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METHACRYLIC ACID GAS-PHASE OBTAINING OVER B_2O_3 – P_2O_5 – MoO_3/SiO_2 CATALYSTS

Propionic acid aldol condensation process with formaldehyde over B_2O_3 – P_2O_5 – MoO_3/SiO_2 catalyst in the gas phase has been investigated. Promoter content effect on the catalyst activity and selectivity has been determined. Optimal condensation process conditions and optimal catalyst composition have been determined.

Keywords: heterogeneous catalysis, aldol condensation, methacrylic acid, methyl methacrylate.

Introduction. Methacrylic acid (MAA) is a bulk product of organic synthesis. Main application area of MAA is methyl methacrylate (MMA) production. MAA and MMA are valuable monomers, and the polymers based on them have good operating ability. Considerable MAA production capacity (about 5 million ton per year) and sustainable increase of demand on the acrylate polymer materials determine high actuality of the existing MAA production methods improvement and the development of new MAA production methods.

Problem statement. Over a long time the acetone cyanohydrin method was the main industrial MAA production method [1, 2]. Today the share of this method in MAA production pattern is still considerable. However, because of the formation of considerable amounts of ammonium wastes in the acetone cyanohydrin method, the researches aimed on displacement of this method are actively conducted world-wide. Thus, 2.5 ton of ammonium hydrogen sulphate are formed per a ton of MAA (MMA) produced by the acetone cyanohydrin method [3]. And ammonium hydrogen sulphate utilization is a very energy-consuming process. In addition, highly toxic cyanic acid is used in the method.

MAA and MMA are also industrially produced by two-stage iso-butylene oxidation via intermediate stage of methacrolein formation [4]. There is more recent MAA production method from ethylene via intermediate stages of propionic aldehyde and methacrolein formation [5]. Main disadvantage of the listed methods is low selectivity of methacrolein oxidation to MAA [5]. This leads to high consumption of raw materials and causes considerable amount of by-products formation and high costs for their separation.

MAA production by propionic acid (PA) gas-phase aldol condensation with formaldehyde (FA) may be the problem solution. The method enables MAA obtaining from ethylene in two stages (ethylene hydrocarboxylation to PA and condensation of the latter to MAA). However, this method has not been industrially implemented to date, because of low efficiency of known catalysts.

State of the art. Aldol condensation of carbonyl compounds may be catalyzed by both basic and acidic catalysts. When using basic catalysts, high selectivity of target product (unsaturated acid) formation is usually achieved at low conversion of reactants, one of which is taken in excess [6]. Such catalysts are unfavorable for industrial implementation because of considerable costs for the separation and recycling of unreacted substances. Using of B_2O_3 – P_2O_5 acidic catalysts supported on highly porous carrier allows to raise the initial reactants conversion substantially [7]. Thus, when using B_2O_3 – P_2O_5/TiO_2 catalyst, FA conversion of 62.0 % is achieved while MAA formation

selectivity is 56 % (PA is taken in excess). Our earlier researches showed considerable increase of the B_2O_3 – P_2O_5 catalyst activity, when the latter is promoted with transition metals oxides. In particular, promotion of the B_2O_3 – P_2O_5 catalyst supported on the “KSK-1” grade silica with molybdenum oxide gives PA conversion 61.7 % under the optimal conditions while MAA formation selectivity is 68.1 % [8]. Using of vanadium oxide as a promoter contributes to strong active sites formation on the catalyst surface [9] and increases MAA formation selectivity up to 80.5 % under the optimal conditions while PA conversion is 48.9 % at equimolar ratio of the reactants [9, 10]. To prepare the latter catalyst the “KSS-3” grade silica with the specific surface area of 600 m²/g was used. Obviously, it is the catalyst high specific surface area coupled with the active promoter that ensure high conversion of the reactants. Anyway, development of more selective catalysts of MAA production by aldol condensation is still very important.

Experimental. Catalytic properties of the developed catalysts were studied in flow setup with fixed-bed catalyst.

Formalin was used as a source of formaldehyde. It is reasonable from both economic (formalin is cheaper than paraformaldehyde or trioxane) and technological point of view (easiness of transportation, storage and use). Use of gaseous FA is undesirable because of its high polymerizability.

Reaction products mixture was analysed chromatographically.

Results and discussion. The present study is aimed on the development of new selective catalysts of PA aldol condensation with FA to MAA. To attain the goal we suggest to promote the B_2O_3 – P_2O_5 catalyst with molybdenum oxide when using the “KSS-3” grade silica as a support. It was assumed that the use of a promoter with temperate acidity would increase the MAA formation selectivity, and the use of a support with high specific surface area would preserve the acceptable PA conversion.

The catalytic systems based on the mixtures of boron and phosphorus oxides with molybdenum oxide at different ratios of the components were prepared for the research. The prepared catalysts composition is given in Tab. 1.

Table 1 – Composition and specific surface area of the catalysts

Designation	Components	Atomic ratio B:P:Mo	Sspec., m ² /g
K1	B ₂ O ₃ – P ₂ O ₅ – MoO ₃	3:1:0.1	347
K2	B ₂ O ₃ – P ₂ O ₅ – MoO ₃	3:1:0.3	374
K3	B ₂ O ₃ – P ₂ O ₅ – MoO ₃	3:1:0.6	389
K4	B ₂ O ₃ – P ₂ O ₅ – MoO ₃	3:1:1.0	390

The process was carried out in temperature range 563 – 683 K at contact time 12 sec. and at equimolar ratio of the reactants with various promoter amounts. At the temperatures below 563 K gas-phase condensation of carboxylic acids with FA occurs with very low rate, in consequence of which conversion of reactants are very low. At the temperatures above 683 K the catalyst work stability is reduced.

With all studied catalysts under the specified conditions the condensation by-product is diethyl ketone (DEK). It is the product of two PA molecules condensation. DEK formed in the reaction may be isolated as a marketable product and used as a solvent or raw material for organic synthesis.

The experimental data (Fig. 1) show that highly selective formation of MAA occurs at low content of the promoter (at the atomic ratio $Mo/P \leq 0.3$). Thus, in case of PA

condensation with FA on the catalysts K1 and K2 at temperatures 563 – 593 K the target product formation selectivity was 89.1 – 91.0 % ($\text{Mo/P} = 0.1$) and 86.2 – 87.2 % ($\text{Mo/P} = 0.3$), respectively. Further rise of molybdenum oxide content in the catalysts causes considerable decrease of the process selectivity.

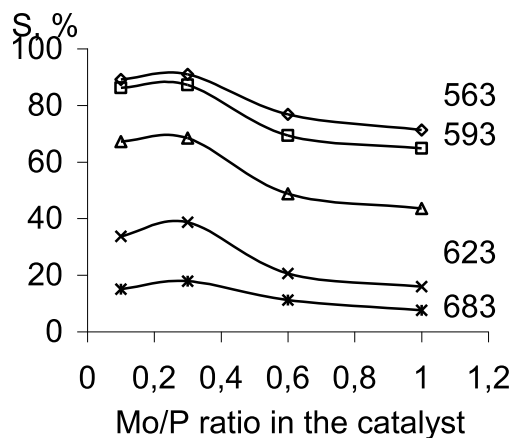


Fig. 1 – Effect of the $\text{B}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{MoO}_3$ catalyst composition on MAA formation selectivity in temperature range 563 – 683 K; contact time – 12 sec.

On the catalyst with the atomic ratio $\text{Mo/P} = 0.6$ (K3) at the same temperatures the unsaturated acid formation selectivity was 76.8 % at 563 K and 69.4 % at 593 K. Considering the insignificant increase of the catalyst activity when raising the promoter content (Table 2), the increase of molybdenum oxide content above the atomic ratio $\text{Mo/P} = 0.3$ (K2) is unreasonable. It is just the catalyst, on which the maximum MAA yield is observed in the whole studied temperature range.

As shown in Fig. 2, the highest yield 40.2 % is achieved at 593 K (catalyst K2). On the catalyst with the lowest molybdenum content (K1) at the same conditions the yield is 37.5 %, and in case of the highest promoter content (K4) – 32.2 %.

So, when the $\text{B}_2\text{O}_3 - \text{P}_2\text{O}_5/\text{SiO}_2$ catalytic system is promoted with molybdenum oxide, the optimal promoter content is that providing the atomic ratio to be $\text{Mo/P} = 0.3$ (K2). It is clear from Fig. 2 that the maximal MAA yield is achieved at 593 K on all the investigated catalysts. That is why this temperature may be considered to be optimal. At these conditions the target product formation selectivity is high (Fig. 1).

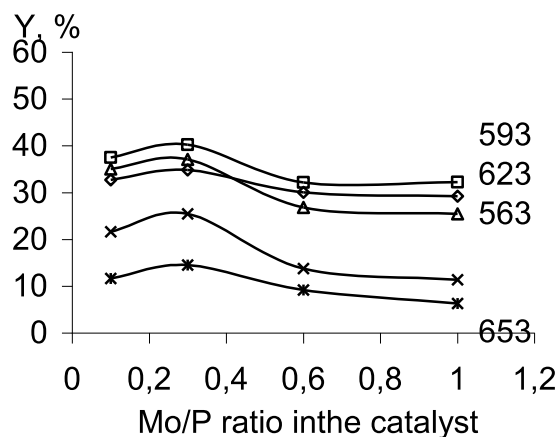


Fig. 2 – Effect of the $\text{B}_2\text{O}_3 - \text{P}_2\text{O}_5 - \text{MoO}_3$ catalyst composition on MAA yield in temperature range 563 – 683 K; contact time – 12 sec

Table 2 – Molybdenum content effect on the $B_2O_3 - P_2O_5 - MoO_3$ catalysts catalytic properties in PA gas-phase aldol condensation with FA
($\tau_c = 12$ sec, PA:FA ratio = 1:1)

T, K	Atomic ratio Mo/P	XPA, %	SMAA, %	SDEK, %	YMAA, %
563	0.1	36.7	89.1	10.9	32.7
	0.3	38.3	91.0	9.0	34.9
	0.6	39.1	76.8	23.2	30.0
	1.0	41.0	71.3	28.7	29.2
593	0.1	43.5	86.2	13.8	37.5
	0.3	46.1	87.2	12.8	40.2
	0.6	46.3	69.4	30.6	32.1
	1.0	49.7	64.8	35.2	32.2
623	0.1	52.1	67.2	32.8	35.0
	0.3	54.2	68.4	31.6	37.1
	0.6	54.9	48.8	51.2	26.8
	1.0	58.3	43.6	56.4	25.4
653	0.1	64.1	33.7	66.3	21.6
	0.3	65.7	38.7	61.3	25.4
	0.6	66.7	20.6	79.4	13.7
	1.0	70.8	16.0	84.0	11.3
683	0.1	77.7	15.0	85.0	11.7
	0.3	81.0	17.9	82.1	14.5
	0.6	82.4	11.2	88.8	9.2
	1.0	83.2	7.6	92.4	6.3

Note: SMAA – MAA formation selectivity; SDEK – DEK formation selectivity; YMAA – MAA yield.

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Conclusions. Thus, use of molybdenum oxide as a promoter compared to vanadium oxide and silica KSS-3 as support allows to raise MAA formation selectivity by 6.7 % at the commensurable MAA yield [10]. On the catalyst with the optimal promoter content (K2) under the optimal conditions at PA conversion equals 46.1 % and MAA formation selectivity equals 87.2 % the target product single-pass yield is 40.2 %.

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Досліджено процес альдольної конденсації пропіонової кислоти з формальдегідом на $B_2O_3-P_2O_5-MoO_3/SiO_2$ каталізаторі в газовій фазі. Встановлено вплив вмісту промотора (оксиду молібдену) на активність та селективність каталізатора. Визначено оптимальні умови здійснення процесу конденсації та оптимальний склад каталізатора.

Ключові слова: гетерогенний каталіз, альдольна конденсація, метакрилова кислота, метилметакрилат.

Исследован процесс альдольной конденсации пропионовой кислоты с формальдегидом на $B_2O_3-P_2O_5-MoO_3/SiO_2$ катализаторе в газовой фазе. Установлено влияние содержания промотора (оксида молибдена) на активность и селективность катализатора. Определены оптимальные условия осуществления процесса конденсации и оптимальный состав катализатора.

Ключевые слова: гетерогенный катализ, альдольная конденсация, метакриловая кислота, метилметакрилат.