

## Effect of CH<sub>2</sub>Br<sub>2</sub>-Addition upon Direct Oxidative Dehydrogenation of Butane into 1,3-Butadiene over Fe-Sb-O Composite Catalyst

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(Received February 27, 1986)

**Synopsis.** Effect of CH<sub>2</sub>Br<sub>2</sub>-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<sub>2</sub>Br<sub>2</sub> to butane in the mole ratio, CH<sub>2</sub>Br<sub>2</sub>/*n*-C<sub>4</sub>H<sub>10</sub>, 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<sub>4</sub>H<sub>10</sub>) 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<sub>4</sub>H<sub>8</sub>) is selectively achieved by the use of composite catalysts such as Fe-Sb-O<sup>1)</sup> and Bi-Mo-O.<sup>2)</sup> On the other hand, the oxidative dehydrogenation of *n*-C<sub>4</sub>H<sub>10</sub> using oxygen or air as the oxidant gives preferentially a large amount of CO<sub>2</sub> and the selectivity to form butenes (C<sub>4</sub>H<sub>8</sub>) or 1,3-butadiene (C<sub>4</sub>H<sub>6</sub>) is generally lowered. It is well known that the addition of small amounts of halogen (I<sub>2</sub>, Br<sub>2</sub>, etc.) or halogen compound (HBr, HCl, KBr, etc.) is effective for the dehydrogenation or oxidative dehydrogenation of paraffinic hydrocarbons or ethylbenzene.<sup>3-5)</sup> In addition, attempts to use COS<sup>6)</sup> or N<sub>2</sub>O<sup>7)</sup> as the oxidant for the dehydrogenation of C<sub>4</sub>H<sub>10</sub> or ethane have recently been made. In these studies, however, a large portion of the dehydrogenated products was C<sub>4</sub>H<sub>8</sub> or olefinic hydrocarbons such as propylene and ethylene, and the extent of C<sub>4</sub>H<sub>6</sub> formation was usually very small.

We have previously reported on the oxidative dehydrogenation of 1-C<sub>4</sub>H<sub>8</sub> to C<sub>4</sub>H<sub>6</sub> over Fe-Sb-O catalyst.<sup>1)</sup> In this paper, we describe a promoting

action of CH<sub>2</sub>Br<sub>2</sub> for the direct oxidative dehydrogenation of *n*-C<sub>4</sub>H<sub>10</sub> to C<sub>4</sub>H<sub>6</sub> over Fe-Sb-O catalyst. It should also be noted that CH<sub>2</sub>Br<sub>2</sub> 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<sub>4</sub>H<sub>10</sub> (expressed by *x*), the selectivity to C<sub>4</sub>H<sub>6</sub> (S<sub>C<sub>4</sub>H<sub>6</sub></sub>), C<sub>4</sub>H<sub>8</sub> (S<sub>C<sub>4</sub>H<sub>8</sub></sub>), etc. were calculated by the usual procedure on the mole basis of *n*-C<sub>4</sub>H<sub>10</sub> fed.

The method of preparation of the Fe-Sb-O catalyst was similar to that previously reported<sup>1)</sup>: Fe(NO<sub>3</sub>)<sub>3</sub> and Sb<sub>2</sub>O<sub>3</sub> were used as the starting materials for the preparation of FeSb<sub>2</sub>O<sub>4</sub> composite catalyst. In order to compare the activity of the Fe-Sb-O catalyst with other catalysts, Cr<sub>2</sub>O<sub>3</sub>(7.5 wt%)/Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>(30 wt%)/SiO<sub>2</sub> 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<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, and Fe<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub>, are summarized in Table 1. Table 1 indicates that an addition of small amounts of CH<sub>2</sub>Br<sub>2</sub> to the reactant mixture is effective for the oxidative dehydrogenation of *n*-C<sub>4</sub>H<sub>10</sub> to give C<sub>4</sub>H<sub>6</sub>. Especially in the case of the Fe-Sb-O catalyst, the high conversion and selectivity (*x*=67%, S<sub>C<sub>4</sub>H<sub>6</sub></sub>=59%) were obtained with the addition of CH<sub>2</sub>Br<sub>2</sub>.

The detailed behavior of the promoting action of

Table 1. Conversion and Selectivities Obtained by Use of Various Catalysts in Oxidative Dehydrogenation of *n*-C<sub>4</sub>H<sub>10</sub> with and without Addition of CH<sub>2</sub>Br<sub>2</sub>

Reaction temperature: 450 °C, Catalyst weight: 3.0 g, Total gas feeding rate: 130 ml min<sup>-1</sup>

Reactant concentration(mole) *n*-C<sub>4</sub>H<sub>10</sub>/Air = 1/12

Catalyst	Without the Addition of CH <sub>2</sub> Br <sub>2</sub>						With the Addition of CH <sub>2</sub> Br <sub>2</sub> <sup>a)</sup>					
	%						%					
	<i>x</i>	S <sub>C<sub>4</sub>H<sub>6</sub></sub>	S <sub>C<sub>4</sub>H<sub>8</sub></sub>	S <sub>CO<sub>2</sub></sub>	S <sub>C<sub>2</sub>H<sub>4</sub></sub>	S <sub>C<sub>3</sub>H<sub>6</sub></sub>	<i>x</i>	S <sub>C<sub>4</sub>H<sub>6</sub></sub>	S <sub>C<sub>4</sub>H<sub>8</sub></sub>	S <sub>CO<sub>2</sub></sub>	S <sub>C<sub>2</sub>H<sub>4</sub></sub>	S <sub>C<sub>3</sub>H<sub>6</sub></sub>
Fe-Sb-O	11	8	b)	92	b)	b)	67	59	5	36	b)	b)
Cr <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	32	5	18	77	b)	b)	40	19	16	58	2	5
Fe <sub>2</sub> O <sub>3</sub> /SiO <sub>2</sub>	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<sub>4</sub>H<sub>10</sub>/Air/CH<sub>2</sub>Br<sub>2</sub> = 1/12/0.12. b) The mark indicates that the numerical value is less than about 1%.

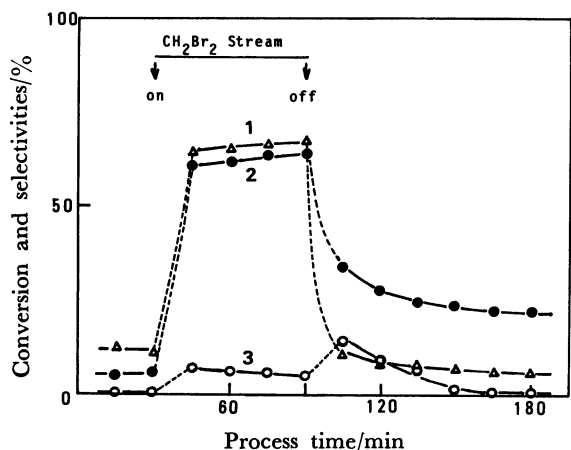


Fig. 1. Influence of  $\text{CH}_2\text{Br}_2$ -addition upon the reaction. 1: Conversion of  $n\text{-C}_4\text{H}_{10}$ , 2: Selectivity to  $\text{C}_4\text{H}_6$  ( $S_{C\gamma}$ ), 3: Selectivity to  $\text{C}_4\text{H}_8$  ( $S_{C\delta}$ )  
Catalyst: Fe-Sb-O, W: 3.0 g, t: 450 °C, F: 130 ml  $\text{min}^{-1}$ , Mole ratio  $n\text{-C}_4\text{H}_{10}/\text{Air}/\text{CH}_2\text{Br}_2$ : 1/12/0.12.

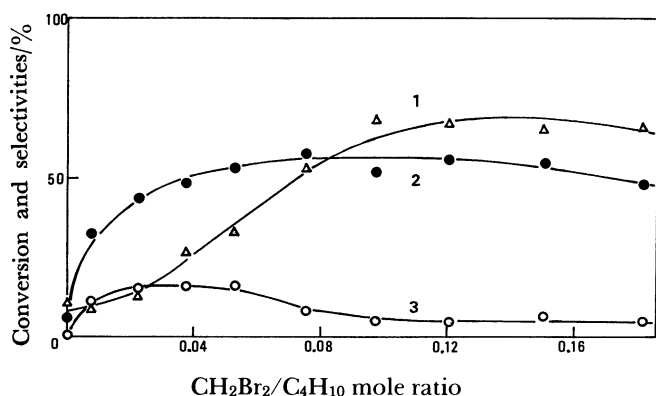


Fig. 2. Influence of  $\text{CH}_2\text{Br}_2/n\text{-C}_4\text{H}_{10}$  ratio upon the reaction. The reaction conditions and the symbols are the same as for Fig. 1.

$\text{CH}_2\text{Br}_2$  for the Fe-Sb-O catalyst is further illustrated in Fig. 1. Figure 1 depicts clearly that the oxidative dehydrogenation to form  $\text{C}_4\text{H}_6$  continues to occur so long as  $\text{CH}_2\text{Br}_2$  is fed into the reaction. When the introduction of  $\text{CH}_2\text{Br}_2$  is stopped, the enhanced activity gradually decreases and tends to resume the original activity.

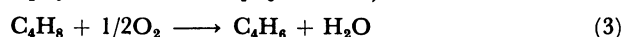
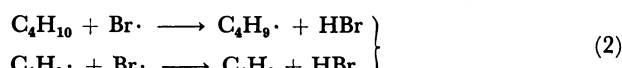
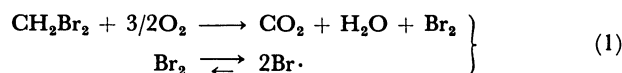
The influence of  $\text{CH}_2\text{Br}_2$  concentration upon the catalytic reaction is shown in Fig. 2. The conversion of  $n\text{-C}_4\text{H}_{10}$  (curve 1) is increased with an increase of the  $\text{CH}_2\text{Br}_2$  concentration and then levels off when the mole ratio of  $\text{CH}_2\text{Br}_2$  to  $n\text{-C}_4\text{H}_{10}$  becomes approximately 1:10. The selectivity to  $\text{C}_4\text{H}_6$  or  $\text{C}_4\text{H}_8$  (curve 2 or 3) is much improved even at a low  $\text{CH}_2\text{Br}_2$  concentration ( $\text{CH}_2\text{Br}_2/n\text{-C}_4\text{H}_{10}=0.03\text{--}0.05$ ).

The activity and selectivity of the Fe-Sb-O catalyst enhanced by the addition of  $\text{CH}_2\text{Br}_2$  stayed at the same level for as long as  $\text{CH}_2\text{Br}_2$  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  $\text{C}_4\text{H}_6$ ,

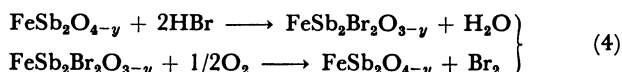
and its yield decreased with a decreasing contact time.

No reaction occurred between  $n\text{-C}_4\text{H}_{10}$  and  $\text{CH}_2\text{Br}_2$  without air over the Fe-Sb-O catalyst. This fact suggests that oxygen is essential for the dissociation of  $\text{CH}_2\text{Br}_2$  to  $\text{Br}_2$  and for the formation of  $\text{C}_4\text{H}_6$  and  $\text{C}_4\text{H}_8$ . As was shown in Table 1, the dehydrogenation of  $n\text{-C}_4\text{H}_{10}$  into  $\text{C}_4\text{H}_8$  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:



Fe-Sb-O cat.



(here,  $\text{FeSb}_2\text{O}_{4-y}$  shows the partially reduced state of the Fe-Sb-O catalyst).

The bromine radical  $\text{Br}\cdot$  generated by Eq. 1<sup>8)</sup> probably plays an important role in the formation of  $\text{C}_4\text{H}_8$ . The resulting  $\text{C}_4\text{H}_8$  is oxidatively dehydrogenated to  $\text{C}_4\text{H}_6$  by the subsequent reaction step, Eq. 3, over the Fe-Sb-O catalyst.<sup>1)</sup>

In addition, it can be speculated that the resulting HBr is converted into  $\text{Br}_2$  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  $x=60\text{--}70\%$ ,  $S_{C\gamma}\approx 60\%$  have been attained even at the low  $\text{CH}_2\text{Br}_2/n\text{-C}_4\text{H}_{10}$  ratio.

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

## References

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- 8)  $\text{Log}_{10} K_p$  for the reaction  $\text{Br}_2 \rightarrow 2\text{Br}$  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  $\text{log} K_p$  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.