Effect of Support Nature on the Efficiency of B–P–V–W–Oₓ Catalysts of Acrylate Synthesis with Aldol Condensation of Acetic Acid with Formaldehyde.

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Abstract – The catalytic systems of the B–P–W–V–Oₓ composition have been investigated on different types of supports. The best by the target product yield is the catalytic system of the composition B–P–W–V–Oₓ/TiO₂ anatase. The optimal conditions for the process are: temperature – 375 °C; residence time – 8 s, at which acetic acid conversion is 63.8 %, acrylic acid selectivity – 92 % and acrylic acid yield – 58.8 %.

Keywords – acrylic acid, aldol condensation, solid catalysts, nature of support.

Introduction

The most valuable representatives of acrylate monomers are acrylic acid and its derivatives, which are the main source material for the production of most acrylic polymeric and composite materials. One of the most promising methods for the production of acrylate monomers is the aldol condensation of carbonyl compounds. A significant advantage of this method is the possibility of using widely available raw materials such as natural gas and coal. The simplicity of technological design and the small number of stages of the process determine the economic and technological feasibility of using this method for the production of acrylate monomers [1, 2]. In previous studies [3] it has been established that the catalyst of the composition B–P–V–W–Oₓ/SiO₂ shows high efficiency in the gas-phase condensation of acetic acid with formaldehyde to acrylic acid and that the porous structure of the catalyst has significant influence on its activity [4]. It is known that the support can also affect the process. For these reasons, the developed active catalyst phase (B–P–V–W–Oₓ) is deposited on a supports of different nature with similar parameters of porous structure (pore diameter of about 10 nm, specific surface area of 200-250 m²/g): SiO₂, TiO₂ anatase, ZrO₂, SnO₂–TiO₂, Al₂O₃. To provide equivalent parameters of the porous structure for all supports, they were pre-treated with hydrothermal methods (hydrothermal treatment (HTT) or mechanochemical treatment (MChT)).

Thus, the purpose of this work is to investigate the effect of the nature of the support of B–P–V–W–Oₓ catalysts in the synthesis of acrylic acid by the aldol condensation of acetic acid with formaldehyde.

The influence of different types of mesoporous supports for B–P–V–W–Oₓ catalysts, namely: SiO₂, SiO₂ (HTT at 150 °C, 3h), SnO₂–TiO₂, Al₂O₃, TiO₂ anatase with TiO(OH)₂, Al₂O₃ (MChT in H₂O at 300 rpm), TiO₂ anatase with TiO(OH)₂ (MChT in H₂O at 300 rpm) and Sn(OH)₄–TiO₂ (MChT at 600 rpm) on their efficiency in the process of aldol condensation of acetic acid with formaldehyde to acrylic acid. The list of synthesized catalysts is given in Table 1.

Various methods of preparation of catalysts and their influence on the main parameters of the process (Table 1) are also investigated in this work.
### Table 1

| №  | Components of the active phase | The support and parameters of its modification | Preparation method |
|----|--------------------------------|-----------------------------------------------|--------------------|
| K1 | SiO₂                           |                                               | Impregnation with evaporation |
| K2 | SiO₂ (HTT at 150 °C 3h)        |                                               | Impregnation without evaporation |
| K3 | SnO₂–TiO₂ (MChT at 600 rpm)    |                                               |                    |
| K4 | Al₂O₃ (MChT in H₂O at 300 rpm) |                                               |                    |
| K5 | TiO₂ anatase (MChT in H₂O at 300 rpm) |                               |                    |
| K6 | B–P–V–W–Oₓ                     |                                               |                    |
| K7 | SiO₂                           |                                               |                    |
| K8 | SnO₂–TiO₂ (MChT at 600 rpm)    |                                               |                    |
| K9 | Al₂O₃ (MChT in H₂O at 300 rpm) |                                               |                    |
| K10| TiO₂ anatase (MChT in H₂O at 300 rpm) |                              |                    |

It has been established that for a series of catalysts prepared by the method of impregnation without evaporation, the best catalyst for the selectivity of the formation of acrylic acid is K₅ (TiO₂ anatase/B–P–V–W–Oₓ) (Fig. 1). The catalyst K₅ shows the following results at 375 °C and the residence time 8 s: OK conversion is 51.8 %, AK selectivity – 94.5 %, AK yield – 48.5 %.

![Fig. 1. Comparison of the selectivity of the AK formation on the catalysts K₁–K₅, temperature 375 °C, residence time 8 s.](image)

And for a series of catalysts prepared by the method of impregnation with evaporation, the best catalyst in the process of aldol condensation is K₁₀ (TiO₂ anatase MChT H₂O at 300 rpm) (Fig. 2). The catalyst K₁₀ shows the following results at 375 °C and residence time 8 s: OK conversion is 63.8 %, AK selectivity is 92 % and AK yield is 58.8 %.

The comparison of the conversion of acetic acid, the selectivity and the yield of acrylic acid on the best catalyst, namely K₁₀, prepared by impregnation with the evaporation of the active phase solution, with the K₅ catalyst, prepared by the method of impregnation without evaporation, is shown in Fig. 2. The catalyst K₁₀ shows better results at 375 °C and residence time 8 s: OK conversion is 63.8 %, AK selectivity – 92 %, and AK yield – 58.8 %. When using the K₅ catalyst, the OK conversion is 51.8 %, AK selectivity – 94.5 %, and AK yield – 48.5 %.
Fig. 2. Comparison of catalytic activity of catalysts ($K_5$ using as support of TiO$_2$ anatase and $K_{10}$ using as support TiO$_2$ anatase MChT H$_2$O at 300 rpm) synthesized by various methods.

Consequently, not only the nature of the support affects both the catalytic properties of catalysts of aldol condensation of acetic acid with formaldehyde, but also the method of catalysts preparation (impregnation with or without evaporation). The most effective in the process of acrylic acid production is the catalytic system B–P–V–W–O/ TiO$_2$ anatase, prepared by impregnating the support with a solution of active phase components, followed by evaporation.

**Conclusion**

New high-performance catalytic systems, based on a mixture of boron oxides, phosphorus, vanadium and tungsten deposited on SiO$_2$, SnO$_2$–TiO$_2$, Al$_2$O$_3$ and TiO$_2$ anatase, have been developed for the process of acrylic acid production using the method of aldol condensation of acetic acid with formaldehyde. It has been established that all developed catalytic systems of the B–P–V–W–O$_x$ composition deposited on a support with a pore size of about 10 nm have high efficiency in the process of aldol condensation of acetic acid with formaldehyde. It is shown that the method of preparation of catalysts (impregnation with or without evaporation) and the nature of the support affects the efficiency of catalysts. The best method is based on the impregnation of the support with the solution of the active phase components with subsequent evaporation; the best support for the B–P–V–W–O$_x$ active phase is TiO$_2$ anatase.

**References**

[1] Patent 9771314 US, Process for preparing acrylic acid from formaldehyde and acetic acid / T. C. Brueggemann, N. T. Woerz, A.Ruppel; assignee: BASF SE, Ludwigshafen am Rhein (DE) – № 14/972,255; filing date: 17.12.2015; publication date: 23.01.2016.

[2] Patent 4165438 US. Synthesis of acrylic acids and its esters / R. A. Schneider; assignee: Chevron Research Comp. – № 734065; filing date: 20.10.1976; publication date: 21.08.1979.

[3] R. Nebesnyi, V. Ivasiv, Y. Dmytruk, N. Lapychak, “Acrylic acid obtaining by acetic acid catalytic condensation with formaldehyde”, *Eastern-European Journal of Enterprise Technologies*, vol. 6/6(66), pp. 40–42, 2013.

[4] R.V. Nebesnyy, Z.H. Pikh, V.V. Ivasiv, V.V. Sydorchuk, I.I. Shpyrka, N.I. Lapychak, “Pidvyshchennya efektyvnosti B$_2$O$_3$–P$_2$O$_5$–WO$_3$–V$_2$O$_5$/SiO$_2$ katalizatora protsesu al’dol’noyi kondensatsiyi ostovoyi kysloty z formal’dehidom shlyakhom hidrotermal’noyi obrobki nosiya”, Visnyk Natsional’noho universytetu "L’vivs’ka politekhnika". Khimiya, tekhnolohiya rechovyn ta yikh zastosuvannya. № 841. pp. 113–118, 2016.