Production of Ethylene and Propylene by the Vapor-phase Catalytic Oxidative Dehydrogenation of Butane with Carbonyl Sulfide

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Synopsis. Ethylene and propylene were produced at high yields, additionally to butenes and butadiene, by the vapor-phase oxidative dehydrogenation of butane with COS over SiO_2, Al_2O_3, MgO, and TiO_2 catalysts at 873—923 K. The results of kinetic and mechanistic studies indicate that ethylene and propylene are produced by the oxidative dehydrogenation through a homolytic mechanism followed by β-scission of the carbon–carbon bond.

Carbonyl sulfide undergoes catalytic decomposition by either of the following two reactions.[1)]

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

$$2COS \rightarrow CO_2 + CS_2. \tag{2}$$

Since the dissociation by the first reaction evolves reactive sulfur atoms, many studies have been made on the use of COS as an oxidant for the oxidative dehydrogenation of lower paraffinic hydrocarbons and alkyl-substituted aromatics.[2,3)] Some mechanistic studies have also been reported.[4,5)] In our recent study on the vapor-phase oxidative dehydrogenation of ethylbenzene by COS over SiO_2, Al_2O_3, MgO, and TiO_2 catalysts, we showed that the role of the metal oxide catalysts is to decompose COS to CO+S, the formed sulfur (maybe sulfur atom) then dehydrogenating ethylbenzene in gaseous phase.[5)] We also showed that in addition to the thermocatalytic mechanism proposed by Haas and Khalafalla[1)] COS is decomposed to CO+S by the action of the reduction sites.[5)] In the present paper, we report the production of ethylene and propylene by the vapor-phase catalytic oxidative dehydrogenation of butane with COS and discuss the mechanism of the formation of these two olefins. The catalytic oxidative dehydrogenation of ethane, propane, and isobutane with COS has been reported.[3,4)] However, no studies have been reported on the catalytic oxidative dehydrogenation of butane with COS and hence no results have been reported of the formation of ethylene and propylene by the catalytic oxidative dehydrogenation with COS.

Experimental

Vapor-phase catalytic oxidative dehydrogenation of hydrocarbons was carried out using a conventional flow fixed-bed reactor under atmospheric pressure. The shape of reactor and method of reaction were the same as those in our previous paper.[5)] Purchased COS of greater than 97.5 % purity and research grade paraffinic hydrocarbons(purity>99%) were used without further purification. The catalysts (32—60 mesh) were prepared by the calcination of their corresponding metal hydroxides at 1073 K (873 K for TiO_2) in air for 5 h. The surface areas determined by the conventional B.E.T. method were 167 $m^2\,g^{-1}$ (SiO_2), 178 $m^2\,g^{-1}$ (Al_2O_3), 40 $m^2\,g^{-1}$ (MgO), and 48 $m^2\,g^{-1}$ (TiO_2), respectively. The gaseous reaction products (paraffins, olefins, COS, CO, CO_2, and H_2S) were analyzed by gas chromatography using propylene carbonate (40 wt% on C-22, 17.0 m, room temperature), Porapak R(2.0 m, 363 K), and molecularsieve 13X(1.5 m, room temperature) as separating columns. Carbon disulfide was not analyzed.

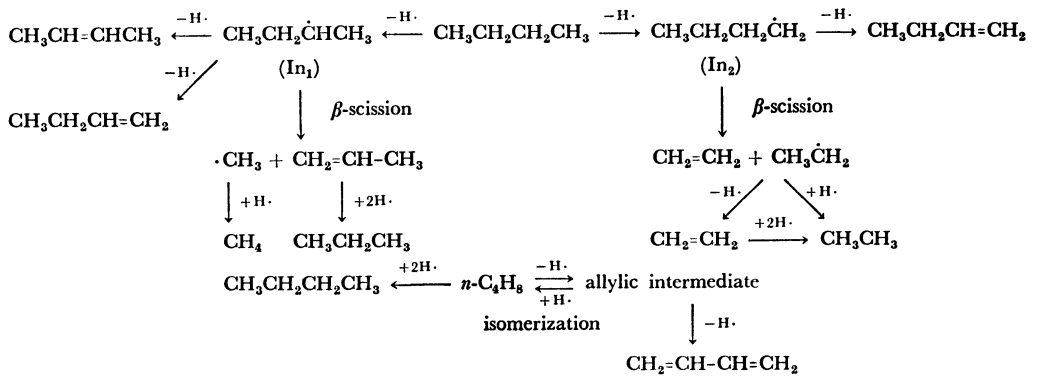
Results and Discussion

Table 1 summarizes the catalytic results obtained in the oxidative dehydrogenation of butane with COS at 873 K. No reaction took place when the mixture of butane and N_2 (butane 30.0 vol%) was fed over these four metal oxide catalysts at 873 K. However, such olefins as ethylene and propylene were produced additionally to butenes and butadiene with an accompanying formation of H_2S when COS was added to the reacant mixture (Table 1. The yield of H_2S is not presented for the sake of simplicity). Both the conversions of butane and COS decreased with time, due to the formation of carboneceous materials at the surface of the catalysts,[5)] and leveled off after a preliminary period of 5 h. However, it is evident that Al_2O_3 had the greatest catalytic activity at the initial stages of the reaction among these four metal oxide catalysts (Table 1,A). This greatest initial catalytic activity of Al_2O_3 correlates its greatest concentration of the reduction sites reported in our previous paper[5)], suggesting the preferential role of the reduction sites in the catalytic decomposition of COS to CO+S. For some catalytic results, the conversion of butane was greater than the yield of sulfur (=[conversion of COS]×[COS decomposition to CO+S]) (Table 1, SiO_2-A,B, MgO-B, and TiO_2-B). It seems that sulfur was also evolved by the catalytic decomposition of

Table 1. Results of the catalytic oxidative dehydrogenation of butane by COS[a)]

Catalyst		Conversion/%		COS decomposition to CO+S/%	Yield/%				Selectivity/%	
		n-C_4H_{10}	COS		C_nH_{2n+2}[e)]	C_2H_4	C_3H_6	C_4 olefins[f)]	$C_2H_4+C_3H_6$	olefins
SiO_2	A[b)]	45.8	49.2	41.1	6.7	4.4	24.3	9.4	62.7	83.2
	B[c)]	29.8	47.9	37.0	3.1	2.9	15.1	7.9	60.4	86.9
Al_2O_3	A[b)]	53.4	96.5	97.7	4.8	2.2	14.3	15.5	30.9	59.9
	B[c)]	26.6	42.0	61.4	2.7	1.4	7.3	13.5	32.7	83.5
MgO[d)]	A[b)]	29.2	63.4	69.9	2.7	1.6	9.6	5.9	38.4	58.6
	B[c)]	12.4	10.4	64.4	1.3	0.5	4.5	2.7	40.3	62.1
TiO_2	A[b)]	47.0	87.3	94.2	4.1	2.0	13.0	12.1	31.9	57.7
	B[c)]	18.9	14.7	73.5	1.0	1.0	4.5	6.3	29.1	62.4

a) Reaction temperature: 873 K. Feed: 100 NTP $cm^3\,min^{-1}$ (n-C_4H_{10} 30.0 vol%, COS 30.0 vol%, N_2 40.0 vol%). Contact time: 11.2 g-catalyst·h·g-mol^{-1}. b) At 10 min. c) At steady state. d) Contact time: 3.7 g-catalyst·h·g-mol^{-1}. e) $CH_4+C_2H_6+C_3H_8$. f) n-$C_4H_8+C_4H_6$.



CS_2 formed during the catalytic oxidative dehydrogenation of butane by COS, as already seen in the reaction of ethylbenzene by COS.[5]

The most important finding that Table 1 provides is that ethylene and propylene were produced additionally to butenes and butadiene in the catalytic oxidative dehydrogenation of butane by COS. The combined yield of ethylene and propylene was high, 18.0—28.7% (selectivity 60.4—62.7%) and 8.7—16.5 % (30.9—32.7%), over SiO_2 and Al_2O_3 catalysts, respectively, and the total selectivity to olefins was also high, 83.2—86.9%, over SiO_2 catalyst. It is to be noted that the yield of propylene was always greater than that of ethylene for all of the catalysts employed (Table 1). At 923 K, the combined yield of ethylene and propylene over SiO_2 catalyst determined after a preliminary period of 10 min increased to 60.3% (selectivity 64.1%) whereas that of butenes and butadiene remained nearly unchanged, 8.2%. In contrast to the reaction of butane, no such olefins as ethylene and propylene were produced when *trans*-2-butene was similarly reacted at 873 K (*e.g.*, SiO_2 catalyst, conversion 48.1%, total yield of butenes 33.2%, and yield of butadiene 10.0%).

In the oxidative dehydrogenation of butane by COS over SiO_2 catalyst at 873 K, the reaction order in butane was unity and that in COS was 0.2—0.3. Assuming the first order kinetics for the oxidative dehydrogenation of paraffinic hydrocarbons, the rate constant for the oxidative dehydrogenation of ethane, propane, and isobutane by COS over SiO_2 catalyst was determined at 873 K using an integral reactor (Table 2). The rate constant k for the paraffinic hydrocarbons follows the order: ethane<propane< isobutane. The order of the reactivity of these hydrocarbons is much more obvious when the value of the rate constant k is normalized to one most-reactive hydrogen (k', Table 2). That is, the reactivity of hydrogen for the oxidative dehydrogenation by sulfur follows the order: primary hydrogen < secondary hydrogen<tertiary hydrogen. This order of the reactivity of hydrogen correlates the value of the C–H bond dissociation energy (Table 2). As reported previously by Haag and Miale,[4] we may thus conclude that the oxidative dehydrogenation of these paraffinic hydrocarbons by sulfur proceeds through a homolytic mechanism. On the other hand, no formation of olefins other than isobutene in the reaction of isobutane (Table 2) indicates that no α-scission of the carbon-carbon bond took place during the oxidative dehydrogenation of paraffinic hydrocarbons by COS at 873 K.

Table 2. Summary of the rate constants for the catalytic oxidative dehydrogenation of lower paraffinic hydrocarbons by COS[a)]

Paraffin	Number and type of hydrogen[b)]	B.D.E.[c)] kJ mol^{-1}	Conversion %	k[d)] $\times 10^2$	k'[e)] $\times 10^2$
C_2H_6	6 p	410	22.3	2.25	0.38
C_3H_8	2 s	395	23.9	2.44	1.22
i-C_4H_{10}	1 t	380	24.9	2.56	2.56

a) Catalyst: SiO_2. Reaction temperature: 873 K. Feed: 100 NTP cm^3 min^{-1} (paraffin 30.0 vol%, COS 30.0 vol%, N_2 40.0 vol%). Contact time: 11.2 g-catalyst·h·g-mol^{-1}. Product: $C_2H_6 \rightarrow C_2H_4$, $C_3H_8 \rightarrow C_3H_6$, i-$C_4H_{10} \rightarrow i$-C_4H_8. b), c) For the weakest C-H bond. C-H bond dissociation energy (B.D.E.): Ref. 6. d) g-mol (g-catalyst·h·atm)$^{-1}$. e) Normalized to one most-reactive hydrogen.

Based on the above findings made in the present work, we propose the following reaction scheme for the oxidative dehydrogenation of butane by COS over these metal oxide catalysts. The oxidative dehydrogenation of butane by sulfur takes place mainly in gaseous phase and it proceeds more preferentially *via* an intermediate In_1 than *via* the another In_2, as indicated by the relative reactivity of the hydrogens (Table 2). The greater yields of propylene than ethylene and no formation of these two olefins from *trans*-2-butene found in the present work (Table 1) support this reaction scheme. The hydrogenation of hydrocarbon species does not take place extensively as seen in the small values of the combined yield of methane, ethane, and propane (Table 1). The hydrogens used for the hydrogenations must have been supplied from HS_x (maybe $x=1$ and/or 2). The mechanism of the formation of carboneceous materials at the surface of the catalysts remains unknown.

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