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

Masamichi Akimoto,* Yoshinori Kashita, and Hiroo Niiyama
Department of Chemical Engineering,Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152
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The vapor-phase catalytic oxidative dehydrogenation of cyclohexane with COS over SiO_2 and Al_2O_3 catalysts (e.g., $C_6H_{12}+COS \rightarrow C_6H_{10}+CO+H_2S$) 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 (C_6H_{12}) to cyclohexene (C_6H_{10}) 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 C_6H_{10} through the oxidative dehydrogenation with gaseous oxygen: Cr_2O_3–CeO_2–K_2O/Al_2O_3,[1] SiO_2–TiO_2–CeO_2,[2] native zeolites,[3] metal ion-exchanged zeolites,[4,5] group 2 metal silicates,[6] and polyquinones[7] have been employed as catalysts. A recent Japanese patent[8] also proposed the production of C_6H_{10} through a similar catalytic oxidative dehydrogenation, but the yield and selectivity to C_6H_{10} reported are as low as 8.0 and 30.8%, respectively, although a noble bimetallic catalyst Ru–Rh/SiO_2 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 H_2S.[10]

$$\mathrm{COS} \longrightarrow \mathrm{CO} + \mathrm{S} \qquad x\mathrm{S} \longrightarrow \mathrm{S}_x (x = 2, 4, 6, \cdots) \tag{1}$$

$$\mathrm{C}_n\mathrm{H}_{2n+2} + 1/x\mathrm{S}_x \longrightarrow \mathrm{C}_n\mathrm{H}_{2n} + \mathrm{H_2S} \tag{2}$$

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 SiO_2 at 873K (e.g., conversion: butane 30% and *trans*-2-butene 48%).[9] Hence we expected to produce C_6H_{10} with high yield and selectivity by the vapor-phase catalytic oxidative dehydrogenation of C_6H_{12} with COS. In the present work, we have tried to find the best reaction conditions for the selective production of C_6H_{10} 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 C_6H_{12} 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 C_6H_{12} and commercially available COS of greater than 97.5 vol% purity (Matheson Co., CO_2 1.4 vol%, N_2+CO 0.6 vol%, CS_2 0.19 vol%, O_2 0.10 vol% and H_2O 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) $cm^3\,min^{-1}$; the standard feed composition was 10 vol% each of C_6H_{12} and COS. The catalysts employed are SiO_2 (20—40 mesh) and the referenced Al_2O_3 catalysts of the Catalysis Society of Japan (JRC-ALO-1 and -4). SiO_2 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 $m^2\,g^{-1}$ (SiO_2), 176 $m^2\,g^{-1}$ (JRC-ALO-1),[11] and 174 $m^2\,g^{-1}$ (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 (N_2, COS, CO_2, CO, CS_2, and H_2S). The liquid products (C_6H_{12}, C_6H_{10}, cyclohexadienes, and benzene) were analyzed with 6.0 m of PEG 6000 (20 wt% on Celite 545, 60—80 mesh, 338K). The yield of H_2S was always calculated on the basis of COS fed.

Results

Production of Cyclohexene. Table 1 summarizes the results of catalytic oxidative dehydrogenation of C_6H_{12} with COS over SiO_2 at different reaction temperatures. Preliminary studies indicated that the yields of C_6H_{10} and benzene (C_6H_6) 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 SiO_2

Reaction temperature	Conversion of C_6H_{12}	Yield/%			Selectivity to $C_6H_{10}+C_6H_8$	Conversion of COS[a]	Conversion to CO+S	Yield of H_2S
K	%	C_6H_{10}	C_6H_8	C_6H_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) cm^3 min^{-1} (C_6H_{12} 10 vol%, COS 10 vol%, N_2 80 vol%). a) The conversion to the side reaction ($2COS \rightarrow CO_2+CS_2$) is included. b) Negligible. c) 1,3-Cyclohexadiene.

Table 2. Effect of the COS/C_6H_{12} Feed Ratio on the Catalytic Oxidative Dehydrogenation of Cyclohexane

COS/C_6H_{12} feed ratio	Conversion of C_6H_{12}	Yield/%			Selectivity to $C_6H_{10}+C_6H_8$	Conversion of COS[a]	Conversion to CO+S	Yield of H_2S
v/v	%	C_6H_{10}	C_6H_8	C_6H_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 Al_2O_3 1.0 g. Total feed rate: 150 (NTP) cm^3 min^{-1} (C_6H_{12} 10 vol% fixed). a) The conversion to the side reaction ($2COS \rightarrow CO_2+CS_2$) is included. b) Yield of H_2S calculated from the yields of C_6H_{10}, C_6H_8, and C_6H_6. c) A small amount of CH_4 (yield=0.3—0.5%) was formed.

10^{12} for C_6H_{10} and C_6H_6 formations, respectively, at 900K[12]). Preliminary experiments showed that no significant change with time in the catalytic activity or selectivity took place during the reaction over SiO_2 and Al_2O_3 catalysts at 723—923K. The conversion of C_6H_{12} 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 C_6H_{10}, but the formation of C_6H_6 was seen at 773K and the yields of these two products increased with further rise in reaction temperature. The formation of 1,3-cyclohexadiene (C_6H_8) was seen only at 873K, but its yield was as low as 0.1%.

Figure 1 shows the variation of the conversion of C_6H_{12}, the yields of $C_6H_{10}+C_6H_8$ and C_6H_6 and the combined selectivity to $C_6H_{10}+C_6H_8$ as a function of the conversion of COS to CO+S at 873K. The conversion of C_6H_{12} and the yield of C_6H_6 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 $C_6H_{10}+C_6H_8$ decreased from 61.4% to 12.1% with such an increase in the conversion to CO+S. The combined yield of $C_6H_{10}+C_6H_8$ showed a maximum at ca. 50% (Fig. 1). The combined yield and selectivity to $C_6H_{10}+C_6H_8$ 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 C_6H_{12}, the yields of $C_6H_{10}+C_6H_8$ and C_6H_6 and the combined selectivity to $C_6H_{10}+C_6H_8$ are determined by the conversion of COS to CO+S, regardless of the catalysts employed (Fig. 1).

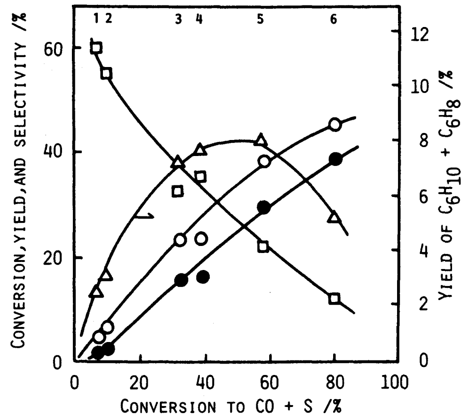

Fig. 1. Variation of the conversion of cyclohexane, the yields of cyclohexene+cyclohexadiene and benzene, and the selectivity to cyclohexene+cyclohexadiene as a function of the conversion of COS to CO+S.
Reaction temperature: 873 K. Total feed rate: 150 (NTP) cm^3 min^{-1} (C_6H_{12} 10 vol%, COS 10 vol%, N_2 80 vol%).
○: Conversion of C_6H_{12}, △: Yield of $C_6H_{10}+C_6H_8$, ●: Yield of C_6H_6, □: Selectivity to $C_6H_{10}+C_6H_8$.
1: SiO_2 1.0 g, 2: SiO_2 2.0 g, 3: JRC-ALO-4 Al_2O_3 0.5 g, 4: JRC-ALO-1 Al_2O_3 1.0 g, 5: JRC-ALO-4 Al_2O_3 1.0 g, 6: JRC-ALO-4 Al_2O_3 2.0 g. The yield of C_6H_8 is 0.1—0.5%.

The catalytic oxidative dehydrogenation of C_6H_{12} was carried out at 873K with JRC-ALO-4 Al_2O_3 at various COS/C_6H_{12} feed ratios (Table 2). When the COS/C_6H_{12} volumetric feed ratio was 5/10, the con-

Table 3. Results of the Vapor-Phase Homogeneous Reaction of Sulfur with Cyclohexane[a)]

Reaction temperature	Conversion of C_6H_{12}	Yield/%			Selectivity to $C_6H_{10}+C_6H_8$	Conversion of COS[b)]	Conversion to CO+S	Yield of H_2S
K	%	C_6H_{10}	C_6H_8	C_6H_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 Al_2O_3 2.0 g. Feed-1: COS 15 (NTP) $cm^3\,min^{-1}$+N_2 80 (NTP) $cm^3\,min^{-1}$. Feed-2: C_6H_{12} 15 (NTP) $cm^3\,min^{-1}$+N_2 40 (NTP) $cm^3\,min^{-1}$. b) The conversion to the side reaction ($2COS \rightarrow CO_2+CS_2$) is included. c) Negligible. d) Yield of H_2S calculated from the yields of C_6H_{10}, C_6H_8, and C_6H_6. e) Yield of CH_4 is 0.2%.

version of C_6H_{12} was 20.7% and the combined yield of $C_6H_{10}+C_6H_8$ was 5.7%. But, they increased to 38.0 and 8.4% at a COS/C_6H_{12} feed ratio of 10/10 and then decreased to 34.0 and 5.1%, respectively, at 15/10. The yield of C_6H_6 showed a similar behavior. In contrast, the combined selectivity to $C_6H_{10}+C_6H_8$ decreased from 27.5% to 15.0% with such a change in the COS/C_6H_{12} feed ratio (Table 2). For the selective production of C_6H_{10}, the COS/C_6H_{12} volumetric feed ratio of 10/10 seems to be optimum at 873K. The observed values of the yields of H_2S (Table 2) give us some information about the mechanism of the oxidative dehydrogenation of C_6H_{12}. That is, the yields of H_2S calculated from the yields of dehydrogenation products (C_6H_{10}, C_6H_8, and C_6H_6) are always greater than the experimentally observed yields of H_2S, although the latter yields of H_2S 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 Al_2O_3 at 873K (Fig. 1), but not over SiO_2 at 723—873K (Table 1). These results indicate that a large portion of the C_6H_8 formed, but not C_6H_{12} or C_6H_{10}, was thermally dehydrogenated to C_6H_6 when the amount of sulfur evolved was smaller than that of hydrocarbons.

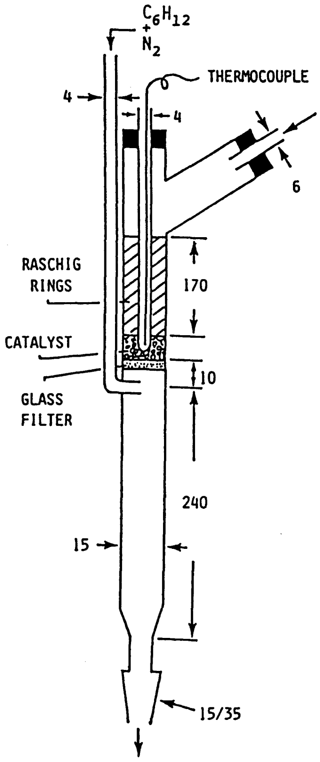

Fig. 2. A schematic figure of the reactor employed in the vapor-phase homogeneous reaction of sulfur with cyclohexane. The dimensions of the reactor are given in millimeters.

Mechanistic Studies. In order to elucidate the role of solid catalysts and the mechanism of oxidative dehydrogenation, the catalytic oxidative dehydrogenation of C_6H_{12} with COS was carried out with a special reactor shown in Fig. 2. In this reactor, only the mixture of COS and N_2 is allowed to come into contact with solid catalyst and the resulting gaseous product containing sulfur is then mixed with another gaseous mixture ($C_6H_{12}+N_2$) in the absence of catalyst. The temperature of the reactor in which the homogeneous reaction of sulfur with C_6H_{12} 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 Al_2O_3 are summarized in Table 3. At these two reaction temperatures, the oxidative dehydrogenation of C_6H_{12} always took place to produce C_6H_{10}, C_6H_8, and C_6H_6 with formation of H_2S. Moreover, the values of the conversion of C_6H_{12}, the yields of $C_6H_{10}+C_6H_8$ and C_6H_6, and the combined selectivity to $C_6H_{10}+C_6H_8$ 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%) 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 H_2S at 823K (8.4%) is nearly the same as that calculated from the yields of C_6H_{10}, C_6H_8, and C_6H_6 (8.1%) (Table 3). This indicates that no thermal dehydrogenation of C_6H_8 to C_6H_6 took place during the oxidative dehydrogenation of C_6H_{12} at 823K.

Kinetic Studies. We estimated the rate constants for the catalytic decomposition of COS to CO+S and for the dehydrogenation of C_6H_{12} and C_6H_{10} with S_2 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

C_6H_{12} with COS at 823K.

$$\mathrm{COS} \longrightarrow \mathrm{CO} + \mathrm{S} \quad x\mathrm{S} \longrightarrow \mathrm{S}_x (x=2, 4, 6,\cdots) \tag{1}$$

$$2\mathrm{COS} \longrightarrow \mathrm{CO_2} + \mathrm{CS_2} \tag{3}$$

$$\mathrm{C_6H_{12}} + 1/x\mathrm{S}_x \longrightarrow \mathrm{C_6H_{10}} + \mathrm{H_2S} \tag{4}$$

$$\mathrm{C_6H_{10}} + 2/x\mathrm{S}_x \longrightarrow \mathrm{C_6H_6} + 2\mathrm{H_2S} \tag{5}$$

We use Reaction 5 instead of two consecutive reactions ($C_6H_{10}+1/xS_x \rightarrow C_6H_8+H_2S$, $C_6H_8+1/xS_x \rightarrow C_6H_6+H_2S$) since the yield of C_6H_8 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 Al_2O_3 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:

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

$$K_{\mathrm{p1}} = \mathrm{[CO_2][CS_2]/[COS]^2} \tag{7}$$

$$\mathrm{d[C_6H_{12}]}/\mathrm{d}(V/F) = -k_1\mathrm{[C_6H_{12}][S}_x] \tag{8}$$

$$\mathrm{d[C_6H_{10}]}/\mathrm{d}(V/F) = k_1\mathrm{[C_6H_{12}][S}_x] - k_2\mathrm{[C_6H_{10}][S}_x] \tag{9}$$

$$\mathrm{d[C_6H_6]}/\mathrm{d}(V/F) = k_2\mathrm{[C_6H_{10}][S}_x] \tag{10}$$

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 Al_2O_3 was determined with liquid C_6H_{12} and a measuring cylinder: the relation $V/F(\mathrm{min})=8.03\times 10^{-5}$ W/F(g-catalyst·min·g-mol^{-1}) was obtained at 823K. Equation 10 shows that the rate-controlling step for the formation of C_6H_6 from C_6H_{10} is the oxidative dehydrogenation of C_6H_{10} to C_6H_8, not that of C_6H_8 to C_6H_6.

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 Al_2O_3 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 CO_2+CS_2 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 CO_2+CS_2 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 S_2 type (Reaction 11).[13] Using the composition of the gaseous product at 300 g-catalyst·min·g-mol^{-1}, the equilibrium constants for Reactions 3 and 11 were calculated to be 8.07×10^{-2}

$$\mathrm{COS} \overset{K_{\mathrm{p2}}}{\rightleftharpoons} \mathrm{CO} + 1/2\mathrm{S_2} \tag{11}$$

and 2.40×10^{-2}, respectively. These values agree well with the thermodynamically calculated values ($K_{p1}=2.29\times10^{-1}$, $K_{p2}=2.21\times10^{-2}$).[12] At a contact time of 15.0 g-catalyst·min·g-mol^{-1}, the conversions to CO+S and CO_2+CS_2 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

$$\mathrm{d[CO]}/\mathrm{d}(W/F) = k_{01}\mathrm{[COS]} - k_{02}\mathrm{[CO][S_2]} \qquad (K_{\mathrm{p2}}=k_{01}/k_{02}) \tag{12}$$

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

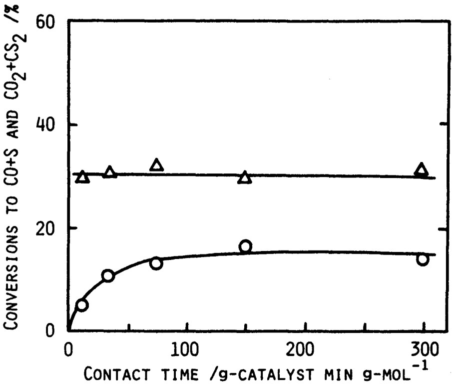

Fig. 3. Effect of contact time on the catalytic conversion of COS.
Catalyst: JRC-ALO-4 Al_2O_3. Reaction temperature: 823K. Total feed rate: 150 (NTP) cm^{-3} min^{-1} (COS 10 vol%, N_2 90 vol%).
○: Conversion to CO+S, △: Conversion to CO_2+CS_2.

Estimation of k_1 and k_2. The rate constants for the oxidative dehydrogenation of C_6H_{12} and C_6H_{10} with S_2 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 Al_2O_3 at 823K and the evolved sulfur (S_2) was reacted with C_6H_{12} 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 C_6H_{12}, the fractional yield of C_6H_{10}, and k_2/k_1, respectively:

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

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 C_6H_{12} with S_2 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) $cm^3 min^{-1}$+N_2 80 (NTP) $cm^3 min^{-1}$ (W/F=467.3 g-catalyst·min·g-mol^{-1}). Feed-2 : C_6H_{12} 15 (NTP) $cm^3 min^{-1}$+N_2 40 (NTP) $cm^3 min^{-1}$. 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 (2X2 mm). b) Yield of C_6H_8 is negligible.

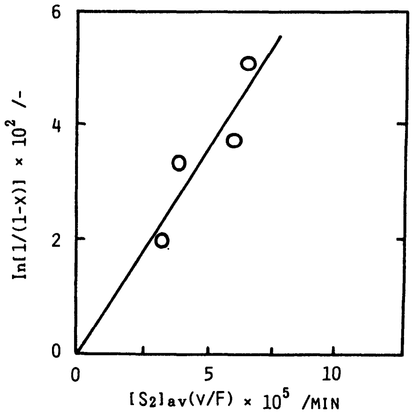

Fig. 4. Determination of k_1 based on Equation 14. Catalyst: JRC-ALO-4 Al_2O_3 2.0—10.0 g. Reaction temperature: 823K. Feed-1: 95—475 (NTP) $cm^3 min^{-1}$ ($COS/N_2=3/16$, fixed. W/F=467.3 g-catalyst·min·g-mol^{-1}). Feed-2: 55—275 (NTP) $cm^3 min^{-1}$ ($C_6H_{12}/N_2=1/3$, fixed). v: 17.10—32.92 cm^3.

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

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 7.38×10^2 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 2.00×10^4 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 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·min·g-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·min·g-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·min·g-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).

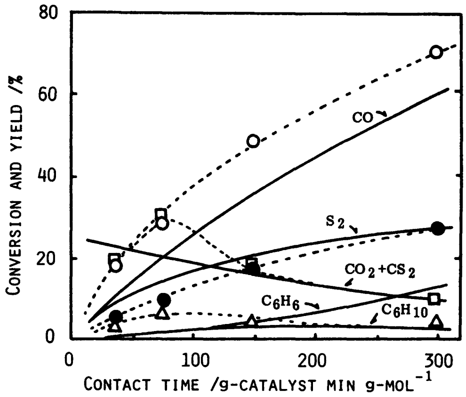

Fig. 5. Simulation of the catalytic oxidative dehydrogenation system.
Catalyst: JRC-ALO-4 Al_2O_3. Reaction temperature: 823K. Feed composition: C_6H_{12} 10 vol%, COS 10 vol%, N_2 80 vol%.
Dotted lines-observed values. Solid lines-simulated values.
$k_0=6.14\times10^{-3}$ g-mol·g-catalyst^{-1}·min^{-1}, $K_{p1}=8.07\times10^{-2}$, $k_1=7.38\times10^2$ min^{-1}, $k_2=2.00\times10^4$ 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.

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

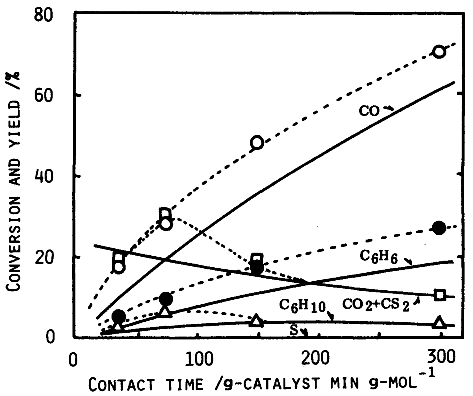

Fig. 6. Simulation of the catalytic oxidative dehydrogenation system.
Reaction conditions and symbols used are the same as those in Fig. 5.
$k_0=6.14\times10^{-3}$ g-mol·g-catalyst^{-1}·min^{-1}, $K_{p1}=8.07\times10^{-2}$, $k_1=2.66\times10^4$ min^{-1}, $k_2=7.20\times10^5$ min^{-1}.

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 CO_2+CS_2 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.

$$C_6H_{12} \xrightarrow{-2H\cdot} C_6H_{10} \xrightarrow{-2H\cdot} C_6H_8 \xrightarrow{-2H\cdot} C_6H_6 \qquad (15)$$

Both the convex behavior of the yield of C_6H_{10}+C_6H_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 C_6H_{10}+C_6H_8 and C_6H_6, and the combined selectivity to C_6H_{10}+C_6H_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 C_6H_{10}+C_6H_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.[8]

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 CO_2+CS_2 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} ($>6.14\times10^{-3}$ g-mol·g-catalyst^{-1}·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]

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

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 ($S \rightarrow 1/2S_2$) is ca. 40 kcal[†]·atom^{-1}.[16] When we assume that ΔQ is equal to 40 kcal·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.