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Oxidative Esterification of Ethanol over Oxide Catalysts

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Oxidative esterification of ethanol has been studied over various oxide catalysts. Acetaldehyde was easily formed by oxidative dehydrogenation, and reacted further with remained ethanol and oxygen to produce ester. Among single oxides, Bi_2O_3, MoO_3, and Sb_2O_4 showed the highest selectivity and yield for ethyl acetate formation, respectively. The ethyl acetate yield was highest and complete oxidation was extremely low over MoO_3-Sb_2O_4 system.

Several kinds of esters have been industrially synthesized by the reaction of alcohol and carboxylic acid in the presence of much excess of alcohol in order to shift the equilibrium to ester formation. Ethyl acetate has been produced by the condensation of acetaldehyde (Tischtschenko reaction). Although Kunugi et al.[1)] reported that ethyl acetate was formed by the vapor-phase oxidation of ethanol over metallic palladium supported on active charcoal (Pd/C), there is no report about the performance of oxide catalysts in this reaction so far. In the present paper, various kinds of oxides and some binary oxides were used to oxidative esterification of ethanol and characteristics of the reaction are discussed.

Single oxides were prepared from their corresponding salts or commercial oxide powders. Composite oxides were prepared by coprecipitation method using aqueous solutions of their corresponding nitrate salts. All of oxides or hydroxide powders underwent calcination in air at 500 °C for 5 h prior to the oxidation reaction. The oxidation of ethanol was carried out at atmospheric pressure in a conventional flow system. Ethanol was introduced by means of a liquid micro-feeder and vaporized in the upper part of reactor. A gaseous mixture of ethanol (20 vol%), oxygen (12-32 vol%), and nitrogen (diluent) was passed through the catalyst bed. Reaction temperature was altered from 200 °C to 450 °C. Activity data were taken 4-5 h after the reaction started, where the reaction attained the steady state. Feed materials and products were analyzed by gas chromatography.

The temperature dependence of ethanol oxidation over MoO_3 catalyst is shown in Fig. 1. Ethanol conversion increased monotonously with a rise in reaction temperature. Main products formed up to 400 °C were acetaldehyde, ethyl acetate, CO and CO_2. As the reaction temperature was raised, the selectivity to ethyl acetate increased below 350 °C but decreased at higher temperatures. The dehydrogenation

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of ethanol to acetaldehyde seems to be oxidative, because hydrogen was scarcely detected in this temperature region. Since the increase in selectivity to ethyl acetate is accompanied by a decrease in that to acetaldehyde at high temperatures and the selectivity of acetic acid is less than 2%, it is probable that ester was formed by the reaction among ethanol, produced acetaldehyde, and oxygen, as suggested by Kunugi et al. for Pd/C catalyst.1-3) The successive oxidation to CO and CO_2 became dominant above 400 °C. Similar behavior was observed with other catalysts except the difference in yields of by-products and the optimum temperature for the ester formation.

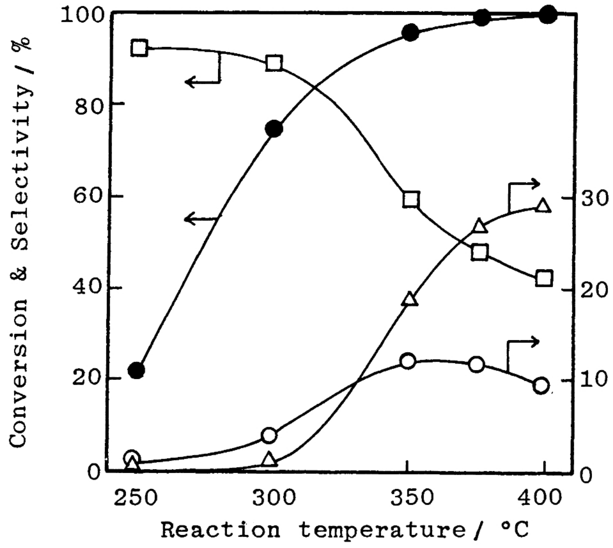

Fig. 1. Effect of reaction temperature on the activity of MoO_3.

● conversion of ethanol
○ selectivity to ethyl acetate
□ selectivity to acetaldehyde
△ selectivity to CO & CO_2

Reaction temperature, partial pressure of reactants, and contact time were changed to find out the optimum condition for the ester formation using MoO_3-Bi_2O_3 catalyst (Mo/Bi = 1). The optimum condition was located at T= 350 °C, W/F = 13.6 g-cat·h/mol, P_{O_2} = 0.2 atm, and $P_{C_2H_5OH}$ = 0.2 atm. Complete oxidation became dominant when either the partial pressure of oxygen or contact time increased. The effect of steam addition to feed gas was also examined but no evident improvement was observed.

Based on the above information, the temperature dependences were tested on every catalyst engaged, as summarized in Table 1,in which selectivities of ethylene and other by-products were not listed. In this table, the activities at two temperatures were given for every catalyst, i.e., one is 350 °C for comparison between these catalysts and the other is the reaction temperature for the higher ester yield. The selectivities to ethyl acetate were generally lower than those to acetaldehyde on most of single oxides in Table 1. Bismuth oxide was the most selective for oxidative esterification but its activity was low. The yield for oxidative esterification was the highest over MoO_3 and Sb_2O_4 among single oxide catalysts. Tin oxide and zinc oxide were selective for oxidation to acetaldehyde. The high oxidation activity of V_2O_5 and CeO_2 led to conversion to CO and CO_2 even though the reaction was operated at low temperature.

Several composite oxides were subjected to oxidative esterification of ethanol to design more active catalysts than the single oxides. The activities and product distributions over the binary oxides were generally different from their component single oxides, as shown in Table 1. Complete oxidation and acetic acid formation (selectivity = 10% at 350 °C) were promoted by mixing of MoO_3 and V_2O_5. There was no obvious improvement on the ester formation by combination of these two oxides.

The ternary system of MoO_3-Bi_2O_3-V_2O_5 was also unselective for oxidative esterification. Mixing of Fe_2O_3 to Sb_2O_4 largely enhanced the catalytic activity and selectivity to acetaldehyde at 350 °C but complete oxidation was too violent at elevated temperatures. The addition of a small amount of Bi_2O_3 to MoO_3 enhances the selectivity to ethyl acetate without lowering the catalytic activity (Fig.2). The selectivity to ethyl acetate was maximum and almost constant at Bi/(Mo+Bi)= 0.09-0.5. Figure 3 shows the dependence of ethanol conversion and product selectivity of MoO_3-Sb_2O_4 system on the composition. It is note that the selectivity to ethyl acetate was strongly enhanced by mixing of Sb_2O_4 with MoO_3 and reached a maximum at Sb/(Mo+Sb) = 0.66. The maximum ethyl acetate selectivity (30%) of MoO_3-Sb_2O_4 was more than 6 and 20 times higher than those of MoO_3 and Sb_2O_4,respec-

Table 1. Oxidative esterification of ethanol over various oxide catalysts ($C_2H_5OH:O_2:N_2$=1:1:3, W/F=13.6 g-cat.h/mol)

Catalyst	Reaction temp /°C	Conv. of ethanol/%	Selectivity a) / %			Yield of $CH_3COOC_2H_5$/%
			CH_3CHO	$CH_3COOC_2H_5$	$CO+CO_2$	
Bi_2O_3	350	40.1	68.8	16.0	11.3	6.4
	300	22.5	72.9	20.9	5.0	4.7
MoO_3	350	96.1	59.5	11.9	18.6	11.4
	300	75.3	89.3	4.0	0.7	3.0
Sb_2O_4	350	32.4	96.6	1.6	0	0.5
	450	90.0	50.7	11.7	35.5	10.5
SnO_2	350	82.3	66.2	6.5	20.3	5.4
	250	20.7	84.2	9.3	0	1.9
ZnO	350	30.5	98.6	0.9	0	0.3
	450	68.4	61.9	7.0	27.8	4.8
V_2O_5	350	94.0	65.4	2.9	28.6	2.7
	250	95.0	81.2	3.5	12.2	3.4
CeO_2	350	68.2	13.5	1.1	75.0	0.7
	200	10.3	66.9	12.2	6.4	1.3
TiO_2	350	53.7	80.0	3.5	9.0	1.9
	400	81.5	54.5	2.1	34.9	1.7
MnO_2	350	76.8	56.7	1.0	35.5	0.8
	300	54.1	79.0	2.3	12.7	1.3
Cr_2O_3	350	95.6	73.0	0.6	25.2	0.5
	250	69.9	88.9	1.0	8.9	0.7
MoO_3-Bi_2O_3	350	94.1	66.2	10.9	17.8	10.3
(Mo:Bi=1:1) b)	400	99.9	44.8	13.1	31.3	13.1
MoO_3-V_2O_5	350	97.8	59.5	0.4	26.2	0.4
(Mo:V=1:1)b)	280	89.6	77.0	9.0	6.0	8.0
MoO_3-Sb_2O_4	350	99.7	79.5	9.0	5.3	9.0
(Mo:Sb=1:2)b)	300	86.3	67.0	29.4	0.7	25.3
Bi_2O_3-V_2O_5	350	98.5	81.4	0.6	14.0	0.6
(Bi:V=1:1) b)	250	60.7	91.4	6.3	1.2	3.8
Sb_2O_4-Fe_2O_3	350	60.4	86.0	3.1	7.2	1.9
(Sb:Fe=2:1) b)	400	87.7	52.2	9.9	34.3	8.7
MoO_3-Bi_2O_3-V_2O_5	350	91.1	80.8	1.0	4.3	0.9
(Mo:Bi:V=1:1:1)b)	250	35.8	90.5	3.6	0	1.3

a) other by-products are ethylene, acetic acid, methyl acetate, ketone,and ether.
b) atomic ratio.

tively. Not only the selectivity, but also the catalytic activity for ethanol oxidation was greatly promoted. About 95% of ethanol was oxidized at Sb/(Mo+Sb)= 0.5-0.67. The highest ethyl acetate selectivity reported for Pd/C catalyst was ca. 69% when the conversion of ethanol was 30.1% at 110 °C. Although the selectivty over MoO_3-Sb_2O_4 catalyst was a little lower, the maximum yield (30%) was much higher than that over Pd/C catalyst. The most striking aspect of the present results is that carbon dioxide was scarcely produced over the MoO_3-Sb_2O_4 catalyst. The by-product over the MoO_3-Sb_2O_4 catalyst was mainly acetaldehyde but that over Pd/C catalyst was CO_2. The formed acetaldehyde can be recycled for ethyl acetate formation from the practical aspect. Although further investigation to mechanism for the ester formation over oxide catalysts is necesary, the condensation of acetaldehyde can be negated because no ester was formed by passing a mixture of nitrogen and acetaldehyde over MoO_3-Sb_2O_4 catalyst at 300 °C.

References
1) T.Kunugi, T.Matsuura, and T. Kono, Kogyo Kagaku Zasshi, 71,1517 (1968).
2) T.Kunugi, and T.Kono, Kogyo Kagaku Zasshi, 72, 1282 (1969).
3) T.Kunugi, T.Kono, T.Yanagisawa, and H.Arai, Nippon Kagaku Kaishi,1972, 2271.

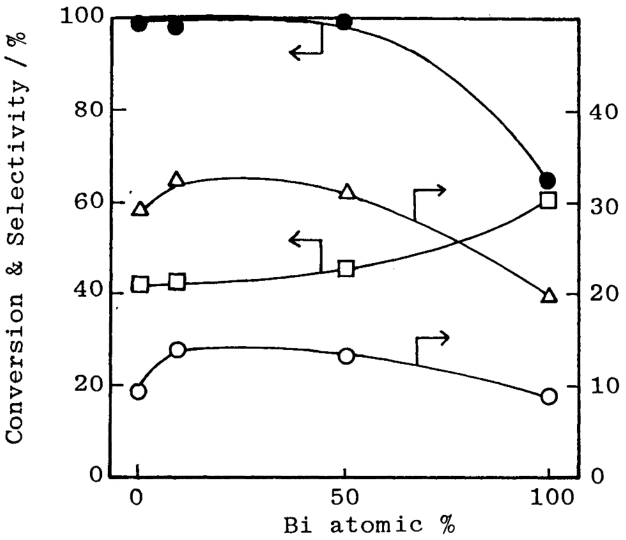

Fig. 2. Dependence of conversion and selectivities at 400 °C on the composition of Mo-Bi binary oxides.

● conversion of ethanol
○ selectivity to ethyl acetate
□ selectivity to acetaldehyde
△ selectivity to CO & CO_2

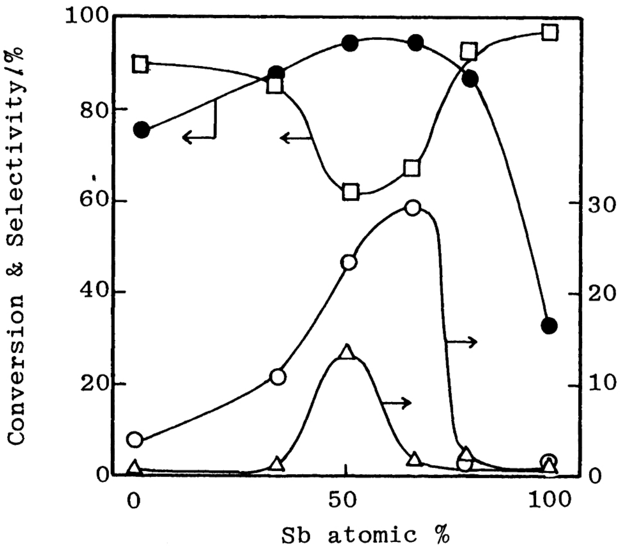

Fig.3. Dependence of conversion and selectivities at 300 °C on the composition of Mo-Sb binary oxides.

● conversion of ethanol
○ selectivity to ethyl acetate
□ selectivity to acetaldehyde
△ selectivity to CO & CO_2

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