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Partial Oxidation of Propane over B-P Mixed Oxide Catalysts

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B-P mixed oxide was the active and selective catalyst for partial oxidation of propane. The selectivity and the yield of the partial oxidation products (propionaldehyde, acetone, acetaldehyde, propylene, etc.) were 50% and 27%, respectively, under the reaction conditions; T=806 K, $P(C_3H_8)$=20 kPa, $P(O_2)$=30 kPa, and W/F=0.67 g h l^{-1}.

Direct conversion of light alkanes such as methane, ethane, and propane into useful chemicals has drawn much attention of chemists from chemical and industrial points of view. Catalytic partial oxidation of propane with oxygen to form oxygenates such as aldehydes and acids is one of the attractive reactions in this field. However, few studies on this reaction have been reported so far.[1,2] Ai[1] has reported that V_2O_5-P_2O_5-based catalysts are active for the reaction to form acrylic acid but that the selectivity for deep oxidation into carbon oxides exceeds that for partial oxidations at higher conversions (>20%). In this communication, we intended to obtain active and selective catalysts for the partial oxidation of propane and to clarify the reaction path over the most active catalyst found in this study.

The apparatus used in the catalytic reaction was an usual flow system with a fixed-bed quartz reactor (i.d.=8 mm). Reactant gases ($P(C_3H_8)=P(O_2)$=15 kPa) were fed with He carrier under atmospheric pressure to the catalyst (W=0.5 g, $F(C_3H_8+O_2)$=1.8 l(STP) h^{-1}). The reaction temperature was usually 823 K. Products were analyzed by gas chromatography. The selectivities and the yields of the products were calculated from the carbon number of the products on the basis of the carbon number of C_3H_8 reacted. Catalysts tested were metal oxides and those modified with boron oxide (denoted as B-M-O) or with phosphorus oxide (P-M-O). The B-M-O catalysts were prepared by an usual impregnation method with the metal oxide powder and aqueous solutions of boric acid. The P-M-O catalysts were prepared similarly with aqueous solutions of phosphoric acid. B-P-O catalyst was prepared by mixing boric acid and P_2O_5. The B/M, P/M, or B/P atomic ratios of these catalysts were 1. These catalysts were calcined in air at 573 K for 2 h and then at 873 K for 2 h.

The catalytic activities of the oxides of V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Mg, and Al were first examined. Only deep oxidation products, CO and CO_2, were

Table 1. Partial oxidation of C_3H_8 over phosphorus-containing mixed oxide catalysts

Catalyst	C_3H_8 conv./%	Selectivity/%				
		C_3-O[a)]	CH_3CHO	C_3H_6	C_2H_4	CO, CO_2
P-V-O	9.2	10	0	25	5	60
P-Mn-O	0.8	4	0	0	16	80
P-Cu-O	1.4	5	0	0	1	94
B-P-O[b)]	22	13	5	47	23	10
blank	0.4	10	4	0	80	6

a) C_3-oxygenates; propionaldehyde, acetone, acrolein and acrylic acid.
b) CH_4 was produced (selectivity=2%).
Reaction temperature=823 K, W/F=0.28 g h l^{-1}.

observed for these oxides. We have reported that boron is an essential component in some mixed oxide catalysts (Mg-B-oxides[3)] and Fe-Nb-B-oxides[4)]) for partial oxidation of CH_4 into formaldehyde. Therefore, the catalytic activities of the oxides modified with boron oxide (B-M-O) were examined. The C_3H_8 conversions at 823 K over the B-M-O catalysts were less than 0.4%, except for B-P-O. Over the B-P-O catalyst, the conversion was 22% and the selectivity for partial oxidation was high (65%). Considering that phosphorus is effective for the reaction, we tested the oxides modified with phosphorus oxide (P-M-O). Some of the P-M-O, that is, P-V-O, P-Mn-O, and P-Cu-O, catalyzed the partial oxidation significantly. Table 1 shows the results obtained with these active P-M-O and B-P-O catalysts together with the result obtained without catalyst (blank). B-P-O gave the highest conversion (22%), followed by P-V-O (9.2%). In the case of the P-V-O, P-Mn-O, and P-Cu-O, products were acrolein and acrylic acid, which were denoted as C_3-O (C_3-oxygenates), C_3H_6, C_2H_4, carbon oxides, and water. The selectivity for deep oxidation observed for these catalysts were fairly high (60, 80, and 94%, respectively). On the other hand, the B-P-O catalyzed mainly the partial oxidation, so that the selectivity of carbon oxides was only 10%. The partial oxidation products observed for this B-P-O were C_3-O (propionaldehyde, acetone,and acrolein), C_3H_6, and acetaldehyde. We conclude that among the catalysts tested, B-P-O is the most active and selective catalyst for the partial oxidation of C_3H_8. Some detailed studies on this B-P-O catalyst will be described below.

Figure 1 shows the C_3H_8 conversion and the selectivities of C_3H_6 and C_3-O as functions of time on stream. The conversion was almost constant during 10 h of the reaction. The selectivities changed a little at the initial stage of the reaction, but became constant after 4 h. The selectivity of carbon oxides was nearly constant (4%) during the run. These observations show that the B-P-O

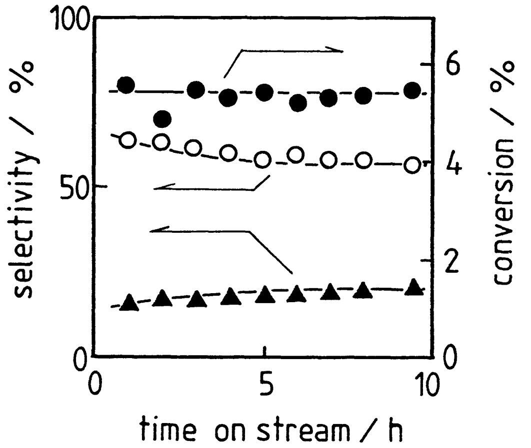

Fig. 1. Change in catalytic activity of B-P-O with time on stream. Reaction temp=773 K, W/F=0.28 g h l^{-1}.
C_3H_8 conversion: ●
C_3H_6 selectivity: O
C_3-oxygenates selectivity: ▲

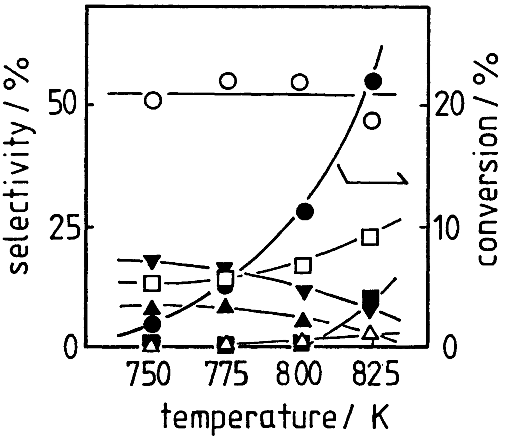

Fig. 2. Effect of reaction temperature on C_3H_8 conversion (●) and on selectivities of C_3H_6 (O), propionaldehyde (▼), acetone (▲), C_2H_4 (□), CO (■) and CH_4 (△). W/F=0.28 g h l^{-1}.

catalyst is stable under the reaction conditions shown in Fig. 1.

The effects of partial pressures of C_3H_8 and O_2 on the formation of C_3-O were examined. The formation rate of C_3-O increased with increasing $P(C_3H_8)$ and $P(O_2)$. This indicates that the B-P-O is the selective catalyst for partial oxidation of C_3H_8 even at higher $P(O_2)$. The B-P-O catalyzed selectively the partial oxidation also at the higher conversion; for example, at the conversion of 53% (T=806 K, $P(C_3H_8)$=20 kPa, $P(O_2)$=30 kPa, and W/F=0.67 g h l^{-1}), the selectivity for the partial oxidation products was 50%. The selectivity of each product was as follows; propionaldehyde (4.5), acetone (2.1), acrolein (1.5), acetaldehyde + acetic acid (8.5), methanol + formic acid (1.9), C_3H_6 (32), C_2H_4 (19), CH_4 (2.4), CO (27), and CO_2 (2.0%). At a lower W/F (=0.056 g h l^{-1}) and at a higher temperature (=863 K), the space time yield (STY) of C_3-O reached 9.2 mmol g^{-1} h^{-1}, when the selectivity for partial oxidation was 49%. This STY is the highest value among those obtained for other catalysts.[1,2]

Figure 2 shows the effects of reaction temperature on the C_3H_8 conversion and on the selectivities of the products. Below 773 K the reaction products were propionaldehyde, acetone, C_3H_6, C_2H_4, a trace of CO and a small amount of acetone (which is not shown in Fig. 2). C_2H_4 may be formed through cracking of C_3H_8. However, the other cracking product, CH_4, could not be found because the amount of CH_4 which should be formed together with C_2H_4 was under the limit of detection. At higher temperatures, the selectivities to propionaldehyde and acetone decreased, while those of C_2H_4, CH_4, and CO increased. These results imply that at higher temperatures, C_2H_4, CH_4, and CO are formed through the decomposition of propionaldehyde and acetone in addition to the cracking of C_3H_8 or deep oxidation.

At such higher conversions, the good carbon balance (< ±3%) between the consumed C_3H_8 and the products was obtained, so that carbon deposits can be neglected.

We examined the effect of W/F on the yields of the products at 773 K to clarify the reaction path. As shown in Fig. 3, the yields of C_3H_6, C_2H_4, propionaldehyde, and acetone increased linearly in proportion to W/F. From these results, we conclude that all these products are formed in parallel directly from C_3H_8, or from a common intermediate. This is the different reaction mechanism from that proposed by Ai$^{1)}$ for P_2O_5-V_2O_5 based catalyst and from that proposed by Giordano et al.$^{2)}$ for Mo, Te, CdX_2 based catalysts. They have reported that C_3-O (acrylic acid or acrolein) is formed via C_3H_6 which is the primary product from C_3H_8. In order to ascertain our conclusion that C_3-O is not formed by the successive reaction via C_3H_6, we have carried out the reaction over the B-P-O with C_3H_6 used as a reactant instead of C_3H_8. Under the similar reaction conditions (T=823 K, $P(C_3H_6)=P(O_2)=15$ kPa, W/F= 0.28 g h l^{-1}) to those of C_3H_8 oxidation, the conversion of C_3H_6 was less than 1% and no C_3-O products were observed. This result supports our above conclusion. The B-P-O is a very unique catalyst for activating alkane (C_3H_8) more easily than alkene (C_3H_6).

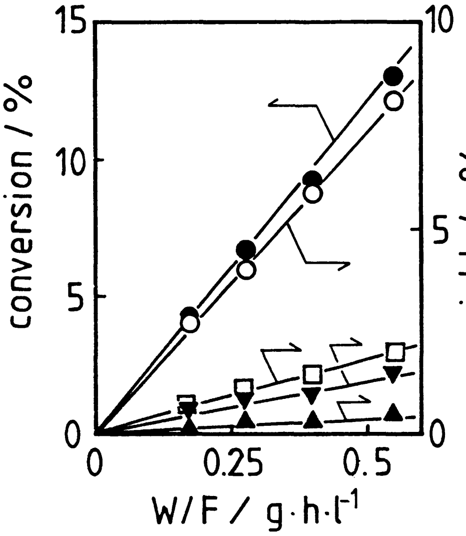

Fig. 3. Effects of W/F on C_3H_8 conversion (●) and on yields of C_3H_6 (○), propionaldehyde (▼), C_2H_4 (□), and acetone (▲). Reaction temp=773 K, W=0.5 g.

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