Conversion of Ethane to Acetaldehyde by Partial Oxidation with Oxygen over BPO₄-based Catalysts

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Direct conversion of ethane to acetaldehyde by partial oxidation with oxygen proceeds selectively on BPO₄ modified with basic oxides.

The contribution of homogeneous reactions in the gas phase to the catalytic process can be neglected under the experimental conditions of this work. The kinetic results obtained for ZnO-added BPO₄ suggest that CH₃CHO and C₂H₄ are produced in parallel *via* a common reaction intermediate. This intermediate was assumed to be ethyl peroxide formed from an ethyl intermediate and O₂.

The role of basic oxides is to increase the basicity of the active site -B-O-, resulting in an increase in the rate of heterolytic splitting of C-H bond on the site.

The NH_3 temperature-programmed desorption (TPD) studies have suggested a weakening of the acidic strength of the host BPO₄ catalyst by addition of ZnO, MgO and CaO. This modification decreases the apparent activation energy of the conversion of C_2H_6 , especially for the conversion to CH_3CHO .

Abundant supplies of natural gas in many countries of the world provide a continuing incentive for research on the conversion of light alkanes (methane, ethane and propane) into more valuable chemical precursors. However, relatively little attention has been paid so far to the selective transformation of ethane into acetaldehyde. At present, the method of thermal cracking of ethane to ethene, followed by the highly selective synthesis of acetaldehyde by the Wacker process prevails, but it is a relatively costly and energy-intensive process. A method of direct conversion would be highly attractive if a suitable catalyst could be developed and the process devised.

There are some reports concerning the direct conversion of ethane to acetaldehyde using N_2O as an oxidant.¹⁻³ However, only a trace of acetaldehyde (yield < 1.0%, selectivity <3%) was obtained when O_2 was used instead of N_2O .³ We have shown earlier that the mixed oxides of boron and phosphorus catalyse the direct transformations of methane, ethane and propane into their alkenes and oxygenates.⁴⁻⁶ We have suggested that a highly dispersed boron oxide on BPO₄ is especially active for the direct synthesis of acetaldehyde.⁶

Recently, we have explored some promising catalysts by addition of foreign metal oxides to BPO_4 . The present work is concerned with the evaluation of a number of BPO_4 -based catalysts for partial oxidation of ethane into acetaldehyde. The role of additives and the reaction mechanism will be discussed on the basis of kinetic studies.

Experimental

Materials

The BPO₄ catalyst was prepared by the addition of an aqueous solution of H_3BO_3 to an equimolar solution of H_3PO_4 . The solution was dried at 373 K and the precipitate calcined in air at 573 K for 2 h and at 873 K for 2 h. The catalyst was washed with distilled water several times followed by drying in air. The surface area of BPO₄ was 6 m² g⁻¹, which decreased slightly (<10%) after the catalytic reaction. Additives in the form of oxides (Mg, Co, Zn, Ce, Sm, Sn, Zr, Ni, Ga), hydroxide (Ca), acid (B) or carbonate (Na) were mixed thoroughly with BPO₄ in a mortar and pestle. The additive concentration was usually adjusted to 2 at.% of metal additives against the amount of B atoms of the host

 BPO_4 . The catalyst with additives was calcined in air at 573 K for 2 h and at 873 K for 2 h. The catalyst in the reactor was heated to the reaction temperature in an He flow.

 C_2H_6 (99.9%) was obtained from Takachiho-Kagaku-Kogyo Co. Oxygen (99.5%) and helium (99.99%) were obtained from Zyonan-Kyodo-Sanso Co. All gases were used as received.

Methods

The catalytic experiments were performed in a fixed-bed continuous flow reactor (quartz) operated at atmospheric pressure. Reactant gases were fed into the reactor (14 cm length, 0.80 cm i.d.) and product gases flowed out from the catalyst bed through a capillary tube (0.30 cm i.d.). The skin temperature of the reactor was monitored by a thermocouple along the length of the reactor. The catalyst and the thermocouple were positioned at the hottest area of the reactor. The temperature gradient was <1 K cm⁻¹ at the hottest zone of the reactor at *ca.* 973 K. The reaction conditions were as follows unless otherwise stated; W = 0.50 g, T = 823 K, F = 100 cm³ min⁻¹, $P(C_2H_6) = P(O_2) = 15$ kPa, and the balance to atmospheric pressure was provided by He.

The reactants and products were analysed by using a Shimadzu GC8AT gas chromatograph equipped with Gaskuropack-54, TSR-1 or active-carbon column packing. The conversion of C_2H_6 and the yield of each product were calculated on the basis of the C_2H_6 reacted. All the kinetic studies described later were carried out at oxygen and C_2H_6 conversions of <15%.

The TPD experiments of NH_3 were carried out as follows. A fresh sample (200 mg) in a quartz tube was treated at 823 K for 1 h *in vacuo*. After cooling to room temperature, NH_3 was preliminarily adsorbed for 1 h at 423 K at a constant pressure of 6.6 kPa. The NH_3 desorbed from the sample was monitored using a quadrupole mass spectrometer (Ulvac MS-300).

Results

Effect of Additives to BPO4 on the Oxidation of C2H6

The effect of additives on the catalytic oxidation of C_2H_6 over BPO₄ is summarized in Table 1. The homogeneous conversion of C_2H_6 , *i.e.* the reaction in the absence of catalysts, did not occur under the experimental conditions of Table 1.

	C_2H_6 conversion (%)	selectivity (%)					
M/BPO ₄		СН₃СНО	C ₂ H ₄	нсно	СО	CO ₂	CH ₃ CHO yield (%)
В	7.23	52.6	16.6	7.7	19.3	3.7	3.80
Na	2.41	49.3	26.5	0	13.6	10.4	1.19
Mg	3.52	42.9	22.1	2.9	20.7	11.2	1.51
Ca	4.60	44.2	21.3	5.6	22.6	6.6	2.03
Со	1.67	61.8	18.1	1.6	14.2	4.2	1.03
Zn	3.85	52.3	20.5	5.5	18.2	3.3	2.01
Ce	1.25	50.1	15.7	0	18.1	15.9	0.63
Sm	1.17	66.9	20.8	0	0	20.8	0.78
Sn	0.58	76.4	20.8	0	0	2.7	0.44
Zr	0.57	68.4	25.9	0	Ō	5.6	0.39
Ni	0.72	62.0	22.0	0	Ō	15.9	0.44
Ga	1.07	74.8	20.4	0	Ő	4.7	0.81
none (BPO₄)	0.69	62.1	27.6	0	1.2	9.1	0.43

Table 1 Effect of additives on the oxidation of C_2H_6 over BPO₄

 $M/BPO_4 = 1/50$ (atomic ratio). Reaction conditions: W = 0.50 g, T = 823 K, $P(C_2H_6) = P(O_2) = 15$ kPa, F(total) = 100 cm³ (STP) min⁻¹.

The predominant products of the catalytic reaction for BPO₄ without additives (last column in Table 1) were CH₃CHO, C₂H₄, CO₂, CO and H₂O. The selectivity to the partial oxidation products (CH₃CHO + C₂H₄) was quite high (90%) for this catalyst, but the catalytic activity (C₂H₆ conversion) was very poor. Addition of foreign metals, all of which must be in the form of metal oxides under the reaction conditions, to BPO₄ increased the catalytic activity with a slight depression in the selectivity to CH₃CHO except for Sn, Zr and Ni. Thus, the yield of CH₃CHO improved appreciably for most of the additives.

Among the additives tested in Table 1, the promoting effect of boron for the formation of CH₃CHO and C₂H₄ is most remarkable. The effects of MgO, CaO and ZnO are also appreciable compared with those of the other oxides in Table 1. The boron-added BPO₄ (denoted as B/BPO₄) was unstable in the presence of water vapour at temperatures >823 K. This is a serious disadvantage for this catalyst at high conversions of C₂H₆, because the reaction is always accompanied by the formation of water. On the other hand, Mg-, Ca- and Zn-added BPO₄ were stable in the presence of water vapour. Kinetic results for these catalysts were reproducible within an error of $\pm 3\%$ when the same sample was used repeatedly. Therefore, we focus our investigation on these three catalysts hereafter.

The results of C_2H_6 oxidation as a function of the quantity of additive are summarized in Fig. 1 for Zn, Mg and Ca additives. The BPO₄ samples used in Fig. 1(*a*), (*b*) and (*c*) and in Table 1 were prepared from different batches. The catalytic performance for the BPO₄ without additives changed from batch to batch. This is the reason why the results for BPO₄ are not identical in Table 1 and Fig. 1(*a*), (*b*) and (*c*).

The effects demonstrated by the additives in Fig. 1 are very similar, *i.e.* (1) the yields of CH₃CHO and C₂H₄ are enhanced appreciably with increasing amount of additive, giving maximum yields at 5 at.% for Mg and Ca and at 3 at.% for Zn, (2) addition of >8 at.% of Mg and Zn decreases the catalytic activity to less than that of BPO₄, (3) the selectivity to C₂H₄ does not change with the amount of additive, while that to CH₃CHO decreases, accompanied by a rise in the CH₃CHO yield, at low additive contents (<5 at.%), and is restored at higher additive contents.

Catalytic reactions for pure MgO, CaO and ZnO were examined under the same reaction conditions as those for Table 1 and Fig. 1 (standard reaction conditions). The catalytic activities of MgO and CaO for C_2H_6 conversion were less than that of BPO₄. The predominant products were C_2H_4 , CO, CO₂ and H₂O. The specific catalytic activity of



Fig. 1 Results of C_2H_6 oxidation on M/BPO₄: Effect of metal oxide content. (a) Zn/BPO₄, (b) Ca/BPO₄, (c) Mg/BPO₄. \bigcirc , CH₃CHO yield; \bigoplus , CH₃CHO selectivity; \triangle , C_2H_4 yield; \blacktriangle , C_2H_4 selectivity. Reaction conditions; W = 0.50 g, T = 823 K, $P(C_2H_6) = P(O_2) = 15$ kPa, F(total) = 100 cm³ (STP) min⁻¹

ZnO (C_2H_6 conversion = 11.8% using 0.50 g of ZnO) was one order of magnitude greater than that of BPO₄. However, the main products were CO₂, C_2H_4 , CO and H₂O. Moreover, the contribution of the reaction on ZnO itself can be neglected in Fig. 1 because the content of ZnO in ZnO/BPO₄ was <10 at.%. Thus, the additives (MgO, CaO and ZnO) without BPO₄ did not produce CH₃CHO at all. Therefore, the observation that the yields of CH₃CHO and C₂H₄ are improved by the addition of Mg, Ca and Zn oxides (Fig. 1) clearly suggests a synergism between additives and BPO₄.

Effect of Additives on NH₃ TPD

We can expect that the addition of basic oxides such as MgO and CaO or of the amphoteric oxide (ZnO) would change the acidic character of BPO_4 . This is demonstrated by the TPD spectra of NH₃ in Fig. 2. As can be seen in Fig. 2, the addition of MgO, CaO and ZnO shifted the maxima of the spectra to lower temperatures compared with the spectrum for BPO₄ without additives. However, the total amount of the desorbed NH₃ was not decreased appreciably by the additives. These observations suggest that the additives would modify the strength of the acid sites of BPO_4 . However, most of the acidic sites on BPO_4 remain intact because only a small quantity of the solid additives has been mixed with the host BPO_4 .

Kinetic Results

The BPO₄ with added 3 at.% ZnO was chosen as a representative of the catalysts in Fig. 1(a)-(c). Kinetic studies for this catalyst have been carried out in detail. The conversions of C_2H_6 at three different temperatures are replotted as functions of 1/F in Fig. 3. The amount of catalyst was kept constant (0.50 g) for the catalytic reaction. The conversions observed in the absence of catalyst (homogeneous reaction) are also plotted in Fig. 3 (filled symbols). The homogeneous reaction was carried out using the same reactor as that for the catalytic reaction. As can be seen in Fig. 3, the homogeneous reaction shows induction periods. This has already been demonstrated in light alkane oxidations.^{7.8} The main products of the homogeneous reaction of C_2H_6 was C_2H_4 under the reaction conditions of Fig. 3. For example, for the



Fig. 2 TPD of ammonia for (a) BPO_4 , (b) Mg/BPO_4 , (c) Zn/BPO_4 and (d) Ca/BPO_4 . Content of metal oxides: Ca (2 at.%), Zn (3 at.%), Mg (2 at.%); heating rate 10 K min⁻¹

3607



Fig. 3 Comparison of catalytic and non-catalytic oxidations of C_2H_6 . \bigcirc , \triangle , \Box , catalytic; \bigcirc , \blacktriangle , \blacksquare , non-catalytic. \bigcirc , \bigcirc , T = 803 K; \triangle , \bigstar , T = 823 K; \Box , \blacksquare , T = 843 K. Reaction conditions; W = 0.50 g, $P(C_2H_6) = P(O_2) = 15$ kPa

homogeneous reaction at 843 K in Fig. 3, the C_2H_4 selectivities were 99, 97, 92 and 95% at C_2H_6 conversions of 0.4, 1.9, 4.3 and 12.2%, respectively. The product distribution for the catalytic reaction was quite different from that of the homogeneous reaction. This is demonstrated in Fig. 4. The predominant products are $CH_3CHO > C_2H_4 > CO >$ HCHO. The selectivity to C_2H_4 does not change with W/F, but that to CH_3CHO decreases with contact time. However, note that the sum of the selectivities of CH_3CHO , CO and HCHO is constant. Moreover, the selectivity to CO is greater than that to HCHO. These observations suggest that CO and HCHO are formed through the oxidation of CH_3CHO [eqn. (1)]. A part of the HCHO formed from CH_3CHO must be oxidized further to CO and H_2O [eqn. (2)] or decomposed into CO and H_2 [eqn. (3)].

$$CH_3CHO + O_2 \rightarrow HCHO + CO + H_2O$$
 (1)

$$HCHO + \frac{1}{2}O_2 \rightarrow CO + H_2O$$
 (2)

$$HCHO \rightarrow CO + H_2$$
 (3)

However, decomposition of CH_3CHO to CH_4 and CO is not probable because only a trace of CH_4 was observed in the effluent gas from the reactor.



Fig. 4 Product selectivities as functions of W/F: \bigtriangledown , CH₃CHO + CO + HCHO; \bigcirc , CH₃CHO; \blacktriangle , C₂H₄; \bigtriangledown , CO; \triangle , HCHO. Reaction conditions; W = 0.50 g, T = 823 K, $P(C_2H_6) = P(O_2) = 15$ kPa

The effects of oxygen pressure on the conversion rate of C_2H_6 and on the product selectivities are depicted in Fig. 6. The experiments were carried out at a constant C_2H_6 pressure (30 kPa). The conversion increased proportionally to oxygen pressure. The selectivity to C_2H_4 did not change with a rise in oxygen pressure. The selectivities to CO and HCHO increased with a decrease in the selectivity of CH₃CHO at higher oxygen pressures. However, the sum of the selectivities of CH₃CHO, CO and HCHO was constant at all the oxygen pressures. The CO/HCHO ratio was far greater than unity. These results suggest again that the oxidation of CH₃CHO gives CO and HCHO [eqn. (1)] and further conversion of HCHO into CO [eqn. (2) or (3)].

The temperature effects on the conversion of C_2H_6 and on the yields of each product are demonstrated in Fig. 7. The yield of C_2H_4 and the conversion of C_2H_6 increased sharply



Fig. 5 Effect of $P(C_2H_6)$ on the rate of C_2H_6 conversion and product selectivities. \bigoplus , C_2H_6 conversion. Selectivity: \bigcirc , CH_3CHO ; \bigstar , C_2H_4 ; \bigtriangledown , CO; \triangle , HCHO. Reaction conditions; W = 0.50 g, T = 823 K, $P(O_2) = 10$ kPa, F(total) = 100 cm³ (STP) min⁻¹



Fig. 6 Effect of $P(O_2)$ on the rate of C_2H_6 conversion and product selectivities. \bullet , C_2H_6 conversion. Selectivity: \lor , $CH_3CHO + CO + HCHO; \bigcirc$, $CH_3CHO; \blacktriangle$, $C_2H_4; \bigtriangledown$, $CO; \bigtriangleup$, HCHO. Reaction conditions; W = 0.50 g, T = 823 K, $P(C_2H_6) = 30$ kPa, F(total) = 100 cm³ (STP) min⁻¹

J. CHEM. SOC. FARADAY TRANS., 1992, VOL. 88



Fig. 7 Conversion of C_2H_6 and yields of products as functions of reaction temperatures. \bigoplus , C_2H_6 conversion: Yield: \bigcirc , CH_3CHO ; \blacktriangle , C_2H_4 ; \bigtriangledown , CO; \triangle , HCHO. Reaction conditions; W = 0.50 g, $P(C_2H_6) = P(O_2) = 15$ kPa, F(total) = 100 cm³ (STP) min⁻¹

with a rise in temperature. The increase in the CH_3CHO yield was depressed at higher temperatures (>825 K), probably because the oxidation of CH_3CHO into CO and HCHO [eqn. (1)] could not be avoided.

A plot of $\ln R vs. 1/T$, where R is the rate of C_2H_6 conversion or of product formation calculated from the data in Fig. 7, showed a good linear correlation at >825 K. The apparent activation energies obtained were 122 kJ mol⁻¹ (C_2H_6 conversion), 180 kJ mol⁻¹ (C_2H_4 formation) and 93 kJ mol⁻¹ ($CH_3CHO + CO + HCHO$ formations). The last value should be considered as the activation energy for the formation of CH₃CHO because CO and HCHO are formed from CH₃CHO as described earlier.

The apparent activation energies obtained for the BPO₄ catalysts with added B, Mg and Ca oxide are compared with the results for Zn/BPO_4 in Table 2. Note that the activation energy for the conversion of C_2H_6 decreases with an increase in the basicity of the additives (order of basicities: $B_2O_3 < ZnO < MgO < CaO$). The apparent activation energies for the formation of C_2H_4 are *ca*. twice as great as those for the formation of CH₃CHO. Therefore, a higher selectivity to CH₃CHO can be expected at lower temperatures for all the catalysts in Table 2.

Discussion

Contribution of Homogeneous Reactions

The results in Fig. 3 for catalytic and non-catalytic reactions show that the presence of catalysts enhances the rate of C_2H_6 conversion by more than two orders of magnitude at short gas residence times. However, the homogeneous reaction at longer residence times could affect the catalytic reaction considerably. It is obvious from the straight lines in Fig. 3 that the catalytic reaction proceeds in a steady manner, in contrast with the homogeneous reaction. A remarkable difference was observed between the product distributions for the catalytic and homogeneous reactions as described earlier. More-

Table 2 Apparent activation energies for C_2H_6 conversion and for C_2H_4 and CH_3CHO formation over various M/BPO4 catalysts

		$E_{a}/kJ \text{ mol}^{-1}$	
catalyst	C_2H_6 conversion	C_2H_4 formation	CH ₃ CHO formation
B (2 at.%)/BPO ₄	166	247	144
Zn (3 at.%)/BPO ₄	122	180	93
Mg (5 at.%)/BPO ₄	112	186	85
Ca (5 at.%)/BPO ₄	102	173	74

over, the product selectivities depended strongly on the additives (Table 1). These observations show that the partial oxidation of C_2H_6 , *i.e.* the rate of conversion, the reaction pathways and the product distributions are definitely controlled by catalysts.

Reaction Mechanism and the Role of Additives

As suggested earlier concerning the results in Fig. 4 and 6, CH₃CHO is the precursor of CO and HCHO. The results in Fig. 3 and 4 indicate that the yield of C_2H_4 and the sum of the yields of CH₃CHO, CO and HCHO increase proportionally with contact time. The selectivity to C_2H_4 and the sum of the selectivities of CH₃CHO, CO and HCHO do not vary with change in the partial pressures of C_2H_6 and O_2 (Fig. 5 and 6). These observations suggest that C₂H₄ and CH₃CHO are formed in parallel with each other. The results in Fig. 1(a)-(c) indicate that the yields of C_2H_4 and CH_3CHO depend on the content of additives in a very similar manner, suggesting the same catalytic active sites on the catalysts and the same intermediate precursor for both products. Therefore, the reaction pathways can be written as follows, where X is a common reaction intermediate for the formation of $CH_3CHO \text{ and } C_2H_4$:

$$C_{2}H_{6} \xrightarrow{O_{2}} X \xrightarrow{CH_{3}CHO} \xrightarrow{O_{2}} HCHO + CO + H_{2}O$$

$$\downarrow O_{2}$$

$$CO + H_{2}O$$

$$(4)$$

The observation that the selectivity to CH_3CHO decreases with an increase in the additive content in Fig. 1(*a*), (*b*) and (*c*) can be ascribed to a further conversion of CH_3CHO into HCHO and CO. However, the selectivity is restored owing to the decrease in the yield of CH_3CHO at high additive contents. The apparent activation energy for the conversion of C_2H_6 depends strongly on the additives (Table 2). The activation energy decreases with increasing basicity of the additives (Table 2). This observation suggests that the activation of C_2H_6 is facilitated with a rise in the basicity of the oxides added. Let us assume here that the activation of C_2H_6 occurs by heterolytic splitting of the C—H bond on a -B-O- site which has been modified with the additives as demonstrated in Fig. 8.

The dissociation of C_2H_6 [step (i)] must be assisted by the formation of $O-H^+$ and $B-C_2H_5^-$ bonds. Here, we can

3609

expect that the more the oxygen of -B-O-M- has a negative charge, the more the $O-H^+$ bond is stabilized. The addition of basic oxides must increase the basicity of the oxygen of -B-O-M- compared with the surface lattice oxygen of BPO_4 . Therefore, we can expect that the activation of C_2H_6 is enhanced with increasing basicity of the additive as described earlier (Table 2). The reaction scheme in Fig. 8 assumes a rapid insertion of O_2 into $B-C_2H_5$, forming $C_2H_5O_2(a)$ in step (ii). Abstractions of the α - and β hydrogens of $C_2H_5O_2$ give CH_3CHO [steps (iii) and (v)] and C_2H_4 [steps (iv) and (vi)], respectively. The former abstraction must be much easier than the latter because of the selective formation of CH_3CHO . This explains the smaller activation energy observed for the former than for the latter (Table 2).

The possibility that CH_3CHO could be formed from C_2H_4 by addition of H_2O (or OH) and subsequent dehydrogenation,

$$C_2H_4 + H_2O \rightarrow CH_3CHO + H_2$$
 (5)

can be neglected for the following reasons: (a) The selectivity to C_2H_4 was independent of contact time (Fig. 5) and partial pressures of reactants (Fig. 5 and 6). (b) The apparent activation energies for the formation of CH_3CHO were much smaller than that for the formation of C_2H_4 for all the catalysts in Table 2. If CH_3CHO is produced from C_2H_4 , the activation energy for CH_3CHO should be close to or larger than that for C_2H_4 . (c) The oxidation of C_2H_4 as the starting reactant did not produce CH_3CHO at all, but the predominant products were CO_2 , H_2O and carbon deposited on the surface.

According to the catalyst model demonstrated in Fig. 8, the role of additives is to modify the basicity of the host BPO₄ catalyst. The NH₃TPD spectra in Fig. 2 showed a decrease in the acidic character/strength of BPO₄ by the addition of ZnO, CaO and MgO. This observation certainly indicates a chemical interaction between the host oxide and the additives. An increase in the additive content should increase the number of active sites at the boundaries between BPO₄ and the additives, which improves the yields of CH₃CHO and C₂H₄ [Fig. 1(a)–(c)]. However, excessive addition of additive sites, thus diminishing the catalytic activity at high additive contents, Fig. 1(a)–(c). Studies on the interactions between BPO₄ and additives have been carried out by applying IR and XPS techniques. However, useful



Fig. 8 Reaction scheme for the partial oxidation of C_2H_6 over M/BPO₄; M represents the metal additives

information has not been obtained at the moment. Further studies are definitely required to obtain a more precise model of the catalytic active species on the BPO₄-based catalysts.

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J. CHEM. SOC. FARADAY TRANS., 1992, VOL. 88

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