CHEMISTRY LETTERS, pp. 535-538, 1989.

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,[1,2] 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_2H_4	CH_3CHO	CO	CO_2	CH_4	C_2H_4	CH_3CHO
none	0.2	89.0	0	0	11.0	0	0.2	0
B_2O_3	3.8	97.1	2.6	0	0.3	0	3.7	0.10
Al_2O_3	22.3	12.4	0.2	55.3	32.0	0	2.8	0.04
SiO_2	4.4	37.4	1.2	54.6	6.8	0	1.6	0.06
B_2O_3-Al_2O_3 a)	38.0	58.0	2.7	31.0	1.6	4.9	14.6	1.03
B_2O_3-La_2O_3 a)	5.7	82.6	6.9	8.2	1.3	1.0	4.7	0.39
B_2O_3-MgO a)	4.6	80.0	7.7	8.5	2.8	1.0	3.7	0.35
B_2O_3-P_2O_5 a)	2.1	89.7	9.4	0	0.9	0	1.9	0.20
B_2O_3-SiO_2 a)	3.6	96.0	2.5	0.3	0.3	0.5	3.5	0.09
B_2O_3-TiO_2 a)	0.4	98.0	2.0	0	0	0	0.4	0.01
B_2O_3-CaO a)	5.8	30.2	0.3	30.3	39.0	0.2	1.7	0.02
B_2O_3-ZnO a)	35.0	40.6	0	2.7	56.5	0.2	14.4	0
B_2O_3-Al_2O_3 b)	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^{-1}, $P(C_2H_6)$ = 20 kPa, $P(O_2)$ = 20 kPa.

a) The content of B_2O_3 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_2O_3-Al_2O_3, B_2O_3-MgO, B_2O_3-La_2O_3 and B_2O_3-P_2O_5 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_2O_3 catalyst without supports. The yields of ethylene and acetaldehyde for B_2O_3-Al_2O_3 were the highest among those for the four catalysts. B_2O_3-SiO_2 and B_2O_3-TiO_2 were also selective for the partial oxidation but less active. On the other hand, deep oxidation mainly proceeded over B_2O_3-CaO and B_2O_3-ZnO.

The stability of B_2O_3(30)-Al_2O_3, 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_2O_3-Al_2O_3 catalyst is stable under the reaction conditions shown in Fig. 1.

Formation rates of products over B_2O_3-Al_2O_3 with the various contents of B_2O_3 are shown in Fig. 2. Though ethane was highly converted over the pure alumina, the main products were CO and CO_2. When 10wt% of B_2O_3 was added, the formation of CO and CO_2 drastically decreased. This observation suggests that the addition of boron oxide on alumina effectively suppresses the formations of CO and CO_2 over alumina. The total selectivity to partial oxidation products (C_2H_4 + CH_3CHO) at the boron oxide content >20wt% was greater than 95%. The specific rate of

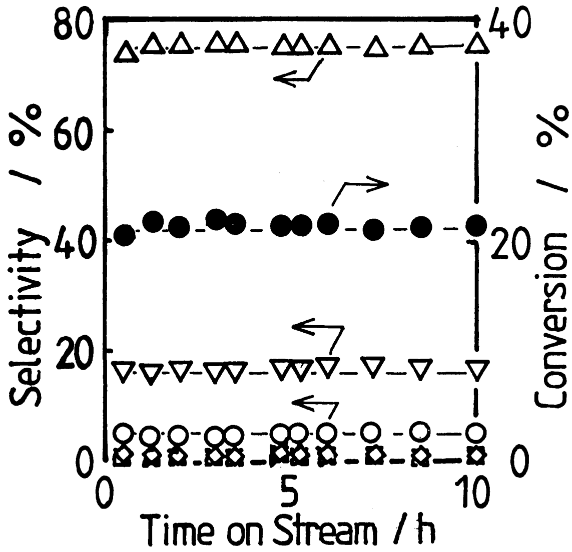

Fig. 1. Stability in catalytic activity of B_2O_3(30)-Al_2O_3 with time on stream. C_2H_6 conversion (●), selectivity of C_2H_4 (△), acetaldehyde (○), CO (▽), CO_2 (□), and CH_4 (◇). Reaction temperature=823 K, weight of catalyst=0.5 g, flow rate=50 ml min^{-1}, $P(C_2H_6)$=10 kPa, $P(O_2)$=10 kPa.

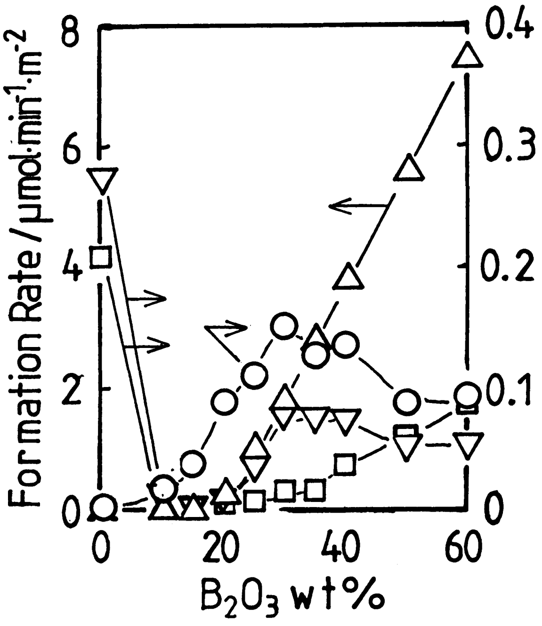

Fig. 2 Formation rates of productions as function of the content of B_2O_3. △:C_2H_4, ○:acetaldehyde, ▽:CO, □:CO_2. Reaction temperature=823 K, weight of catalyst=0.05 g, flow rate=100 ml min^{-1}, $P(C_2H_6)$=10 kPa, $P(O_2)$=10 kPa.

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 m^2 g^{-1}, was restored to the original value of alumina, i.e. 258 m^2 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.

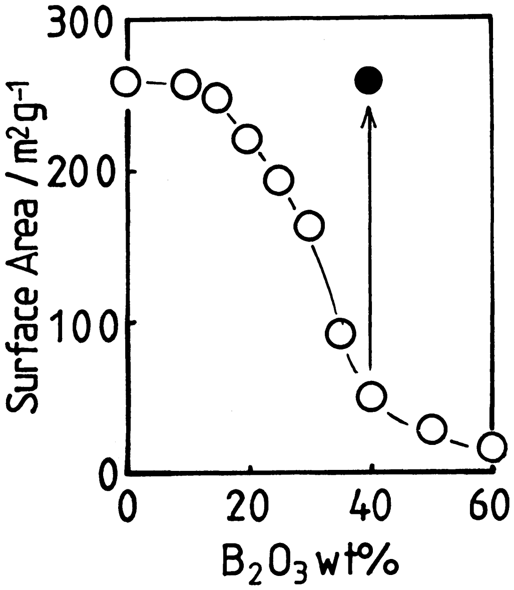

Fig. 3. Surface areas of B_2O_3-Al_2O_3 with various contents of B_2O_3.
●: after washing with distilled water.

References
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2) L. Mendelovici, and J. H. Lunsford, J. Catal., 94, 37 (1985).

(Received December 12, 1988)