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HETEROGENEOUS-HOMOGENEOUS MECHANISM FOR VAPOR-PHASE CATALYTIC OXIDATIVE DEHYDROGENATION OF ETHYLBENZENE BY CARBONYL SULFIDE

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A mechanistic study on vapor-phase oxidative dehydrogenation of ethylbenzene to styrene by COS over SiO_2, Al_2O_3, MgO, and TiO_2 catalysts has been carried out. The results obtained indicate that the sulfur evolved by the heterogeneous catalytic decomposition of COS dehydrogenated ethylbenzene in the homogeneous phase.

Carbonyl sulfide undergoes catalytic decomposition by either of two reactions:[1)]

$$COS \rightarrow CO + S \quad (1) \qquad 2COS \rightarrow CO_2 + CS_2 \quad (2)$$
$$xS \rightarrow S_x \ (x = 2,4,6,\text{and } 8)$$

Since dissociation by the first reaction can evolve reactive sulfur atom, many studies have been made on the use of COS as an oxidant for the catalytic oxidative dehydrogenation of lower saturated hydrocarbons and alkyl-substituted aromatics.[2-4)] The most striking feature of this dehydrogenation compared with the usual oxidative dehydrogenation by oxygen is to be able to produce unsaturated hydrocarbons with high selectivities. Nevertheless, only a few papers[4)] have been published on the mechanism of the oxidative dehydrogenation of these hydrocarbons by COS. In this paper, we report the results obtained in the mechanistic study on vapor-phase oxidative dehydrogenation of ethylbenzene(EB) by COS over SiO_2, Al_2O_3, MgO, and TiO_2 catalysts.

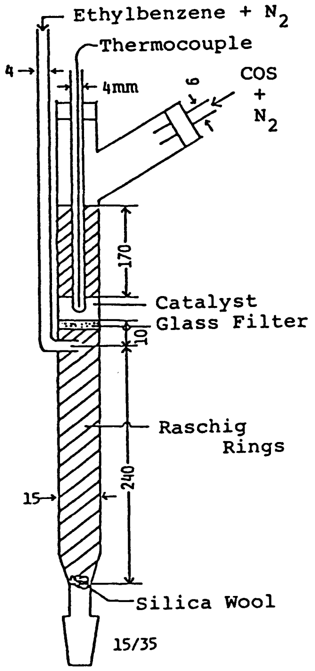

Fig.1 Reactor(II)

Vapor-phase oxidative dehydrogenation of ethylbenzene was carried out at 600°C using a conventional flow fixed-bed reactor(Reactor(I)) and a specially made flow fixed-bed reactor(Reactor(II),Fig.1). Purchased COS of greater than 97.5% purity was used without further purification. The catalysts (32 - 60 mesh) were prepared by the calcination of their corresponding metal hydroxides at 800°C in air for 5 hr. The surface areas determined by the conventional B.E.T. method were 182 $m^2/g(SiO_2)$, 175 $m^2/g(Al_2O_3)$, 52 $m^2/g(MgO)$, and 11 $m^2/g(TiO_2)$, respectively. The reaction products (EB, styrene, COS, CO, CO_2, and H_2S) were analyzed by gas chromatography, but CS_2 was not analyzed. The ESR measurements were carried out at room temperature and radical concentrations were estimated by comparing with the standard solution of 2,2-diphenyl-1-pycrylhydrazyl in benzene.

Table 1 summarizes the catalytic results obtained in the oxidative dehydrogenation of ethylbenzene by COS over SiO_2,MgO,and TiO_2 catalysts at 600°C using the reactor(I). No styrene was produced when the mixture of ethylbenzene and N_2(EB 5.0 vol%) was fed over these catalysts at 600°C. However,styrene was produced with accompanying formation of H_2S when COS was added to the reactant mixture. The yields of styrene were always nearly the same as the conversions of ethylbenzene,i.e.,the selectivity to styrene was always nearly 100%. The yields of H_2S were always smaller than those of H_2S expected from the formation of styrene,presumably due to the strong adsorption of H_2S in the separating column used.[5] The results of Table 1 show that SiO_2,MgO,and TiO_2 catalysts could produce styrene at the yields of 20.4 - 21.6%,27.3 - 58.5%,and 16.1 - 34.6%,respectively,by the oxidative dehydrogenation at 600°C. The decreases in the catalytic activity of MgO and TiO_2 with time,which are indicated by the values of the conversions and the yields of styrene and H_2S(Table 1),are caused by the formation of carboneceous materials at the surface of the catalysts. 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. It is also seen that the yields of styrene with the exception of the steady state yield over MgO catalyst are greater than those of sulfur(=[conversion of COS]×[COS decomposition to CO + S]). This suggests that sulfur was also evolved by the catalytic decomposition of CS_2 formed during the oxidative dehydrogenation of ethylbenzene by 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 oxides at 600°C(i.e.,$CS_2 \rightarrow C + 2S$). The result of X-ray diffraction analysis revealed that these metal oxide catalysts were not sulfided during the course of the oxidative dehydrogenation of ethylbenzene by COS at 600°C. This suggests that the oxidative dehydrogenation did not proceed through an usual redox-type reaction mechanism. It is to be noted that the catalytic activity determined after an interval of 10 min followed the order $SiO_2 < TiO_2 <$ MgO.

Table 1 Results of the oxidative dehydrogenation of ethylbenzene by COS(Reactor(I))[a]

Catalyst		Conversion/% of		Yield/% of		COS decomposition/% to	
		EB	COS	Styrene	H_2S	CO + S	$CO_2 + CS_2$
SiO_2	A[b]	21.6	46.0	21.6	10.0	22.5	77.5
	B[c]	20.4	46.0	20.4	10.0	22.5	77.5
MgO	A[b]	58.5	74.1	46.4	42.3	76.1	23.9
	B[c]	27.3	53.5	27.3	24.5	53.5	46.5
TiO_2	A[b]	34.6	35.0	34.6	14.5	61.5	38.5
	B[c]	16.1	18.0	16.1	7.5	61.5	38.5

[a] Reaction temp.: 600°C, Catalyst: 1.0g, Feed: EB + COS + N_2(EB 5.0vol%,COS 5.0vol%) 100 NTPml/min.

[b] At 10 min. [c] At steady state.

The catalytic decomposition of COS over SiO_2,Al_2O_3,MgO,and TiO_2 was carried out at 600°C in order to clarify the role of the metal oxide catalysts in the oxidative dehydrogenation of ethylbenzene by COS. As summarized in Table 2, these four metal oxides are capable of decomposing COS to CO + S at 600°C. Moreover, the conversions of COS over these four metal oxide catalysts, 51.0 - 52.8%, are close to each others irrespective of the kind of catalyst used. This is also the case of the values of the decomposition of COS to CO + S, 35.8 - 37.0% (Table 2). The observation of nearly the same values of conversion of COS and its decomposition to CO + S over these four metal oxide catalysts suggests that the equilibrium for the catalytic decomposition of COS was established in these reaction conditions employed.

Table 2 Results of the catalytic decomposition of COS[a)]

Catalyst	Conversion of COS/%	COS decomposition/% to CO + S	COS decomposition/% to CO_2 + CS_2
SiO_2	52.1	36.2	63.8
Al_2O_3	51.0	35.8	64.2
MgO	52.8	36.6	63.4
TiO_2	52.0	37.0	63.0

a) Reactor (I), Reaction temp.: 600°C, Catalyst: 1.0g, Feed: COS + N_2 (COS 5.0vol%) 100 NTPml/min.

It has been reported that COS is thermocatalytically decomposed to CO + S.[1)] It has also been reported that COS is easily decomposed to CO + S through formation of COS^- when adsorbed on reduction sites.[6)] Then, the concentration of reduction sites at the surface of these four metal oxide catalysts was determined as the amount of SO_2^- formed ($g_\perp$ = 2.002 - 2.003, $g_\parallel$ = 2.008 - 2.009[7)]). The results obtained (Table 3) indicate that these four metal oxides have reduction sites: the concentration of reduction sites followed the order $TiO_2 < SiO_2 < MgO \ll Al_2O_3$. The concentration of reduction sites, 10^{15} - 10^{18} spins/g-catalyst, at the surface of these metal oxides is not high as the concentration of catalytically active sites. However, we may consider that in addition to the thermocatalytic mechanism, COS was also decomposed to CO + S by the role of the reduction sites. The observation of the highest initial catalytic activity for the oxidative dehydrogenation of ethylbenzene over MgO (Table 1, A) supports this view. At any rate, it is evident that these four metal oxides are able to catalyze the decomposition of COS to CO + S at 600°C.

Table 3 Summary of the concentration of reduction sites[a)]

Catalyst	SO_2^- /spins g-catalyst^{-1}
SiO_2	3.0×10^{15}
Al_2O_3	4.8×10^{17}
MgO	6.2×10^{15}
TiO_2	8.9×10^{14} b)

a) Catalyst: 1.0g, previously evacuated at 500°C for 1 hr, and then exposed to 20 Torr SO_2 at room temperature and thermally treated at 400°C for 30 min.

b) Treated at room temperature.

The oxidative dehydrogenation of ethylbenzene by COS was also carried out using the reactor (II). That is, the mixture of COS and N_2 (COS 9.3 vol%) was passed through the catalyst bed at 600°C and the resulting gaseous mixture was then reacted with ethylbenzene at 600°C in the absence of catalyst (Table 4). There was no change in the catalytic activity of these metal oxides with time during the course of the oxidative dehydrogenation. 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 4) suggests that the equilibrium for the catalytic decomposition of COS was also established in this reaction method. The most important finding which Table 4 provides is that styrene could be produced in this reaction method.

Table 4 Results of the oxidative dehydrogenation of ethylbenzene by COS(Reactor(II))[a)]

Catalyst	Conversion/% of		Yield/% of		COS decomposition/% to	
	EB	COS	Styrene	H_2S	CO + S	CO_2 + CS_2
SiO_2	21.0	49.1	21.0	8.0	32.3	67.7
Al_2O_3	24.6	49.9	24.6	10.8	33.8	66.2
MgO	17.2	50.3	17.2	7.9	34.5	65.5
TiO_2	20.0	51.7	20.0	9.3	32.0	68.0

a) Reaction temp.: 600°C,Catalyst: 1.0g,Feed-1: COS + N_2(COS 9.3 vol%) 54 NTPml/min,Feed-2: EB + N_2(EB 10.9 vol%) 46 NTPml/min.

That is,it appears that these metal oxide catalysts are not always requisite for the oxidative dehydrogenation of ethylbenzene by formed sulfur although they are requisite for the decomposition of COS to CO + S. Both the degree of the contribution of catalyst surface to the dehydrogenation step in a conventional flow fixed-bed reactor and the nature of sulfur species dehydrogenating ethylbenzene remain unknown. Nevertheless,we may conclude that the role of the metal oxide catalysts is to decompose COS to sulfur atom through a "heterogeneous" mechanism,the formed sulfur(maybe sulfur atom) then dehydrogenating ethylbenzene in the "homogeneous" phase(heterogeneous-homogeneous reaction mechanism). This reaction mechanism proposed in the present work does not agree with the previously reported one[4)] in which sulfur atoms adsorbed on the surface of MgO and SiO_2 catalysts play a role of the dehydrogenation of hydrocarbons. In the case of Al_2O_3 catalyst,styrene was produced with a selectivity of 95% when the mixture of ethylbenzene and N_2(EB 5.0 vol%) was fed at 600°C. However, styrene will also be produced through the heterogeneous-homogeneous reaction mechanism just proposed when ethylbenzene and COS are fed over the catalyst at 600°C.

References

1) L.A.Haas and S.E.Khalafalla, J.Catal.,30,451(1973).
2) D.E.Boswell, U.S.Patent 3,399,243(1968).
3) W.O.Haag and J.N.Miale, U.S.Patent 3,787,517(1974); U.S.Patent 3,821,278(1974); U.S.Patent 3,875,252(1975).
4) W.O.Haag and J.N.Miale, Proc.6th Intern.Congr.Catal., London(1976),Vol.1, p.397.
5) M.Akimoto and I.G.Dalla Lana, Nippon Kagaku Kaishi,1979,579,1662.
6) M.J.Lin,D.P.Johnson,and J.H.Lunsford, Chem.Phys.Lett.,15,412(1972).
7) J.H.Lunsford and J.P.Jayne, J.Phys.Chem.,69,2182(1965) etc.

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