Catalysts of Aldol Condensation of Acetic Acid with Formaldehyde

Iryna Shpyrka[1], Roman Nebesnyi[1], Volodymyr Sydorchuk[2], Svitlana Khalameida[2], Volodymyr Ivasiv[1], Kateryna Zavalii[1]

1. Technology of Organic Products Department, Lviv Polytechnic National University, UKRAINE, Lviv, S. Bandery street 12, E-mail: *iryna.i.shpyrka@lpnu.ua*

2. Institute for Sorption and Problems of Endoecology of NAS of Ukraine, UKRAINE, Kyiv, Naumova street 13, E-mail: bilychi@ukr.net

Abstract – it had been demonstrated that mechanochemical and hydrothermal treatment of support allows increasing activity and selectivity of the catalyst in the studied process. Hydrothermal treatment (HTT) of silica increases mechanical strength of silica gel granules subjected to hydrothermal treatment, also reduction of coke formation takes place, as well as prolongation of the catalysts life. Similarly, the same approaches allow to optimize the pore structure of titanium phosphates.

Keywords – acrylic acid, aldol condensation, mechanochemical treatment, hydrothermal treatment, porous structure.

I. Introduction

Acrylic acid (AA) is a valuable substance in the industry of organic synthesis and is widely used in the production of high-quality paint and varnish, organic glass, as an auxiliary substance in the textile industry, in the production of superabsorbents, in medicine [1-4]. World production of AA amounts to over 5 million tons per annum, and according to analytical studies, the market of acrylate monomers has a steady upward trend [5]. One of the most promising methods of AA production is aldol condensation of acetic acid (AcA) with formaldehyde (FA) [6]. The production of AA by aldol condensation is not implemented in industry because of comparably low efficiency of known catalysts and short working life due to coke formation on catalysts' surface [7].

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 synthesized the catalysts of both types and found that acid catalysts have higher activity and efficiency than the base ones [8,9]. Also the correlation between the strength of acid sites of the catalysts and their selectivity was found [10]. But despite of some success in the catalysts development, the desirable level of their efficiency isn't still achieved.

It is well known that porous structure of solid catalysts has a huge effect on their catalytic properties. So we decided to continue our developments of catalytic systems for aldol condensation reaction and to apply different kinds of treatment of the catalysts in order to modify their crystal structure, activate surface and, as a result, change their catalytic properties [11]. This kind of modification also allows to vary parameters of porous structure (specific surface area (S), pore size (d) and pore size distribution (PSD)) in wide limits [12].

II. Results and Discussion

It is well known that efficiency of catalysts of aldol condensation reactions depends on many physical and chemical characteristics, namely specific surface area, porous and crystal structure, surface acidity. So, different kinds of catalysts were tested in this process: acid and basic type catalysts, supported and bulk solid catalysts, the catalysts with various carriers. Recently using of structured carriers for aldol condensation catalysts was reported as well as the huge effect of porous structure of catalysts on their chemical properties. So in this context, application of different kinds of catalysts treatment (hydrothermal, microwave and mechanochemical), which are able to vary the physical and chemical characteristics of catalysts within wide limits, can be considered as the alternative method for porous structure regulation and optimization of the catalytic properties [12]. Therefore, the goal of present work is to study the efficiency of hydrothermal methods for the regulation of porous structure of the catalysts for aldol condensation reaction as well as optimization of their catalytic performance in acrylic acid synthesis, for which we tested the effect of hydrothermal treatment of B_2O_3–P_2O_5–WO_3–V_2O_5/SiO_2 and hydrothermal and mechanochemica treatments of $TiPO_4$ catalysts which are moderately efficient in gas-phase acrylic acid synthesis via aldol condensation.

It has been found that hydrothermal treatment (HTT) of silica support of B–P–V–W–O_x catalyst at 150 °C allows increasing the one-pass yield of acrylic acid synthesis from 58 % to 68 % at acrylic acid selectivity of 91 %. 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.

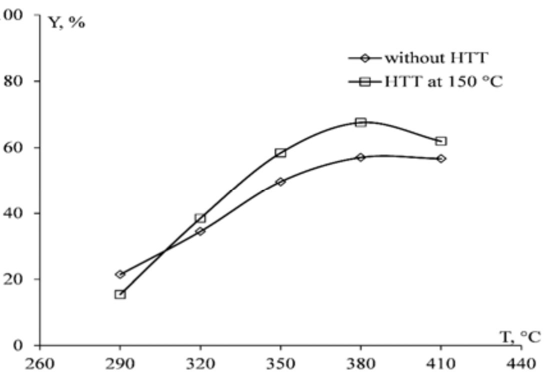

Fig.1 The effect of HTT temperature on Acrylic Acid yield (Y, %) at different reaction temperatures.

As expected, mechanochemical and hydrothermal treatment of TiPO4 catalyst also modifies its porous structure (Table 1). But in this case specific surface area changes are insignificantly.

As for catalytic properties in aldol condensation reaction of AcA with FA, the formation of AA on pure $TiPO_4$ was negligible (Fig. 2).

TABLE 1

PARAMETERS OF POROUS STRUCTURE OF THE CATALYSTS

Catalysts	Porous Structure			
	SSA, m^2/g	V_Σ, cm^3/g	d, nm	Total acidity, mmol/g
$TiPO_4$ (Initial)	109	1.60	32; 52	0.434
$TiPO_4$ (MChT)	86	1.23	9.0	0.080
$TiPO_4$ (HTT)	107	1,72	3.7; 49	0.510

SSA – specific surface area, V_Σ – total pore volume, d – pore size

Mechanochemical and hydrothermal treatment of titanium phosphate dramatically changes its catalytic properties in test reaction. Thus both mechanochemically and hydrothermally treated catalysts exhibit much better catalytic performance. On the treated by MChT catalyst AA yield increases to 14 %, and on the treated by HTT catalyst AA yield reaches maximum value 61 % at 623 K.

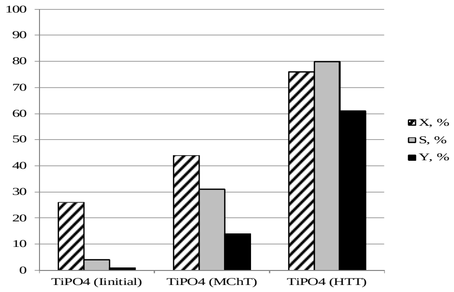

Fig. 2 Catalytic properties of initial titanium phosphate and titanium phosphates after MChT and HTT at 623 K, residence time 8s.

Conclusion

It had been demonstrated that mechanochemical and hydrothermal treatment of support allows increasing activity and selectivity of the catalyst in the studied process. Hydrothermal treatment (HTT) of silica support of B–P–V–W–O_x catalyst at 150 °C allows increasing the one-pass yield of acrylic acid synthesis from 58 % to 68 % at acrylic acid selectivity of 91 %. 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. Similarly, the same approaches allow to optimize the pore structure of titanium phosphates. On the treated by MChT catalyst AA yield increases to 14 %, and on the treated by HTT catalyst AA yield reaches maximum value 61 % at 623 K.

References

[1] H. Danner, M. Ürmös, M. Gartner, R. Braun, “Biotechnological Production of Acrylic Acid from Biomass”, Applied Biochemistry and Biotechnology, vol. 70, pp. 887-894, 2008,doi:10.1007/BF02920199.

[2] Cuncun Zuo, Yaping Li, Chunshan Li, Shasha Cao, Haoyu Yao, Suojiang Zhang, “Thermodynamics and separation process for quaternary acrylic systems”, AlChE J., 62, 228–240, 2015, doi:10.1002/aic.15015.

[3] Valentina T.Shashkova, Irina A.Matveeva, Nikolay N.Glagolev, Tatyana S.Zarkhina, Anastasiya V.Cherkasova, Svetlana L.Kotova, Peter S.Timashev, Anna B.Solovieva, “Synthesis of polylactide acrylate derivatives for the preparation of 3D structures by photo-curing”. Mendeleev Communications, , vol. 26, pp. 418-420, 2016doi: 10.1016/j.mencom.2016.09.018.

[4] Killian Flégeau, Richard Pace, HélèneGautier, Gildas Rethore, Jerome Guicheux, Catherine Le Visage, PierreWeiss, “Toward the development of biomimetic injectable and macroporous biohydrogels for regenerative medicine”, Advances in Colloid and Interface Science, 2017,doi: 10.1016/j.cis.2017.07.012.

[5] X. Li, Y. Zhang, “Highly Efficient Process for the Conversion of Glycerol to Acrylic Acid via Gas Phase Catalytic Oxidation of an Allyl Alcohol Intermediate”, ACS Catalysis, vol. 6, pp. 143-150, 2016, doi: 10.1021/acscatal.5b01843.

[6] Zhyznevs'kyy V.M., Nebesnyy R.V., Ivasiv V.V., S. V. Shybanov. “Obtaining of acrylic monomers by gas-phased catalytic condensation of carbonyl compounds in gas phase”, Reports of NAS Ukraine, vol. 10, pp. 114–118, 2010.

[7] Patent 0343319 US, Process for preparing acrylic acid with high space-time ield / M. Goebel // BASF SE., filing date: 18.05.2013; publication date: 08.04.2014.

[8] R.V. Nebesnyi, V.V. Ivasiv, V.M. Zhyznevskyy, S.V. Shybanov, S.V. Maykova, “Condensation of acetic acid with formaldehyde to acrylic acid over B-P-Mo-Cs-Ox catalysts in the gas phase”, Visnyk NU ”LP” “Chemistry, technology of substances and their applications”, no 667, pp. 196-199, 2010.

[9] R. Nebesnyi, V. Ivasiv, Y. Dmytruk, N. Lapychak, “Acrylic acid obtaining by acetic acid catalytic condensation with formaldehyde”, Eastern-European Journal of Enterprise Technologies, Vol. 6, no 6(66), pp. 40-42, 2013.

[10] V.V. Ivasiv, Z.G. Pikh, V.M. Zhyznevskyy, R.V. Nebesnyi, “Physical-chemical properties of surface of B_2O_3 – P_2O_5 – MeO_x/SiO_2 catalysts and their influence on parameters of propionic acid aldol condensation with formaldehyde”, Reports of NASc of Ukraine, no. 11, pp. 126-130, 2011.

[11] E. Skwarek, S. Khalameida, W. Janusz, V. Sydorchuk, N. Konovalova, V. Zazhigalov, J. Skubiszewska-Zięba, R. Leboda Influence of mechanochemical activation on structure and some properties of mixed vanadium-molybdenum oxides. Journal of Thermal Analysis and Calorimetry, vol.106, no3, pp.881-894, 2011.

[12] J. Skubiszewska-Zieba, S. Khalameida, V. Sydorchuk. Comparison of surface properties of silica xero- and hydrogels hydrothermally modified using mechanochemical, microwave and classical methods. Colloids and Surfaces A: Physicochemical and Engineering Aspects, vol. 504, pp. 139-153, 2016.