1. Introduction

For today, there has been a significant increase in the world production of monomers and polymers, with significant segment of which is acrylic acid (AA) and its derivatives, in particular, methyl acrylate (MA) and butyl acrylate. Thanks to the ability to chemically interact with acrylic acid and its esters, it is possible to form homopolymers or copolymers. The above-mentioned products are widely used in the manufacture of paints, glues, various coatings, organic glass, modifying additives to concrete [1, 2]. It is predicted that the total production of AA and methyl acrylate will increase to 8 million tons/year by 2020 due to their use as superabsorbents, detergent components, textiles, medical products [3]. Therefore, research aimed at finding new and improving existing methods for the production of acrylate monomers, in particular AA and methyl acrylate, is promising.

2. Literature review and problem statement

The main industrial method for AA production is the two-stage oxidation of propylene through the intermediate formation of acrolein and its oxidation to AA [4]. Methyl acrylate is obtained by the esterification of AA with methanol on acid-type catalysts [5]. Taking into account that propylene is produced from petroleum raw materials, the prices for which are not stable and have a steady tendency to increase, the search for methods of AA synthesis from alternative sources of raw materials is being conducted. Significant prospects for implementation are the methods of AA production by aldol condensation of acetic acid (AcA) with formaldehyde (FA) [6] and oxidative condensation of methanol with acetic acid [7]. In the processes of aldol condensation reagents are AcA and FA, which are synthesized from methanol [8]. The raw material base for methanol production is synthesis gas, produced from methane and coal [9].

**ACRYLIC ACID SYNTHESIS BY OXIDATIVE CONDENSATION OF METHANOL AND ACETIC ACID ON B–P–V–W–Ox/SiO2 CATALYST**

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**UDC 541.128.13**

**DOI: 10.15587/1729-4061.2019.156764**
Consequently, significant reserves of coal and methane can be used as sources of alternative raw materials for AA production as the oil reserves become depleted. That is why active research has been going on the development of technologies and effective catalysts for this process. An important task on the way of the implementation of acrylic acid and methyl acrylate production by condensation reactions is to find efficient catalysts. One of the most effective catalysts of AcA and FA aldol condensation reaction are acid-type catalysts [10–12]. In particular, catalysits based on a mixture of boron oxides and phosphorus deposited on silica have been developed. These catalysts are promoted by molybdenum, vanadium and tungsten oxides, which are effective in the process of aldol condensation. The ability to regulate the acidic properties of the catalysts surface by adding appropriate promoters opens the prospects for the development of efficient catalysts for condensation processes [6, 7, 10–12]. In recent years, acid-type catalysts have been also used for the production of formaldehyde [13, 14]. Since these reactions are key in the transformation system for oxidative condensation [7], there are reasons to believe that acid catalysts of aldol condensation will be effective in the oxidative condensation of AcA with methanol.

There are not much of systematized research data concerning the processes of oxidative condensation, even though the process itself is promising and interesting due to the possibility of reducing the number of synthesis stages [7]. The process involves simultaneous combination of two reactions: the oxidation of methanol to formaldehyde and AcA aldol condensation with the FA formation.

The known method for the implementation of combined process of acetic acid and methanol oxidative condensation is performed with V-Ti-P catalyst [7, 15]. At 623 K, the yields of AA and methyl acrylate reached 42 and 13 %, however, the selectivity of target products was low and did not exceed 73 % [7]. Nevertheless, these studies relate only to the effect of changes in the quantitative composition of the catalyst and the ratio of the components of reaction mixture on the acrylates yield. The change of porous structure of catalysts without changing their quantitative and qualitative composition remains unexplored for this process.

The use of the B–P–V–W–Ox/SiO 2 catalyst has been studied, which proved to be very effective in the process of aldol condensation of AcA with FA for the one-step production of AA from methanol and AcA in the presence of air. In this case AA and MA were obtained with 93.9 % total selectivity, however, the yield of acrylates remains low – 30.4 % [16]. Thus, the efficiency of known catalysts at oxidative condensation of methanol with AcA remains insufficient, which is the reason for scientific research.

It has been established that the preliminary modification of the B–P–V–W–Ox/SiO 2 catalyst carrier by hydrothermal treatment allows to significantly increase its efficiency in the process of aldol condensation of AcA with FA [17–18]. Hydrothermal treatment of the catalyst or carrier can substantially alter its porous structure, including the specific surface area, pore size, pore size distribution and, therefore, affect its catalytic properties in chemical transformations.

### 3. The aim and objectives of the study

The aim of this work is the effectiveness determination of the hydrothermal treatment of catalyst B–P–V–W–Ox/SiO 2 in the oxidative condensation of methanol with acetic acid. To achieve this aim, the following tasks have to be solved:

- to investigate the porous structure of the used catalyst;
- to determine the influence of technological parameters (temperature, contact time, ratio of methanol: acetic acid, oxygen concentration) on the yield, selectivity of reaction products and the conversion of acetic acid;
- to choose the best technological parameters of the oxidative condensation of methanol with acetic acid.

### 4. Materials and methods to study the oxidative condensation of methanol with acetic acid

Materials that were used for the research:

- acetic acid (H 3C–COOH) (ice) 100 %, anhydrous, for analysis;
- methanol (H 3C–OH), 99.9 %, high purification, for chromatography;
- B–P–V–W–Ox/SiO 2 catalyst subjected to hydrothermal treatment. The atomic ratio of components in catalyst B:P:V:W is 3:1:0.18:0.12.

The catalytic activity of the developed catalyst was investigated in a flow reactor with a stationary layer of catalyst with constant mass (0.88 g) located on a fixed grid. A stainless steel reactor of tubular type with an external electric heating with a length of 230 mm and an internal diameter of 6 mm was used. The composition of the reaction products was determined by the chromatographic method. The studies were performed on a HP-5890 series II (USA) chromatograph.

The carrier, silica (SiO 2) of the KSKG brand with a specific surface area of 365 m 2/g, was hydrothermally treated in an autoclave in a gas phase at 150 °C temperature and a pressure of water vapour of 0.5 MPa within 3 hours. Upon completion of the treatment, the autoclave was cooled abruptly. The treated silica was first dried in a drying oven, and then calcined. On the prepared carrier, the active phase of the catalyst was applied by the method of impregnation. The active phase content (B–P–V–W–Ox) is 20 % of the total weight of the catalyst. As a boron source, boric acid was used, phosphorus – diammonium hydrogen phosphate, vanadium – ammonium metavanadate, tungsten – phosphotungstic acid. The calculated amounts of inorganic compounds were dissolved in water; a solution of salts was precipitated on prepared silica. Surface moisture was removed by placing the samples in the drying oven for 8 hours at 150 °C. The residual and chemically bound moisture was removed by calcining at 673 K for 6 hours.

Conversion of reagents (X), selectivity of AA (S) and AA yield (Y) were calculated by following equations:

\[ X = \left( \frac{n_{0} - n_{e}}{n_{0}} \right) \times 100 \% \]  
\[ S = \left( \frac{n_{A}^{AA}}{n_{0} - n_{e}} \right) \times 100 \% \]  
\[ Y = \left( \frac{n_{A}^{AA}}{n_{0}} \right) \times 100 \% \]

where \( n_{0} \) – AcA quantity that enters into reactor, mol; \( n_{e} \) – AcA quantity that exits reactor, mol; \( n_{A}^{AA} \) – AcA quantity that participated in the formation of AA, mol.

The specific surface area and pore size were calculated by the Barrett-Joiner-Khalenda method with adsorption-desorption nitrogen isotherms at –196 °C, which were obtained using the QuantaChrome AutoSorb gas sorption analyser.
The influence of the contact time on the selectivity and yield of the reaction products and on the conversion of the AcA was studied at 623 K temperature, molar ratio of AcA:M=1:1 at atmospheric pressure and contact time of 4–16 sec. in a flow reactor with a stationary layer of the catalyst. When the influence of temperature was studied, the reaction was carried out in the range 573–673 K at an interval of 25 K. The influence of the oxygen: acetic acid ratio on the process of oxidation condensation of methanol with AcA was carried out within the molar ratio of 1:5 (0.2); 1:2 (0.5); 1:1 (1.0); 1:5:1 (1.5); 2:0:1 (2.0).

The resulting experimental data was processed in Origin and Microsoft Excel programs. Dependences are described by approximating curves of a polynomial structure. As a result of the experiment, the average arithmetic value of three independent measurements was used. The general dispersion of the reproducibility of the values of the reagents conversion is 2.5, and the values of the target product selectivity – 1.8.

5. Results of B–P–V–W–Ox/SiO₂ catalyst’s activity tests

5.1. The study of catalyst’s porous structure

The initial stage of the research was to establish the structure of the porous surface of a hydrothermally treated carrier (silica) and a catalyst (Table 1).

| Sample                  | 𝑆, m²/g | 𝑉₉, cm³/g | 𝑉ₘ, cm³/g | 𝑑, nm |
|-------------------------|---------|-----------|-----------|-------|
| Silica                  | 365     | 1.05      | 1.04      | 7.9   |
| Catalyst (without HTT)  | 238     | 0.74      | 0.72      | 9.7   |
| Silica (HTT at 150 °C)  | 275     | 1.04      | 1.02      | 9.7   |
| Catalyst (HTT at 150 °C)| 193     | 0.72      | 0.72      | 12.6  |

For silica, the value of the total pore volume 𝑉₉ and the volume of mesopore 𝑉ₘ practically does not differ. Thus, we can conclude that the carriers do not contain micro and macropores, and all samples are mesoporous. As a result of the HTT, the specific surface area of the carrier decreases, and the pore size increases as compared to the untreated sample. The application of the active phase on the carrier is accompanied by decrease in both the specific surface area and the pore volume. This is due to the partial filling of the pore with the active phase. Hydrothermal treatment of the carrier allows to increase the average pore size of the catalyst, which provides better availability of surface to reagents.

5.2. Study of the contact time effect on the selectivity, the yield of reaction products and the conversion of acetic acid

Since oxygen is present in the reaction system (air), the processes of complete oxidation of the starting reagents are likely to happen with carbon dioxide and water formed as products. That is why it is important to study the possibility of destructive oxidation processes and determine the allowable temperature regime of the process. For these reasons, the dependence of the CO₂ release on temperature was studied and it was found that in the temperature range of 563–623 K the amount of formed carbon monoxide coincides with its amount formed as a result of the condensation (ketonization) reaction of acetic acid (at a molar ratio of AcA:oxygen=1:1). Therefore, under the stated conditions, products of destructive oxidation of reagents have not been recorded. That is why further research was carried out at a temperature of 623 K for the equilibrium ratio of the starting reagents and with the interval of contact time 4–16 sec., the oxidizer – air. With a shortage of oxygen (molar ratio of AcA:oxygen=1:0.5), the destructive oxidation of reagents is negligible at temperatures up to 673 K.

The simultaneous presence of acid, alcohol and catalytic acid in the system result not only in the processes of oxidation and aldol condensation but also creates the possibility for the processes of esterification and aldol condensation of the formed products to occur.

In particular, in the case of esterification of AcA and methanol, methyl acetate (Mac) is formed. Methyl acrylate may be formed as a result of the aldol condensation of Mac with FA, and the esterification of AA with methanol. Acetone (AC) is also formed in the process, which is consistent with known literature data [19].

The dependence of products selectivity and their yield on the time of contact is shown in Fig. 1. For AA and MA, selectivity gradually increases with increase of contact time from 4 sec. to 8 sec., and then remains unchanged and is more than 21 % for AA and increases for MA. The selectivity of the Mac with increase of contact time to 8 sec. smoothly decreases, and with increase of contact time to 16 sec. reaches the plateau.

The growth of target products yields with increase of contact time up to 8 sec. indicates the positive effect of this parameter increase. With further increase of contact time, the proportion of MA formation increases and, therefore, its yield. The total selectivity of AA and MA is calculated without taking into account the conversion of AcA to Mac, since Mac, as well as AcA, is the starting material for MA.

It was established that with increase of contact time from 4 to 16 sec., the total selectivity of AA and MA is slightly increasing, which may indicate the formation of MA with Mac and AcA (Fig. 2). However, when contact time is increased to 8 sec. the total yield is initially increasing, and after 8 sec. remains practically unchanged. The conversion of AcA also increases up to 8 sec. of contact time, and in the range of 8–16 sec. remains basically unchanged.

![Fig. 1. Dependence: a – selectivity; b – yield Mac (1), AA (2), AC (3), MA (4) on contact time. T=623 K; molar ratio AcA:M=1 : 1](image-url)
The criteria for choosing a better contact time are the AA selectivity, the MA selectivity, and the yields of these products. After analysing the experimental data, it is considered that 8 sec. is the best time of contact in the studied range, because further increase of contact time does not lead to a significant increase of AA and MA yield.

5.3. Determination of the temperature influence on the process of oxidative condensation of methanol with acetic acid

To determine the optimum temperature of the process for acrylic acid production by oxidative condensation of acetic acid with methanol, the study was carried out at the established temperature limits with a contact time of 8 sec. (Fig. 3).

At the lowest temperature, high selectivity for Mac and very low for other products are observed. Probably, in the temperature interval 573–623 K FA practically does not form, therefore the only possible process is the esterification of AcA and M in Mac [7].

With increase of temperature, the proportion of aldol condensation reactions increases and, therefore, the selectivity increases smoothly for AA, AC and MA and the selectivity of Mac decreases (Fig. 3, a). At 673 K temperature, the selectivity of AA, AC and MA reaches the maximum value – 56.8 %, 27.6 % and 6.1 %, respectively.

Gradual increase in yield is observed for all reaction products in the range 573–623 K (Fig. 3, b). With an increase of temperature in the range of 623–673 K, a rapid accumulation of AA, AC and MA was observed.

With the increase of temperature from 573 to 673 K, the total selectivity of AA and MA, as well as the yield of AA and MA are increasing (Fig. 4). Therefore, at the maximum value of temperature, the highest performance rates of the proposed catalyst are observed.

Further increase in the temperature of the process is impossible due to the limited thermal stability of the catalyst.

5.4. Determination of the reagents ratio influence (methanol : acetic acid) on the process of their oxidative condensation

To establish the corresponding patterns, samples with fixed molar ratio of reagents M:AcA were prepared. The dependence of the AA and MA selectivity and their yields on the ratio of reagents is shown in Fig. 5.
With the increase of the methanol part in the ratio of reagents to 1.5:1, the selectivity of AA and MA increases (Fig. 5, a), but further increase of methanol content in the samples from 1.5:1 to 5:1, basically does not affect the selectivity of AA, MA and other products. With the increase of methanol amount, the yields of Mac, AA and MA are doubled, but AC yield decreases. Further increase of the methanol part in the reaction mixture does not lead to an increase of the studied parameters. These patterns are also confirmed by the study of the total selectivity and yield of acrylates (Fig. 6).

The reaction of oxidative condensation in the best conditions in terms of yield (temperature 673 K, contact time 8 sec., ratio AcA:methanol=1:1.2, ratio AcA:O₂=1:1.5) allows to reach the 53 % yield of AA and 1.7 % yield of MA (total yield of acrylates is 54.7 %) (Fig. 8).

6. Discussion and selection of the best technological parameters for the process of oxidative condensation of methanol with acetic acid

Based on the results of the technological parameters, influence on the process of oxidative condensation of methanol with AcA, the following conditions for the implementation of the process are chosen:

- the best temperature of the process is 673 K. At this temperature the highest activity rates of the proposed catalyst are recorded.
- the contact time is 8 seconds. The increase in contact time contributes to the growth of the AA yield, however, when the contact time exceeds 8 sec., the specific catalyst productivity (the amount of the product formed per time unit per mass unit of the catalyst) is significantly reduced.
- the molar ratio of reagents methanol:AcA=1:2.1. With a slight excess of methanol, growth of the selectivity of methyl acrylate and AA was observed, and significant decrease in the selectivity of the formation of a by-product – acetone. The further increase of the excess of methanol is not accompanied by significant improvement of the indicated parameters. The ratio of the target products AA:MA changes from 10.6:1 at a ratio of methanol:AcA=1:1 to 3.4:1 at a ratio of methanol:AcA=1:2.1. Thus, a slight change in the ratio of reagents can regulate the ratio of target products of the process (AA and MA), depending on market needs.
– as an oxidizer, it is proposed not to use air, but the ratio of oxygen: acetic acid (1:5:1). The growth of the ratio of oxygen: acetic acid contributes to reduce of acetone and methyl acetate selectivity, does not change the selectivity of the MA, and significantly increases the selectivity and yield of the target product – AA.

For the catalyst, which has undergone a preliminary hydrothermal treatment, the maximum total yield of acrylates is 54.7% with total selectivity of 80.1%, which exceeds the known results [7, 15, 16]. It has been established that the previous HTT of carrier allows to modify the pore structure of the catalyst – to increase the size of the pores of the catalyst at a constant total pore volume. In this way, the availability of reagents to active catalyst centres is facilitated, which makes it possible to increase its catalytic properties in the process of oxidative condensation of AcA with methanol to AA and MA. However, the application of the developed catalyst has certain limitations, in particular the narrow temperature interval of its application in the investigated process. The highest conversion rates of reagents and acrylate yields were obtained at a temperature of 673 K, and given the thermal stability of the catalyst in the range of 573–683 K, it is impossible to conduct a study at higher temperatures. Therefore, the question arises of improving catalysts in the direction of extending the working interval of temperatures of catalysts application and increasing the efficiency of catalysts at temperatures below 673 K. The obtained results indicate that the modification of the surface of the catalyst carrier by hydrothermal treatment with the consistent quality and quantity of the catalyst can have a positive effect on its efficiency. Therefore, further research in the direction of optimization of the porous structure of catalysts in order to regulate their catalytic properties in the process of oxidative condensation of methanol with AcA to AA and MA is promising.

7. Conclusions

1. It has been established that as a result of hydrothermal treatment of the carrier, the physical and chemical properties of the B-P-V-W-Ox/SiO2 catalyst surface changes: the pore size increases from 9.7 to 12.6 nm with constant total pore volume (0.72–0.74 cm³/cm³), the specific surface area of the catalyst (238–193 m²/g) slightly decreases. This ensures better availability of reagents to its surface, increases the efficiency of the catalyst.

2. Increasing the contact time to 8 sec, leads to the increase in the yields of the target products of the reaction. The highest catalytic activity of the proposed catalyst was obtained at a maximum temperature of 673 K. Increasing the proportion of methanol in the ratio of methanol: acetic acid to 1.5:1 leads to the increase in the selectivity of the acrylic acid and methyl acrylate. Process of oxidative condensation of methanol with acetic acid is the most effective from the point of view of products yield and selectivity at the ratio of oxygen: acetic acid 1:5:1.

3. For hydrothermally treated B-P-V-W-Ox/SiO2 catalyst at a temperature of 673 K, the contact time of 8 seconds, the molar ratio of acetic acid:methanol=1:2:1, the total yield of acrylates is 54.7% with the total selectivity of 80.1%.

References

1. Acrylic block copolymer and thermoplastic resin composition: Pat. No. US7309736B2 USA / Taniguchi A., Kokubo T., Take-sada K., Kondo K., Chiba T., Kumasaki A., Kaneda Yu. No. 10/522,869; declared: 31.07.2003; published: 18.12.2007.
2. Olson J. M., Srinivasan K. R. Chemically prepared toners with size limiting binders: Pat. No. US7435523B2 USA. No. 4301374; declared: 1.06.2005; published: 14.10.2008.
3. James S. Acrylic Acid Market Size. San Francisco: Grand View Research, 2016. 115 p.
4. SBA-15-supported highly dispersed copper catalysts: Vacuum–thermal preparation and catalytic studies in propylene partial oxidation to acrolein / Liu C.-H., Lai N.-C., Lee J.-F., Chen C.-S., Yang C.-M. // Journal of Catalysis. 2014. Vol. 316. P. 231–239. doi: https://doi.org/10.1016/j.jcat.2014.05.013
5. Sert E., Atalay F. Esterification of Acrylic Acid with Different Alcohols Catalyzed by Zirconia Supported Tungstophosphoric Acid // Industrial & Engineering Chemistry Research. 2012. Vol. 51, Issue 19. P. 6666–6671. doi: https://doi.org/10.1021/ ie202609f
6. Processes for producing acrylic acids and acrylates: Pat. No. US658441B2 USA / Peterson C. J., Chapman J. T., Gallacher J., Pan T. No. WO201302471A1; published: 11.04.2013.
7. Ai M. Vapor-phase reaction of methanol with methyl acetate and acetic acid in the presence of oxygen // Journal of Catalysis. 1988. Vol. 112, Issue 1. P. 194–200. doi: https://doi.org/10.1016/0021-9517(88)90133-9
8. Ormsby G., Hargreaves J. S., Ditzel E. J. A methanol-only route to acetic acid // Catalysis Communications. 2009. Vol. 10, Issue 9. P. 1292–1295. doi: https://doi.org/10.1016/j.catcom.2009.02.005
9. Da Silva M. J. Synthesis of methanol from methane: Challenges and advances on the multi-step (syngas) and one-step routes (DMTM) // Fuel Processing Technology. 2016. Vol. 145. P. 42–61. doi: https://doi.org/10.1016/j.fuproc.2016.01.023
10. Nebesnyi R. Complex oxide catalysts of acrylic acid obtaining by aldol condensation method // Eastern-European Journal of Enterprise Technologies. 2015. Vol. 1, Issue 6 (73). P. 13–16. doi: https://doi.org/10.15587/1729-4061.2015.37405
11. Nebesna Yu., Ivasiv V., Nebesnyi R. The study of technological and kinetic regularities of simultaneous methacrylates obtaining over zirconium-containing catalysts // Eastern-European Journal of Enterprise Technologies. 2015. Vol. 5, Issue 6 (77). P. 49–52. doi: https://doi.org/10.15587/1729-4061.2015.51348
12. Catalytic aldol condensation of formaldehyde with acetic acid on titanium phosphates modified by different techniques / Khalameida S., Nebesnyi R., Pikh Z., Ivasiv V., Sydorchuk V., Nebesna Y. et. al. // Reaction Kinetics, Mechanisms and Catalysis. 2018. Vol. 125, Issue 2. P. 807–825. doi: https://doi.org/10.1007/s11144-018-1443-8

13. Vanadium promoted molybdenum phosphate catalysts for the vapour phase partial oxidation of methanol to formaldehyde / Whiting G. T., Bartley J. K., Dummer N. F., Hutchings G. J., Taylor S. H. // Applied Catalysis A: General. 2014. Vol. 485. P. 51–57. doi: https://doi.org/10.1016/j.apcata.2014.07.029

14. Behera G.C., Parida K. Selective gas phase oxidation of methanol to formaldehyde over aluminum promoted vanadium phosphate // Chemical Engineering Journal. 2012. Vol. 180. P. 270–276. doi: https://doi.org/10.1016/j.cej.2011.11.047

15. Ai M. Reaction of acetic acid with methanol over vanadium-titanium binary phosphate catalysts in the presence of oxygen // Applied Catalysis. 1990. Vol. 59, Issue 1. P. 227–235. doi: https://doi.org/10.1016/s0166-9834(00)82200-9

16. Oderzhannia akrylovoi kysloty z metanolu ta otstovoi kysloty v prysutnosti skladnykh oksydnykh katalizatoriv / Nebesnyi R., Pikh Z., Shpyrka I., Ivasiv V., Nebesna Yu., Fuch U. // Visnyk NTU “KhPI”. Novi rishennia v suchasnykh tekhnolohiyakh. 2015. Vol. 62. P. 125–130.

17. Improving the efficiency of $B_2O_3$–$P_2O_5$–$WO_3$–$V_2O_5$/$SiO_2$ catalyst of aldol condensation of acetic acid with formaldehyde by hydrothermal treatment of the carrier / Nebesnyi R. V., Pikh Z. G., Ivasiv V. V., Sydorchuk V. V., Shpyrka I. I., Lapychak N. I. // Visnyk Natsionalnoho universytetu “Lvivska politekhnika”. Khimiya, tekhnolohiya rechovyn ta yikh zastosuvannia. 2016. Vol. 841. P. 113–117.

18. Leboda R., Charmas B., Sidorchuk V. V. Physicochemical and Technological Aspects of the Hydrothermal Modification of Complex Sorbents and Catalysts. Part II. Modification of Phase Composition and Mechanical Properties // Adsorption Science & Technology. 1997. Vol. 15, Issue 3. P. 215–236. doi: https://doi.org/10.1177/026361749701500306

19. Zirconia catalysed acetic acid ketonisation for pre-treatment of biomass fast pyrolysis vapours / Jahangiri H., Osatiashtiani A., Bennett J. A., Isaacs M. A., Gu S., Lee A. F., Wilson K. // Catalysis Science & Technology. 2018. Vol. 8, Issue 4. P. 1134–1141. doi: https://doi.org/10.1039/c7cy02541f