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ACRYLIC ACID OBTAINING BY ACETIC ACID CATALYTIC CONDENSATION WITH FORMALDEHYDE

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Досліджено процес одержання акрилової кислоти методом альдольної конденсації оцтової кислоти з формальдегідом на $V_2O_3-P_2O_5-WO_3/SiO_2$ катализаторі в газовій фазі. Показано перспективність даного методу як такого, що не потребує використання сировини нафтового походження. Встановлено вплив температури та часу контакту на процес конденсації; визначено оптимальні умови його здійснення

Ключові слова: акрилова кислота, гетерогенний катализ, газова фаза, альдольна конденсація, акрилатні мономери

Исследован процесс получения акриловой кислоты методом альдольной конденсации уксусной кислоты с формальдегидом на $V_2O_3-P_2O_5-WO_3/SiO_2$ катализаторе в газовой фазе. Показана перспективность данного метода как такого, который не требует использования сырья нефтяного происхождения. Установлено влияние температуры и времени контакта на процесс конденсации, определены оптимальные условия его осуществления

Ключевые слова: акриловая кислота, гетерогенный катализ, газовая фаза, альдольная конденсация, акрилатные мономеры

1. Introduction

Acrylic acid (AA) is a valuable organic synthesis product having wide application in production of high-quality polymer materials, super sorbents, paint-and-varnish materials etc. Wide application of AA and its derivatives causes annual expansion of AA production capacity. The latter reaches over 4.5 million ton per year to date. Main industrial method of AA production is propylene oxidation. However, the expedience of propylene use as raw material is directly related to petroleum and oil products availability in certain region and to the costs for them persistently trending to grow. Besides, when AA is produced by propylene oxidation, great number of various oxidation by-products, in particular CO and CO₂, is formed [1]. That is why development and improvement of alternative AA production methods is very topical.

2. Problem statement

The most promising AA production methods include:

- 1) AA synthesis from renewable raw materials using enzymes [2];
- 2) AA synthesis by direct propane oxidation [3];
- 3) AA synthesis by acetic acid (AcA) aldol condensation with formaldehyde (FA) [4].

The main disadvantage of the enzymatic AA production method is considerable process duration [5] negatively affecting the reaction equipment productivity. Direct propane oxidation to AA has very low target product formation selectivity [3]. Among listed methods the method of AA

production by AcA aldol condensation with FA has fair implementation prospects.

The great interest of chemical products manufacturers in the implementation of condensation processes by carbonyl group is related to the possibility of acrylic monomers production in low number of stages [6]. In addition, advantages of AA obtaining by condensation method include:

- expanding of raw materials base for the synthesis of AA and the possibility to avoid using of oil-derived raw materials. It is known that in industry FA and AcA are synthesized from methanol produced from synthesis gas, and a feedstock for synthesis gas obtaining is methane or coal. Considering the much larger global reserves of methane and coal compared to oil, the use of these raw materials for organic synthesis is more promising;
- more complete utilization of raw materials. This is achieved by the higher selectivity of the desired product formation.

However, industrial production of unsaturated acids, in particular AA, by carbonyl compounds aldol condensation method has not been set up, because of low efficiency of the process catalyst known.

3. Latest research review

In scientific and technical literature there are much information about AA gas-phase production when using both basic [7] and acidic catalysts [8]. However, most of them provide high conversion of AcA and FA only in case of considerable excess of one of the reactants.

In our earlier researches it has been determined that the $B_2O_3-P_2O_5/SiO_2$ catalyst promoting by transition metals oxides allows achieving high conversion of propionic acid (PA) and FA to the methacrylic acid (MAA) production process even at equimolar ratio of the reactants [9, 10]. The catalytic system $B_2O_3-P_2O_5-WO_3/SiO_2$ is most efficient among developed ones in methacrylic acid production by aldol condensation [10].

4. Optimal conditions of the process determination

The present study is aimed on determination of main regularities of AcA aldol condensation with FA to AA on the $B_2O_3-P_2O_5-WO_3/SiO_2$ catalyst.

The catalytic systems based on mixtures of boron, phosphorus and tungsten oxides with different components ratios have been prepared for the research. All catalysts were prepared by impregnation method. Silica was used as a support.

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

Formalin obtained from paraformaldehyde immediately before usage was used as a FA source.

The process was carried out at temperature ranged from 563 to 683 K and contact time ranged from 2 to 16 sec at equimolar initial reagents ratio. The reaction products were analyzed by chromatography.

As is shown on Fig. 1, when increasing contact time AcA, conversion substantially increases until the contact time value is 8 sec. Further contact time increase has almost no effect on AcA conversion. When raising the process temperature, AcA conversion rapidly increases reaching maximal value – 65.8 % at contact time of 16 sec.

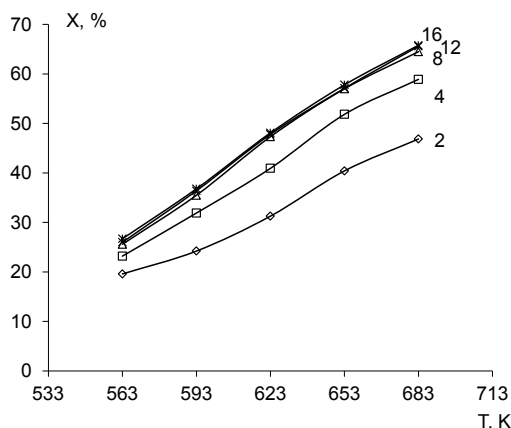


Fig. 1. Temperature T and contact time effect on acetic acid conversion X; contact time is 2-16 sec

The contact time dependence of AA formation selectivity is shown on Fig. 2. There is almost no effect of contact time on AA formation selectivity in the whole studied temperature range. The process temperature decrease results in the target product formation selectivity increase.

The higher selectivity values, namely 92.5 – 96.1 %, are observed in the temperature range 563 – 623 K. It should be noted that at high temperatures of AcA condensation with FA the unsaturated acid formation selectivity is considerably higher than in case of PA condensation with FA [11]. Thus, at

683 K and contact time 8 sec. the least AA formation selectivity is 74.7 %, while MAA formation selectivity under the same conditions is only 32.4 % [11].

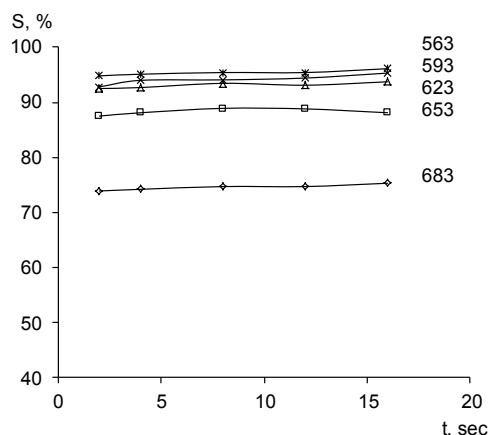


Fig. 2. Contact time t effect on acrylic acid formation selectivity S; temperature is 563 – 683 K

The contact time effect on AA yield is similar to its effect on AcA conversion. As is clear from Fig. 3, the rapid increase of the product yield is observed until contact time reaches 4 sec. hereafter until 8 sec. the yield increases more gradually. The further contact time increase over 8 sec. virtually does not lead to AA yield increase due to the insignificant AcA conversion increase under these conditions. So, 8 sec. may be considered to be the optimal contact time of AcA condensation with formaldehyde on the studied catalyst. It is also clear from Fig. 3 that 653 K is the optimal temperature in terms of AA yield.

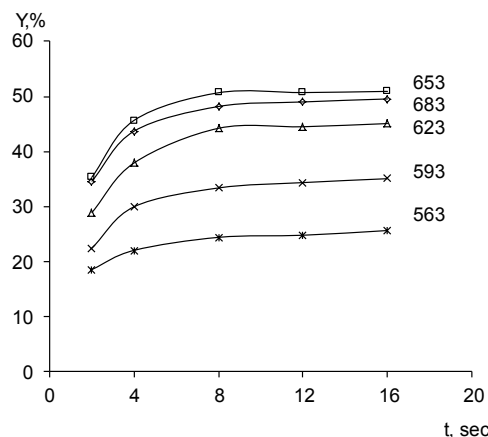


Fig. 3. Contact time t effect on acrylic acid yield Y; temperature is 563 – 683 K

When comparing the experimental results of the FA condensation with PA and AcA, it becomes clear that AA yield is higher than MAA yield [11]. It is because of the higher selectivity of the target product formation in case of AcA, that allows carrying out the process at higher temperature, at which the reactants conversion is considerably higher.

Thus, the research showed that the catalytic system $B_2O_3 - P_2O_5 - WO_3/SiO_2$ is efficient in FA condensation

with AcA. Using of the developed catalyst under the optimal conditions (temperature 653 K, contact time 8 sec.) allows to achieve AA yield equal to 50.6 %, while AA formation selectivity is 88.8 % and AcA conversion is 57.0 %. When recycling the unreacted AcA and FA, the AA yield would be 88.8 %.

5. Results approbation

The method of AA acid obtaining by AcA aldol condensation with FA when using the catalyst developed by us has not been industrially implemented to date. But in prospect it may be used for acrylic and methacrylic acid production from ethylene at operating ethylene producing plants, in particular at „Karpatnaftokhim” Ltd., Kalush, Ivano-Frankivsk region.

6. Acknowledgement

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7. Conclusions

The $B_2O_3-P_2O_5-WO_3/SiO_2$ catalyst use in AcA aldol condensation with FA allows AA obtaining with selectivity – 88,0%, single-pass yield – 50,6% and AcA conversion – 57,0% at equimolar reactants ratio. Acrylic acid production by the aldol condensation method would enable diversifying the raw materials base of acrylic monomers production. High efficiency of the developed catalyst confirms the expedience of the method as an alternative.

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