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A Mechanistic Study on Vapor-Phase Catalytic Oxidative Dehydrogenation of Ethylbenzene with Carbonyl Sulfide

Carbonyl sulfide undergoes catalytic decomposition by either of the following two reactions (*1*).

$$COS \rightarrow CO + S \qquad (1)$$

$$xS \rightarrow S_x \qquad (x = 2,4,6, \text{ and } 8)$$

$$2COS \rightarrow CO_2 + CS_2 \qquad (2)$$

Since the dissociation by the first reaction evolves reactive sulfur atom, many studies have been made on the use of COS as an oxidant for the vapor-phase catalytic oxidative dehydrogenation of lower paraffinic hydrocarbons and alkylaromatic compounds (*2–4*). The most striking feature of this dehydrogenation compared to the usual oxidative dehydrogenation with oxygen is to be able to produce unsaturated hydrocarbons with high selectivity even over such SiO_2, Al_2O_3, MgO, and TiO_2 catalysts as have conventionally been used as carriers (*2–4*). Although this feature is important in view of the industrial dehydrogenation process, only a few papers (*4*) have been published on the mechanism of the catalytic oxidative dehydrogenation of hydrocarbons with COS. In the present note, we have mechanistically investigated the vapor-phase oxidative dehydrogenation of ethylbenzene (EB) with COS over SiO_2, Al_2O_3, MgO, and TiO_2 catalysts and discussed the role of these metal oxide catalysts, the nature of surface sites active for the decomposition of COS, and the mechanism of the dehydrogenation reaction.

Vapor-phase oxidative dehydrogenation of EB was carried out using a conventional flow fixed-bed reactor at atmospheric pressure. The reactor system comprised a 15-mm-i.d. quartz tube, 470-mm long, and a concentric thermowell. The catalyst of 32–60 mesh was used, and Raschig rings (2 × 2 mm) were added above and below the catalyst bed. Guaranteed reagent grade EB and purchased 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%) was used as the diluent, and the total feed rate was held constant at 100 (NTP)ml/min: the standard feed composition was EB 5.0 vol% and COS 5.0 vol%. The catalysts were prepared by the calcination of their corresponding metal hydroxides at 800°C (600°C for TiO_2) in air for 5 h. Silica sol (Snowtex-O, Nissan Chemical Industries, Ltd.), alumina sol (No. 200, Nissan Chemical Industries, Ltd.), and reagent grade magnesium hydroxide were used as the catalyst sources. Titanium hydroxide was prepared by the hydrolysis of reagent grade titanium isopropoxide in water at room temperature. The BET surface areas were 182 m^2/g (SiO_2), 175 m^2/g (Al_2O_3), 52 m^2/g (MgO), and 11 m^2/g (TiO_2). The reaction products (EB, styrene, COS, CO, CO_2, and H_2S) were analyzed by gas chromatography. CS_2 was not analyzed. The ESR measurements were carried out with a JEOL JES-PE spectrometer operating in the *X* band, adopting a 100-kHz modulation frequency. The *g* values of paramagnetic species were determined by the use of Mn^{2+} dissolved in MgO, and radical concentrations were estimated by comparing with the standard solution of 2,2-diphenyl-1-picrylhydrazyl in benzene.

Table 1 summarizes the results of catalytic oxidative dehydrogenation of EB with

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TABLE 1

Results of the Catalytic Oxidative Dehydrogenation of Ethylbenzene with COS[a]

Catalyst		Conversion (%)		Yield (%)		COS decomposition to CO + S (%)	Yield of sulfur (%)[d]
		EB	COS	Styrene	H_2S		
SiO_2	A[b]	21 6	46 0	21 6	10 0	22 5	10 4
	B[c]	20 4	46 0	20 4	10 0	22 5	10 4
MgO	A[b]	46 4	74 1	46 4	42 3	76 1	56 4
	B[c]	27 3	53 5	27 3	24 5	53 5	28 6
TiO_2	A[b]	34 6	35 0	34 6	14 5	61 5	21 5
	B[c]	16 1	18 0	16 1	7 5	61 5	11 1

[a] Reaction temperature 600°C, catalyst 1 0 g, feed EB + COS + N_2 (EB 5 0 vol%, COS 5 0 vol%) 100 (NTP) ml/min

[b] At 10 min

[c] At steady state

[d] Calculated by (conversion of COS) × (COS decomposition to CO + S)

COS at 600°C With the exception of Al_2O_3 catalyst, no styrene was produced when the mixture of EB and N_2 (EB 5 0 vol%) was fed over SiO_2, MgO, and TiO_2 catalysts at 600°C As reported previously (*3*, *4*), however, styrene was produced with a selectivity of nearly 100% with an accompanying formation of H_2S when COS was added to the reactant mixture (Table 1) Unlike SiO_2 catalyst, the catalytic activity of MgO and TiO_2 decreased with time and leveled off after a preliminary period of 5 h The decrease in the catalytic activity of these two metal oxides with time is caused by the formation of carbonaceous materials at the surface of the catalyst This view is supported by the realization of the initial catalytic activities (Table 1,A) upon calcination of the used catalysts at 600°C in air The yield of styrene determined after a preliminary period of 10 min was 21 6, 46 4, and 34 6% over SiO_2, MgO, and TiO_2 catalysts, respectively, the value of yield of styrene followed the relation $SiO_2 < TiO_2 <$ MgO This relation is also seen in the yield of sulfur determined after a preliminary period of 10 min (Table 1) Thus, the yield of styrene in the catalytic oxidative dehydrogenation of EB with COS was determined by the catalytic activity of these metal oxides for the catalytic decomposition of COS to CO + S

However, the yields of styrene with the exception of the yields over MgO catalyst were greater than those of sulfur calculated by (conversion of COS) × (COS decomposition to CO + S) (Table 1) This suggests that sulfur was also evolved by the catalytic decomposition of CS_2 formed during the oxidative dehydrogenation of EB with COS Really, formation of sulfur (yellow solid) was observed at the outlet of the reactor when the mixture of CS_2 and N_2 (CS_2 5 0 vol%) was fed over these metal oxide catalysts at 600°C The yields of H_2S were always less than those of H_2S expected from the formation of styrene (Table 1), presumably due to the strong adsorption of H_2S in the separating column used (*5*) As reported previously (*4*), these three metal oxide catalysts were hardly sulfided in the oxidative dehydrogenation of EB with COS even at 600°C

The nature of active sites for the catalytic decomposition of COS to CO + S was investigated A reactant mixture (COS + N_2, COS 5 0 vol%, 100 (NTP)ml/min) was fed over the catalyst (1 0 g) and the effect of reaction temperature on the catalytic decomposition of COS to CO + S was determined The decomposition of COS to CO +

TABLE 2

Summary of the Concentration of Reduction Sites[a]

Catalyst	SO_2^- (spins g-catalyst^{-1})
SiO_2	$3\ 0 \times 10^{15}$
Al_2O_3	$4\ 8 \times 10^{17}$
MgO	$6\ 2 \times 10^{15}$
TiO_2	$8\ 9 \times 10^{14}$[b]

[a] Catalyst 0 10 g, previously degassed at 500°C for 1 h and then exposed to 20 Torr SO_2 at room temperature and heated at 400°C for 30 min

[b] Exposed to 20 Torr SO_2 at room temperature for 30 min

S over SiO_2 catalyst was initiated at ca 550°C and the conversion of COS to CO + S increased with increasing reaction temperature Unlike SiO_2 catalyst, the decomposition of COS to CO + S over Al_2O_3, MgO, and TiO_2 catalysts was initiated at relatively low temperatures, ca 400, 440, and 450°C, respectively, and the conversion of COS to CO + S similarly increased with increasing reaction temperature It has been reported that COS is thermocatalytically decomposed to CO + S (1) That is, COS is adsorbed on the catalyst surface and is then thermally decomposed to CO + S (1) As found in the present work, however, the temperature at which the catalytic decomposition of COS to CO + S was initiated varied for SiO_2, Al_2O_3, MgO, and TiO_2 catalysts and the temperature followed the relation 400°C (Al_2O_3) < 440°C (MgO) < 450°C (TiO_2) < 550°C (SiO_2) although the relation of BET surface area was 11 m^2/g (TiO_2) < 52 m^2/g (MgO) < 175 m^2/g (Al_2O_3) < 182 m^2/g (SiO_2) This contradiction suggests that a mechanism other than the thermocatalytic one played the important role of catalytic decomposition of COS to CO + S over these four metal oxide catalysts

It has been reported that COS is readily decomposed to CO + S via a formation of COS^- when COS is adsorbed on the reduction sites of MgO (*6*) Then, the concentration of reduction sites at the surface of these four metal oxide catalysts was estimated by determining the amount of SO_2^- ($g_\perp$ = 2 002–2 003, $g_\parallel$ = 2 008–2 009) (*7*) formed on adsorption of SO_2 The results obtained (Table 2) indicate that these four metal oxide catalysts have reduction sites the concentration of reduction sites follows the relation $TiO_2 < SiO_2 < MgO < Al_2O_3$ This relation agrees with the relation of the catalytic activity of these four metal oxides for both the decomposition of COS to CO + S (see above) and the oxidative dehydrogenation of EB with COS at 600°C (Table 1,A) when we take account of the possibility that a fairly reduction of TiO_2 catalyst took place during these two catalytic reactions (i e , concentration of reduction sites $SiO_2 < TiO_2$) Although the observed concentration of reduction sites, 10^{15}–10^{18} spins/g-catalyst, at the surface of these metal oxides are not high as the concentration of catalytically active sites, we may conclude that the reduction sites played the predominant role of catalytic decomposition of COS to CO + S over these four metal oxide catalysts

Formation of styrene by the vapor-phase homogeneous reaction of EB with sulfur at 500–700°C has been reported (*8*) This report suggests the possibility that sulfur evolved by the catalytic decomposition of COS dehydrogenates EB in gaseous phase without any aid of the catalyst during the oxidative dehydrogenation of EB with COS over SiO_2, Al_2O_3, MgO, and TiO_2 catalysts In order to ascertain this possibility, the vapor-phase oxidative dehydrogenation of EB with COS was carried out at 600°C using a specially made flow fixed-bed reactor (Fig 1) That is, a mixture of COS and N_2 (COS 9 3 vol%, 54 (NTP)ml/min) was passed through the catalyst bed (1 0 g) at 600°C and the resulting gaseous product was then reacted with EB at 600°C in the absence of catalyst (Table 3) In contrast to the catalytic reaction with the conventional flow

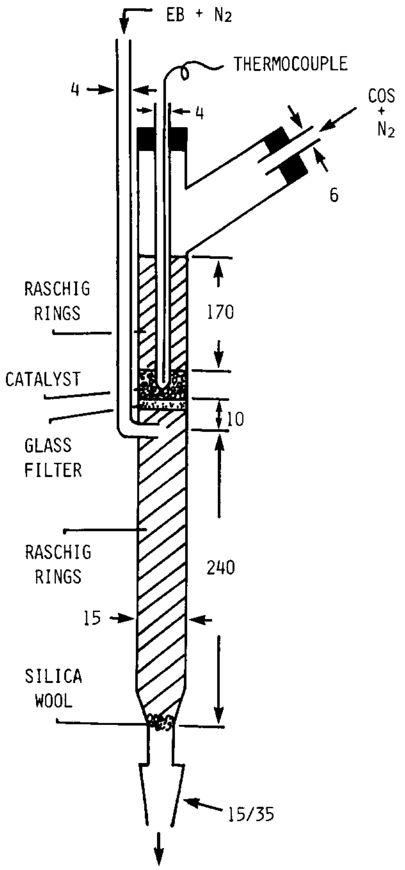

FIG 1 A schematic figure of the reactor employed in the vapor-phase noncatalytic reaction of sulfur with ethylbenzene The dimensions in the reactor are given in millimeters

TABLE 3

Results of the Oxidative Dehydrogenation of Ethylbenzene with COS[a]

Catalyst	Conversion (%)		Yield (%)		COS decomposition to CO + S (%)
	EB	COS	Styrene	H_2S	
SiO_2	21 0	49 1	21 0	8 0	32 3
Al_2O_3	24 6	49 9	24 6	10 8	33 8
MgO	17 2	50 3	17 2	7 9	34 5
TiO_2	20 0	51 7	20 0	9 3	32 0

[a] Reaction temperature 600°C catalyst 1 0 g feed 1 COS + N_2 (COS 9 3 vol%) 54 (NTP) ml/min Feed 2 EB + N_2 (EB 10 9 vol%) 46 (NTP) ml/min The reactor employed is shown in Fig 1

fixed-bed reactor (Table 1), there was no change in the catalytic activity of SiO_2, Al_2O_3, MgO, and TiO_2 with time during the course of the oxidative dehydrogenation of EB at 600°C This indicates that no back-mixing of EB onto the catalyst took place during the oxidative dehydrogenation of EB Additionally, the observation of nearly the same values of COS conversion (49 1–51 7%) and its decomposition to CO + S (32 0–34 5%) over these four metal oxide catalysts (Table 3) suggests that the equilibrium for the decomposition of COS was nearly established in this reaction method The most important finding which Table 3 provides is that styrene could be produced in this reaction method, although the yields of styrene obtained were not always very close to each others It appears that these metal oxide catalysts are not always requisite for the oxidative dehydrogenation of EB with formed sulfur although they are requisite for the decomposition of COS to CO + S

Haag and Miale (*4*) already proposed that sulfur atoms adsorbed on the surface of SiO_2 and MgO catalysts play the role of dehydrogenation of hydrocarbons at 538°C Although both the degree of contribution of the catalyst surface to the dehydrogenating step in the conventional flow fixed-bed reactor and the nature of sulfur species dehydrogenating EB remain unknown, the finding made in the present work (Table 3) suggests that some portion of styrene produced in the conventional flow fixed-bed reactor (Table 1) was via the vapor-phase noncatalytic reaction of sulfur with EB In this reaction mechanism just suggested by us, the role of these metal oxide catalysts is to decompose COS to CO + S through a "heterogeneous" catalytic reaction the evolved sulfur, maybe sulfur atom, then dehydrogenates EB to styrene through a "homogeneous" noncatalytic reaction Hence, the mechanism of the oxidative dehydrogenation of EB with COS found in the present work is a "heterogeneous–homogeneous mechanism "

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