

# Catalysts for Oxidative Dehydrogenation of Isobutyric Acid

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The catalytic oxidative dehydrogenation of isobutyric acid has been studied with an Mo—V—P oxide catalyst coated on Aerosil. The oxidation main products involve methacrylic acid, acetone, propylene, and CO<sub>2</sub>. Lowering of the oxidation state of vanadium in the catalyst to V<sup>IV</sup> is connected with a distinct decrease in the catalyst activity and its selectivity for methacrylic acid. Increasing phosphorous content in the catalyst causes a mild increase in its activity along with an increased yield of methacrylic acid. A modification of the said catalyst with cobalt results in its activity decrease and lowers the yield of methacrylic acid. By means of IR spectroscopy it has been found that isobutyric and methacrylic acids are adsorbed on the surface of the catalysts studied already at room temperature, which is connected with formation of the corresponding carboxylates.

Methacrylic acid (MAA) is an important intermediate in the production of methacrylic esters and a number of important polymers. The world consumption of methyl methacrylate reached  $1.4 \times 10^6$  t in 1988 with anticipated increase of 6 % per year. Although most MAA (about 90 %) is still being produced by the classical acetone cyanohydrin route, intensive research has been directed in the last decade to finding other alternatives of its production [1, 2]. This fact has its reason in the problems connected with the ammonium sulfate effluents and in ecological restrictions to the transport of HCN. One of the new possibilities consists in production of MAA by the method of oxidative dehydrogenation of isobutyric acid (IBA) in gas phase on a suitable catalyst. It was found that the most promising catalysts are heteropolyacids of the type H<sub>3</sub>P<sub>1</sub>Mo<sub>12</sub>O<sub>40</sub> and H<sub>4</sub>P<sub>1</sub>V<sub>1</sub>Mo<sub>11</sub>O<sub>40</sub> and their salts. The yield of MAA on the said catalysts reaches up to 70 % with total conversion of IBA. However, the catalysts mentioned have a serious drawback preventing their industrial application in that they are rapidly deactivated during the oxydehydrogenation of IBA. This is mainly caused by the destruction of Keggin's structure and connected with formation of volatile molybdenum compounds [3—11].

The present paper is focused on a study of Mo—V—P oxide catalysts coated on Aerosil used in the oxidative dehydrogenation of IBA in gas phase, paying special attention to the effects of amount of water vapours in the reaction mixture, of vanadium oxidation state, of phosphorus amount in the catalyst, and of addition of another component (cobalt) to the oxide catalyst mentioned.

## EXPERIMENTAL

### Catalysts

The investigated Mo—V—P(Co) oxide catalysts coated on Aerosil (always 30 mass % of the catalyst) were prepared from solutions of (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, H<sub>3</sub>PO<sub>4</sub>, NH<sub>4</sub>VO<sub>3</sub>, and Co(NO<sub>3</sub>)<sub>2</sub>. The resulting solution with added Aerosil was evaporated with intensive stirring at 80 °C to give a microcrystalline paste which was dried at 120 °C for 6 h, at 180 °C for 6 h, and annealed at 370 °C for 9 h, and at 420 °C for 3 h. The product was crushed and the fraction of 0.315—0.5 mm grain size was separated by means of sieves. For IR spectral measurements the finely ground catalysts were pressed ( $p = 15$  MPa) to obtain thin plates of  $(10 \text{ to } 15) \times 10^{-3}$  g cm<sup>-2</sup> surface area density.

### Apparatus

The activity and selectivity of the catalysts prepared was studied in a through-flow apparatus with integral reactor with fixed bed. The reactor of 2.5 cm diameter was equipped with a thermocouple. The composition of the reaction mixture ( $\varphi$ /vol. %): isobutyric acid (IBA) 3.7, O<sub>2</sub> 10.1, H<sub>2</sub>O 0, 20.3, and 40.6, the rest was N<sub>2</sub>. The total feed of reaction mixture was  $F(\text{STP}) = 4.93$  dm<sup>3</sup> h<sup>-1</sup>. The gases (oxygen and nitrogen) were dosed by means of capillary flow meters, IBA and water vapour were added into the reaction mixture from saturators kept at a calculated temperature. The catalyst was always diluted in the mass ratio of 1:1 with SiC of the same grain size, hence

the bed height in the reactor was always greater than 1 cm. At such conditions both outer and inner diffusions can be neglected. The liquid reaction products were condensed in a water absorber placed at the end of the through-flow apparatus.

The character of interactions between IBA, oxygen, MAA, and the surface of the catalysts prepared was investigated with the help of a two-beam Perkin—Elmer 684 IR spectrometer. The prepared catalyst plates with surface area density of  $(10 \text{ to } 15) \times 10^{-3} \text{ g cm}^{-2}$  exhibited a sufficient transmittance in the range of  $\tilde{\nu} = 1300 \text{ to } 2000 \text{ cm}^{-1}$  enabling both the adsorption and desorption measurements. Before each measurement the catalyst plate was heated in vacuum ( $p = 10^{-3} \text{ Pa}$ ) at  $320^\circ\text{C}$  for 1 h. The subsequent sorption of substances studied was carried out at room temperature at the pressure  $p = ca. 5 \times 10^3 \text{ Pa}$ . After measuring the IR spectrum, we studied their desorption in vacuum at temperatures continuously increasing from  $100^\circ\text{C}$  to  $250^\circ\text{C}$  (the spectra were measured after cooling the samples from the corresponding temperatures to room temperature). All the measurements were carried out in a glass cell with NaCl windows.

### Analysis of Reaction Products

The conversion of IBA and the yields of the main products of reaction – methacrylic acid (MAA), acetone (AC), propylene, and  $\text{CO}_2$  – were determined by means of GC Chrom 5 with TCD or FID 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 its passing through the reactor. The columns of 2.5 m length and 3 mm inner diameter were packed with Porapak Q for determination of  $\text{CO}_2$ , AC, and  $\text{C}_3\text{H}_6$  and with Chromosorb 101 for determination of  $\text{C}_3\text{H}_6$ , AC, IBA, and MAA. In addition to that, the total amount of acids in the reaction mixture was verified by titration of the absorbate from the water absorber using NaOH standard solution and a pH-meter. The relative error of the determination of the conversion of IBA was  $\leq 3 \%$ ; the relative error of determination of the yields of the reaction products was *ca.* 1%. The conversion, selectivity, and yields of products were determined in the following way:

$$\begin{aligned} \text{conversion of IBA:} & X_{\text{IBA}} = (n_{\text{R}}/n_{\text{A}}) \cdot 100 \% \\ \text{selectivity for} & S_i = (1/\nu_i) \cdot (n_i/n_{\text{R}}) \cdot 100 \% \\ \text{the } i\text{-th product} & \\ \text{yield of} & Y_i = (1/\nu_i) \cdot (n_i/n_{\text{A}}) \cdot 100 \% \\ \text{the } i\text{-th product} & \end{aligned}$$

where  $n_{\text{A}}$  is the number of moles of IBA fed per hour,  $n_{\text{R}}$  the number of moles of IBA reacted per hour,  $n_i$  the number of moles of the *i*-th product formed per hour, and  $\nu_i$  the stoichiometric coefficient of the *i*-th product.

**Table 1.** Mole Ratio of Components in the Catalysts

Catalyst	Mole ratio of components						
	$n(\text{Mo})$	:	$n(\text{V})$	:	$n(\text{P})$	:	$n(\text{Co})$
C1	4.7	:	1	:	–	:	–
C2	5.0	:	1 <sup>a</sup>	:	0.5	:	–
C3	5.0	:	1	:	0.5	:	–
C4	5.0	:	1	:	0.2	:	–
C5	5.0	:	1	:	0.4	:	–
C6	5.0	:	1	:	0.6	:	–
C7	5.0	:	1	:	0.5	:	0.1
C8	5.0	:	1	:	0.5	:	0.2
C9	5.0	:	1	:	0.5	:	0.5

a) Vanadium in the oxidation state of  $\text{V}^{\text{IV}}$ .

## RESULTS AND DISCUSSION

All the experiments were carried out with freshly prepared catalysts. Aerosil was chosen for the catalyst support on the basis of the finding [8] that silica ( $\text{SiO}_2$ ) as a support increases the service life of catalysts of similar type (heteropolyacids). For preparations of the Mo—V—P—Co—O catalysts the masses of individual components were chosen in such a way as to obtain the catalyst type  $\text{Mo}_A\text{V}_B\text{P}_C\text{Co}_D\text{O}_N$  with the mole ratios of elements  $n(\text{Mo}):n(\text{V}):n(\text{P}):n(\text{Co}) = A:B:C:D$ . The oxygen content in the catalysts was not determined. The mole ratios of the elements in the individual catalysts are given in Table 1.

We studied the effects of four parameters on the course of oxidative dehydrogenation of IBA in gas phase:

1. The effect of water vapour amount in the reaction mixture: This effect was studied using the catalysts C1 ( $\text{Mo}_{4.7}\text{V}_1\text{O}_N$ ) and C2 ( $\text{Mo}_5\text{V}_1\text{P}_{0.5}\text{O}_N$ ) in the temperature interval from  $253^\circ\text{C}$  to  $359^\circ\text{C}$  with the time factor  $m/F_{\text{IBA}} = 61.3 \text{ g h mol}^{-1}$  (where  $m$  and  $F_{\text{IBA}}$  are the catalyst mass in g and the IBA feed in  $\text{mol h}^{-1}$ , respectively). The water vapour content in the reaction mixture was 0 vol. %, 20.3 vol. %, and 40.6 vol. %. The results obtained are given in Figs. 1 and 2. With the catalyst without phosphorus, the conversion of IBA distinctly increases with increasing water content, which is obviously caused by water substantially accelerating the desorption of the chemisorbed components (especially MAA and IBA) from the catalyst surface [12, 13]. The MAA yields also increase with increasing water content, especially in the temperature interval from  $253^\circ\text{C}$  to  $280^\circ\text{C}$ . On the other hand, activity of the catalyst C2 (which contains phosphorus and, hence, also a higher number of acidic active centres on its surface) decreases with increasing water content. *Ernst et al.* [4] proved that the presence of water on catalysts of similar type decreases the number of free active centres due to strong absorption of water at such centres.

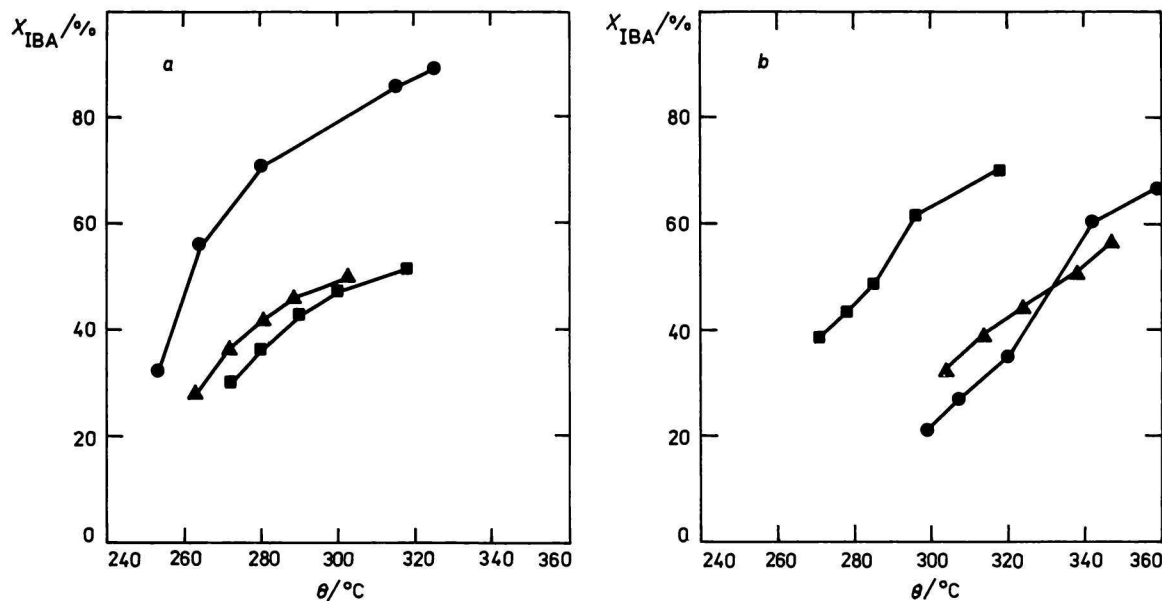


Fig. 1. Dependence of conversion of isobutyric acid,  $X_{IBA}$ , upon reaction temperature,  $\theta(m/F_{IBA} = 61.3 \text{ g h mol}^{-1})$ . a) For catalyst C1; b) for catalyst C2. Water content ( $\varphi(H_2O)/\text{vol. \%}$ ): ■ 0, ▲ 20.3, ● 40.6.

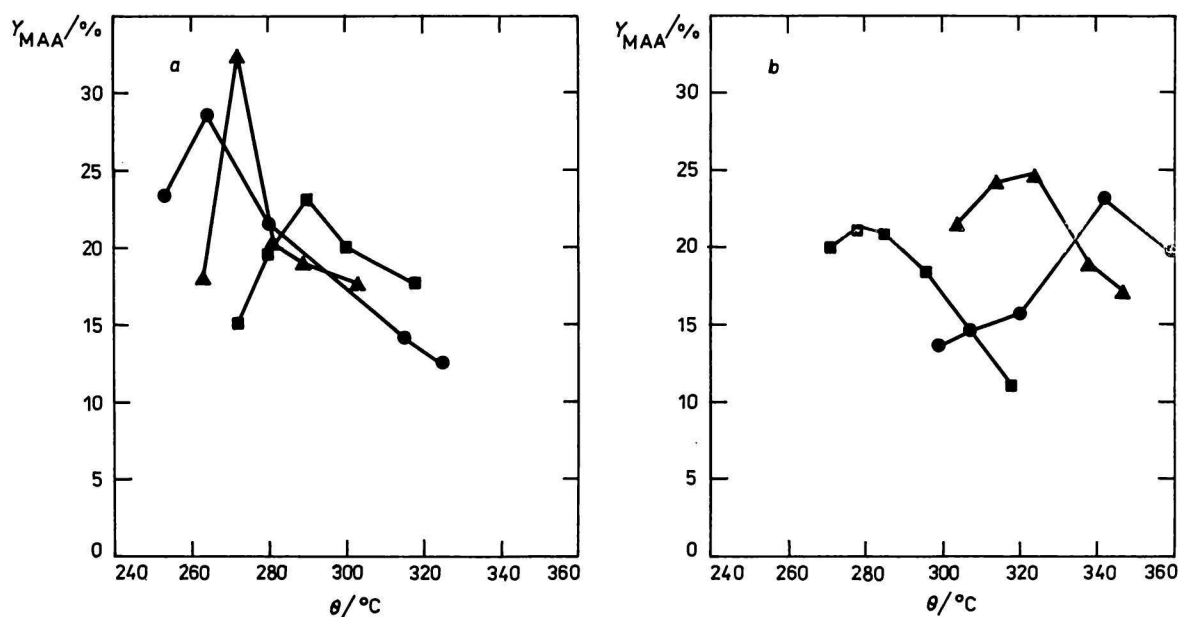


Fig. 2. Dependence of yield of methacrylic acid,  $Y_{MAA}$ , upon reaction temperature,  $\theta(m/F_{IBA} = 61.3 \text{ g h mol}^{-1})$ . a) For catalyst C1; b) for catalyst C2. Water content ( $\varphi(H_2O)/\text{vol. \%}$ ): ■ 0, ▲ 20.3, ● 40.6.

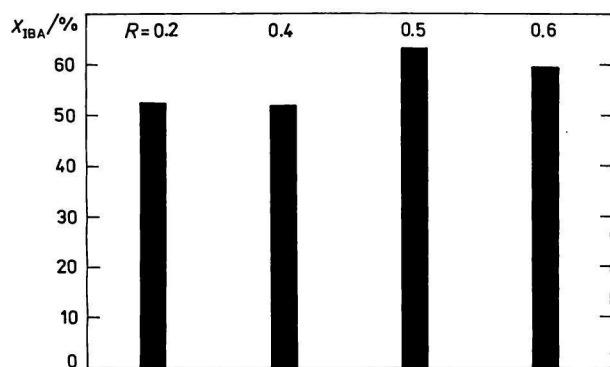
2. The effect of vanadium oxidation state: For this purpose we prepared catalysts C2 ( $\text{Mo}_5\text{V}^{\text{IV}}_1\text{P}_{0.5}\text{O}_N$ ) and C3 ( $\text{Mo}_5\text{V}^{\text{V}}_1\text{P}_{0.5}\text{O}_N$ ) with the same composition, but with the use of ethylenediamine as the reducing agent for the preparation of C2 catalyst, which ensures the presence of vanadium at the oxidation state of  $\text{V}^{\text{IV}}$  [14]. Table 2 presents the values of conversion of IBA ( $X_{IBA}$ ), selectivities ( $S_i$ ), and yields ( $Y_i$ ) of the individual reaction products at the temperature of 304 °C, time factor  $m/F_{IBA} = 61.3 \text{ g h mol}^{-1}$ , and 20.3 %

content of water vapour in the reaction mixture. The change in oxidation state from  $\text{V}^{\text{IV}}$  to  $\text{V}^{\text{V}}$  results in a large activity increase of the catalyst along with the increase in the selectivity for MAA. The selectivity for acetone remained practically unchanged, whereas that for  $\text{C}_3\text{H}_6$  decreased.

3. The effect of phosphorus content in the catalyst: This effect was studied using the catalyst type  $\text{Mo}_5\text{V}_1\text{P}_R\text{O}_N$ , where  $R = 0.2, 0.4, 0.5$ , and  $0.6$  for the catalysts C4, C5, C3, and C6, respectively. All these

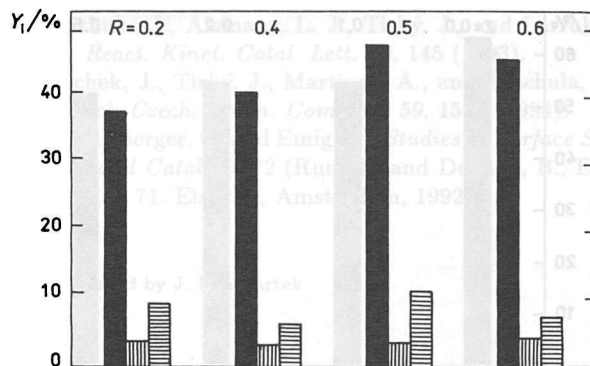
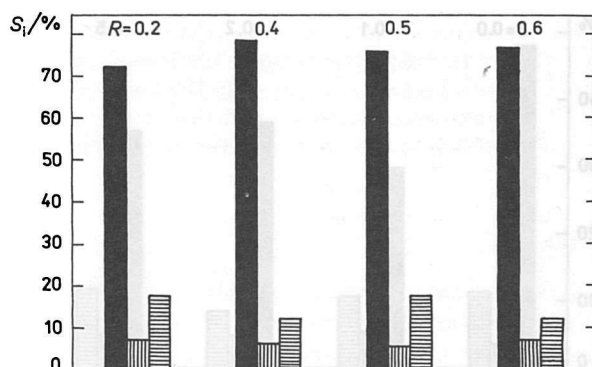
**Table 2.** Comparison of Conversion of IBA ( $X_{\text{IBA}}$ ), Selectivity ( $S_i$ ), and Yield ( $Y_i$ ) of the  $i$ -th Product on the Catalysts C2 and C3

Parameter	Catalyst	
	C2	C3
$X_{\text{IBA}}/\%$	32.8	68.6
$Y_{\text{MAA}}/\%$	21.5	50.6
$Y_{\text{propylene}}/\%$	3.3	4.1
$Y_{\text{AC}}/\%$	5.3	12.2
$S_{\text{MAA}}/\%$	65.5	73.8
$S_{\text{propylene}}/\%$	10.1	5.9
$S_{\text{AC}}/\%$	16.1	17.8


**Fig. 3.** Dependence of conversion of isobutyric acid,  $X_{\text{IBA}}$ , upon phosphorus amount in catalyst,  $R$  ( $\text{Mo}_5\text{V}_1\text{P}_R\text{O}_N$ ) (reaction temperature  $298^\circ\text{C}$ ;  $m/F_{\text{IBA}} = 61.3 \text{ g h mol}^{-1}$ ).

catalysts contained vanadium at the  $\text{V}^{\text{V}}$  oxidation state. The experiments were carried out at the reaction temperature of  $298^\circ\text{C}$ , time factor  $m/F_{\text{IBA}} = 61.3 \text{ g h mol}^{-1}$ , and the water vapour content 20.3 vol. % in the reaction mixture. The results obtained are given in Figs. 3–5. With increasing content of phosphorus in the catalyst and, hence, increasing number of acidic centres on the catalyst surface the yield of MAA increases, too, and on the catalyst with  $\text{Mo}_5\text{V}_1\text{P}_{0.5}\text{O}_N$  composition (C3) it reaches the maximum. The selectivity for MAA reaches 76 % and is almost the same for the catalysts C3, C5, and C6. The yield of propylene (product of partial destruction of the carbon chain) is not affected by increasing number of phosphorus atoms in the catalyst.

4. The effect of addition of cobalt: For the investigation of this effect we prepared the catalyst type  $\text{Mo}_5\text{V}_1\text{P}_{0.5}\text{Co}_Z\text{O}_N$ , where  $Z = 0.1, 0.2, \text{ and } 0.5$  for the catalysts C7, C8, and C9, respectively. Cobalt was used as an additional component in an attempt at preventing the formation of volatile compounds of molybdenum. Long-term tests of a polycomponent catalyst with molybdenum and cobalt in an industrial reactor during catalytic oxidation of propylene


**Fig. 4.** Dependence of yields of reaction products,  $Y_i$ , upon phosphorus amount in catalyst,  $R$  (reaction temperature  $298^\circ\text{C}$ ;  $m/F_{\text{IBA}} = 61.3 \text{ g h mol}^{-1}$ ). ■ MAA, ▨  $\text{C}_3\text{H}_6$ , ▩ AC.

**Fig. 5.** Dependence of selectivities for reaction products,  $S_i$ , upon phosphorus amount in catalyst,  $R$  (reaction temperature  $298^\circ\text{C}$ ;  $m/F_{\text{IBA}} = 61.3 \text{ g h mol}^{-1}$ ). ■ MAA, ▨  $\text{C}_3\text{H}_6$ , ▩ AC.

to acrolein showed that the catalyst retained its excellent parameters even after 6 500 h of operation and no volatile compounds of molybdenum were formed [15]. The experiments with catalysts C7–C9 were carried out at the reaction temperature of  $298^\circ\text{C}$ , time factor  $m/F_{\text{IBA}} = 61.3 \text{ g h mol}^{-1}$ , and 20.3 vol. % content of water vapour in the reaction mixture. The results obtained are given in Figs. 6–8 which show that even a small addition of cobalt (catalyst C7) results in a decrease of not only the conversion of IBA but also the selectivity for MAA (the latter decrease being distinct). Although the selectivity for MAA again increases with further increasing the cobalt content, it, nevertheless, remains about 10 % lower than that with the catalyst C3 without this element. Hence it is obvious that in the case of Mo–V–P oxide catalysts used for oxidative dehydrogenation of IBA, cobalt plays a negative role, obviously decreasing the number of active centres on the catalyst surface.

The IR spectral measurements showed that the sorption of both IBA and MAA proceeds in almost the same way. The acids are sorbed on the catalyst

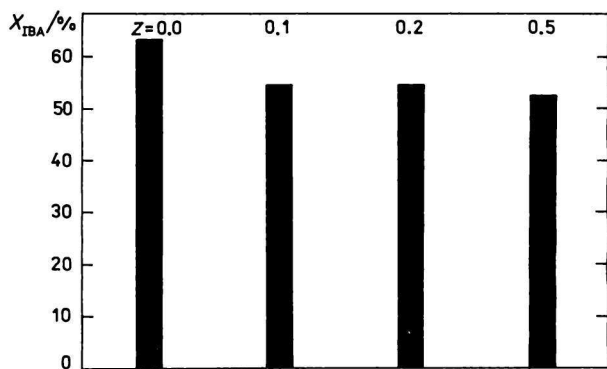


Fig. 6. Dependence of conversion of isobutyric acid,  $X_{IBA}$ , upon cobalt amount in catalyst,  $Z(\text{Mo}_5\text{V}_1\text{P}_{0.5}\text{Co}_Z\text{O}_N)$  (reaction temperature 298 °C;  $m/F_{IBA} = 61.3 \text{ g h mol}^{-1}$ ).

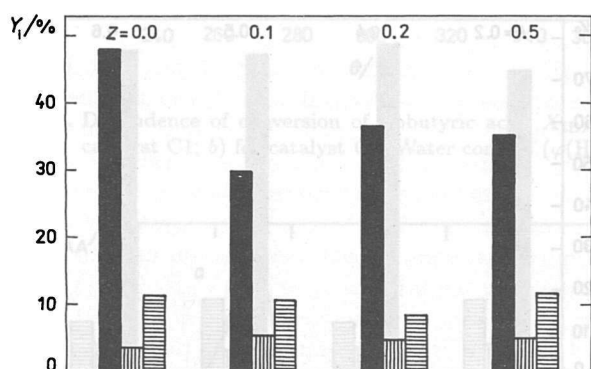


Fig. 7. Dependence of yields of reaction products,  $Y_i$ , upon cobalt amount in catalyst,  $Z$  (reaction temperature 298 °C;  $m/F_{IBA} = 61.3 \text{ g h mol}^{-1}$ ). ■ MAA, ▨  $\text{C}_3\text{H}_6$ , ▩ AC.

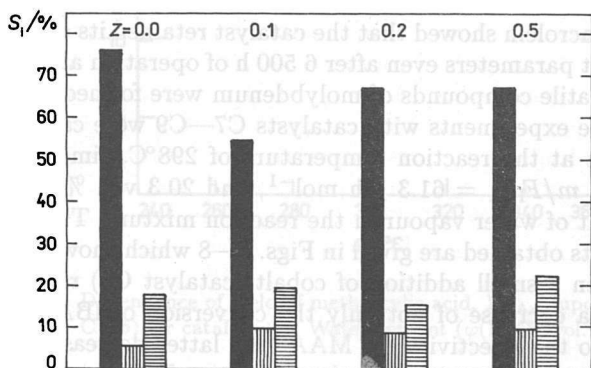


Fig. 8. Dependence of selectivities for reaction products,  $S_i$ , upon cobalt amount in catalyst,  $Z$  (reaction temperature 298 °C;  $m/F_{IBA} = 61.3 \text{ g h mol}^{-1}$ ). ■ MAA, ▨  $\text{C}_3\text{H}_6$ , ▩ AC.

surface by a donor—acceptor interaction, which is manifested by distinctly lowered  $\tilde{\nu}$  values of  $\nu(\text{CO})$  (1710—1720  $\text{cm}^{-1}$ ) for IBA and MAA. The sorption of IBA is, with great probability, immediately followed

by partial oxidative dehydrogenation of IBA with a lattice oxygen which is manifested by the formation of a weak band at  $\tilde{\nu}$  about 1620  $\text{cm}^{-1}$  ( $\nu(\text{C}=\text{C})$ ). It seems to be confirmed by increasing intensity of this band in sorption of IBA on catalyst C9 with preadsorbed oxygen. However, already at room temperature there takes place a distinct acid-base reaction of the acids sorbed on the catalyst surface to give the corresponding carboxylates. This fact is connected with formation of new intense bands at  $\tilde{\nu} = 1420 \text{ cm}^{-1}$  ( $\nu_s(\text{COO})$ ) and 1540  $\text{cm}^{-1}$  ( $\nu_s(\text{COO})$ ). With respect to the relatively small wavenumber difference between these bands, the bonding to the catalyst surface can be formulated as a bidentate one. On heating to 100 °C, most of the molecules of acids disappear from the catalyst surface (ca. 80 %), and the spectrum practically exhibits weak carboxylate bands only, especially on the catalysts with cobalt (C8 and C9). On further increasing the desorption temperature these bands are diminished and at 200 °C the desorption of IBA and MAA is practically complete.

With all the catalysts, even with those containing cobalt, a gradual decrease in conversion of IBA and a distinct decrease in selectivity for MAA were observed after ca. 30 h of operation. This deactivation of catalysts, which is also observed with the heteropolyacids containing Keggin's structure, is obviously due to not only the formation of volatile compounds of molybdenum but also the adsorption of IBA and MAA on the reduced centres (whereby the reoxidation of the catalyst is considerably slowed down) [16]. Hence, at present it does not seem likely that the production of methacrylic acid by oxidative dehydrogenation of isobutyric acid could successfully replace the acetone cyanohydrin route or the method of isobutene oxidation [2].

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