Simultaneous Methyl Methacrylate and Methacrylic Acid Obtaining over Zirconium-containing Catalysts

Yuliia Nebesna, Roman Nebesnyi, Volodymyr Ivasiv, Nazarii Lapychak

Technology of Organic Products Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: yulia_lemberg@ukr.net

Abstract – Methyl methacrylate and methacrylic acid are widely used monomers. The aldol condensation of methyl propionate and formaldehyde is perspective process for simultaneous obtaining of this methacrylate monomers. It was found that zirconium-containing catalysts are active in this process. The effect of zirconium content in the catalyst on methyl propionate conversion and yield of methyl methacrylate and methacrylic acid has been determined. The best catalyst for methyl propionate condensation with formaldehyde has been found.

Key words – methyl methacrylate, methacrylic acid, aldol condensation, methacrylates, catalyst, zirconium oxide.

I. Introduction

Methyl methacrylate (MMA) and methacrylic acid (MAA) are important monomers in industrial organic chemistry. Polymeric materials, made of MMA and MAA, have good transparency, lightness, UV light and weather resistance. Methacrylates are widely used in the production of organic glass, electronic and semiconductor devices, fiber optic cables, lighting equipment, paints, lacquers and other coatings, in medicine and so on. Demand for MMA and MAA has grown year-on-year over decades, so it is an actual task to improve these monomers obtaining methods or find alternatives.

One of the promising methods of methacrylate monomers producing is gas phase aldol condensation of carbonyl compounds [1]. This method has substantial advantages, such as small number of process steps and possibility to use by-products as commercial products [2]. Methacrylic acid and methyl methacrylate can be obtained simultaneously in one process, through aldol condensation reaction of methyl propionate (MP) and formaldehyde (FA) in the gas phase over heterogeneous catalysts. In our previous studies it was found that acid type catalysts containing oxides of boron and phosphorus and promoted by tungsten oxide are active in this process [3, 4]. These catalysts provide high conversion of methyl propionate (up to 99 %), but MMA and MAA selectivity is low [3].

As is known from the literature [5, 6], basic type catalysts which contain compounds of alkali and alkaline earth metals are active in the aldol condensation of MP with FA. One of such catalysts is based on cesium oxide or hydroxide deposited on silica gel [5]. These catalysts show high total MMA and MAA selectivity (up to 86 %), but due to low conversion of MP yield of unsaturated products was only 12.0 %. In order to increase selectivity of our B-P-O_x/SiO_2, we added basic oxides to this catalyst instead of acidic tungsten oxide, but this replacement did not have positive effect on catalyst activity and selectivity [7].

Recent publications show that zirconium oxide is effective promoter to the catalysts for condensation of MP with FA [8, 9]. In particular, the addition of zirconium increased MMA selectivity [8]. The aim of this paper is to study the effect of zirconium oxide addition to the catalyst based on boron and phosphorus oxides deposited on silica gel in aldol condensation of MP and FA.

II. Results and Discussions

Catalysts B_2O_3–P_2O_5–ZrO_2/SiO_2 were prepared for the study. The total amount of active components in the catalyst was 20 % by weight. Molar ratio of B_2O_3 and P_2O_5 oxides in each catalyst was 3:1 respectively. Zirconium oxide content in the catalyst was changed so that ZrO_2/P_2O_5 molar ratio in the catalyst was 0.1; 0.3; 0.6 and 1.0. The activity of these catalytic systems was studied in flow reactor with impulse feeding of the reactants and fixed-bed catalyst.

The reaction mixture of MP and FA with their equimolar ration was used for the research. Temperature was changed in the range of 563 ÷ 683 K, contact time was 12 s. The reaction products were analyzed by gas chromatography. Methanol and propionic acid (products of methyl propionate hydrolysis) also formed during the process, and diethylketone is another product, which can be separated and used as a commercial product.

The results show that in the presence of B_2O_3-P_2O_5-ZrO_2/SiO_2 catalytic systems MP conversion increases with temperature increasing over all studied catalysts (Fig. 1). The highest MP conversion was over the catalyst with ZrO_2/P_2O_5 molar ratio of 0.3 at all temperatures, e.g., 84.7 % at 563 K and 99.6 % at 683 K.

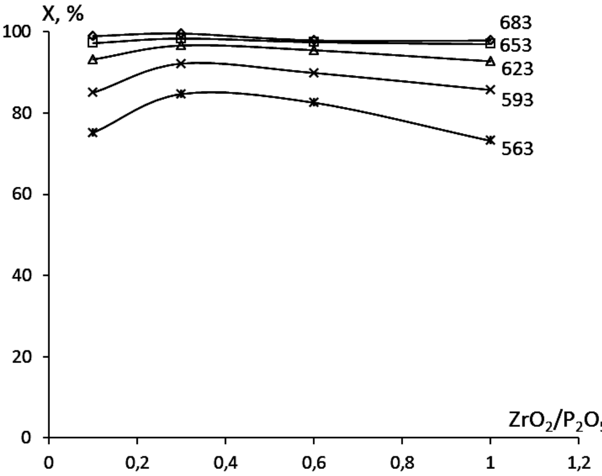

Fig. 1. Methyl propionate conversion dependence on zirconium oxide content in the catalyst in the temperature range 563 – 683 K

The total MMA and MAA selectivity increases with zirconium content increasing until molar ratio of ZrO_2/P_2O_5 is 0,3, and then slightly decreases. The highest selectivities were at 623 K over all studied catalysts, because at temperatures over 623 K side reactions occurs actively, particularly, diethylketone formation. The maximum methacrylates selectivity (65.4 %) was at 623 K over the catalyst with zirconium oxide content of 0.3, and at 683 K over the catalyst with zirconium oxide content of 0.1 the selectivity was only 13.7 %.

The highest total yield of methacrylate monomers was over the catalyst in which molar ratio of ZrO_2/P_2O_5 is 0.3, at all studied temperatures of the process (Fig. 2). Also methacrylate yield increases with temperature increasing up to 623 K, then yield decreases. At 683 K yield was 13.4 % over the catalyst with zirconium oxide content 1.0 and 23.3 % over the catalyst with zirconium oxide content 0.3 At 623 K over the same catalysts MAA and MMA yield was 50.3 % and 63.3 % respestively, and at 563 K – 19.0 % and 31.5 % respectively.

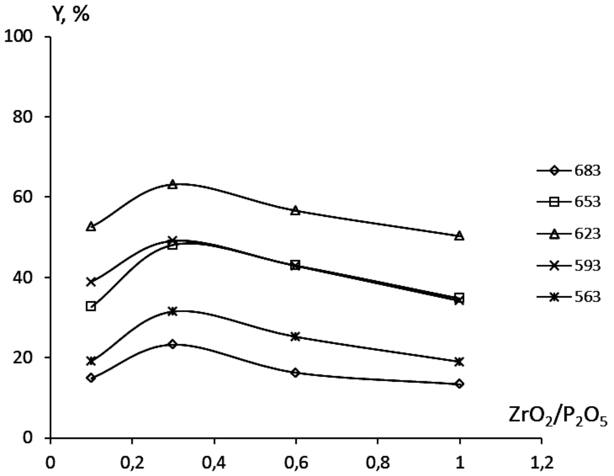

Fig. 2. The effect of zirconium oxide content in the catalyst on total methyl methacrylate and methacrylic acid yield at 563 – 683 K

As the yield of target products is a criterion for choosing the best catalyst for the process, the optimum catalyst for methyl propionate condensation process with formaldehyde is catalyst in which the molar ratio of ZrO_2/P_2O_5 is 0.3, as at 623 K this catalyst provides the highest total yield of methacrylates (63.2 %).

The experiments showed that B_2O_3-P_2O_5-ZrO_2/SiO_2 catalysts are active in methyl propionate aldol condensation with formaldehyde in the gas phase. Compared to the previously studied catalysts promoted by tungsten oxide and basic oxides, zirconium-containing catalysts provide significantly higher methyl methacrylate and methacrylic acid selectivity. Particularly in the presence of B_2O_3-P_2O_5-WO_3/SiO_2 catalyst the highest selectivity was 49.1 % at 653 K [4]; potassium-containing catalyst provided selectivity up to 42.4 % at 653 K [7], and in the presence of B_2O_3-P_2O_5-ZrO_2/SiO_2 catalyst the highest selectivity (65.4 %) was achieved at lower temperature – 623 K. So, adding zirconium oxide to B-P-O_x/SiO_2 catalytic system allowed to increase the selectivity of the process by 16.3% and to reduce optimum temperature of the process by 30 K.

Conclusion

It was found that zirconium-containing catalysts based on boron and phosphorus oxides are active in the process of methyl methacrylate and methacrylic acid simultaneous obtaining by aldol condensation of methyl propionate and formaldehyde. It was determined, that catalyst which has molar ratio of ZrO_2/P_2O_5 of 0.3 provides the highest methyl propionate conversion, methacrylate monomers selectivity and yield. Also this catalyst allows to reduces optimum temperature of the process by 30 K, which is positive for the economical aspect of this process.

References

[1] K. Nagai, "New developments in the production of methyl methacrylate", Appl. Catal. A: Gen., vol. 221 (1-2), pp. 367-377, Dec. 2001.

[2] H. A. Wittcoff, et al., Industrial organic chemicals, 3rd ed. New York: J. Wiley and Son, 2013.

[3] Yu. Dmytruk, et al., "Optimum conditions determination of methyl methacrylate obtaining over tungsten-containing catalyst," Eastern-European J. of Enterprise Technologies., vol. 6, is. 6 (76), pp. 4-7, Aug. 2015.

[4] Yu. V. Dmytruk, et al., "Aldolna condensatsiia metylpropionatu z formaldehidom na B_2O_3 – P_2O_5 – WO_3/SiO_2 katalizatorah [Aldol condensation of methyl propionate with formaldehyde over B_2O_3 – P_2O_5 – WO_3/SiO_2 catalysts]," Visnyk Natsionalnoho tehnichnoho universytetu "Kharkivskyi politehnichnyi instytut" – National Technical University "Kharkiv Polytechnic Institute" Bulletin, vol. 39, pp. 98-102, Sep. 2015 (in Ukraininan).

[5] M. Ai, "Formation of methyl methacrylate by condensation of methyl propionate with formaldehyde over silica-supported cesium hydroxide catalysts", Appl. Cat. A: Gen., vol. 288 (1-2), p. 211-215, Apr. 2005.

[6] S. Ding, et. al., "Condensation of methyl propionate with formaldehyde to methyl methacrylate over Cs-Zr-Mg/SiO_2 catalysts", Adv. Mat. Res., vol. 396-398, pp. 719-723, 2012.

[7] Yu. V. Nebesna, et al., "Promotuvannia osnovnymy oksydamy B_2O_3 – P_2O_5/SiO_2 katalizatora protsesu sumisnoho otrymannia metylmetakrylatu ta metakrylovoi kysloty [Promoting by basic oxides of B_2O_3 – P_2O_5/SiO_2 catalyst of the process of methyl methacrylate and methacrylic acid simultaneous obtaining]," Naukovyi Visnyk NLTU Ukrainy – Scientific Bulletin of NLTU of Ukraine, vol. 25.6, pp. 211-216, Oct. 2015 (in Ukrainian).

[8] B. Li, et. al., "SBA-15 Supported cesium catalyst for methyl methacrylate synthesis via condensation of methyl propionate with formaldehyde", Ind. & Eng. Chem. Res., vol. 53, pp. 1386-1384, Jan. 2014.

[9] S. D. Jackson, "Catalysts for the production of unsaturated acids or esters thereof," U.S. Patent 6 544 924, April 8, 2003.