Effect of CH_2Br_2-Addition upon Direct Oxidative Dehydrogenation of Butane into 1,3-Butadiene over Fe-Sb-O Composite Catalyst

Hitoshi SAITOH, Satoshi SATOH, Toshiaki SODESAWA, and Fumio NOZAKI*
Department of Industrial Chemistry, Faculty of Engineering, Chiba University, Yayoi-cho, Chiba 260
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Synopsis. Effect of CH_2Br_2-addition upon direct oxidative dehydrogenation of butane into 1,3-butadiene has been investigated in a conventional flow apparatus. The activity and selectivity of Fe-Sb-O catalyst were much improved by the addition of CH_2Br_2 to butane in the mole ratio, CH_2Br_2/n-C_4H_{10}, of 0.03 to 0.10 at temperatures near 450 °C.

The dehydrogenation of paraffinic hydrocarbons such as butane (hereafter referred to as n-C_4H_{10}) is endothermic, so that high temperature is required to facilitate the reaction. The oxidative dehydrogenation has no such difficulty; however, catalytic selectivity is often poor.

The oxidative dehydrogenation of olefin such as 1-butene (1-C_4H_8) is selectively achieved by the use of composite catalysts such as Fe-Sb-O[1] and Bi-Mo-O.[2] On the other hand, the oxidative dehydrogenation of n-C_4H_{10} using oxygen or air as the oxidant gives preferentially a large amount of CO_2 and the selectivity to form butenes (C_4H_8) or 1,3-butadiene (C_4H_6) is generally lowered. It is well known that the addition of small amounts of halogen (I_2, Br_2, etc.) or halogen compound (HBr, HCl, KBr, etc.) is effective for the dehydrogenation or oxidative dehydrogenation of paraffinic hydrocarbons or ethylbenzene.[3-5] In addition, attempts to use COS[6] or N_2O[7] as the oxidant for the dehydrogenation of C_4H_{10} or ethane have recently been made. In these studies, however, a large portion of the dehydrogenated products was C_4H_8 or olefinic hydrocarbons such as propylene and ethylene, and the extent of C_4H_6 formation was usually very small.

We have previously reported on the oxidative dehydrogenation of 1-C_4H_8 to C_4H_6 over Fe-Sb-O catalyst.[1] In this paper, we describe a promoting action of CH_2Br_2 for the direct oxidative dehydrogenation of n-C_4H_{10} to C_4H_6 over Fe-Sb-O catalyst. It should also be noted that CH_2Br_2 is chosen as a promoter because of its appropriate magnitude of vapor pressure and its low cost.

Experimental

The catalytic tests were conducted in a conventional tubular-flow reactor operating at atmospheric pressure. The reaction products were analyzed by the gas chromatography on a 4 m column of VZ-7 (Gasukuro-kogyo Co.) operated at room temperature. The conversion of n-C_4H_{10} (expressed by x), the selectivity to C_4H_6 ($S_{C_4'}$), C_4H_8 (S_{C_4}), etc. were calculated by the usual procedure on the mole basis of n-C_4H_{10} fed.

The method of preparation of the Fe-Sb-O catalyst was similar to that previously reported[1]: $Fe(NO_3)_3$ and Sb_2O_3 were used as the starting materials for the preparation of $FeSb_2O_4$ composite catalyst. In order to compare the activity of the Fe-Sb-O catalyst with other catalysts, Cr_2O_3(7.5 wt%)/Al_2O_3 and Fe_2O_3(30 wt%)/SiO_2 were also used in the catalytic tests. These two materials were commercially supplied from Nissan-Girdler Co., Ltd.

Results and Discussion

The results of catalytic tests obtained by three kinds of catalysts, Fe-Sb-O, Cr_2O_3/Al_2O_3, and Fe_2O_3/SiO_2, are summarized in Table 1. Table 1 indicates that an addition of small amounts of CH_2Br_2 to the reactant mixture is effective for the oxidative dehydrogenation of n-C_4H_{10} to give C_4H_6. Especially in the case of the Fe-Sb-O catalyst, the high conversion and selectivity (x=67%, $S_{C_4'}$=59%) were obtained with the addition of CH_2Br_2.

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Table 1. Conversion and Selectivities Obtained by Use of Various Catalysts in Oxidative Dehydrogenation of n-C_4H_{10} with and without Addition of CH_2Br_2
Reaction temperature: 450 °C, Catalyst weight: 3.0 g, Total gas feeding rate: 130 ml min^{-1}
Reactant concentration(mole) n-C_4H_{10}/Air = 1/12

Catalyst	Without the Addition of CH_2Br_2						With the Addition of CH_2Br_2[a]					
	%						%					
	x	$S_{C_4'}$	S_{C_4}	S_{CO_2}	S_{C_2}	S_{C_3}	x	$S_{C_4'}$	S_{C_4}	S_{CO_2}	S_{C_2}	S_{C_3}
Fe-Sb-O	11	8	b)	92	b)	b)	67	59	5	36	b)	b)
Cr_2O_3/Al_2O_3	32	5	18	77	b)	b)	40	19	16	58	2	5
Fe_2O_3/SiO_2	38	3	2	89	6	b)	48	11	20	65	b)	4
None	17	7	9	49	21	14	6	13	67	17	3	b)

a) The catalytic reaction was carried out with the mole ratio n-C_4H_{10}/Air/CH_2Br_2 = 1/12/0.12. b) The mark indicates that the numerical value is less than about 1%.

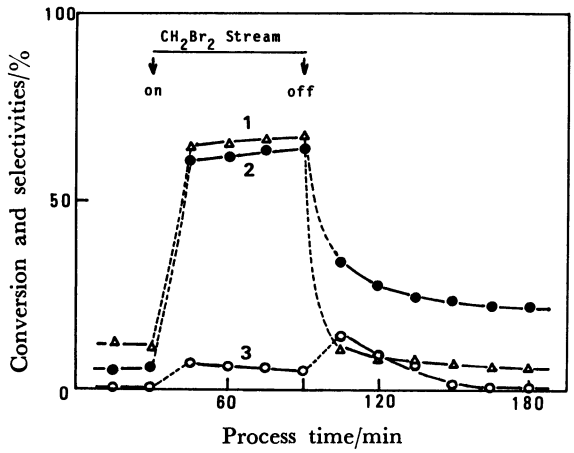

Fig. 1. Influence of CH_2Br_2-addition upon the reaction. 1: Conversion of n-C_4H_{10}, 2: Selectivity to C_4H_6 (S_{C4}), 3: Selectivity to C_4H_8(S_{C4})
Catalyst: Fe–Sb–O, W: 3.0 g, t: 450 °C, F: 130 ml min^{-1}, Mole ratio n-C_4H_{10}/Air/CH_2Br_2: 1/12/0.12.

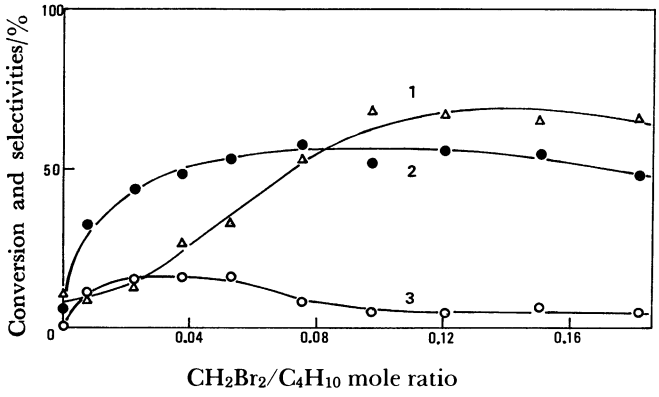

Fig. 2. Influence of CH_2Br_2/n-C_4H_{10} ratio upon the reaction. The reaction conditions and the symbols are the same as for Fig. 1.

CH_2Br_2 for the Fe–Sb–O catalyst is further illustrated in Fig. 1. Figure 1 depicts clearly that the oxidative dehydrogenation to form C_4H_6 continues to occur so long as CH_2Br_2 is fed into the reaction. When the introduction of CH_2Br_2 is stopped, the enhanced activity gradually decreases and tends to resume the original activity.

The influence of CH_2Br_2 concentration upon the catalytic reaction is shown in Fig. 2. The conversion of n-C_4H_{10} (curve 1) is increased with an increase of the CH_2Br_2 concentration and then levels off when the mole ratio of CH_2Br_2 to n-C_4H_{10} becomes approximately 1:10. The selectivity to C_4H_6 or C_4H_8 (curve 2 or 3) is much improved even at a low CH_2Br_2 concentration (CH_2Br_2/n-C_4H_{10}=0.03—0.05).

The activity and selectivity of the Fe–Sb–O catalyst enhanced by the addition of CH_2Br_2 stayed at the same level for as long as CH_2Br_2 was being supplied. The changes in the conversion and selectivity with reaction temperature and contact time were also investigated. The results indicated that the reaction temperature near 450 °C was the best for the formation of C_4H_6, and its yield decreased with a decreasing contact time.

No reaction occurred between n-C_4H_{10} and CH_2Br_2 without air over the Fe–Sb–O catalyst. This fact suggests that oxygen is essential for the dissociation of CH_2Br_2 to Br_2 and for the formation of C_4H_6 and C_4H_8. As was shown in Table 1, the dehydrogenation of n-C_4H_{10} into C_4H_8 took place to a certain extent even in the absence of the Fe–Sb–O catalyst.

In accordance with the above findings and with other information, we have tentatively speculated the reaction pathways as follows:

$$\left.\begin{aligned} CH_2Br_2 + 3/2O_2 &\longrightarrow CO_2 + H_2O + Br_2 \\ Br_2 &\rightleftarrows 2Br\cdot \end{aligned}\right\} \quad (1)$$

$$\left.\begin{aligned} C_4H_{10} + Br\cdot &\longrightarrow C_4H_9\cdot + HBr \\ C_4H_9\cdot + Br\cdot &\longrightarrow C_4H_8 + HBr \end{aligned}\right\} \quad (2)$$

$$C_4H_8 + 1/2O_2 \xrightarrow{\text{Fe-Sb-O cat.}} C_4H_6 + H_2O \quad (3)$$

$$\left.\begin{aligned} FeSb_2O_{4-y} + 2HBr &\longrightarrow FeSb_2Br_2O_{3-y} + H_2O \\ FeSb_2Br_2O_{3-y} + 1/2O_2 &\longrightarrow FeSb_2O_{4-y} + Br_2 \end{aligned}\right\} \quad (4)$$

(here, $FeSb_2O_{4-y}$ shows the partially reduced state of the Fe–Sb–O catalyst).

The bromine radical Br· generated by Eq. 1[8] probably plays an important role in the formation of C_4H_8. The resulting C_4H_8 is oxidatively dehydrogenated to C_4H_6 by the subsequent reaction step, Eq. 3, over the Fe–Sb–O catalyst.[1]

In addition, it can be speculated that the resulting HBr is converted into Br_2 by the redox mechanism of the Fe–Sb–O catalyst, as is shown by Eq. 4. This is probably responsible for the experimental fact that such a high conversion and selectivity as x=60—70%, $S_{C4}\cong$ 60% have been attained even at the low CH_2Br_2/n-C_4H_{10} ratio.

However, the more definitive reaction scheme must remain to be the subject for a further study.

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8) $Log_{10} K_p$ for the reaction $Br_2 \rightarrow 2Br$ has been estimated to be about −7.9 at 450 °C by the use of data listed in "JANAF Thermochemical Tables," 2nd ed., p. 290 and p. 318 (National Bureau of Standards). The low value of log K_p appears to be unfavorable to the proposed mechanism; however, a small amount of Br can be formed and it can initiate the subsequent reaction steps represented by Eqs. 2—4.