

# Acrylic and Methacrylic Acids Obtaining by Gas-Phase Aldol Condensation of Carbonyl Compounds on $B_2O_3-P_2O_5-WO_3-V_2O_5/SiO_2$ Catalysts

Roman Nebesnyi, Oksana Petelka,  
Iryna Shpyrka

Department of Organic Products Technology, Lviv Polytechnic  
National University, UKRAINE, Lviv, S. Bandery street 12,  
E-mail: nebesnyi@lp.edu.ua

**Abstract – Prospects of acrylic acid obtaining by acetic acid aldol condensation with formaldehyde are considered. Complex oxide catalysts of the process have been developed. It is shown that raw materials costs in case of acrylic acid production by the condensation method are commensurable with those in case of its production by oxidation method (main industrial method of acrylic acid production). This method of acrylic acid obtaining may be used as an alternative and enables diversifying the raw materials base of acrylic monomers production. It is shown that the developed catalyst is also efficient in propionic acid aldol condensation with formaldehyde to methacrylic acid.**

Key words – acrylic acid, methacrylic acid, acrylic monomers, aldol condensation, gas phase, heterogeneous catalysis.

## I. Introduction

Acrylic acid (AA) and methacrylic acid (MAA) are bulk products of organic synthesis industry. Main industrial method of AA production is propylene oxidation through intermediate acrolein formation stage [1, 2]. Main industrial production methods of methylmethacrylate (MMA) and MAA, as an intermediate when producing MMA, include acetone cyanohydrin process [3, 4], isobutylene oxidation to MAA through intermediate methacrolein formation stage [5, 6] and propionic aldehyde aldol condensation with formaldehyde to methacrolein followed by oxidation of the latter to MAA [7, 8]. Disadvantage of AA and MAA production by corresponding olefins (propylene and isobutylene) oxidation include is formation of great number of various oxidation by-products, in particular CO and CO<sub>2</sub> (especially in case of isobutylene oxidation). MAA obtaining via intermediate stage of propionic acid aldehyde aldol condensation and acetone cyanohydrin method are multistage processes. In addition, highly toxic cyanic acid is used in acetone-cyan-alcohol method and great amount of ammonium wastes are formed.

It is important to underscore that the expedience of propylene and isobutylene use as raw materials is directly related to petroleum and oil products availability in certain region and to the costs for them persistently trending to grow.

Our researches are aimed on the development of alternative resource-saving and environmentally safe

method of AA and MAA obtaining based on non oil-derived raw materials. Having regard to all this things, we suggest to obtain AA by gas-phase catalytic condensation of acetic acid (AcA) with formaldehyde (FA), as well as MAA by gas-phase catalytic condensation of propionic acid (PA) with FA.

The main problem of industrial implementation of this AA and MAA production method is lack of the catalysts efficiency in the aldol condensation of AcA and PA with FA.

The main advantages of AA obtaining by condensation method are:

1. Expanding of raw materials base for the synthesis of AA and the possibility to avoid using of oil raw materials. It is known that in industry AcA and formaldehyde (FA) 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.

2. More complete utilization of raw materials. This is achieved by the higher selectivity of the desired product formation.

3. Environmentally safe method. Substantially fewer amounts of CO and CO<sub>2</sub> are formed compared to propylene oxidation method.

Concerning MAA obtaining by PA condensation with FA, the latter may also be obtained from synthesis gas through intermediate stage of methanol formation. However, the most reasonable industrial method of propionic acid production is ethylene hydrocarbonilation. So, in case of MAA obtaining by condensation method only part of the raw materials can be of non-oil origin.

In our earlier researches [9 – 12] we have ascertained that complex catalytic oxide systems based on boron oxide, phosphorus oxide and the oxide chosen from the range: zinc oxide, vanadium oxide, molybdenum oxide and tungsten oxide, are highly efficient in AcA (PA) Aldol condensation with FA to AA (MAA). It has been shown that the high catalytic activity is related to surface acidity of the catalysts. Thus, the catalyst containing vanadium oxide has highest catalytic activity and highest value of surface acidity. It has also been shown that there is inverse dependence of MAA formation selectivity on acid sites strength [7]. The highest selectivity of target product formation is observed in case of the catalyst with lowest acid sites strength (the catalyst containing tungsten oxide).

In consideration of such regularities we decided to modify the most efficient catalyst of AA and MAA obtaining ( $B_2O_3-P_2O_5-WO_3/SiO_2$  with the components atomic ratio B:P:W = 3:1:0.3), by introducing vanadium oxide into its composition. It was expected that this would increase the catalyst surface acidity (i.e. number of active sites) and, consequently, raise the initial reactants conversion.

## II. Results and Discussion

The catalysts based on silica-supported mixture of oxides  $B_2O_3$ ,  $P_2O_5$ ,  $WO_3$ ,  $V_2O_5$  were used for the research. All catalysts were prepared by impregnation

method. Atomic ratio of the components B:P:(W+V) was equal to 3:1:0,3.  $WO_3$  and  $V_2O_5$  content was changed in such a manner to provide the vanadium fraction in the mixture of transition metals oxides ( $WO_3 + V_2O_5$ ) to be equal to 20 % ( $K_1$ ), 40 % ( $K_2$ ), 60 % ( $K_3$ ) and 80 % ( $K_4$ ).

The condensation reactions were carried out in flow reactor with impulse feeding of the reactants and fixed-bed catalyst. Reaction products mixture was analysed chromatographically. AR grade chemicals were used for the aldol condensation reactions and for the catalyst preparation. Formalin with formaldehyde content of 36 % by wt. was used as a source of FA. The formalin was prepared from polyformaldehyd immediately before its application.

To determine the best ratio of tungsten and vanadium oxides in the catalyst of AcA condensation with FA the experiments were carried out at the reactants molar ratio AcA (PA):FA = 1:1, temperature 563 – 683 K and contact time 12 sec.

The only by-product under reaction conditions used is acetone (it is a product of two AcA molecules condensation inter se). It should be isolated as a marketable product.

In the case of MAA obtaining diethylketone is formed as a by-product (it is a product of two PA molecules condensation inter se).

As can be seen in Fig. 1, AcA conversion increases when increasing vanadium content in vanadium-tungsten mixture and raising the process temperature. The increase of the catalyst activity is, probably, caused by the increase of active acid sites number due to vanadium oxide addition. The highest conversion value registered is 78.5%. It has been reached at 683 K and vanadium content in vanadium-tungsten mixture equal to 20%.

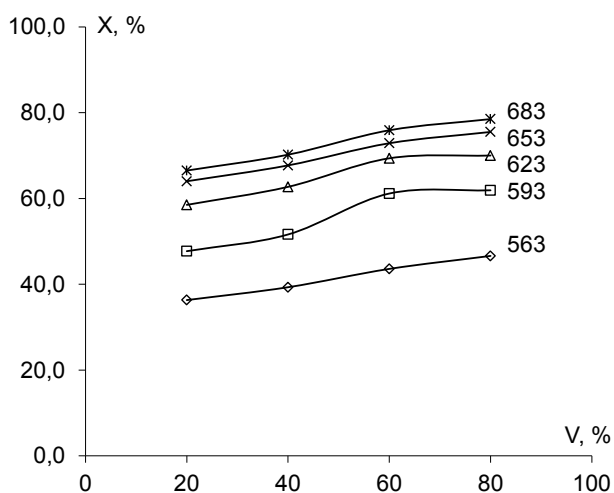


Fig. 1. Acetic acid conversion dependence on vanadium content in the mixture vanadium-tungsten, entering into the catalysts composition

Dependence of AA formation selectivity has the appearance of extreme curve (Fig. 2). Initially, vanadium content raise leads to very weak change (gradual increase) of target product formation selectivity, but after reaching 60 % content of vanadium in vanadium-tungsten mixture the selectivity starts reducing. High selectivity of AA

formation is observed at 563 – 593 K. Temperature raise above 593 K results in significant decrease of the selectivity at all studied ratios V:W. Maximum selectivity was reached at 563 K and vanadium content in the mixture equal to 60 % – 95.5 %.

AA yield dependence on vanadium content (Fig. 3) has a maximum at 60 % of vanadium in vanadium-tungsten mixture in all studied temperature range. Thus, vanadium content in vanadium-tungsten mixture equal to 60 % is optimal in terms of the target product yield.

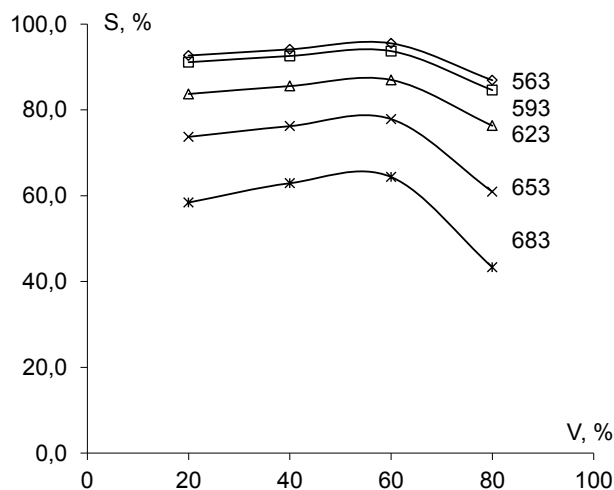


Fig. 2. Dependence of acrylic acid formation selectivity on vanadium content in the mixture vanadium-tungsten, entering into the catalysts composition

Maximal value of AA yield (60.3 %) is achieved at 623 K. However, AA formation selectivity is only 87.0 % at this temperature. At the same time, when the process temperature is lower by 30 K (593 K) AA formation selectivity is considerably higher – 93.9 %, while AA yield is lower only by 2.9 %. From this point of view it is unreasonable to carry out the process at 623 K.

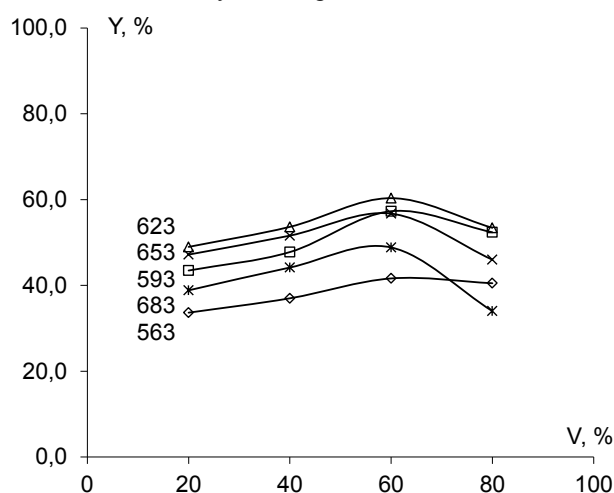


Fig. 3. Acrylic acid yield dependence on vanadium content in the mixture vanadium-tungsten, entering into the catalysts composition

Thus, temperature of 593 K is the optimal temperature of AcA aldol condensation with FA to AA. The best catalyst is one with vanadium content in vanadium-

tungsten mixture equal to 60 %. Under such conditions AA yield is 57.4 % and selectivity of its formation is 93.9 %.

When using the catalyst without vanadium oxide ( $B_2O_3-P_2O_5-WO_3/SiO_2$ ) under the optimal conditions AA yield is 50.6 %, when selectivity of its formation is 88.8 % and AcA conversion is 57.0 %. Thus, the partial substitution of tungsten oxide by vanadium oxide in the catalyst composition made it possible to improve the catalyst activity (conversion) by 4.1 %, while the target product formation selectivity rises by 5.1 % and AA yield increases by 6.8 %. Moreover, the optimal temperature of the process is reduced from 653 K to 593 K, enhancing the production energy efficiency.

Based on the results obtained let us compare the economic efficiency of AA production by propylene oxidation method (basic industrial AA synthesis method) and by the method of AcA aldol condensation with FA on the developed catalyst.

TABLE 1

COMPARISON OF ECONOMIC EFFICIENCY OF AA PRODUCTION METHODS

Raw material	Raw material price, €/t	Existing method		Developed method	
		kg/t of MMA	€/t of MMA	kg/t of MMA	€/t of MMA
Propylene	1210	720.2	871.4	-	-
Acetic acid	600	-	-	887.5	532.5
Formalin	284	-	-	1126.1	319.8
Total			871.4		852.3

*Note: Discharge coefficients for propylene, AcA and FA were calculated based on material balances of the processes. Calculations were made in terms of overall selectivity of AA formation with regard to propylene to be equal 81.0 % at conversion of the latter equal to 92.5 % [7]. AA formation selectivity with regard to AcA is 93.9 % at AcA conversion equal to 61.1 %. Discharge coefficients were calculated subject to recycling of unreacted raw materials. In such case AA yield is 81 % (propylene oxidation method) and 93.9 % (method of AcA condensation with FA).*

As is clear from Table 1, the raw materials costs in case of AA production by the condensation method is less by 2.2 %. Herewith one should bear in mind that world AA production capacity exceeds 4 million tons per year and keeps growing.

The  $B_2O_3-P_2O_5-WO_3-V_2O_5/SiO_2$  catalyst with atomic ratio V:W = 3:2 has been investigated in PA aldol condensation with FA to MAA. The developed catalyst is highly active in this process. As is shown in Fig. 4, PA conversion increases rapidly in whole temperature range and reaches 67.4 % at 683 K (contact time 12 sec.). The target product (MAA) formation selectivity, in contrast, decreases, when raising the temperature. Acceptable selectivity of MAA formation (93.4 – 77.6 %) is achieved at 593 – 623 K. At 653 K MAA formation selectivity is only 54.4 %. Optimal temperature in terms of MAA yield is 623 K. At this temperature MAA yield is maximal – 46.2 %, and selectivity of its formation is 77.6 % and PA conversion is 59.5 %. When using the original  $B_2O_3-$

$P_2O_5-WO_3/SiO_2$  catalyst (without vanadium oxide) under the same conditions MAA yield is less – 43.3 %, however, MAA formation selectivity is higher – 81.4 %. However, optimal conditions of the process with  $B_2O_3-P_2O_5-WO_3/SiO_2$  catalyst are: temperature – 593 K and contact time – 12 sec. At this conditions MAA yield is 44.1 %, while PA conversion is 47.1 % and MAA formation selectivity is considerably higher – 93.7 %. When using the  $B_2O_3-P_2O_5-WO_3-V_2O_5/SiO_2$  catalyst at 593 K, MAA yield is 44.4 %, while MAA formation selectivity is relatively low – 85.5 %.

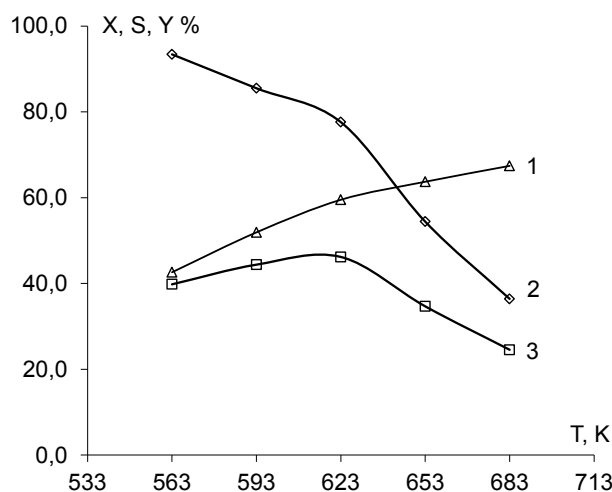


Fig. 4. Propionic acid conversion (1), methacrylic acid formation selectivity (2) and methacrylic acid yield (3) dependence on temperature. Atomic ratio V:W = 3:2

## Conclusion

New efficient catalysts of acetic acid Aldol condensation with formaldehyde to acrylic acid have been developed. Optimal quantitative composition of the catalytic system  $B_2O_3 - P_2O_5 - WO_3 - V_2O_5/SiO_2$  and optimal conditions of its application has been found out. Use of the developed catalyst enable acrylic acid obtaining with yield – 57.4 % at selectivity of its formation – 93.9 % and acetic acid conversion – 61.1 %. In case of unreacted substances recycling acrylic acid yield is 93.9 %.

Acrylic acid production by the aldol condensation method would enable diversifying the raw materials base of acrylate monomers production (makes it possible to use non-oil sources of the raw materials). High economic efficiency of the AA production method by aldol condensation when using the catalyst developed by us confirms the expedience of the method using as an alternative.

Use of the same catalytic system in propionic acid aldol condensation with formaldehyde enable methacrylic acid obtaining with yield – 46.2 % at selectivity of its formation – 77.6 % and propionic acid one-pass conversion – 59.5 %.

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