

## Partial Oxidation of Ethane over Boron Oxide Added Catalysts

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$B_2O_3$ - $Al_2O_3$ ,  $B_2O_3$ - $MgO$ ,  $B_2O_3$ - $La_2O_3$ , and  $B_2O_3$ - $P_2O_5$  are selective catalysts for the partial oxidation of ethane. Among these catalysts,  $B_2O_3$ (30wt%)-added  $Al_2O_3$  showed the highest catalytic activity in the formations of acetaldehyde (yield 1.03%) and ethylene (14.6%). Acetaldehyde is formed not via ethylene but directly from ethane. The formations of ethylene and acetaldehyde occur on different active sites.

Partial oxidation of light alkanes with oxygen to ethylene and oxygenated compounds is of significance from the standpoint of effective use of alkanes as a chemical resource. Direct conversion of ethane to  $C_2$  oxygenates such as acetaldehyde and acetic acid has been studied with nitrous oxide,<sup>1,2)</sup> but no successful work on the reaction with oxygen as an oxidant has been reported. Therefore, we have carried out a screening test of metal oxides with and without supported metal oxides to find active and selective catalysts for partial oxidation of ethane to ethylene and acetaldehyde using oxygen.

The metal oxides used were purchased from WAKO Chemical Co. and the alumina was the reference catalyst, JRC-ALO-2, supplied by Catalysis Society of Japan. The boron oxide supported on various oxides was prepared by an impregnation method with metal oxide powders and an aqueous solution of boric acid. These catalysts were calcined in air at 873 K. The contents of boron oxide in the catalysts are denoted in the parentheses, for example, the  $Al_2O_3$  added with 30wt%  $B_2O_3$  as  $B_2O_3$ (30)- $Al_2O_3$ . A conventional gas-flow system with a fixed-bed reactor made of quartz was used in the experiments. Ethane and oxygen gases were fed with helium gas carrier to the catalyst under atmospheric pressure. The reaction temperature for the test of catalysts was 823 K. Products were analyzed by gas chromatography. The selectivities and the yields of the products were expressed on the bases of ethane converted into each product.

The catalytic activities were examined over the oxides of B, Mg, Al, Si, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Sr, Y, Zr, Nb, Mo, Cd, In, Sn, Sb, Te, Ba, La, Ce, W, Pb, and Bi. No oxygenated hydrocarbons were formed over the oxides except for the oxides of B, Al, and Si.  $B_2O_3$  was a more selective catalyst for formations of ethylene and acetaldehyde than  $Al_2O_3$  and  $SiO_2$  which produced mainly CO and  $CO_2$  (See Table 1). However, the yield of acetaldehyde for  $B_2O_3$  was low, i.e., less than 0.1%.

Table 1. Partial Oxidation of Ethane over Various Oxide Catalysts at 823 K

Catalyst	Conv. /%	Selectivity /%					Yield /%	
		C <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> CHO	CO	CO <sub>2</sub>	CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	CH <sub>3</sub> CHO
none	0.2	89.0	0	0	11.0	0	0.2	0
B <sub>2</sub> O <sub>3</sub>	3.8	97.1	2.6	0	0.3	0	3.7	0.10
Al <sub>2</sub> O <sub>3</sub>	22.3	12.4	0.2	55.3	32.0	0	2.8	0.04
SiO <sub>2</sub>	4.4	37.4	1.2	54.6	6.8	0	1.6	0.06
B <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>a)</sup>	38.0	58.0	2.7	31.0	1.6	4.9	14.6	1.03
B <sub>2</sub> O <sub>3</sub> -La <sub>2</sub> O <sub>3</sub> <sup>a)</sup>	5.7	82.6	6.9	8.2	1.3	1.0	4.7	0.39
B <sub>2</sub> O <sub>3</sub> -MgO <sup>a)</sup>	4.6	80.0	7.7	8.5	2.8	1.0	3.7	0.35
B <sub>2</sub> O <sub>3</sub> -P <sub>2</sub> O <sub>5</sub> <sup>a)</sup>	2.1	89.7	9.4	0	0.9	0	1.9	0.20
B <sub>2</sub> O <sub>3</sub> -SiO <sub>2</sub> <sup>a)</sup>	3.6	96.0	2.5	0.3	0.3	0.5	3.5	0.09
B <sub>2</sub> O <sub>3</sub> -TiO <sub>2</sub> <sup>a)</sup>	0.4	98.0	2.0	0	0	0	0.4	0.01
B <sub>2</sub> O <sub>3</sub> -CaO <sup>a)</sup>	5.8	30.2	0.3	30.3	39.0	0.2	1.7	0.02
B <sub>2</sub> O <sub>3</sub> -ZnO <sup>a)</sup>	35.0	40.6	0	2.7	56.5	0.2	14.4	0
B <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub> <sup>b)</sup>	21.9	12.5	0.2	55.5	31.8	0	2.8	0.04

Reaction temperature = 823 K, Weight of catalyst = 0.5 g,  
Flow rate = 50 ml min<sup>-1</sup>, P(C<sub>2</sub>H<sub>6</sub>) = 20 kPa, P(O<sub>2</sub>) = 20 kPa.

a) The content of B<sub>2</sub>O<sub>3</sub> is 30wt%.

b) After washing with distilled water.

The catalytic activities of the boron oxides supported on various metal oxides were tested (Table 1). B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>, B<sub>2</sub>O<sub>3</sub>-MgO, B<sub>2</sub>O<sub>3</sub>-La<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> were effective catalysts for the partial oxidation of ethane to acetaldehyde. These catalysts were more active and selective for the formation of acetaldehyde than the B<sub>2</sub>O<sub>3</sub> catalyst without supports. The yields of ethylene and acetaldehyde for B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> were the highest among those for the four catalysts. B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> were also selective for the partial oxidation but less active. On the other hand, deep oxidation mainly proceeded over B<sub>2</sub>O<sub>3</sub>-CaO and B<sub>2</sub>O<sub>3</sub>-ZnO.

The stability of B<sub>2</sub>O<sub>3</sub>(30)-Al<sub>2</sub>O<sub>3</sub>, the most active catalyst, in the catalytic activity and selectivity with time on stream is shown in Fig. 1. The conversion and the selectivity was constant during 10 hours of the reaction. Thus, the B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst is stable under the reaction conditions shown in Fig. 1.

Formation rates of products over B<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> with the various contents of B<sub>2</sub>O<sub>3</sub> are shown in Fig. 2. Though ethane was highly converted over the pure alumina, the main products were CO and CO<sub>2</sub>. When 10wt% of B<sub>2</sub>O<sub>3</sub> was added, the formation of CO and CO<sub>2</sub> drastically decreased. This observation suggests that the addition of boron oxide on alumina effectively suppresses the formations of CO and CO<sub>2</sub> over alumina. The total selectivity to partial oxidation products (C<sub>2</sub>H<sub>4</sub> + CH<sub>3</sub>CHO) at the boron oxide content >20wt% was greater than 95%. The specific rate of

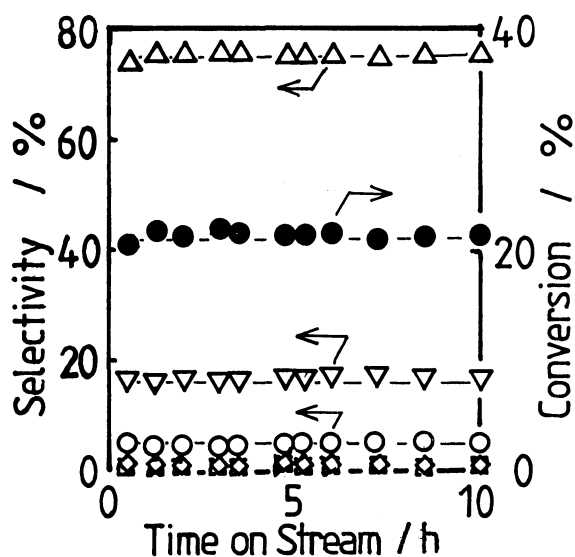


Fig. 1. Stability in catalytic activity of  $B_2O_3(30)-Al_2O_3$  with time on stream.  $C_2H_6$  conversion (●), selectivity of  $C_2H_4$  (Δ), acetaldehyde (○), CO (▽),  $CO_2$  (□), and  $CH_4$  (◇). Reaction temperature=823 K, weight of catalyst=0.5 g, flow rate=50 ml  $min^{-1}$ ,  $P(C_2H_6)=10$  kPa,  $P(O_2)=10$  kPa.

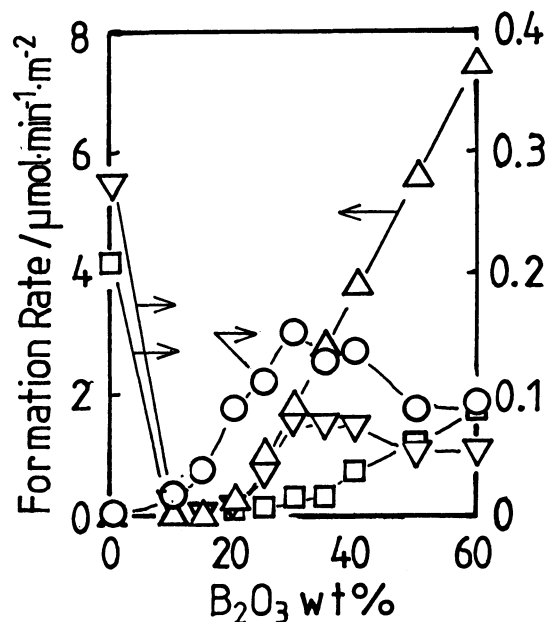


Fig. 2. Formation rates of productions as function of the content of  $B_2O_3$ . Δ:  $C_2H_4$ , ○: acetaldehyde, ▽: CO, □:  $CO_2$ . Reaction temperature=823 K, weight of catalyst=0.05 g, flow rate=100 ml  $min^{-1}$ ,  $P(C_2H_6)=10$  kPa,  $P(O_2)=10$  kPa.

formation of ethylene increased linearly with the addition of boron oxide above 20wt%. On the other hand the formation rate of acetaldehyde showed a maximum value at 30wt%. These observations strongly suggest that the formations of ethylene and acetaldehyde occur on different active sites. The selectivities to acetaldehyde at 15, 20, 25, and 30wt%  $B_2O_3$  are 31.1, 25.0, 9.2, and 7.1%, respectively. These values are considerably higher than that observed for pure  $B_2O_3$  in Table 1 (2.6%). This observation may suggest the generation of new active sites for the selective formation of acetaldehyde. No acetaldehyde was formed from ethylene on  $B_2O_3(30)-Al_2O_3$  when the ethylene was used as a reactant. This experiment was carried out under the same partial pressure of ethylene as that observed in the experiment of ethane oxidation. This result indicates that acetaldehyde is formed not via ethylene but directly from ethane. Supported boron oxide is assumed to play two roles for the catalytic reaction. One is to suppress the catalytic activity of alumina for the complete oxidation. The other is to generate the catalytically active site for the formation of acetaldehyde.

XRD spectra of  $B_2O_3-Al_2O_3$  with various contents of  $B_2O_3$  showed that the pattern attributed to crystalline  $B_2O_3$  was observed for the  $B_2O_3-Al_2O_3$  containing more than 20wt% of  $B_2O_3$ , and the intensity of the peaks in the spectra increased

with a rise in the content of  $B_2O_3$ . As described earlier, the formation rate of ethylene increased linearly with the content of  $B_2O_3$  (Fig.2). Therefore, the crystalline  $B_2O_3$  could be active sites for the formation of ethylene.  $B_2O_3$  would spread over the surface of alumina below the content of 20wt% in high dispersion and agglomerate above this value. The added  $B_2O_3$  at contents below 10wt% must react with the active sites for the deep oxidation, resulting in deactivation of this reaction.

The surface areas of the catalysts of the various contents of  $B_2O_3$  are shown in Fig. 3. It slightly decreased until 20wt%  $B_2O_3$  content, but was significantly lowered above this content probably due to the plugging of the pores in alumina by an agglomerate of  $B_2O_3$ .

This assumption was supported by the observation that the surface area of the  $B_2O_3(40)-Al_2O_3$ , of which surface area was  $48 \text{ m}^2 \text{ g}^{-1}$ , was restored to the original value of alumina, i.e.  $258 \text{ m}^2 \text{ g}^{-1}$ , after washing with distilled water at room temperature (indicated by the arrow in Fig. 3). The catalytic activity and selectivity after the washing treatment became comparable to those observed over alumina (see Table 1). The catalytic active species for both formations of ethylene and acetaldehyde must be easily washed away by distilled water. The catalytic active species for the formation of acetaldehyde is poorly characterized at present. Further investigation is necessary to reveal the details of the active species.

#### References

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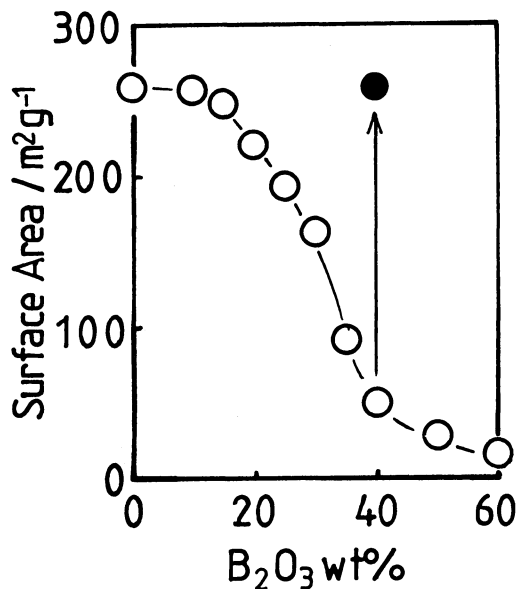


Fig. 3. Surface areas of  $B_2O_3-Al_2O_3$  with various contents of  $B_2O_3$ .

●: after washing with distilled water.

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