IMPROVEMENT OF PROPERTIES OF CATALYST FOR INDUSTRIAL PRODUCTION OF ACROLEIN FROM PROPYLENE

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The catalytic gas-phase oxidation of propylene on a multicomponent Mo–Co–Fe–Bi–K–O catalyst gives up to 85% yield of acrolein and acrylic acid along with undesirable side products – formaldehyde and acetaldehyde. Effects of four factors have now been studied with the aim of suppressing of formation of the by-products viz. the effect of potassium content in the catalyst, that of final annealing temperature of the catalyst, and those of addition of other components (tungsten, nickel). It has been found that a change in potassium content in catalyst affects distinctly its activity and also selectivity for products of total oxidation of propylene but does not practically affect the yields of formaldehyde and acetaldehyde. The yields of the said side products decreased with increasing annealing temperature, however, with concomitant considerable decrease in the catalyst activity. Whereas a partial substitution of molybdenum atoms in the catalyst by tungsten atoms is accompanied by an increase in production of formaldehyde and acetaldehyde, some catalysts with nickel gave acrolein as the only aldehyde.

At present acrolein is produced on industrial scale almost exclusively by gas-phase catalytic oxidation of propylene on multicomponent catalysts. The modern oxide catalysts are usually based on Mo–Bi (Sohio catalyst) which in 1959 was found to produce acrolein in a higher yield than the copper catalyst used up to that time[1]. Beside the mentioned Mo–Bi system the multicomponent catalysts[1,2] often contain also Co, Fe, W, P, Tl, Sb, Sn, Li, K etc. forming thus complex systems both chemically and structurally. The above-mentioned catalysts work at the temperatures of 300 – 400 °C, when the yield of acrolein reaches up to 85% with 5 – 8% propylene content in the reaction mixture. The by-products involve acrylic and acetic acids beside (in most cases) formaldehyde, acetaldehyde, acetone, allyl alcohol, CO_2, and CO. The service life of these catalysts in industrial reactors reaches 2 – 5 years[3].

In the present paper we have focused our attention on improving the properties of the Mo–Bi–Co–Fe–K–O catalyst[4] which at the temperatures of 310 – 340 °C allowed an up to 95% conversion of propylene with 75% yield of acrolein and 15% yield of acrylic acid; the yields of formaldehyde, acetaldehyde, and acetone reached up to 3% depending upon the way of controlling the oxidation. As, in most cases, acrolein together with the other products of propylene oxidation is immediately introduced into another reactor where it is oxidized to acrylic acid (on a different catalyst and at different conditions), formaldehyde–acetaldehyde–acetone by-products represent an undesirable admixture lowering the yields of acrylic acid. Therefore, such a composition of catalyst was looked for as to remove this drawback and to produce acrolein as the only aldehyde.

EXPERIMENTAL

Catalysts

The investigated oxide catalysts based on Mo–Co–Fe–Bi–X–K–O where X represents W or Ni were prepared from the solutions of ammonium heptamolybdate, nitrates of the respective metals, KOH, and tartaric acid.

Tungsten was added in the form of 5 $[(NH_4)_2O] . 12 WO_3 . 4 H_2O$. A detailed procedure of preparation of the catalysts is given elsewhere[4,5]. The application of tartaric acid ensures the final mixture of all the components to be in the form of a solution, which in turn ensures the homogeneity and reproducibility of the catalysts prepared. The pH value of the final solutions was adjusted at 6 – 7 by adding aqueous ammonia, whereafter the solutions were evaporated with continuous stirring at 90 °C to give a microcrystalline paste which was dried at 120 °C 12 h, annealed at 160 and 180 °C 3 h, at 360 °C 5 h, and at 420 °C 24 h (and at 460 and 500 °C for another 24 h in the case of the catalysts C1(460) and C1(500), respectively). The samples obtained were ground and sieved to give the fraction of 0.40 – 0.63 mm grain size.

Apparatus

The activity and selectivity of the catalysts produced were investigated with the help of a through-flow apparatus with integral reactor with solid bed. The reactor was heated by means of an electric oven with two coilings out of which one was controlled by an automatic controller Radelkis, which made it possible to maintain the chosen temperature in catalyst bed with the accuracy of ±2 °C. The reactor had a diameter of 2.5 cm and contained a coaxial tube for a thermocouple. The flow rates of gases (propylene, O_2, N_2) were measured by means of capillary flow meters, the water vapour was dosed into the reaction mixture from a saturator thermostated at a calculated temperature. The composition of reaction mixture: C_3H_6 5, O_2 12, H_2O 35, N_2 48 vol.%. The whole feed of reaction mixture $F = 5\ dm^3\ h^{-1}$ ($p = 1.013 . 10^5$ Pa, $T = 273.13$ K), weight of catalyst 1 – 5 g. The catalyst was always diluted with SiC of the same grain size at a volume ratio of 1 : 1, hence the bed height in the reactor was always greater than 1 cm. It was proved that at this set of conditions the effects of inner and outer diffusion can be neglected. At the end of the through-flow apparatus there was a water absorber where the liquid products of oxidation (carbonyl compounds and acids) were absorbed.

Analysis of Reaction Products

The conversion of propylene (the measure of catalyst activity), selectivity, and yields of the individual oxidation products (for their definition see ref.[6]) were calculated from analyses carried out on a GC Chrom 5 apparatus with thermal-conductivity (TCD) or flame-ionization (FID) detectors attached to the through-flow apparatus. A system of three six-way cocks (Perkin–Elmer) was adopted to provide the dosing of reaction mixture into the gas chromatograph before and after passing the catalyst bed of reactor. The columns of 2.5 and 1.2 m length and 3 mm i.d. were packed with Porapak Q for determinations of CO, CO_2, C_3H_6, acetone, and aldehydes, and with Chromosorb 101 for determinations of acids.

In addition, the overall yield of acids was checked by the titration of absorbate from the water absorber with an NaOH solution titrant and with the help of a pH meter. The qualitative composition of the carbonyl compounds formed was determined via the corresponding 2,4-dinitrophenylhydrazones using descending paper chromatography[7]; the overall yield was determined according to Smith and Mitchel[8]. The amount of the acrolein formed was also checked polarographically according to Moshier[9].

RESULTS AND DISCUSSION

For preparing the basic oxide catalyst C1 with the type designation $Mo_{12}Co_4Fe_1Bi_1K_{0.08}O_Z$ the amounts of the respective components were chosen in such a way as to obtain the molar ratios of the metals Mo : Co : Fe : Bi : K = 12 : 4 : 1 : 1 : 0.08 (the oxygen content in the catalysts was not determined). The study of propylene conversion and of yields of individual oxidation products in the temperature interval of 308 – 362 °C were carried out for various values of the time factor $W/F_{C_3H_6}$, and the results are presented in Table I. It can be seen that the summary yield of useful reaction products, i.e. acrolein and acrylic acid, is above 80% in most cases. However, in all the

TABLE I
Conversion of propylene and yields of some oxidation products (in %) on the basic catalyst C1

$W/F_{C_3H_6}$, g h mol^{-1}	Reaction temperature, °C	$X_{C_3H_6}$	Y_{AC}	Y_{AA}	Y_{ALD}
194	315	80.0	69.3	8.0	0.5
	325	83.2	71.6	9.2	1.3
	334	85.8	70.1	10.4	2.5
243	335	87.0	75.4	8.6	1.2
	345	89.1	76.0	9.9	1.7
	362	92.2	70.1	11.8	2.8
280	327	94.2	79.5	10.7	2.4
	340	96.0	75.1	10.6	2.9
320	318	89.5	77.4	9.7	0.8
	330	93.6	75.8	12.2	1.7
	336	95.5	72.6	12.3	1.6[a]
404	308	85.3	77.6	5.5	1.3
	318	94.0	76.6	11.0	1.7
	327	95.5	76.4	15.6	2.6
	340	96.8	74.2	16.3	3.0[a]

[a] Traces of acetone were formed too.

cases formaldehyde and acetaldehyde were also formed, sometimes with traces of acetone.

With the aim to suppress these undesirable reactions connected with partial destruction of carbon chain we studied the effects of four factors upon the oxidation course: the effect of potassium amount, that of the temperature of annealing of catalyst, and those of additions of other components (tungsten or nickel).

The effect of amount of potassium: For this purpose we prepared (in the above-mentioned way) five oxide catalysts of $Mo_{12}Co_4Fe_1Bi_1K_NO_Z$ type where N = 0, 0.04, 0.055, 0.07, and 0.12 for the catalysts C2, C3, C4, C5, and C6, respectively. Table II presents the results of tests of the given catalysts at the temperature of 320 °C and at the time factor value $W/F_{C_3H_6}$ = 171 g h mol^{-1}. The catalyst C2, which does not contain potassium, is highly active at the conditions given but, at the same time, also highly selective for the products of total oxidation. With increasing content of potassium and, hence, increasing number of basic centres at the catalyst surface both the catalyst activity and its selectivity for products of total oxidation decrease. The maximum selectivity for acrolein was reached with the C5 catalyst, of course, it decreased by 10% with increasing the time factor value to $W/F_{C_3H_6}$ = 314 g h mol^{-1}.

With the catalyst C1 the same change in the time factor caused almost no change in the selectivity for acrolein, and the selectivity for acrylic acid even increased. The catalyst with the highest potassium content (C6) shows a marked decrease in the conversion of propylene accompanied by a distinct decrease in selectivity for acrolein. In all the cases, however, a change in potassium content of the catalysts did not affect the formation of formaldehyde and acetaldehyde. Hence it is obvious that even slight

TABLE II
Effect of amount of potassium upon activity and selectivity (in %) of catalysts of $Mo_{12}Co_4Fe_1Bi_1K_NO_Z$ type (reaction temperature 320 °C, $W/F_{C_3H_6}$ = 171 g h mol^{-1}

Catalyst	N	$X_{C_3H_6}$	S_{AC}	S_{AA}	S_T	S_{ALD}
C2	0	95.6	70.3	10.5	18.8	1.5
C3	0.04	95.0	81.0	7.6	9.9	1.8
C4	0.055	91.5	78.3	9.8	9.1	2.1
C5	0.07	81.3	93.5	3.0	3.1	0.7
		94.0[a]	83.5	8.5	6.1	1.6
C1	0.08	65.6	91.5	3.9	2.6	0.5
		90.5[a]	90.1	5.8	3.0	1.4
C6	0.12	54.4	74.7	13.5[b]	2.8	3.6

[a] The measurements were repeated for $W/F_{C_3H_6}$= 314 g h mol^{-1}. [b] Acetic acid is formed together with acrylic acid.

changes in the potassium content in the catalysts affect distinctly the numbers of active centres at the catalyst surface which are responsible primarily for the total oxidation of propylene but do not affect the active centres causing the partial destruction of carbon chain in propylene or acrolein.

The effect of the final temperature of annealing: For these experiments we selected the basic oxide catalyst C1 of $Mo_{12}Co_4Fe_1Bi_1K_{0.08}O_Z$ type which gave 90% selectivity for acrolein at 90% conversion of propylene (Table II). A part of the catalyst mentioned was annealed at 460 °C for 24 h and another part at 500 °C for 24 h to give the samples denoted as C1(460) and C1(500), respectively. These catalysts were tested at the temperatures of 320 and 335 °C and at the time factor value $W/F_{C_3H_6}$ = 314 g h mol^{-1}. As expected, the increased temperature of annealing resulted in decreased activity of catalyst (Table III). The catalyst C1(500) produces acrolein as the only aldehyde (without even traces of formaldehyde and acetaldehyde), of course, with distinct drop in activity. Hence, it can be presumed that formaldehyde and acetaldehyde are probably formed only from acrolein by a consecutive reaction. The effect of final temperature of annealing upon the phase composition of the catalyst C1 was studied with the help of a JEOL JDX-85 diffractograph at the following conditions: CuKα radiation, LiF monochromator. All the three catalysts contain MoO_3, which is indicated by the presence of the diffraction peaks[10] with the values of interplane distances d_{hkl} = 3.82, 3.46, 2.66, and 2.31 10^{-10} m, and furthermore $Bi_2O_3 . 3 MoO_3$ (α-phase) with the values[11] d_{hkl} = 6.96, 3.19, 3.06, and 2.86 . 10^{-10} m. Again, intensive diffraction peaks with the values d_{hkl} = 3.80, 3.38, 3.26, and 2.66 . 10^{-10} m were detected in all the three catalysts, which indicates the presence of α-phase $CoMoO_4$ (ref.[12]). The diffraction peaks of the values d_{hkl} = 3.26, 3.19, and 3.07 . 10^{-10} m can also be due to the β-phase of the Bi–Mo system[13] (i.e. $Bi_2O_3 . 2 MoO_3$). The presence of this phase in the catalysts also seems to be confirmed by a fairly marked diffraction peak[13] with the value d_{hkl} = 4.91 . 10^{-10} m.

TABLE III
Effect of final annealing temperature upon activity and selectivity (in %) of basic catalyst of $Mo_{12}Co_4Fe_1Bi_1K_{0.08}O_Z$ type (time factor $W/F_{C_3H_6}$ = 314 g h mol^{-1})

Catalyst	Reaction temperature, °C	$X_{C_3H_6}$	S_{AC}	S_{AA}	S_T	S_{ALD}
C1	320	90.5	90.1	5.8	3.0	1.4
	335	94.2	76.6	9.6	8.0	3.0
C1(460)	320	79.2	91.0	5.1	2.5	1.1
	335	81.4	91.6	6.0	2.8	0.2
C1(500)	320	22.0	96.5	3.8	–	–
	335	30.4	95.5	4.1	–	–

Interestingly, no diffraction peak due to Mo–Fe system could be observed. After precipitation of ammonium heptamolybdate with $Fe(NO_3)_3$ and subsequent annealing, three different Mo–Fe forms are formed[14,15]: mixed $Fe_2(MoO_4)_3 \, . \, MoO_3$, β-phase of $FeMoO_4$, and $Fe_2(MoO_4)_3$. The presence of any given crystalline form of iron molybdate should make itself felt by a more distinct diffraction peak of the value d_{hkl} = $3.87 \, . \, 10^{-10}$ m. However, this peak was detected in none of the catalysts. Although the catalysts C1, C1(460), and particularly C1(500) markedly differ in their activities in catalytic oxidation of propylene, the X-ray diffraction analysis gave practically identical results for the three samples.

The effect of tungsten: Two catalysts were prepared for investigating the tungsten effect, molybdenum being partially replaced by tungsten. The amounts of individual components were chosen in such a way that the catalysts prepared corresponded to the types $Mo_9W_3Co_4Fe_1Bi_1K_{0.08}O_Z$ (denoted as C7) and $Mo_{10}W_2Co_4Fe_1Bi_1K_{0.08}O_Z$ (referred to as C8). Again the final temperature of annealing was 420 °C. The tests of catalytic activity and selectivity of these two catalysts were carried out at the value of time factor $W/F_{C_3H_6}$ = 267 g h mol^{-1}, and the results are presented in Table IV. The partial replacement of molybdenum atoms by tungsten resulted in a decreased propylene conversion (as compared with C1), abrupt decrease in acrolein yield, and also distinct increase in the yields of formaldehyde and acetaldehyde. Hence it is obvious that introduction of tungsten atoms into the catalyst results in formation of active centres causing partial destruction of propylene or acrolein to formaldehyde and acetaldehyde, i.e. the effects of tungsten upon the properties of the Mo–Co–Fe–Bi–K–O catalyst are quite obviously negative.

The effect of nickel: Four catalysts were prepared for testing the effect of nickel differing from C1 by gradual replacement of cobalt atoms by nickel. The amounts of starting components were chosen in such way that the catalysts prepared corresponded to the types: $Mo_{12}Co_3Ni_1Fe_1Bi_1K_{0.08}O_Z$ (referred to as C9), $Mo_{12}Co_2Ni_2Fe_1Bi_1K_{0.08}O_Z$ (C10), $Mo_{12}Co_1Ni_3Fe_1Bi_1K_{0.08}O_Z$ (C11), and $Mo_{12}Ni_4Fe_1Bi_1K_{0.08}O_Z$ (C12). Moreover,

TABLE IV

Effect of introduction of tungsten upon properties of Mo–Co–Fe–Bi–K–O catalyst (time factor $W/F_{C_3H_6}$ = 267 g h mol^{-1}, conversion and yields in %)

Catalyst	Reaction temperature, °C	$X_{C_3H_6}$	Y_{AC}	Y_{AA}	Y_{ALD}
C7	321	71.5	48.2	12.0	5.3
	337	82.3	49.1	14.6	8.3
C8	324	69.8	43.2	10.1	7.7
	335	71.0	44.8	12.3	8.8
	347	73.5	41.4	14.2	10.2

two catalysts were prepared in which nickel was used as additional component of the catalyst C1: $Mo_{12}Co_4Ni_2Fe_1Bi_1K_{0.08}O_Z$ (C13) and $Mo_{12}Co_4Ni_1Fe_1Bi_1K_{0.08}O_Z$ (C14). From data in Table V it follows that the presence of nickel in catalyst increases abruptly its activity in the catalytic oxidation of propylene, whether nickel is used instead of cobalt (C9 – C12) or in addition to it (C13 and C14). It was possible to attain 90%

TABLE V
Effect of introduction of nickel on properties of Mo–Co–Fe–Bi–K–O catalyst (conversion and yields in %)

Catalyst	$W/F_{C_3H_6}$ g h mol^{-1}	Reaction temperature, °C	$X_{C_3H_6}$	Y_{AC}	Y_{AA}	Y_T	Y_{ALD}
C9	179	340	95.0	80.1	10.2	4.6	–
		355	96.2	76.3	14.2	5.8	–
	202	305	86.3	78.5	6.6	1.2	–
		325	92.7	77.0	9.2	4.8	–
		340	94.0	77.1	11.0	5.7	–
		350	95.1	75.0	13.1	7.2	–
	269	265	90.2	80.3	6.7	3.2	–
		275	96.0	77.5	10.0	8.4	–
C10	179	275	84.7	75.8	5.4	3.8	–
		300	94.1	76.9	9.3	7.8	–
		320	96.3	76.0	12.0	8.5	–
C11	269	250	80.2	70.3	4.4	5.0	–
		265	94.0	74.5	9.1	10.0	0.3
C12[a]	269	250	62.8	52.3	3.7	7.2	–
		281	72.6	60.9	5.5	6.9	0.5
		295	92.0	65.8	14.7	10.6	0.8
C13	269	265	77.0	66.2	3.3	6.8	–
		280	87.4	68.9	5.0	11.9	0.2
		301	90.2	70.8	8.9	12.0	0.2
C14	179	305	82.2	75.4	4.5	2.1	–
		325	92.1	82.6	6.8	3.0	–
	269	255	53.7	46.8	4.0	3.7	–
		265	75.0	65.4	4.8	4.9	–
		281	92.1	73.6	8.0	8.8	0.1
		290	93.2	76.6	9.5	8.0	0.1
		301	95.0	73.4	8.8	12.7	0.6

[a] In the catalyst C12 all cobalt atoms are replaced by nickel.

conversion of propylene at the value of time factor $W/F_{C_3H_6}$ = 269 g h mol^{-1} and at the temperatures below 300 °C. The best results were achieved with the catalyst C9. This catalyst is sufficiently stable in a relatively wide temperature interval (265 – 355 °C) which is indicated by the selectivity for the valuable oxidation products (acrolein and acrylic acid) reaching 96.6% at 265 °C and at 90% conversion of propylene, and 94% at 355 °C and at 96% conversion of propylene. The most important experimental result, however, consists in the finding that the catalysts C9 and C10 only produce acrolein and no other aldehydes (not even traces of CH_2O and CH_3CHO).

The service life of catalyst C9 was tested in a long interval in one tube of an industrial reactor for two-step production of acrylic acid (Mitsubishi Chemical Company) using the following set of conditions: The tube diameter 27 mm, tube length 5 m, reaction temperature 300 – 340 °C, composition of reaction mixture: C_3H_6 – 8, O_2 – 14, H_2O – 25.5, N_2 – 52.5 vol.%, total feed of reaction mixture F = 870 dm^3 h^{-1}. The catalyst in the form of pellets of 4 mm diameter and height was diluted with inert particles. The composition of reaction mixture and the temperature somewhat varied according to actual situation in the reactor. The experiment was performed in such a way that the analysis of reaction components was carried out at the outlet of the tube in the second reactor (oxidation of acrolein to acrylic acid). From data of Table VI it is

TABLE VI
Long-term tests of C9 catalyst in a tube of industrial reactor

Time of working load of catalyst, h	$X_{C_3H_6}$, %	Nonreacted acrolein, %	Y_{AA}, %
500	99.5	0.2	83.5
1 000	99.5	0.3	83.0
1 500	100.0	1.8	82.0
2 000	99.2	0.5	87.0
3 000	99.4	0.2	86.0
3 500	99.0	0.5	85.0
4 000	99.1	1.5	85.0
4 500	99.0	3.0	82.5
5 000	99.0	2.4	83.5
5 500	99.2	1.5	84.2
6 000[a]	98.2	8.4	80.0
6 500	99.0	1.6	83.9

[a] When the technology was put out of action, the catalyst of the second step was reactivated with air 23 h.

obvious that even after 6 500 h working load in an industrial reactor, the catalyst C9 retains its excellent parameters. The yield of acrylic acid lower by ca 1% than that guaranteed by the Japanese producer (84.6%) is most likely due to the somewhat lower selectivity of the catalyst of the second step (oxidation of acrolein to acrylic acid).

SYMBOLS

d_{hkl}	interplane distance, m
F	total feed of reaction mixture, dm^3 h^{-1} (p = 1.013 . 10^5 Pa, T = 273.13 K)
$W/F_{C_3H_6}$	time factor, g h mol^{-1}, where W is catalyst weight, g, and $F_{C_3H_6}$ is propylene feed, mol h^{-1}
S_i	selectivity for the i-th product, %
$X_{C_3H_6}$	conversion of propylene, %
Y_i	yield of the i-th product, %
Abbreviations	
AA	acrylic acid
AC	acrolein
ALD	formaldehyde plus acetaldehyde
T	products of total oxidation (CO_2 and CO)

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