Досліджено процес одержання метилметакрилату альдольною конденсацією метилпропіонату з формальдегідом на B_2O_3–P_2O_5–WO_3/SiO_2 каталізаторі в газовій фазі. Встановлено вплив додавання метанолу в реакційну суміш на побічну реакцію гідролізу естерів. Визначено оптимальні умови (температура, час контакту) здійснення процесу конденсації метилпропіонату з формальдегідом в присутності даного каталізатора

Ключові слова: метилметакрилат, метакрилова кислота, метилпропіонат, формальдегід, каталізатор, гетерогенний каталіз, альдольна конденсація

Исследован процесс получения метилметакрилата альдольной конденсацией метилпропионата с формальдегидом на B_2O_3–P_2O_5–WO_3/SiO_2 катализаторе в газовой фазе. Установлено влияние добавления метанола в реакционную смесь на побочную реакцию гидролиза сложных эфиров. Определены оптимальные условия (температура, время контакта) осуществления процесса конденсации метилпропионата с формальдегидом в присутствии данного катализатора

Ключевые слова: метилметакрилат, метакриловая кислота, метилпропионат, формальдегид, катализатор, гетерогенный катализ, альдольная конденсация

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OPTIMUM CONDITIONS DETERMINATION OF METHYL METHACRYLATE OBTAINING OVER TUNGSTEN-CONTAINING CATALYST

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1. Introduction

Methyl methacrylate (MMA) is an important monomer of the organic synthesis industry. The main field of use of MMA is production of poly(methyl methacrylate) (organic glass) and copolymers based on it. The materials made of MMA have good transparency, lightness, UV light and weather resistance; they can be easily colored, formed and recycled. These properties make poly (methyl methacrylate) an ideal light and impact-resistant substitute for glass in electronics – in laptops and mobile phones screens, photonics, semiconductor devices, in lighting equipment. MMA-based polymers are highly compatible with the human body, that's why they are used for making artificial lenses, bone cement and dentures. This wide range of MMA applications causes a 4 % annual demand growth for it. However, the problems in the production of this monomer limit its availability.

2. State of the art and problem statement

The main and most common method of MMA producing is acetoncyanohydrin process [1]. However, this method has significant drawbacks, namely the use of toxic cyanide acid and the need for utilization of large amount of by-product (ammonium sulfate). The preparation of MMA by oxidation of isobutylene or tert-butanol via intermediate stage of methacrolein formation is characterized by low selectivity and low efficiency of known catalysts, and therefore it is not widely implemented in the industry [2].

The most promising process for MMA obtaining is methyl propionate aldol condensation with formaldehyde in the gaseous phase over solid catalysts. The advantages of this method are the use of widely available materials and a low number of process stages [3–6], as methyl propionate can be obtained by carbonylation of ethylene in the presence of methanol, and formaldehyde can also be synthesized from methanol, which is obtained from synthesis gas. In addition, byproducts formed in this process can be separated and used as commercial products.

The process of condensation of methyl propionate (MP) with formaldehyde (FA) is mainly carried out over the basic catalysts [3, 4]; there is no enough information about acidic catalysts for this process, so they need to be studied in more detail [5, 6].

It has been found in our earlier studies that B_2O_3–P_2O_5–WO_3/SiO_2 catalytic system is active in the processes of acrylic and methacrylic acids obtaining by gas-phase

condensation of acetic and propionic acid respectively with formaldehyde [7–9]. The highest yield of unsaturated acid was in the presence of catalyst with atomic ratio of components B:P:W respectively 3:1:0.6. Therefore, we decided to test this catalyst in the condensation of MP with FA.

Obtaining of MMA by aldol condensation is mainly carried out with excess of saturated ester [10, 11]. However, the aforementioned catalyst based on boron, phosphorus and tungsten oxides is active in the condensation process of propionic acid with FA at their equimolar ratio. Therefore, we decided to study the process of MP condensation with FA with molar ratio of the initial reagents 1:1.

3. The purpose and objectives of the study

The aim of this study is to research aldol condensation process of methyl propionate with formaldehyde to methyl methacrylate over B_2O_3–P_2O_5–WO_3/SiO_2 catalyst in the gaseous phase.

The following objectives were set to reach the work purpose:

– to determine optimum conditions (temperature and contact time) of the aldol condensation process of MP with FA in the gaseous phase;

– to determine the effect of adding methanol to the reaction mixture on the side reaction of methyl propionate and methyl methacrylate hydrolysis.

4. Methodology of the research of tungsten-containing catalyst activity in the aldol condensation process

The study was carried out using a catalyst based on a mixture of boron, phosphorus and tungsten oxides, deposited on silica gel. The total amount of active components in the catalyst was 20 % by weight. The atomic ratio of the elements B:P:W in the catalyst was 3:1:0.6 respectively. The activity of this catalyst was studied in flow reactor with fixed-bed catalyst. To determine the effect of methanol (M) it was added to the reaction mixture so that the molar ratio of M:MP was (0,5÷10):1.

The research on methanol effect in the reaction mixture was carried out at a temperature 653 K and contact time 8 s. In order to determine optimum conditions for methyl propionate condensation process with formaldehyde temperature was changed in the range of 563÷÷683 K (at temperatures below 563 K MMA was not formed, and at temperatures over 683 K catalyst was coked and reactants were decomposed). Contact time was changed in the range of 4÷16 s. The reaction products were analyzed by gas chromatography. The main byproducts are diethylketone which can be separated and used as a commercial product, propionic acid formed by hydrolysis of MP, and methacrylic acid (MAA), which can be used for further esterification to form MMA.

5. Determining of optimum conditions for the process of aldol condensation of methyl propionate with formaldehyde to methyl methacrylate

The results of research of MP condensation process with FA in the presence of the aforementioned catalyst at contact time 8 s in the temperature range 503÷683 K are shown on Fig. 1. Conversion of the saturated ester is high and it increases with temperature rising, and at temperatures above 563 K it is above 90 %. However, a large amount of propionic acid is formed in the process by hydrolysis of MP, resulting in low MMA selectivity. Formed propionic acid (PA) also reacts with FA resulting in methacrylic acid formation. Moreover, methacrylic acid also can be formed by MMA hydrolysis. Fig. 1 also shows that at temperatures of 503 and 533 K MMA and MAA are practically not formed, therefore it is not practical to carry out the condensation process of MP with FA at these temperatures.

In order to resolve the problem of MP and MMA hydrolysis it was decided to add methanol to the reaction mixture, which in theory should shift the balance of ester hydrolysis reaction towards the esters formation. The results of these experiments are shown on Fig. 2.

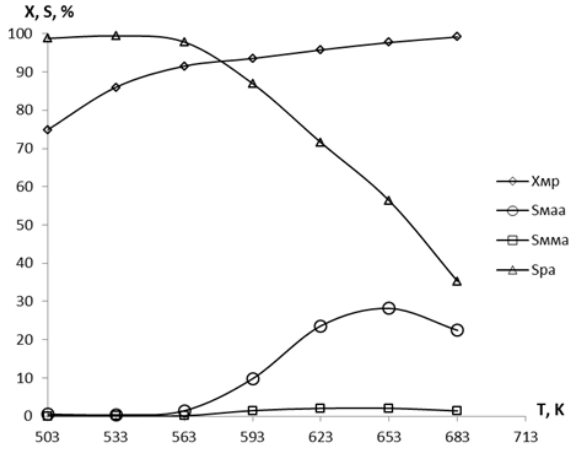

Fig. 1. Parameters of MP condensation process with FA at temperature range 503÷683 K and contact time 8 s

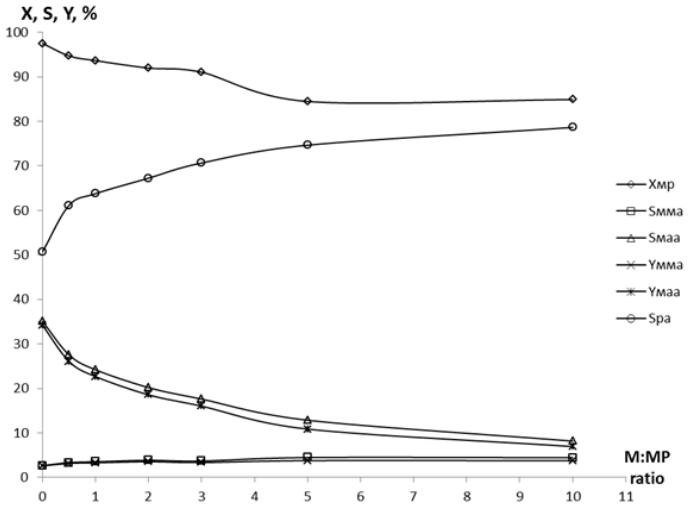

Fig. 2. The effect of methanol adding to the reaction mixture on parameters of MP condensation process with FA at temperature 653 K and contact time 8 s

It was found that adding methanol to the reaction mixture decreases conversion of methyl propionate. MMA selectivity increases with the increasing of methanol content

in the reaction mixture, but PA selectivity significantly increases too, resulting in a decreasing of total yield of unsaturated products (MMA and MAA).

Thus, adding methanol to the reaction mixture does not solve the problem of methyl propionate hydrolysis. Therefore, further research was done using a mixture of MP and FA with molar ratio of 1:1 without adding methanol.

The results of studies of the reaction contact time effect on MP conversion and MMA and MAA selectivity are shown in Table 1. Conversion of MP gradually increases with the contact time rising at all temperatures.

Table 1

Conversion of MP and selectivity of MMA, MMA and PA at contact time 4÷16 s; temperature range 563÷683 K

Contact time, s	Temperature, K	X, %	S_{MMA}, %	S_{MAA}, %	S_{PA}, %
4	683	95,17	3,16	17,81	54,37
	653	89,85	3,48	15,06	76,37
	623	86,93	1,73	7,89	88,45
	593	83,32	0,59	2,54	96,39
	563	77,43	0,40	1,49	97,41
8	683	99,16	1,37	22,46	35,25
	653	97,72	2,08	28,19	56,32
	623	95,77	2,06	23,62	71,55
	593	93,53	1,46	9,81	86,97
	563	91,53	0,11	1,41	97,85
12	683	99,50	0,74	17,05	30,97
	653	98,79	1,01	31,29	52,57
	623	96,41	2,00	30,16	63,69
	593	92,66	1,45	14,47	82,85
	563	88,38	0,46	4,02	95,04
16	683	99,37	0,45	17,29	23,20
	653	99,62	0,47	31,66	37,63
	623	98,10	1,50	30,14	56,48
	593	95,71	1,71	20,87	74,99
	563	92,72	0,70	4,70	93,51

Note: X – conversion of MP, %; S_{MMA} – MMA selectivity, %; S_{MAA} – MAA selectivity, %; S_{PA} – PA selectivity, %

Propionic acid selectivity significantly decreases with temperature and contact time rising. MMA and MAA selectivity have extremum dependence from the temperature during contact times 8÷16 s, and at 4 s contact time MMA and MAA selectivity slightly increases with temperature increasing.

The dependence of the total yield of MMA and MAA from temperature and contact time is shown on Fig. 3. Unsaturated products yield increases with temperature rising up to 623 K at all contact times, due to the MP conversion and selectivity increase at these temperatures.

The maximum yield was observed at contact time 12 s at temperatures of 623 K and 653 K – 31.0 % and 31.91 % respectively, and at contact time 16 s at 623 K – 32.02 %. So, optimum conditions for MMA and MAA obtaining over this catalyst can be considered the following: contact time of 12 s and temperature 653 K, as a lower contact time ensures better productivity of the process.

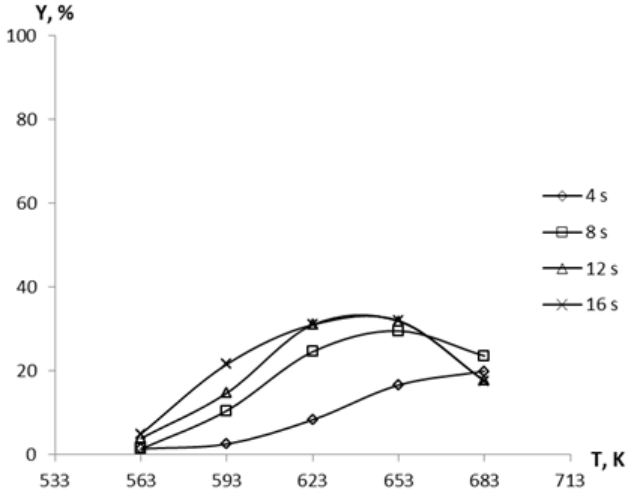

Fig. 3. Dependence of total yield of MMA and MAA (Y, %) from temperature (T, K) at different contact times (4÷16 sec)

6. Discussion of the research results of adding methanol to the reaction mixture and determining of optimum conditions of the process

The research showed that B_2O_3–P_2O_5–WO_3/SiO_2 catalyst is active in the methyl propionate aldol condensation with formaldehyde. However, MMA selectivity is very low, due to the esters hydrolysis (MP and MMA) and consequently large amounts of propionic and methacrylic acids formation. In [3, 6] adding methanol to the reaction mixture reduces esters hydrolysis. It should be noted however that in these works condensation process was carried out over base-type catalysts. Tungsten-containing catalyst studied in this paper is of acid type [7], which causes different mechanism of the process. PA selectivity increasing in the presence of this catalyst with increasing of methanol content in the reaction mixture (Fig. 2), despite the theoretical shift of the equilibrium towards the esters formation, can be explained by strong adsorption of methanol on the acid active sites of the catalyst, which causes inhibition of the condensation reaction. This fact also explains the reduction of the MP conversion, despite the increased PA selectivity.

Acid type catalysts are more promising for the process, as the base catalysts typically provides low conversion in the aldol condensation reactions. However, studied tungsten-containing catalyst does not provide sufficient selectivity of methyl methacrylate formation, so it is necessary to study in more detail the problem of selectivity increasing and hydrolysis supression in the presence of acid type catalytic systems in aldol condensation process.

The results will be used for further study of the methyl methacrylate obtaining process by aldol condensation, in particular for the analysis and prediction of catalytic systems properties and the development of efficient catalysts with the necessary characteristics that will reduce the cost of production of MMA by this method. The optimum conditions for MP condensation with FA to form MMA (temperature 653 K and contact time 12 s) can also be used for developing the technology for this monomer producing.

7. Conclusions

The optimum conditions for MP condensation process with FA, namely temperature 653 K and contact time 12 s were determined. Under these conditions, in the presence of B_2O_3–P_2O_5–WO_3/SiO_2 catalyst with an atomic ratio of components B:P:W 3:1:0.6 respectively total yield of MMA and MAA was 31.91 % and their total selectivity was 32.3 %.

The effect of adding methanol to the initial reaction mixture was determined. It was found that adding methanol causes a slight increase in MMA selectivity, but the yield of unsaturated products decreases, and therefore adding methanol to the reaction mixture for the MP condensation with FA over B_2O_3-P_2O_5-WO_3/SiO_2 catalyst is impractical.

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