} \cdot \text{min}^{-1}$, $K_{p1} = 8.07 \times 10^{-2}$, $k_1 = 2.66 \times 10^4 \text{ min}^{-1}$, $k_2 = 7.20 \times 10^5 \text{ min}^{-1}$.

yield of sulfur in this calculation is always negligible within the contact time of the reaction studied (Fig. 6). Both the calculated values of the yields of C_6H_{10} and C_6H_6 increased to be nearer to the observed values than the case in Fig. 5: the calculated values of the yield of C_6H_6 at the contact time of 75, 150, and 300 g-catalyst·min·g-mol⁻¹ are 7.1, 10.8, and 18.8%, respectively. In contrast, the values of the conversions of COS to CO+S and CO₂+CS₂ remained unchanged in this calculation (Fig. 6).

Discussion

We first discuss the role of solid catalyst and the mechanism of the oxidative dehydrogenation of C_6H_{12} with COS. But, we do not refer here to the mechanism of the catalytic decomposition of COS since it was already reported.¹⁴⁾ Although the yield of C_6H_8 over SiO_2 was negligibly small between 723 and 823K, the observed behavior of the yields of C_6H_{10} and C_6H_6 with rising reaction temperature, i.e., formation of C_6H_{10} at 723K, that of C_6H_{10} and C_6H_6 at 773K, and the increase in the yields of these two products with further rise in reaction temperature (Table 1) suggest that the oxidative dehydrogenation of C_6H_{12} with COS proceeds through the following consecutive reaction steps.



Both the convex behavior of the yield of $\text{C}_6\text{H}_{10} + \text{C}_6\text{H}_8$ against the conversion of C_6H_{12} and the decrease in the selectivity to these two products with increasing conversion of C_6H_{12} (Fig. 1) support this reaction scheme.

The occurrence of the catalytic oxidative dehydrogenation of C_6H_{12} with COS in the special reactor, in which only COS contacts with the catalyst and the evolved gaseous sulfur reacts with C_6H_{12} in the

absence of solid catalyst (Table 3, Fig. 2), indicates that the role of solid catalysts is to decompose COS into CO+S and that the evolved sulfur can dehydrogenate C_6H_{12} , C_6H_{10} , and C_6H_8 even in the absence of solid catalysts. Since the values of the conversion of C_6H_{12} , the yields of $\text{C}_6\text{H}_{10} + \text{C}_6\text{H}_8$ and C_6H_6 , and the combined selectivity to $\text{C}_6\text{H}_{10} + \text{C}_6\text{H}_8$ at 873K obtained with the special type reactor were nearly equal to the values at 873K obtained with the conventional fixed-bed reactor (Table 3, Fig. 1), we believe that the oxidative dehydrogenation of C_6H_{12} with sulfur proceeded homogeneously also in the conventional fixed-bed reactor. The decisive effect observed of the conversion of COS to CO+S on the conversion of C_6H_{12} and the product distributions (Fig. 1) supports this view. The heterogeneous-homogeneous reaction mechanism for the catalytic oxidative dehydrogenation of C_6H_{12} with COS proposed in the present work agrees with the reaction mechanism for the cases of ethylbenzene and paraffinic hydrocarbons reported.^{9,10)} The representative values of the combined yield and selectivity to $\text{C}_6\text{H}_{10} + \text{C}_6\text{H}_8$, 8.0 and 34.0%, obtained in the present work (Fig. 1) are comparable to those, 8.0 and 30.8%, reported in a recent Japanese patent.⁹⁾

Next we discuss the nature of sulfur species responsible for the oxidative dehydrogenation of C_6H_{12} . Although the calculated values of the conversion of COS to CO+S and CO₂+CS₂ and the yields of C_6H_{10} and C_6H_6 in the simulation at 823K did not always agree with the experimentally observed values, the behavior of these calculated values versus the contact time of the reaction is similar to that of the observed values (Figs. 5 and 6), thus supporting the reasonability of the simulation method employed in the present work. The big difference between the calculated and observed values of the conversion of COS to CO+S at 823K (Figs. 5 and 6) must have been caused by the low estimation of the value of the rate constant k_{01} for the catalytic decomposition of COS to CO+S at 823K. We believe that by the use of a larger value of k_{01} ($> 6.14 \times 10^{-3} \text{ g-mol} \cdot \text{g-catalyst}^{-1} \cdot \text{min}^{-1}$) not only the calculated value of the conversion of COS to CO+S but also that of the yields of C_6H_{10} and C_6H_6 can be increased to be much nearer to the observed values than those in Fig. 6.

The most important implication suggested by the results of simulation concerns the nature of sulfur species responsible for the oxidative dehydrogenation of C_6H_{12} . The agreement of the negligibly small yields of sulfur between the calculated and observed values caused by the assumption of the participation of atomic sulfur and the rise of the values of the rate constants for the dehydrogenation of C_6H_{12} and C_6H_{10} with sulfur (k_1 and k_2) by 36 times (Figs. 5 and 6) suggests that the sulfur species responsible for the oxidative dehydrogenation in the conventional fixed-bed reactor is mainly of atomic type, although some degree of the contribution of diatomic sulfur to

the reaction can not be rejected. This view can be supported by the following discussion based on the Evans & Polanyi rule (Equation 16).¹⁵⁾

$$\Delta E = -\alpha \Delta Q \quad (\alpha=0.25) \quad (16)$$

Where ΔE and ΔQ are the differences in activation energy and heat of reaction, respectively. The heat of formation of S_2 from atomic sulfur ($S \rightarrow 1/2 S_2$) is ca. 40 kcal $\cdot$ atom $^{-1}$.¹⁶⁾ When we assume that ΔQ is equal to 40 kcal $\cdot$ atom $^{-1}$, the value of $e^{-\Delta E/RT}$ at 823K is calculated to be 417. This means that the reactivity of atomic sulfur is at the greatest nearly 400 times greater than that of diatomic one in exothermal reactions. The value of the relative reactivity to C_6H_{12} and C_6H_{10} of atomic sulfur to diatomic sulfur employed in the present work, 36, is smaller than the calculated one, 417. This supports our view concerning the nature of the sulfur species responsible for the dehydrogenation reactions. In the present work, the relative degree of contribution of atomic and diatomic sulfurs to the oxidative dehydrogenation of C_6H_{12} was not determined.

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[†]1 cal=4.184J.