Single Stage Acrylic Acid Obtaining based on Methanol and Acetic Acid

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Abstract – The new complex oxide acid type catalysts were developed and their performance in the process of aldol condensation of acetic acid with formaldehyde to acrylic acid was studied. The optimum conditions of the process were determined. It was established that these catalysts are effective in the process of methanol to formaldehyde oxidation, and also in the process of single stage acrylic acid obtaining from acetic acid and methanol in the presence of air.

Key words – aldol condensation, oxidation, catalysts, acrylic acid, acetic acid, methanol, formaldehyde.

I. Introduction

Acrylic acid (AA) is a valuable product of chemical industry with a world production over 4 million tons per year. AA and its derivatives are used for production of the wide variety of valuable polymeric materials, paints, superabsorbents. AA also is used as intermediate for different functional materials production (microgels, hydrogels, drugs delivery systems, e.g.) [1].

The main industrial method of AA production is two stage propylene oxidation via the intermediate stage of acrolein obtaining [2]. This method is characterized by good economic efficiency and simplicity of technological designing but as it based on the oil raw material it is suitable only for the regions with good petroleum products availability. So in recent years growing of interest for extending of raw material base of AA obtaining and developing new methods of AA synthesis was observed. The promising method is AA production from renewable raw material – biomass (by using biological catalysts – enzymes) [3, 4].

Another one method which is of great interest to scientists is AA production based on formaldehyde (FA) and acetic acid (AcA) [5]. Both AcA and FA in industry are obtained from methanol (via carbonylation and oxidation reactions respectively) [6 – 8], and the common raw material for methanol production is synthesis gas which is obtained from natural gas or coal. Considering the much larger global reserves of natural gas and coal compared to oil, the use of these raw materials for organic synthesis is more promising.

The key for successful implementation of AA production based on AcA and FA is effective catalyst for this process. It is known that the reactions of aldol condensation may proceed through both, base and acidic catalysis. We have developed the catalysts of both types, and it also was found that acid catalysts have higher activity and efficiency than the base one [5, 9]. Also the correlation between the strength of acid sites of the catalysts and their selectivity was found [10]. It is an interesting fact that in recent years a lot of publications have been appearing which declare high efficiency of acid catalysts, particularly the catalysts based on metal oxides (Fe_2O_3, MoO_3, V_2O_5 etc.) in the process of methanol oxidation [8]. So we decided to continue our developments of acid catalysts for aldol condensation reaction and to test the best of them in the process of single stage AA obtaining based on methanol and AcA, combining methanol oxidation and subsequent reaction of the formed FA with AcA in one reactor on the same catalyst.

II. Results and Discussion

The first stage of present work is developing the new efficient catalysts for AA obtaining by aldol condensation of AcA with FA. So the new B–P–W–V–O_x/SiO_2 catalyst was developed and its catalytic properties were investigated at temperature range from 563 to 683 K, residence time 2 – 16 sec at equimolar initial reagents ratio.

The results showed that increase of residence time results in considerable increase of AA yield (Fig. 1). The exception is in temperature range 653 – 683 K where the maximum of yield is observed.

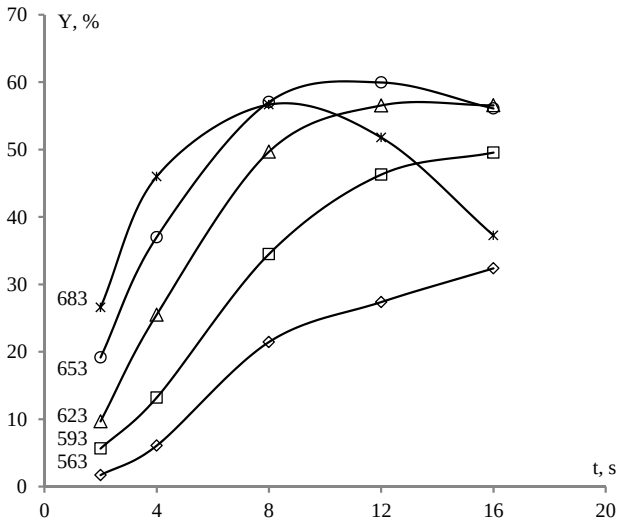

Fig. 1. Residence time effect on acrylic acid yield, temperature range 563 – 683 K

The maximum yield of AA obtaining within temperature range 653 – 683 K is caused by the specific dependence of selectivity of AA formation from residence time (Fig. 2). While the conversion of AcA is increasing within the whole residence time range (2 – 16 sec.) the selectivity of AA formation tends to decrease at longer residence time, especially at 653 – 683 K (Fig. 2). Within 563 – 623 K temperature range the selectivity of AA formation is high and almost is not influenced by residence time and temperature.

The investigated catalyst is developed for the industrial application, therefore the optimal conditions are chosen based on the maximum productivity of AA obtaining. The selectivity of AA formation is also an important factor. The desirable level of selectivity of AA formation (over 80 %) is achieved up to 653 K at contact time range 2-12 s. The maximum one pass yield of AA obtaining (60 %) was

obtained at 653 K at residence time 12 sec. But the optimum conditions of AA obtaining in terms of catalyst's productivity and selectivity is temperature 653 K and residence time 4 sec. At these conditions the one pass yield of AA obtaining is 37 % at selectivity of its formation 92 %.

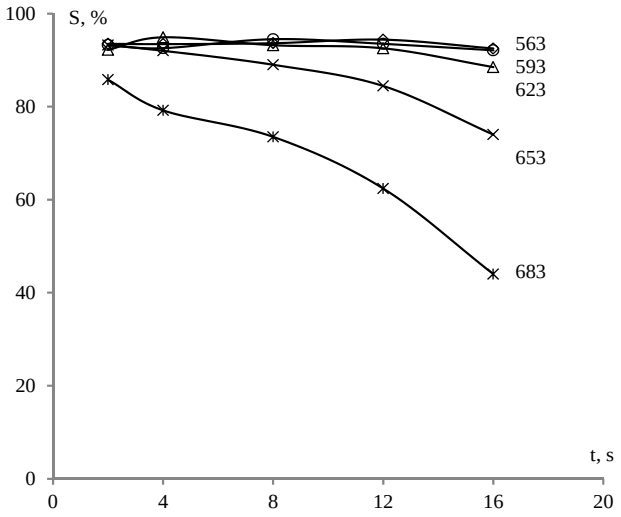

Fig. 2. Dependence of acrylic acid formation selectivity on residence time, temperature range 563 – 683 K

At these reaction conditions the developed catalyst was tested in the process of single stage AA obtaining based on methanol and AcA in the presence of air. The formation of AA has been detected. The reaction products were analyzed by chromatography. Under reaction conditions the one pass yield of AA obtaining is over 20 %.

Conclusion

Acrylic acid production by the aldol condensation of acetic acid with formaldehyde will provide diversifying the raw materials base of acrylate monomers production (makes it possible to use non-oil sources of the raw materials). Use of the developed B–P–W–V–O_x/SiO_2 catalyst allows for acrylic acid obtaining with one pass yield 37 % at selectivity of its formation 92 % and acetic acid conversion 40 % (residence time 4 sec., 653 K). In case of unreacted substances recycling, acrylic acid yield will be up to 92 %.

The very important fact is the same catalytic system shows efficiency in the process of single stage acrylic obtaining based on acetic acid and methanol in the presence of air. The one pass yield of AA obtaining is near 20 % at the same reaction conditions as in common aldol condensation method based on acetic acid and formaldehyde.

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