

Synthesis of Methacrylate Monomers Combined Condensation of Propionic Acid and Methylpropionate in the Gas Phase

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Abstract – Development of active and selective catalyst for the process of obtaining methacrylate monomers from methyl propionate, propionic acid and formaldehyde is one of important stages to industrial implementation of this process. In order to solve this problem, we designed catalyst based on oxides of boron and phosphorus that were promoted by mixture oxides of zirconium and tungsten. The total yield of the target products at optimum temperature of 593 K is 52.3 % with the total selectivity of their formation at 96.4 % and the conversion of reagents of 54.2 %. We determined the effect of adding methanol on the ratio of products MMA/MAA.

Key words: methacrylic acid, methyl methacrylate, propionic acid, condensation, catalyst, methyl propionate, formaldehyde, methanol.

I. Introduction

Existing methods of obtaining acrylate monomers have a number of shortcomings – producing large amounts of by-products of oxidation, formation of toxic wastes, as well as a big number of stages of the process. It is promising to obtain acrylate monomers by aldol condensation of carbonyl compounds in the gas phase, which is characterized by a small amount of by-products, the absence of toxic waste and the availability of raw materials.

In particular, at papers [1-2] established that for the process of aldol condensation of MP with FA, the active boron-phosphorus-oxide catalyst was developed, applied on the silica gel, promoted by zirconium oxide ($B_2O_3:P_2O_5:ZrO_2=3:1:0.3$), however, due to the hydrolysis of part of the MP to PA and methanol, the total selectivity of the formation of acrylates is low – 65.4 %.

It is reasonable to explore a new process of combined condensation of MP and PA with FA, which on one hand should reduce the MP hydrolysis due to the presence of PA in the reaction mixture and, on the other hand, will allow to recirculate the PA that formed in the process of hydrolysis of MP. It is also advisable to examine the effect of methanol on the course of the process because this can also reduce the MP hydrolysis and increase the share of more valuable MMA in the products of the reaction.

II. Experimental

The research was carried out with the use of catalyst on the base of a mixture of oxides of boron and phosphorus promoted by the mixture of oxides zirconium and tungsten, applied on the silica gel. The total number of active components in the catalyst was 20% mass. The

molar ratio of the oxides in catalytic system $B_2O_3:P_2O_5:ZrO_2:WO_3$ 3:1:0.15:0.15. Catalyst was prepared by the impregnation method [3].

The catalytic system was examined in a flow reactor with a stationary layer of catalyst. For the research we used a mixture with the ratio of reagents MP:PA:FA=1:1:2. Two molecules of FA were chosen considering for one per every molecule of PA and MP. For the study of the process in the presence of methanol, the ratio of reagents was MP:PA:methanol:FA=1:1:1:2. As the source of FA we used formalin 37 %, which was prepared from paraform directly before the experiments. The temperature of the process changed in the range of 563–683 K, the residence time was 12 s because it was found previously that these conditions are optimal for the process of condensation of MP with FA [4, 5]. The reaction products were analyzed by the gas chromatography method.

III. Results and Discussion

The research results of the process of combined condensation of MP and PA with FA in the presence of $B_2O_3-P_2O_5/SiO_2$ catalytic system with mixture promoters of oxides zirconium and tungsten allowed us to establish that the conversion of ester and acid increases with increasing temperature (Fig. 1). The maximum conversion value of 75 % was obtained at the temperature of 683 K.

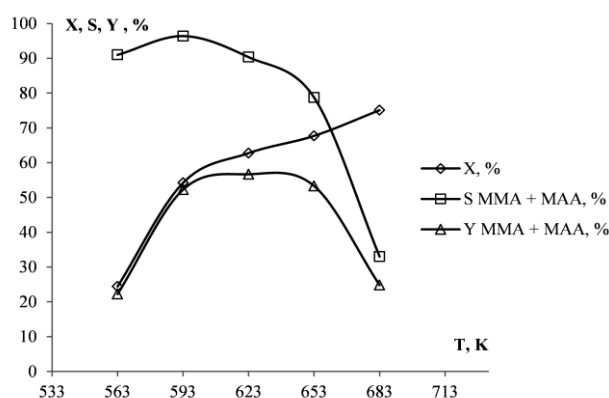


Fig. 1. Dependency of parameters of the process conversion (X, %), selectivity (S, %), yield (Y, %) on temperature (T, K) in the presence of catalyst, residence time 12 s

The total selectivity of formation of MMA and MAA decreases with increasing temperature (Fig. 1). The highest values of selectivity are achieved at temperatures of 563–593 K. This is due to the fact that at temperatures over 623 K, the process of formation of a by-product, diethyl ketone, actively occurs. The maximum total selectivity of formation of MAA and MMA is 96.4 % at a temperature of 593 K.

The total yield of the unsaturated products significantly increases with increasing temperature to 653 K on examined catalysts (Fig. 1). When the temperature exceeds 653 K, the total yield of MMA and MAA is reduced due to a decrease in the selectivity of formation of the target products and increase in the output of by-products at high temperatures. The highest yield of

products was obtained at a temperature of 623 K – 56.7 %. However, the temperature of the process implementation at 593 K can be considered optimal, because the selectivity is slightly higher and the yield is only slightly lower.

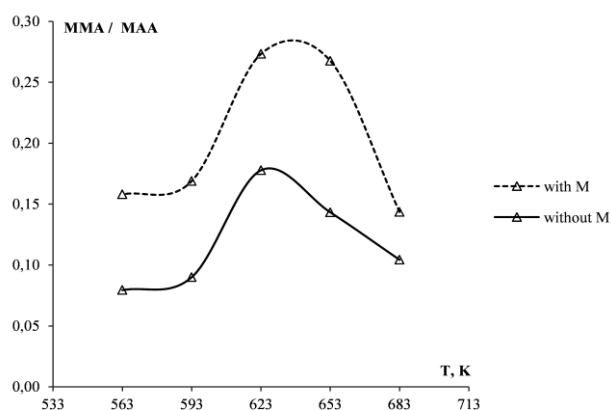


Fig. 2. Dependency of the ratio of MMA/MAA on temperature (T, K) with and without adding of methanol, residence time 12 s

We also determined the total selectivity and the total yield of the target products in the presence of methanol (Fig. 2). Adding methanol not only increases the ratio of MMA/MAA but also increases the total selectivity of formation of acrylates. However, the conversion of reagents is lower than in process without methanol, due to that fact the total yield is lower too. The total yield and selectivity of the acrylates formation on the catalyst in the process with methanol, at temperature 623 K are 46.7 % and 93.3 %, respectively.

Compared to the previously studied catalysts for the process of condensation of MP and FA, promoted by individual tungsten oxide and zirconium oxide, the developed catalyst provide for a much higher selectivity of formation of the target products – methyl methacrylate and methacrylic acid. For example, in the presence of the $B_2O_3-P_2O_5-WO_3/SiO_2$ catalyst, the maximum selectivity of formation of acrylates reached 49.1% and was achieved at a temperature of 653 K [4], while in the presence of the $B_2O_3-P_2O_5-ZrO_2/SiO_2$ catalyst, they managed to achieve the selectivity is 65.4 % at a temperature of 623 K [5]. Thus, the designed $B_2O_3-P_2O_5/SiO_2$ catalytic system promoted by $ZrO_2:WO_3 = 0.15:0.15$ allowed us to increase the selectivity of formation of the target products to 96.4 %, which is 31 % higher, and made it possible to carry out the process of condensation of MP and PA with FA at a lower optimum temperature of 593 K than in the process without propionic acid, confirming possibility and feasibility of the PA recycling in the process of condensation of MP and FA.

It was found that addition of methanol in reaction mixture increase of the of MMA / MAA ratio. In addition,

despite the fact that at the optimum temperature of 593 K total selectivity of acrylates decreases by 3 %, and the yield by 11 %, however substantially larger MMA yield in the products is obtained.

Conclusion

We created highly selective catalyst of combined condensation of methyl propionate and propionic acid with formaldehyde. The selectivity of the formed catalyst varies within 90–96 % in the process without the use of methanol at the temperature range 563–623 K.

The optimal temperature was determined of conducting the process of condensation of propionic acid and methyl propionate with formaldehyde, which is 593 K. At this temperature on the catalyst with the molar ratio $B_2O_3:P_2O_5:ZrO_2:WO_3 = 3:1:0.3:0.15:0.15$, the single-pass yield of methyl methacrylate and methacrylic acid in one run is 52.3 % with the total selectivity of their formation at 96.4 %.

It was established that adding methanol to the reagent mixture increases the ratio of methyl methacrylate to methacrylic acid in the composition of the products and the overall selectivity of the process on created catalyst. It was found that in the process with methanol, the share of MMA is highest at the optimum temperature of 623 K, at which the single-pass yield of MMA and MAA in one run is 46.7 % at the total selectivity of their formation of 93.3 %.

References

- [1] Yu., V., Dmytruk, V., Ivasiv, R., Nebesnyi, S. Maykova, "Optimum conditions determination of methyl methacrylate obtaining over tungsten-containing catalyst," Eastern-European Journal of Enterprise Technologies, vol. 4, Issue 6 (76), pp. 4–7, 2015.
- [2] Yu., V., Nebesna, V., V., Ivasiv, R., V. Nebesnyi, "Doslidzhennia tekhnolohichnykh ta kinetychnykh zakonmirnostei sumisnoho oderzhannia metakrylativ na tsyrkoniivmisnykh katalizatorakh," Skhidno-Yevropeyskyi zhurnal peredovykh tekhnolohii, vol. 5, T. 6 (77), pp. 49–52, 2015.
- [3] S., L., Ding, R., Y., Wang, Y., Y., Yan, Z., Li, "Condensation of Methyl Propionate with Formaldehyde to Methyl Methacrylate over Cs-Zr-Mg/SiO₂ Catalysts," Advanced Materials Research, vol. 396–398, pp. 719–723, 2012.
- [4] R., Nebesnyi, V., Ivasiv, Z., Pikh, V., Zhyznevskiy, Y. Dmytruk, "The kinetic of the gas phase aldol condensation reaction of propionic acid with formaldehyde on $B_2O_3 - P_2O_5 - WO_3/SiO_2$ catalyst," Chemistry & Chemical Technology, vol. 8, pp. 29–34, 2014.
- [5] R. Nebesnyi, "Complex oxide catalysts of acrylic acid obtaining by aldol condensation method," Eastern-European Journal of Enterprise Technologies, vol. 1, Issue 6 (73), pp. 13–16, 2015.