

ACRYLIC ACID SYNTHESIS. CONVENTIONAL (OIL-BASED) METHOD VS NEW APPROACHES

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Acrylic acid (AA) is a valuable monomer, world production of which amounts near 5 million tons annually. AA is used for production of paints, dispersants, textile auxiliaries etc. [1 – 5]. In last decade the amount of superabsorbent polymers production based on AA was rapidly increased [5]. It causes AA market growing by 3 – 6 % annually and this growing will continue in long run trend.

The conventional method of AA production is the two-step propylene oxidation via intermediate stage of acrolein formation [6]. This method is characterized by good economic efficiency and simplicity of technological design, but it is based on oil feedstock and therefore is strongly dependent on highly volatile oil market. During 2005 – 2014 oil prices were high enough to cause a problem of diversification of AA raw materials base and high relevance of new methods of AA production development. And development of methods of renewable AA synthesis has become a new trend. Based on this point of view the most promising methods are AA synthesis based on glycerol and AA synthesis based on biomass. Another method which also can be considered as a method of renewable AA synthesis is aldol condensation of acetic acid with formaldehyde (via the scheme: biomass – syngas – methanol – acetic acid and formaldehyde – acrylic acid).

The aim of this paper is to compare the most promising methods of AA production with the conventional (oil-based) one.

Glycerol based acrylic acid. An interest to this approach increased with biodiesel boom. The reason is the by-product of biodiesel production is glycerol which became widely accessible and comparably inexpensive raw material (Fig. 1). There are numerous publications regarding glycerol oxidehydration into acrolein and acrylic acid. And W–V–Nb–O bronzes catalysts are among the most efficient ones [7]. It was also reported one-pot glycerol oxidehydration to acrylic acid over multifunctional catalysts [8]. But the highest AA yield does not exceed 50.5 %.

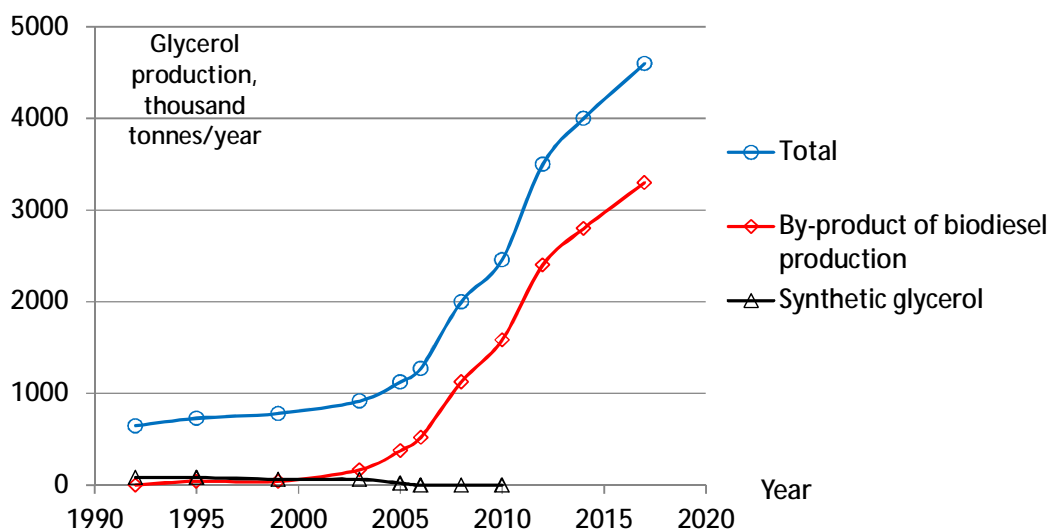


Fig. 1 Global glycerol production

Biomass based acrylic acid. Production of AA from renewable raw materials is carried out by fermentation of biomass to lactic acid with further dehydration to AA. Ca–Cu–Na–K sulfates were reported as efficient catalysts of lactic acid to AA dehydration [9]. The separation and purification of lactic acid from fermentation broth is a difficult process because of the unlimited solubility of lactic acid in water. An alternative procedure was achieved by forming methyl lactate first and then purifying it via distillation, followed by hydrolysis of methyl lactate to lactic acid. It was reported methyl lactate could be used as feedstock for the production of other chemicals such as acrylic acid and save energy costs [10]. The AA yield or the total AA and methylacrylate yields are near 63 %. The principal weakness of this approach (biomass based AA) is considerable duration of the process [11] and consequently low productivity of reaction equipment.

Condensation methods. The reactions of aldol condensation of carbonyl compounds are among the most promising methods of acrylic monomers production. AA synthesis via the route: biomass – syngas – methanol – acetic acid and formaldehyde – acrylic acid can be considered as a renewable method of acrylic acid synthesis. All stages of the specified method, except the last one, are implemented industrially. However, aldol condensation of acetic acid (AcA) with formaldehyde (FA) to AA is not realized in practice due to insufficient performance of known catalysts for this stage. Nevertheless, the number of studies devoted to this process has been increased recently.

Different approaches were used for efficient catalysts development: acid type catalysts [12], base type catalysts [13], as well as bi-functional type catalysts [14] were synthesized and tested for acrylic monomers synthesis via aldol condensation reaction. Also different supports were used for catalyst synthesis: SiO₂, TiO₂, ZrO₂, Nb₂O₅, Sb₂O₃, Al₂O₃, and the effect of support-oxide interaction on catalytic performance in aldol condensation processes was reported [15]. So the qualitative and quantitative composition of the catalyst, acid-base characteristics of the catalysts surface and support-oxide interaction were found as the factors affecting its catalytic performance in aldol condensation of carbonyl compounds.

In recent researches it was reported that the use of SBA-15 carrier for V-P-O catalyst may be efficient in AA and methylacrylate synthesis [16]. And, like in other papers, the catalytic performance was associated just with acid–base properties of catalyst which is caused by support type and the P/V atomic ratio.

In our previous researches it was determined that B–P–W–V–O_x/SiO₂ catalysts are rather efficient in gas-phase aldol condensation of AcA with FA to AA [17]. It was found out that the optimal atomic ratio of the catalyst components B:P:(W+V) is 3:1:0.3; and the optimal atomic ratio W:V is 2:3. The application of this catalyst allows to achieve 57 % AA one pass yield.

It is well known that efficiency of its use as a catalyst depends on many physical-chemical characteristics, namely specific surface area, porous and crystal structure, surface acidity. The latter can be varied within wide range by hydrothermal treatment (HTT). So it was interesting to determine the effect of hydrothermal treatment of the silica support of B–P–W–V–O_x/SiO₂ catalysts on its properties in condensation reactions. Thus, to regulate the porous structure of the support, latter was subjected to HTT in the temperature range 100-250°C for 3 h.

As it can be seen from the Fig. 2, the maximum on curves of pore size distribution (PSD) is shifted towards higher values of pore diameter when temperature of HTT increases. The catalyst supported on silica and subjected to HTT at 150 °C is characterized by the highest catalytic performance. We associate the increasing of catalysts performance mostly with changing of pore size distribution of the catalysts surface. In addition to increase of mechanical strength of silica gel granules subjected to hydrothermal treatment, reduction of coke formation takes place, as well as prolongation of the catalysts life.

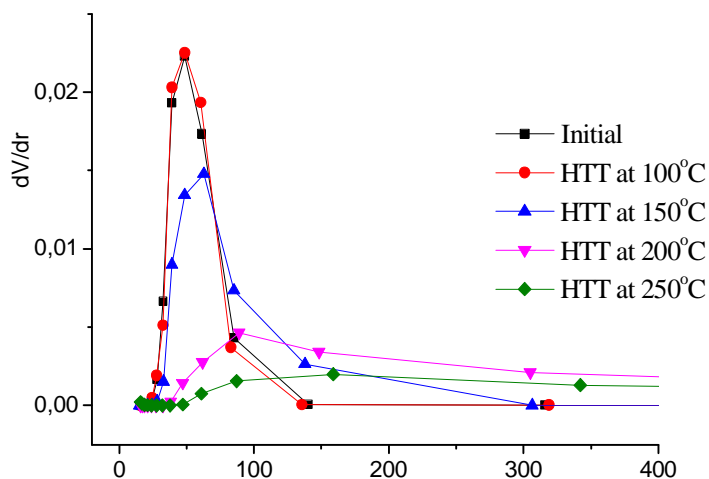


Fig. 2. PSD-curves for B-P-W-V-O_x catalyst supported on silica and treated by HTT at various temperatures

B-P-W-V-O_x/SiO₂ catalysts are also efficient in oxidative condensation process (oxidative condensation of methanol with acetic acid to acrylic acid and methylacrylate (Table. 1)). The feature of this process is simultaneous obtaining of two valuable monomers – AA and methylacrylate.

Table 1

Performance of the B-P-W-V-O_x/SiO₂ catalysts in aldol condensation and oxidative condensation processes (at optimal conditions)

Parameter \ Process	Aldol condensation		Oxidative condensation	
	Untreated catalyst	Treated catalyst	Untreated catalyst	Treated catalyst
Conversion, %	64	75	38	57
Selectivity, %	89	91	93	93
One pass yield, %	57	68	32*	50*

* - Total yield of acrylic acid and methylacrylate

Oil based acrylic acid. The method of AA production from propylene via intermediate stage of acrolein formation became quite popular since 80s of the 20th century. AA yield based on propylene is near 81 % [18]. Both stages are carrying out in flow rate reactors with fixed catalyst bed. The regular temperature for propylene oxidation is 350 °C and for acrolein oxidation 320 °C. The reaction steam moves to the second stage without separation.

Relative oil market stabilization after 2014 remains this method of AA production as the most preferable in terms of economic efficiency. But there are series of publications regarding direct propane oxidation to AA [19]. The reason is propane is much cheaper raw material. But due to low AA selectivity this method is still under development.

Taking into account that fact acrolein is the intermediate product of high scale AA production (conventional method) and also intermediate product of one of the most promising alternative (green) methods of AA production (based on glycerol), improving the performance of acrolein oxidation catalysts is of high interest.

Thus, highly selective unsaturated aldehydes oxidation in the presence of inorganic Se-containing catalysts was reported [20]. But the use of water soluble catalysts causes the problem of reagents separation and catalysts separation and reuse. To solve this problem we use novel type

of acrolein oxidation catalysts – Se-containing microgel-based colloidal organocatalysts. Use of these catalysts allows us to convert acrolein to AA or methylacrylate (in methanol medium) at high one pass yield as well as high selectivity (up to 97 %). Another huge advantage of these catalysts is simplicity of catalysts separation and reuse. Besides, the process is carrying out at mild reaction conditions (at 50 °C and atmospheric pressure) (Table 2).

Table 2

Comparison of the methods of acrylic acid and methylacrylate synthesis

Method of acrylic acid production	Reagent conversion, %	Acrylic acid selectivity, %	Methylacrylate selectivity, %	Total acrylates one pass yield, %	Temperature, °C
Acrolein oxidation (industrial process)	94	89	0	84	320
Glycerol oxidehydration	100	50.5	0	50.5	265
Biomass conversion via lactic acid	-	-	-	63.7	330
Biomass conversion via methylactate	76	54.3	26.4	61.3	400
Aldol condensation of acetic acid with formaldehyde	75	91	0	68	380
Oxidative condensation of methanol with acetic acid	57	89	4	50	400
Oxidative esterification of acrolein with methanol using Se-containing microgel catalysts	93	0	97	90	50

Taking into account the summarising results (Table 2), all considered approaches of acrylic acid (methylacrylate) synthesis are highly competitive. And industrial implementation of them will facilitate the expansion of raw materials base of AA production as well as reduction of its price.

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References:

- [1] X. Zhang, L. Lin, T. Zhang, H. Liu, Chem. Eng. J., 2016, 284, 934–941.
- [2] G.Nafe, M. López-Martinez, M. Dyballa et al. J. Catal., 2015, 329, 413–424.
- [3] C. Peterson, J. Chapman and J. Gallacher, US Pat., 8864950 B2, 21 Oct 2014.
- [4] C. Peterson and J. Chapman, US Pat., 20130085303 A1, 4 Apr 2013.
- [5] H. S. Chu, J. H. Ahn, J. Yun, I. S. Choi, T. W. Nam and K. M. Cho, Metab. Eng., 2015, 32, 23–29.
- [6] M. Tanimoto, D. Nakamura, T. Kawajiri, US Pat., 6545178, 08 Apr 2003.
- [7] A. Chierogato, F. Basile, P. Concepción et al. Catal. Today J., 2012, 197, 58-65.
- [8] A. Chierogato, M. D. Soriano, F. Basile et al. J. Applied Catal. B: Environmental, 2014, 150-151, 37-46.
- [9] J. Zhang, J. Lin, P.Cen, Canadian J. of Chem. Eng., 2008, 86, 1047-1053.
- [10] J. Zhang, J. Lin, X. Xu, P.Cen, Chinese J. of Chem. Eng., 2008, 16, 263-264.
- [11] C. Gao, C. Ma, P. Xu. J. Biotechnology Advances, 2011, 29, 930–939.
- [12] D. Yang, C. Sararuk, K. Suzuki, Z. Li, C. Li, Chem. Eng. J., 2016, 300, 160-168.
- [13] X. Guo, D. Yang, C. Zuo, Z. Peng, C. Li, S. Zhang, Ind. Eng. Chem. Res., 2017, 56, 5860–5871.
- [14] D. Yang, D. Li, H. Yao, G. Zhang et al., Ind. Eng. Chem. Res., 2015, 54, 6865–6873.
- [15] H. Zhao, C. Zuo, D. Yang, C. Li, S. Zhang, Ind. Eng. Chem. Res., 2016, 55, 12693–12702.
- [16] J. Hu, Z. Lu, H. Yin, W. Xue, A. Wang, L. Shen, S. Liu, J. of Ind. and Eng. Chem., 2016, 40, 145-151.
- [17] R. Nebesnyi, East.-Eur. J. of Ent. Tech., 2015, 73, 13-16.
- [18] J-I. Dubois, F. Desdevises, F. Desdevises, S. Serreau, US Pat., 734519, 18 Mar 2008.
- [19] C. Klanner, M. Dieterle, G-P. Schindler, US Pat 7388106, 17 June 2008.
- [20] Z. Pikh, R. Nebesnyi, V. Ivasiv, A. Pich, S. Vynnytska, J. Chem. & Chem. Tech., 2016, 10, 401-411.