The Effect of Hydrothermal Treatment of Silica-based Catalysts on their Efficiency in Acrylic Acid Synthesis via Oxidative Condensation of Methanol with Acetic Acid

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Abstract – The effect of modification of the catalyst of oxidative condensation of methanol with acetic acid on acrylic acid and methyl acrylate selectivity and yield was determined. Hydrothermal treatment of the catalyst has been shown to significantly improve its catalytic properties during the oxidative condensation of acetic acid with methanol compared to the untreated catalyst. The maximum total acrylates yield (54.7 %) was obtained on the catalyst modified at 150 °C.

Keywords – acrylic acid, methyl acrylate, hydrothermal treatment, heterogeneous catalysis, oxidative condensation.

Introduction

Acrylic acid (AA) and methyl acrylate (MA) are valuable substances in the industry of organic synthesis, the total world production of which amounts to over 6 million tons annually [1]. One of the most promising methods of AA synthesis, which is of great interest to scientists, is based on formaldehyde (FA) and acetic acid (AcA) [2]. It is well known that in the industry FA and AcA are synthesized from methanol [3], produced from the synthesis gas, which in turn is produced from methane or coal. Considering a lot more abundant world reserves of methane and coal as compared to oil, use of these types of raw materials for organic synthesis is more promising.

The AA production by this method comprises of many stages, which can be reduced by combining methanol to formaldehyde oxidation stage with subsequent aldol condensation of formaldehyde with acetic acid stage on one catalyst in one reactor producing acrylic acid and methyl acrylate. However, currently there are no known catalysts that allow to efficiently produce the acrylic acid by the oxidative condensation of methanol with acetic acid.

It is well known that specific surface and porous structure of solid catalysts has a great influence on their catalytic properties in the processes of condensation carbonyl compounds. It was established that the preparation of catalysts has a essential effect on its physico-chemical properties, and therefore on catalytic properties in chemical reactions [4].

From previous studies[5], it is known that the catalytic system of the B-P-W-V-Ox is effective in the process of condensation of acetic acid with formaldehyde with the formation of acrylic acid and the porous structure of the catalysts has significant effect on the reaction parameters [6].

So, we decided to take this catalytic system as the base, modify it by hydrothermal treatment and test its efficiency in the process of oxidative condensation of AcA with methanol to AA and MA.

Experimental

To study the oxidative condensation process of AcA with methanol, catalytic systems were prepared based on mixtures of oxides of boron, phosphorus, vanadium and tungsten. First, a

support, such as silica gel of the KSKG brand (with a specific surface of 365 m^2/g), was submitted to hydrothermal treatment (HTT) in the gas phase in temperature range 100 – 250 °C (K_{1-7}) in a steps of 25 °C. Atomic ratio of components in catalyst B:P:W:V=3:1:0.18:0.12. The catalyst properties were investigated in a flow type reactor with a fixed catalyst bed, at the process temperature 400 °C, residence time 8 s and molar ratio of M:AcA=1,2:1.

Results and Discussion

The effect of the temperature of the HTT on the total selectivity of AA and MA and the total yield of AK and MA (Fig. 1) has been determined. As can be seen from fig. 1, the total selectivity of AA and MA decreases with increasing temperature of the HTT, and the total yield of AA and MA increases up to a temperature of 150 °C, and further increase in the temperature of the HTT leads to a gradual decrease in the total yield of AK and MA. Best results were obtained on the catalyst based on the support with HTT temperature 150 °C – acetic acid conversion – 68,2 %, total selectivity of AA and MA 80,1 % and total yield of AA and MA 54,7 % under optimum conditions of the process temperature 400 ºC and residence time 8 s.

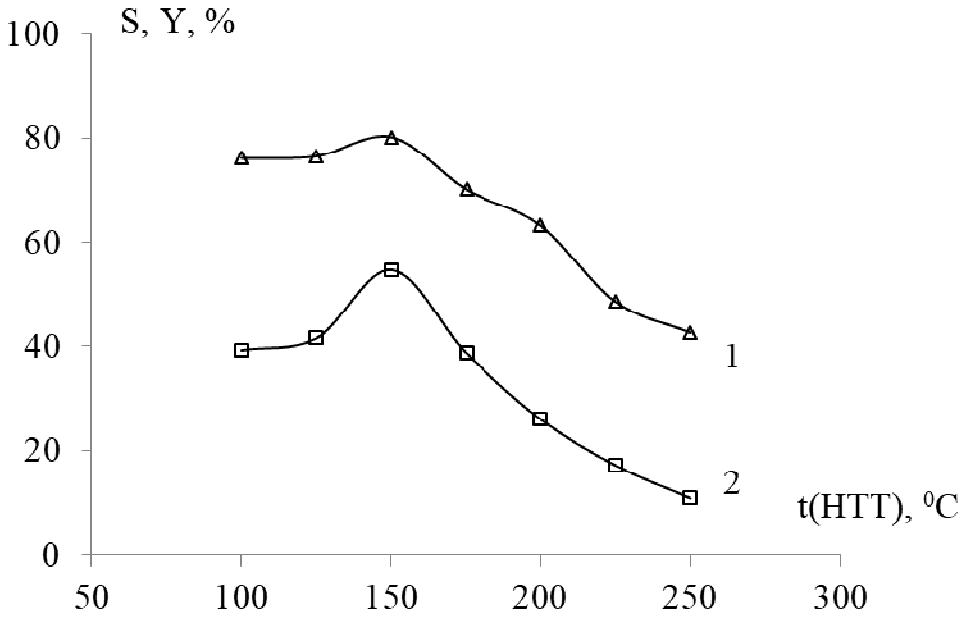

Fig.1. The effect of the support HTT temperature on the total selectivity of AA and MA (1) and the total yield of AA and MA (2). Residence time 8 s; temperature of the process 400 ºC.

On the catalyst with untreated support maximum total yield of acrylates is 34,9 % with a total selectivity 76,1 % and AcA conversion of 47,9 %. Comparing the results obtained on a catalysts with treated and untreated support shows that HTT of the catalyst support can significantly improve its catalytic properties in the oxidative condensation of AcA with methanol in AA and MA (Fig. 2).

Conclusion

The silica gel of KSKG brand was hydrothermally treated and used as support for B_2O_3-P_2O_5-WO_3-V_2O_5 catalytic system with the atomic ratio of components B:P:W:V=3:1:0.18:0.12. It was found that the best catalyst for the process of acrylic acid and methyl acrylate synthesis by oxidative condensation of AcA with methanol is the catalyst with support treated with HTT at temperature 150 °C. Under the optimum conditions of the process temperature 400 ºC and residence time 8 s it is possible to obtain acrylic acid and methyl acrylate with 54,7 % total yield

and 80,1 % total selectivity, at acetic acid conversion 68,2 %. It was confirmed that hydrothermal treatment of the catalyst's support can significantly improve its catalytic properties in the oxidative condensation of AcA with methanol in AA and MA compared to the catalyst on untreated support. Therefore the hydrothermal treatment of the catalyst's support can be considered as an instrument to control selectivity of the oxidative condensation of methanol with acetic acid to acrylic acid and methyl acrylate.

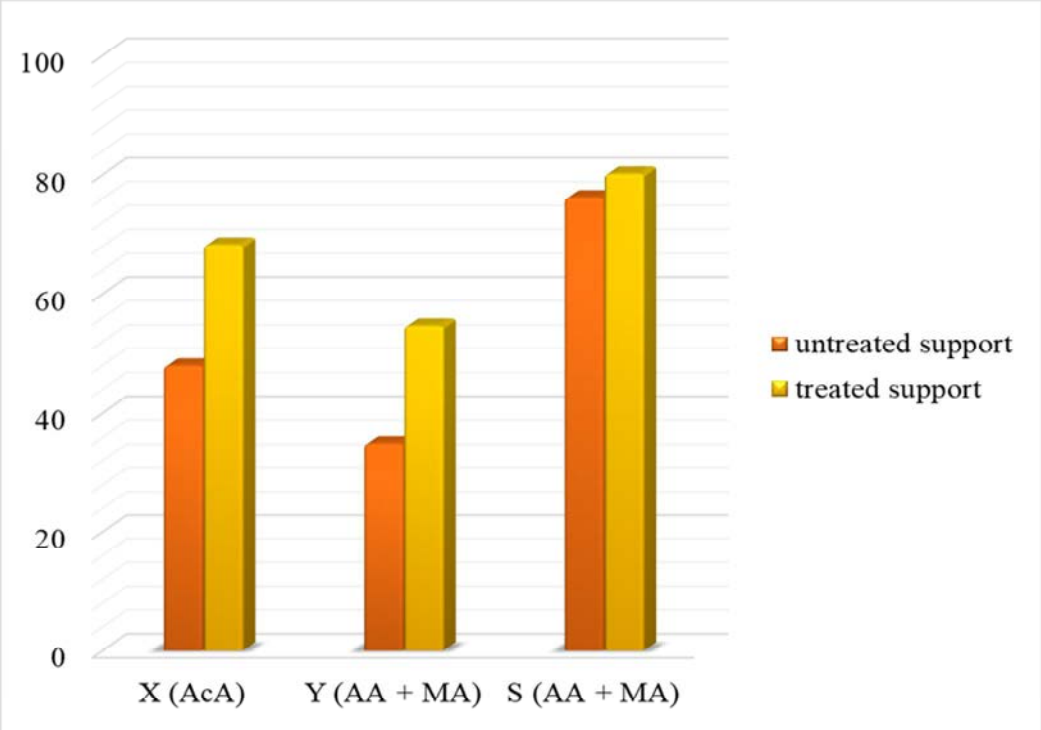

Fig.2. Comparison of catalytic activity under optimal conditions on the catalysts with treated and untreated supports in oxidative condensation of methanol with acetic acid.

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