CATALYTIC OXIDATION OF ISOBUTENE ON A POLYCOMPONENT CATALYST

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Received January 21, 1993
Accepted May 26, 1993

The catalytic gas-phase oxidation of isobutene has been studied on polycomponent Mo-Co-Ni-Bi-Fe-K oxide catalysts suitable for industrial preparation of propenal from propene. It has been found that within the temperature interval of 290 – 350 °C the main oxidation products are 2-methylpropenal, acetone, 2-methylpropenoic acid, acetic acid and carbon dioxide. A modification of the mentioned catalyst by addition of a further component (W, P, Te, and Zn) showed that zinc increases the conversion of isobutene and at the same time markedly increases its selectivity for 2-methylpropenal, whereas the additions of tungsten and phosphorus decrease the conversion of isobutene with a simultaneous increase of selectivity for CO_2. If *tert*-butyl alcohol is used as the starting material instead of isobutene, then the extent of reaction is slightly decreased with simultaneous increase of selectivity for 2-methylpropenal, whereas the selectivities for the acids remain almost unchanged.

Multicomponent oxide catalysts based on the Mo-Bi-X where X represents one or several elements from the series Fe, Ni, Sb, Co, W, Sn, P etc. have been used successfully for the industrial production of propenal from propene which usually represents the initial step in the production of propenoic acid. The increased demand for methyl 2-methylpropenoate was accompanied also by an interest in a similar reaction – catalytic oxidation of isobutene or *tert*-butyl alcohol to 2-methylpropenal and 2-methylpropenoic acid[1 – 5]. Most catalytic systems studied are based on the above-mentioned Mo-Bi-X oxide catalysts[6 – 11], on the Sn-Sb-O system[12], or on Mo-V-P heteropolyacids[13]. The present paper is focused on the oxidation of isobutene on the Mo-Co-Ni-Bi-Fe-K oxide catalysts used in the industrial production of propenal from propene[14] and on their modifications by the addition of a further component (W, P, Te, Zn).

EXPERIMENTAL

Catalysts

In the preparation of the basic catalysts S1 and S2 differing distinctly in the Fe and Bi content, the amounts of the respective components were chosen in such a way as to make the molar ratio of the metals Mo : Co : Ni : Bi : Fe : K equal to 6.8 : 3 : 1 : 0.89 : 1.11 : 0.08 and 7 : 3 : 1 : 2.2 : 0.2 : 0.08

for the catalysts S1 and S2, respectively[14]. Both the catalysts mentioned were prepared from the solutions of ammonium heptamolybdate, tartaric acid, nitrates of the respective metals, and potassium hydroxide. The pH value of final solutions was adjusted at 6 – 7 by addition of ammonia, whereupon each solution was evaporated at 90 °C with vigorous stirring to give a microcrystalline paste. This paste was always dried at 120 °C 12 h, and annealed at 160 and 180 °C 3 h, at 350 °C 5 h, and at 460 °C 6 h. The samples obtained were ground and separated on sieves to get a fraction of 0.315 – 0.500 mm grain size. The catalysts S1K1 – S1K4, containing additional tungsten, and the catalysts S1K5 – S1K8, containing additional phosphorus, were prepared in the same way as S1; tungsten and phosphorus were added to the solutions in the form of WO_3 and $(NH_4)_2HPO_4$, respectively.

The catalysts S2C1 – S2C5, containing additional tellurium, and the catalysts S2C6 – S2C8, containing additional zinc, were prepared in the same way as S2; the metallic tellurium was dissolved in HNO_3 and then added to the resulting solution, zinc was added in the form of zinc(II) acetate.

Apparatus

The activity and selectivity of the catalysts prepared were studied on a through-flow apparatus with integral reactor with solid bed. In the reactor there was a coaxial tube of 1.7 cm diameter with a thermocouple. The reactor was heated with an electric oven with two windings one of which was controlled by an automatic regulator Radelkis, which allowed maintaining the chosen temperature with the accuracy of ±1.8 °C. The flow rates of gases (N_2, O_2, $CH_2=C(CH_3)_2$) were measured with capillary flow meters. Water vapour and *tert*-butyl alcohol were dosed into the reaction mixture from saturators temperated at a calculated temperature. The composition of reaction mixture (% v/v): isobutene (IB) or *tert*-butyl alcohol (TB) 5, O_2 12, H_2O 20, N_2 63; total feed of the reaction mixture $F = 5$ dm^3 STP h^{-1}, the amount of catalyst used 1 – 6 g. The catalyst was always diluted with SiC of the same grain size in the ratio of 1 : 1, hence the bed height in the reactor was always greater than 1 cm. At the conditions given the effect of inner and outer diffusion is negligible. The liquid reaction products (aldehydes and acids) were condensed in a water absorber placed at the end of the through-flow apparatus. The specific surface area of catalysts was measured by the method of thermal desorption of nitrogen.

Analysis of Reaction Products

The qualitative analysis of liquid reaction products was carried out on apparatuses GC/MS Hewlett Packard and Kratos 25 RFA, the quantitative analysis on a GC Chrom 5 with heat conductivity detector connected to the through-flow apparatus. A system of three six-way cocks enabled dosing of the reaction mixture into the gas chromatograph before and after the passage through the reactor bed. A column of 2.5 m length and 3 mm inner diameter packed with Porapak Q or T was used with helium as the carrier gas. After finished elution of air, water, and unreacted IB at 123 °C the temperature in the column was raised to 195 °C to accomplish the elution of acetone, 2-methylpropenal, acetic acid, and 2-methylpropenoic acid. Carbon dioxide was determined in the same column at 30 °C.

RESULTS AND DISCUSSION

The qualitative analysis of aqueous absorbate showed ca 20 products of the catalytic oxidation of isobutene, the main products including 2-methylpropenal (methacrolein, MA), acetone (AC), 2-methylpropenoic (methacrylic) acid (MAA), acetic acid (AA), and CO_2. The yields of the other oxidation products were below 0.5% and were not determined. The conversion of IB and the yields of products on the S1 catalyst (specific surface area 8.0 $m^2 g^{-1}$) were studied for various values of time factor W/F_{IB} (where W is the catalyst weight in g, and F_{IB} is the isobutene feed in mol h^{-1}) and showed that at 320 °C the catalyst is relatively highly active but with an only average selectivity for 2-methylpropenal and 2-methylpropenoic acid (Fig. 1). At an almost 100% conversion of IB the yields of MA and MAA are only 66% and 5.1%, respectively, whereas the propene oxidation on the same catalyst at the same reaction conditions gives 85% and 7.9% yields of propenal and propenoic acid, respectively[14]. The conversion (as a measure of the catalyst activity), selectivity, and yields of products were estimated in the following way:

conversion of IB or TB	$X = (n_R/n_A)\ 100\%$,
selectivity for the *i*-th product	$S_i = (1/\nu_i)(n_i/n_R)\ 100\%$,
yield of the *i*-th product	$Y_i = (1/\nu_i)(n_i/n_A)\ 100\%$,

where n_A is the number of mols of IB (TB) fed per hour, n_R is the number of mols of IB (TB) reacted per hour, n_i is the number of mols of the *i*-th product formed per hour, ν_i is the stoichiometric coefficient of the *i*-th product (ν_i = 1 for MA and MAA, 4/3 for AC, 2 for AA, and 4 for CO_2).

The formation of acetone indicates partial destruction of carbon chain of the oxidized molecule. Most patent literature dealing with the catalytic oxidation of isobutene to 2-methylpropenal gives also *tert*-butyl alcohol (TB) as starting material. Therefore, we

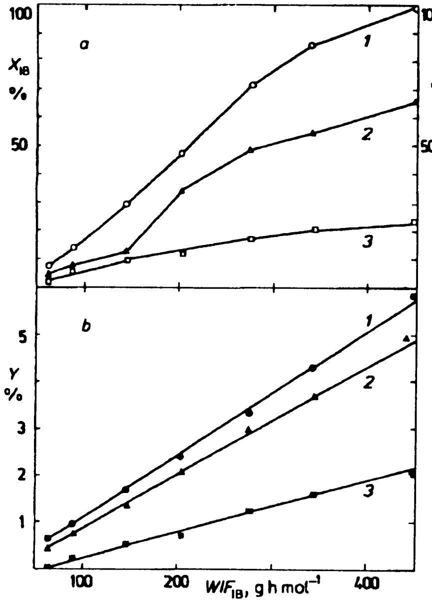

FIG. 1

Dependence of: *a* conversion of isobutene X_{IB} (*1*) and yields of 2-methylpropenal Y_{MA} (*2*) and carbon dioxide Y_{CO_2} (*3*) and *b* yields of acetone Y_{AC} (*1*), 2-methylpropenoic acid Y_{MAA} (*2*), and acetic acid Y_{AA} (*3*) upon time factor W/F_{IB}; t = 320 °C compared the effect of reaction temperature upon the activity and selectivity of the S1 catalyst with isobutene and *tert*-butyl alcohol as the starting materials. From the data of Table I it follows that particularly at lower temperatures the oxidation of TB proceeds to a smaller extent but with higher selectivity for 2-methylpropenal as compared with the oxidation of IB. The selectivities for MAA and AA did not practically change, the selectivity for CO_2 somewhat decreased. It is interesting to compare the selectivities for AC. Whereas in the oxidation of IB the selectivity for AC practically does not change with temperature, in the oxidation of TB the temperature increase is connected with a more distinct destruction of carbon chain. Since even at low conversions of TB the latter was not detected among the reaction products (only IB was always detected), the oxidation of TB at the active centres must be preceded by its dehydration to IB. The effect of tungsten upon the properties of the catalyst S1 in the oxidation of IB was studied with the catalysts having the molar ratios of Mo : Co : Ni : Bi : Fe : K : W = 6.8 : 3 : 1 : 0.89 : 1.11 : 0.08 : n, where $n = 0.5$, 1.0, 1.5, and 2.0 for the catalyst S1K1, S1K2, S1K3, and S1K4, respectively, with the specific surface area values of 7.3, 7.6, 5.5, and 5.9 $m^2 g^{-1}$, respectively. The effect of phosphorus was studied with the catalysts having the molar ratios of Mo : Co : Ni : Bi : Fe : K : P = 6.8 : 3 : 1 : 0.89 : 1.11 : 0.08 : m, where $m = 0.4$, 0.8, 1.2, and 1.6 for the catalysts S1K5, S1K6, S1K7, and S1K8, respectively, with the specific surface area values of 7.5, 7.6, 8.1, and 7.9 $m^2 g^{-1}$, respectively. The reaction temperature was 320 °C, the time factor $W/F_{IB} = 342$

TABLE I
Effect of reaction temperature upon activity and selectivity of S1 catalyst in oxidation of IB and TB. Time factor $W/F_A = 342$ g h mol^{-1} (where A is either IB or TB); X conversion of IB or TB (%), S_i selectivity for the i-th product (%)

Reaction temperature, °C	X_A	S_{MA}	S_{AC}	S_{MAA}	S_{AA}	S_{CO_2}
			A = IB			
298	32.7	68.8	6.1	2.4	2.1	18.3
310	50.7	64.7	6.1	2.7	2.6	21.9
320	84.2	65.1	5.0	4.1	2.7	22.7
330	90.4	55.2	6.7	4.3	2.8	30.5
342	96.1	49.8	5.4	5.0	3.6	36.8
			A = TB			
295	20.6	78.2	2.0	2.8	2.0	14.5
312	43.8	73.1	3.1	2.4	2.3	17.0
327	81.5	60.8	7.3	4.8	3.2	23.4
344	90.6	53.1	7.0	5.6	4.0	28.5

g h mol^{-1}. It was found that even a small admixture of tungsten markedly decreases the catalyst activity which further decreases with increasing tungsten content (Fig. 2). The selectivity for 2-methylpropenal has a similar course, although its decrease at the lowest admixture of W is not as distinct as the decrease in conversion. The selectivity for CO_2 increases with increasing W content to a maximum (the S1K3 catalyst) and then decreases. Hence, tungsten markedly reduces the number of active points for partial oxidation of IB and – at the amount exceeding 10.4 mole % (related to metals) – also the number of active points for total oxidation of IB.

The influence of phosphorus is similar. Again, its small admixture (the catalyst S1K5) already markedly reduces the activity of the S1 catalyst, but the further decrease with increasing phosphorus content is insignificant. Generally, phosphorus increases the number of acidic centres at the catalyst surface but it seems that at these centres there takes place the total oxidation of either IB or the 2-methylpropenal formed or both of them. This is indicated by the continuous increase in selectivity for CO_2 (Fig. 3). To sum up, it can be stated that the effects of P and W upon the activity and selectivity of S1 catalyst are negative in the partial oxidation of IB to 2-methylpropenal.

Furthermore, the oxidation of IB was studied with the S2 catalyst (specific surface area 6.1 m g^{-1}) which has a lower Fe content and a higher Bi content than those in S1. The effect of tellurium upon the properties of this catalyst was studied with the catalysts having the molar ratios of metals Mo : Co : Ni : Bi : Fe : K : Te = 7 : 3 : 1 : 2.2 : 0.2 : 0.08 : a, where a = 0.1, 0.2, 0.3, 0.4, and 0.5 for the catalysts S2C1 – S2C5 with the specific surface area values of 4.1, 3.5, 4.2, 4.1, and 3.0 $m^2 g^{-1}$, respectively. The effect of zinc upon the properties of the S2 catalyst in the oxidation of IB was studied with the catalysts of the metals molar ratios Mo : Co : Ni : Bi : Fe : K : Zn = 7 : 3 : 1 : 2.2 : 0.2 : 0.08 : b, where b = 0.5, 1.0, and 2.0 for the catalysts S2C6 – S2C8 with the specific surface area values of 8.4, 4.6, and 7.5 $m^2 g^{-1}$, respectively. The lowering of Fe

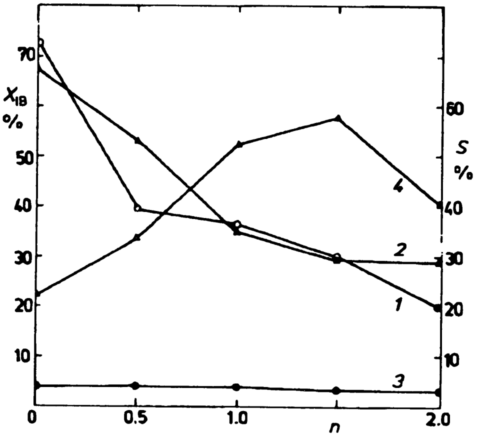

FIG. 2

Dependence of conversion of isobutene X_{IB} (*1*) and selectivities for 2-methylpropenal S_{MA} (*2*), 2-methylpropenoic acid S_{MAA} (*3*) and carbon dioxide S_{CO_2} (*4*) on molar proportion of tungsten, n, in catalysts S1K1 – S1K4; W/F_{IB} = 342 g h mol^{-1}, t = 320 °C content was accompanied by the catalyst activity decrease, hence the measurements were carried out at the temperature of 340 °C and the time factor W/F_{IB} = 359 g h mol^{-1}. In comparison with S1, the S2 catalyst is substantially less active and less selective for CO_2 (Tables I and II). The increasing Te content markedly reduces the catalyst activity. The selectivity for MA goes through an indistinct minimum at the Te content about 3 mole % (referred to metals, the S2C4 catalyst), whereafter it again increases. Weng et al.[15] found that in a mechanic mixture of MoO_3 and TeO_2 the latter oxide behaves as an oxygen donor in the oxidation of IB and ensures regeneration of deactivated surface centres whereby the properties of the MoO_3–TeO_2 catalyst are improved. In the

TABLE II

Effect of Te and Zn admixtures upon activity and selectivity of S2 catalyst in oxidation of IB (%). Time factor W/F_{IB} = 359 g h mol^{-1}, reaction temperature 340 °C

Catalyst	X_{IB}	S_{MA}	S_{AC}	S_{CO_2}	S_{ac} [a]
S2	54.8	65.0	2.5	16.0	9.6
S2C1	54.9	69.5	4.2	10.3	9.7
S2C2	51.5	68.2	4.2	15.3	2.4
S2C3	47.6	59.5	9.9	17.8	9.6
S2C4	41.6	57.9	14.4	14.2	6.1
S2C5	22.5	69.5	14.3	11.0	3.3
S2C6	85.6	74.2	5.2	7.2	9.6
S2C7	73.6	86.2	2.9	7.1	3.8
S2C8	59.0	78.6	1.8	12.8	3.4

[a] S_{ac} Selectivity for sum of acetic and 2-methylpropenoic acids.

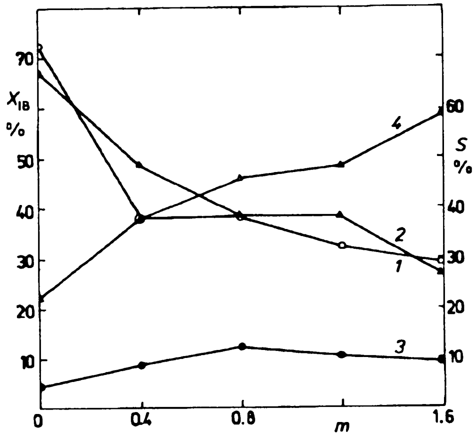

FIG. 3

Dependence of conversion of isobutene X_{IB} (*1*) and selectivities for 2-methylpropenal S_{MA} (*2*), acetone S_{AC} (*3*), and carbon dioxide S_{CO_2} (*4*) on molar proportion of phosphorus, *m*, in catalysts S1K5 – S1K8; W/F_{IB} = 342 g h mol^{-1}, *t* = 320 °C example given, where the form of Te present in the catalyst was not determined, it can be presumed that it creates or regenerates the surface centres causing a partial destruction of carbon chain of IB, which is indicated by the marked increase in selectivity for acetone. Beside that, the catalysts containing tellurium produce small amounts of ethyl and vinyl acetates along with the products given in Table II. As little as 3.6 mole % added zinc (referred to the metals content, the S2C6 catalyst) distinctly increases the activity of S2 catalyst which, however, decreases with further increasing the Zn content (Table II). It can be anticipated that Zn will increase the number of basic centres at the catalyst surface and, hence, improve the desorption of the MA formed, which also has basic character and, hence, low affinity to these centres. If the Zn content reaches 12.9 mole % (referred to the metals content, the S2C8 catalyst), the selectivity for CO_2 is increased, which is obviously due to the subsequent oxidation of MA to CO_2 also indicated by the unchanged yield of acids. The best result was obtained with the catalyst S2C7 containing 6.9 mole % Zn (referred to metals): 73% conversion of IB with 86% selectivity for MA. This catalyst was experimentally studied from the standpoint of the dependence of selectivities for MA and CO_2 upon the conversion of IB, the increase in conversion of IB being achieved either by increasing the time factor in the interval of 108 – 543 g h mol^{-1} at a temperature of 340 °C or by increasing the reaction temperature in the interval of 320 – 360 °C at a constant time factor W/F_{IB} = 359 g h mol^{-1}. The data of Table III show that the temperature increase by 40 °C will cause an only small selectivity decrease for MA and an about 4% selectivity increase for CO_2, which, how-

TABLE III
Effect of reaction temperature and time factor W/F_{IB} upon activity and selectivity of S2C7 catalyst in oxidation of IB (%)

Parameter	X_{IB}	S_{MA}	S_{AC}	S_{CO_2}	S_{ac}
Reaction temperature[a], °C					
320	21.0	86.7	1.8	5.6	4.6
340	73.6	86.2	2.9	7.1	3.8
360	89.9	80.6	2.7	9.3	7.3
W/F_{IB}[b], g h mol^{-1}					
108.5	28.6	85.2	2.1	5.2	1.4
217.1	50.0	86.8	2.7	7.2	3.3
305.6	60.5	86.5	3.3	7.7	3.9
359.0	73.6	86.2	2.9	7.1	3.8
542.7	85.9	82.9	2.9	9.4	3.8

[a] Time factor W/F_{IB} = 359 g h mol^{-1}; [b] reaction temperature 340 °C.

ever, can be due to free radical total oxidation of MA in gas phase at 360 °C. Similarly, a ca threefold increase in conversion of IB due to the increased time factor is not accompanied – with the S2C7 catalyst – by any distinct drop in selectivity for MA, the selectivity for CO_2 being increased by only 4% again. From among the admixtures investigated, only zinc improved the properties of the polycomponent catalysts in the oxidation of IB. At present it seems improbable that the classic acetone cyanohydrin route for production of methyl 2-methylpropenoate (methyl methacrylate, MMAC) could successfully be replaced by the two-step catalytic oxidation IB – 2-methylpropenal – 2-methylpropenoic acid and subsequent esterification of the acid to MMAC. The price of 1 kg MMAC prepared by the Sumitomo–Nippon–Shokubai procedure of oxidation of IB is 1.76 USD while that in Europe and U.S.A. (of the product manufactured via acetone cyanohydrin[16]) is 1.17 – 1.48 USD.

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Translated by J. Panchartek.