IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

Kinetics and Mechanism of the Vapor-Phase Synthesis of Vinyl Acetate from Ethylene

Firdavsiy Buronov
Karshi Engineering Economics Institute

Abstract: The article discusses in detail the kinetic laws and kinetics and mechanism of the oxidation-acetylation reaction of ethylene in the vapor phase of the catalyst of order 0,4%Pd+4%Cu+7%CH_3COOK/HSZ. It was found that the total rate of the reaction was proportional to the amount of unmodified and modified active sites of palladium (not clusters). Excessive amounts of the modifier (both potassium acetate and copper) have been found to reduce catalyst efficiency and block active sites. As a result of the study, the following optimal conditions were selected for the reaction to occur: in the middle zone of the reactor at a temperature of 165 ℃, volumetric speed - 2000 h^{-1}, at a pressure of 4 atm, ethylene to acetic acid ratio 4: 1 and oxygen content 7%. Under these optimal conditions, the formation energies of vinyl acetate (VA) and the activation energies of ethylene oxidation reactions are as follows: $E_{a(VA)}$ = 8,17 kcal/(mol·K) and $E_{a(CO_2)}$ = 19.61 kcal/(mol·K), respectively.

It was found that the oxidation state of ethylene at temperatures above 220 ℃ is higher than the rate of formation of VA. A reaction mechanism for the formation of VA from ethylene and acetic acid in the presence of a palladium catalyst has been proposed. Based on the results obtained, the following kinetic equation of the reaction to obtain VA in the oxidized acetylation of ethylene was proposed:

$$W_{VA} = \frac{K_5 K_1 K_2^{0.5} K_3 K_4 P_{C2H4} \cdot P_{O2}^{0.5} P_{\text{acetic acid}}}{(1 + K_1 P_{C2H4} + (K_2 P_{O2})^{0.5} + K_3 P_{\text{acetic acid}})^2}$$

W_{VA}- catalyst activity, g/(l cat.*s); P- pressure, atm.

The aim of the work is to study the kinetics and mechanism of the oxidative acetylation reaction of ethylene.

Keywords: ethylene, oxygen, acetic acid, vinyl acetate, kinetic equation, mechanism.

Introduction

Vinilacetate is a colorless, easily flammable liquid with a distinctive odor. Manufacturer of polyvinyl acetate (PVA), polyvinyl alcohol and PVA resins. Vinilacetate is also polymerized by forming commercial and acrylic fibers for vinyl chloride and ethylene as a secondary raw material.

Vinilacetate is the primary raw material for the production of PVA homopolymers and copolymers for a wide range of industrial and consumer goods. In terms of application of VA is divided into PVA - polyvinyl acetal, polyvinyl alcohol, ethylene, vinyl alcohol, ethylene-vinyl acetate and others[1-3].

About 80% of the VA produced is used to produce PVA and polyvinyl alcohol. PVA is widely used in the glue industry, exhibits good adhesive properties to various substrates such as wood, paper, metals and plastic films. PVA directly derived from PVA plays an important role in the production

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

of safe glass intermediate layer, washable primers, coatings and magnetic wire insulation. Industrial production of VA is carried out in two ways:

1. On the basis of acetylene and acetic acid [4-7];

2. Based on ethylene, acetic acid and oxygen.

The first method is based on a vinyllation reaction consisting of the addition of acetic acid to acetylene:

$$CH_3COOH + C_2H_2 \rightarrow CH_3OCOCH = CH_1$$

$$\Delta H^0_{298} = -98\,kJ / mol$$

The process of obtaining VA from acetylene is carried out in the liquid phase as well as in the vapor phase. Vinilacetate was first obtained as a by-product in the liquid phase synthesis reaction of ethylidendiacetate. This method was later developed as the first industrial method of obtaining VA: the reaction was carried out in acetic acid at 40-100 °C in the presence of strong acids such as mercury salts ($HgSO_4, HgO$) and H_2SO_4, oleum, BF_3, CF_3SO_3H and others. By changing the catalyst composition, temperature, mixing speed, it is possible to influence the process selectivity and obtain 80% yield of VA or ethylidendiacetate in acetic acid. Production of VA in non-heterogeneous catalysts began in Germany in the late 1930s, and this method is still relevant today: the reaction is carried out (activated carbon) in a catalytic system of zinc acetate $Zn(OA)_2$ in the carrier at a temperature range of 160-240 ℃ and a pressure close to atmospheric pressure [8-10].

To reduce the yield of ethylidendiacetate, the reaction is carried out in an excess of acetylene (ratio of acetylene to acetic acid = 4-10: 1) [4-8]; the process is carried out either in tube reactors, or in forged liquefied layered reactors of the catalyst. Volumetric loading is 100 - 500 ch-1, acetic acid conversion is about 50%, and productivity in VA is 40-80 kg/m^3 cat. h. zinc acetate loses its activity over time due to the accumulation of polymers and resins in the catalyst, forcing the temperature of the process to gradually rise from 160-180 ℃ to 220-240 ℃ [11-12].

Synthesis of VA on the basis of ethylene is carried out by passing a vapor-gas mixture of primary reagents through a layer of acetic acid and oxygen catalyst, at a temperature of 140-200 °C and a pressure of 0.8 MPa. process chemistry is approached by mass reactions of formation of target by-products [13-18]:

$$C_2H_4 + CH_3COOH + 0{,}5\,O_2\,CH_3COOCH = CH_2 + H_2O$$

$$C_2H_4 + 3\,O_2\,2CO_2 + 2\,H_2O$$

The process is significantly linked to the supply of imported catalyst, which represents porous aluminosilicate bubbles of 5-6 mm, in the porous course of which was carried out in the form of fine dispersion of metallic palladium (3,3 g/l), copper (1,5 g/l) and potassium acetate (30 g/l). Over time, the catalytic complex becomes obsolete and its activity decreases. To maintain the constant activity of the catalyst, the process of VA synthesis is carried out by slowly raising the temperature from 140 to 200 ℃ for 1 year. The service life of the imported catalyst is 1 year. A relatively small number of publications have been devoted to modeling and controlling the synthesis of ethylene, acetic acid, and oxygen-based VA [15 - 19]. A mathematical model for the synthesis of VA is used in the catalyst of "Bayer" to control this process at the current production facility [20-21]. To avoid costly import dependence, it is important to shift this production to a catalyst produced locally or in CIS countries [22, 23].

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

Experimental part

The VA synthesis process was carried out at a temperature of 145–200 ℃ (the temperature rises slowly depending on the catalyst activity), the pressure was 0.4 MPa, and the volumetric rate of delivery of the vapor-gas mixture (VGM) was 2000 h^{-1}. The molar ratio of ethylene and acetic acid is 4:1; the volume concentration of oxygen in dry gas (without acetic acid) is 7.5%. VA synthesis is accomplished by incomplete conversion of the starting materials. The unreacted ethylene, oxygen, and acetic acid are purified and the vapor-gas mixture is returned to the preparation node.

The conversion rate is average in one conversion: for ethylene - 8%, for acetic acid - 18%, for oxygen - 47%. VA synthesis takes place in an experimental device for the preparation of a complex catalyst. The process consists of two stages. Catalyst for catalyst preparation was hydrothermally treated at 200 ℃ for 6 hours, specific surface area of 150 $m^{2/}g$, pile density of 54 g/cm^3, porosity of 0.78 cm^3/g and particle diameter of 4.5-5 mm high silicon zeolite used.

The catalysts were tested in a tube-reactor with a diameter of 20 mm and a height of 900 mm (heated oil is sent to remove the heat of the exothermic reaction of VA and CO_2 formation) in a demonstration device of VA synthesis.

Each of the catalyst samples was tested for 36-40 hours at a load of 100 cm^3 of catalyst in the reactor, and the optimal process parameters found experimentally for this device were: 165 ℃, 0.4 MPa, ethylene: acetic acid ratio 4:1, volumetric rate 6000 h^{-1} , the amount of oxygen in the dry gas is 7.0 vol.%. Under the specified conditions, the reaction of formation of VA and CO_2 proceeds with a slight effect of diffusion in the kinetic field, which begins to manifest only with an increase in the time of vapor-gas mixture in the reactor - at a volumetric rate of 3000 h^{-1}.

Results and discussion.

The effect of pressure change. Pressure 1-9 atm. changed at intervals. Other initial parameters were left constant: T = 165 ℃, volumetric velocity - 2000 h^{-1}, the ratio of ethylene to acetic acid was 4: 1, and the oxygen content was 7 vol.%. The data from these experiments are given in Figure 1.

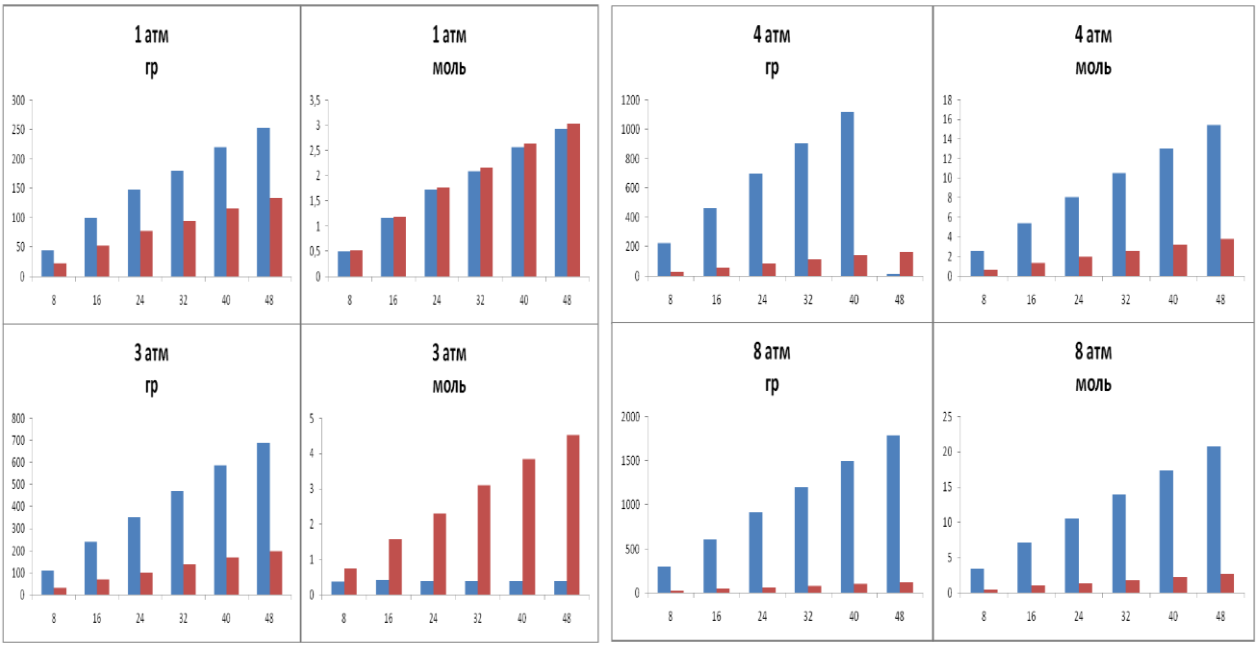

Figure 1. Influence of process pressure

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

The relationship between VA output and CO_2 formation is linear. The rates of formation of reaction products by processing them were calculated.

The effect of changes in the oxygen concentration in the reaction mixture. Oxygen concentration change range: 1-7 vol.%. the upper limit is limited by the explosion-safe concentration limit of ethylene mixed with oxygen.

The initial parameters of the series of experiments: T = 165 ℃, volumetric velocity - 7500 h-1, the ratio of ethylene to acetic acid 4: 1 and the amount of oxygen 7 vol.%. the data for this series of experiments are given in Figure 2.

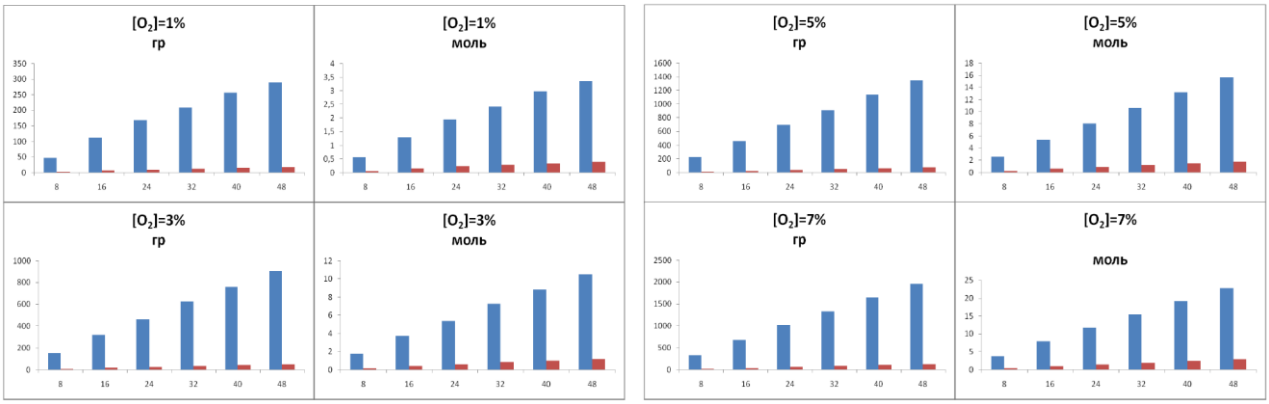

Figure 2. Influence of oxygen concentration in VGM

A decrease in the amount of oxygen to 1.0% in the specified parameters does not lead to a significant increase in the amount of carbon monoxide.

The kinetic curves of the dependence of VA output and CO_2 formation are nonlinear. From the formed kinetic curves, the rates of formation of the reaction products described in Figure 2 and Figure 3 were calculated.

As can be seen from the given data, the increase in the amount of oxygen leads to a linear increase in the formation of VA and the oxidation rate of ethylene to CO_2 at a constant selectivity of the formation of VA on ethylene. Since the relative amounts of ethylene and acetic acid in the VGM are virtually unchanged, it can be calculated that the reactions that take place in parallel with the formation of VA and CO_2 have the first orders of magnitude for oxygen. No reverse braking of the reaction with oxygen is observed. The rate equations of the reactions are as follows:

- as the dependence of oxygen on the mole fraction in ethylene:

$W_{VA} = (6{,}54 \pm 0{,}5)\cdot[O_2 \text{ percentage}]$ mol/h

$W_{CO2} = (0{,}92 \pm 0{,}07)\cdot[O_2 \text{ percentage}]$ mol/h

- as the dependence of the partial pressure of oxygen:

$W_{VA} = (1{,}07 \pm 0{,}07)\cdot[P(O_2)]$ mol/h

$W_{CO_2} = (0{,}156 \pm 0{,}01)\cdot[P(O_2)]$ mol/h

The calculated selectivity of vinylacetate formation on ethylene using the obtained equations well describes the experimental values.

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

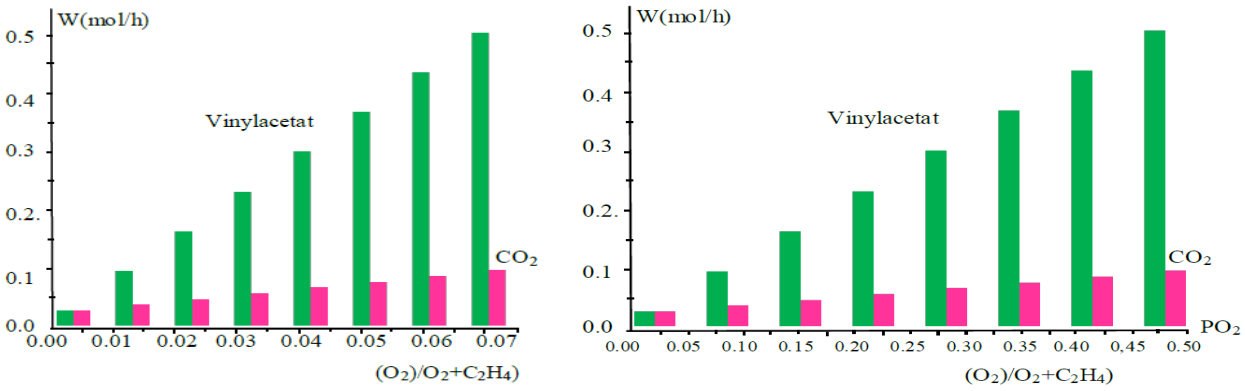

Figure 3. Graphs of changes in the rates of formation of reaction products depending on the amount of oxygen in ethylene: the mole fraction of O_2 in ethylene at a total pressure of 4 atm and the partial pressure of oxygen in VGM, P (O_2) atm.

The primary components are the effect of the ethylene and acetic acid ratio. The mole ratio of ethylene and acetic acid ranged from 2: 1 to 8: 1. The experiments were carried out under the following conditions: the middle zone of the reactor T = 165 ℃, P = 4 atm, volumetric speed - 7500 h^{-1}. The amount of oxygen in the mixture with ethylene is 7%. The amount of catalyst is 100 cm^3. The experimental data are presented in Figure 4. The output of VA and the formation of CO_2 are nonlinear. The rates of formation of reaction products by processing them were calculated.

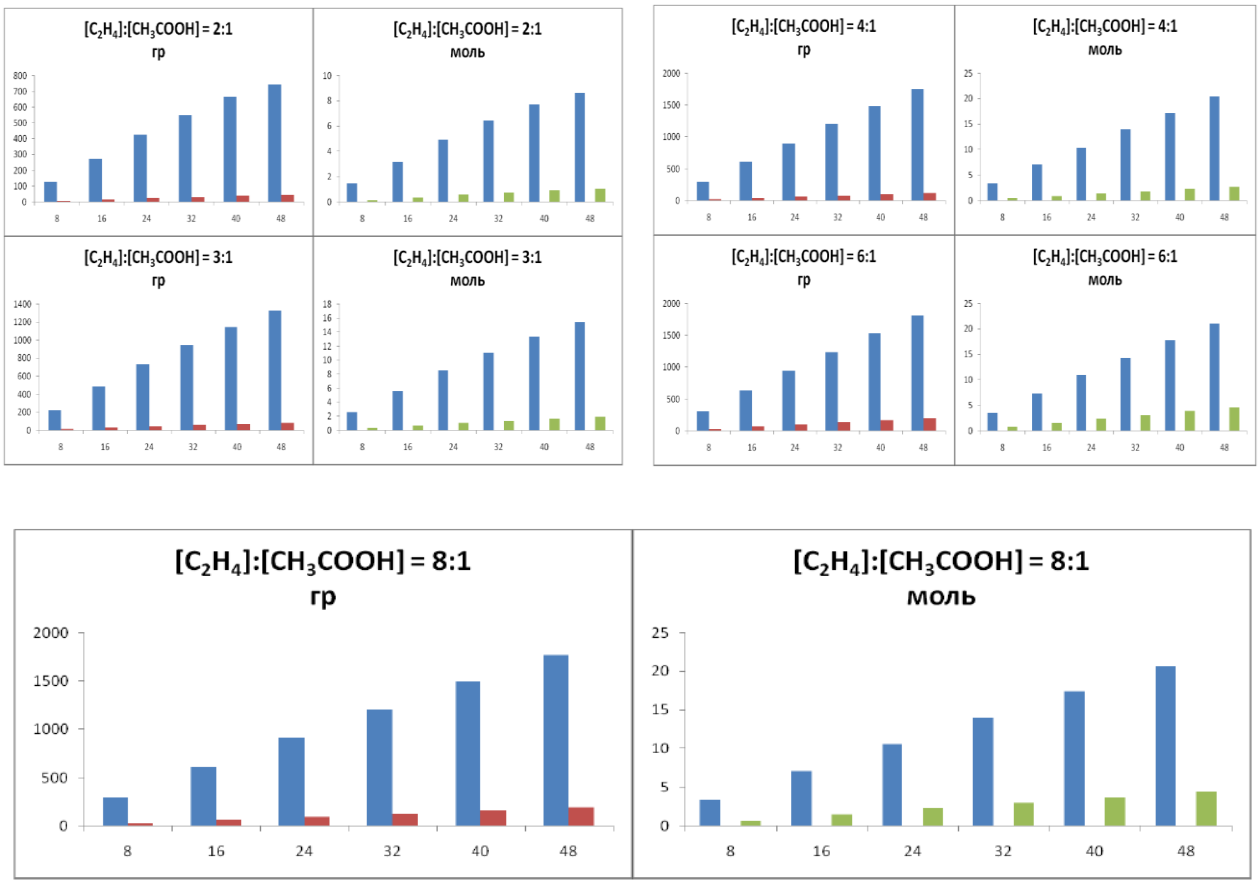

Figure 4. The starting components are the effect of the ratio of ethylene and acetic acid

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

An increase in the ratio of ethylene to acetic acid leads to a nonlinear increase in the formation of VA and the oxidation rates of ethylene to CO_2. When the mutual ratio reaches ≈5, the increase in reaction rate stops. In this series of experiments, the concentration of all reagents changes, which makes it much more difficult to find functional dependences of the rates of formation of VA and CO_2 on the $[C_2H_4]$/[Acetic acid] ratio and their partial pressures.

Influence of synthesis temperature. The temperature was varied from 140 to 200 ℃. A series of experiments were performed on the following parameters: P = 4 atm, VGM volume rate 7500 h^{-1}, the ratio of ethylene to acetic acid 4: 1, and the oxygen content 7% vol. The experimental data are presented in Figure 5.

The relationship between VA output and CO_2 formation is linear. From the formed kinetic curves, the rates of formation of reaction products were calculated. Processing the experimental results in Arrenius coordinates results in obtaining the linear relationships shown in Figure 5. Thus, under the conditions of these experiments, the reaction rates are determined by the following equations:

Formation of VA:

$$W_{VA} = exp(8,63) \cdot exp(-4086 / T°K)\, mol / h$$

$$W_{CO_2} = exp(20,1) \cdot exp(-9810 / T°K)\ mol / h$$

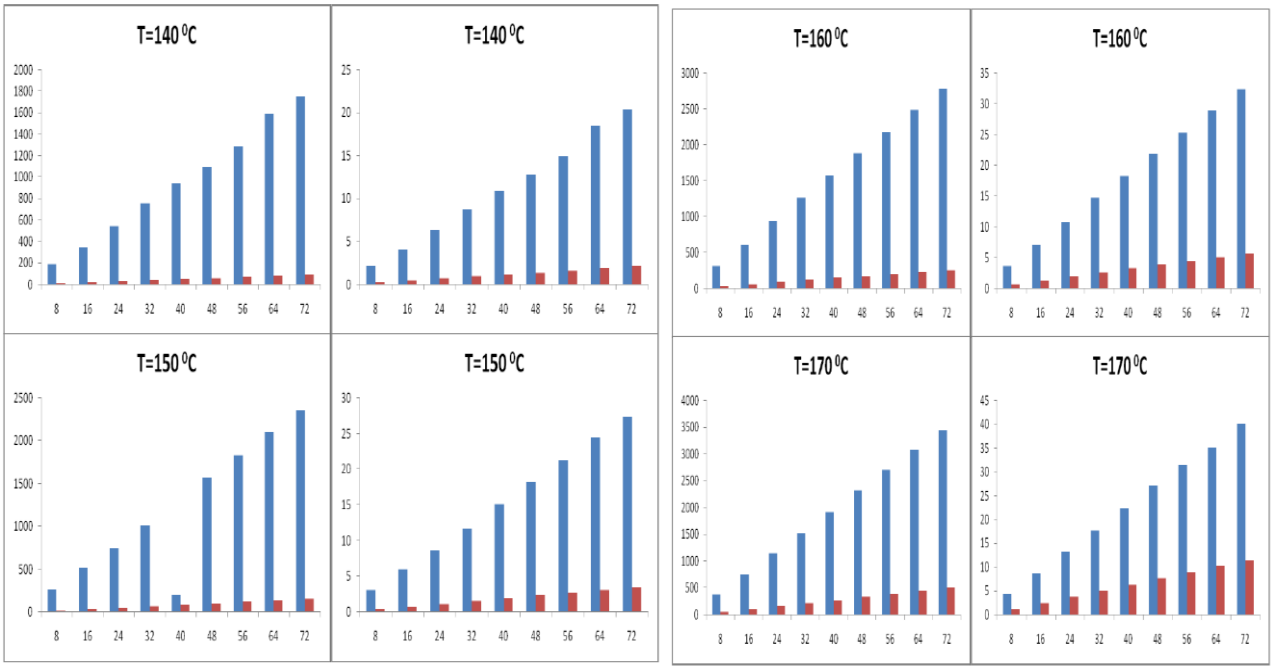

Figure 5. Influence of synthesis temperature

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

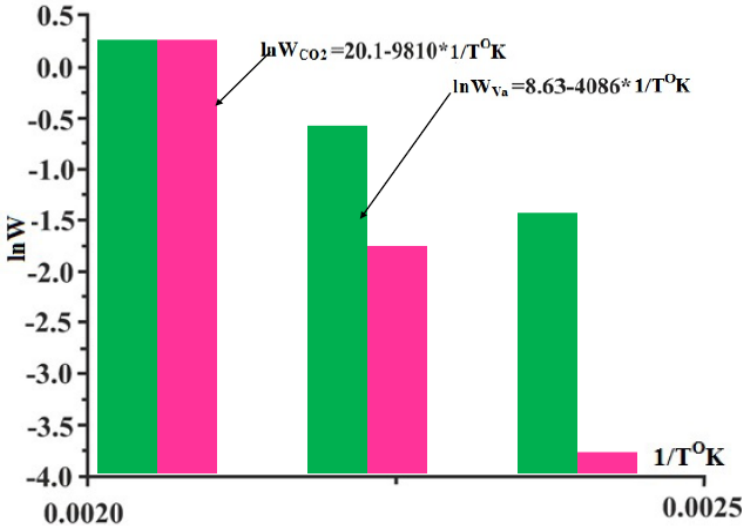

Figure 6. The inverse temperature dependence of the logarithms of the rates of formation of VA and CO_2

The calculated activation energies for VA formation and ethylene oxidation reactions are as follows:

$$E_a / R = 4086 / {}^{\circ}K \ and \ 9810 K^{-1} or$$
$$E_{a(VA)} = 8{,}17 \ kcal / (mol \cdot K) \ and$$
$$E_{a(CO_2)} = 19{,}61 \ kcal / (mol \cdot K).$$

As can be seen from the figure, increasing the reaction temperature above 220 ℃ leads to the fact that the oxidation rate of ethylene is higher than the rate of formation of VA. The mechanism of the reaction of formation of VA from ethylene and acetic acid in the presence of a palladium catalyst can be proposed as follows:

$$\mathbf{C}_2\mathrm{H}_4 + 2\mathrm{Pd} \underset{K1}{\overset{K1K}{\Leftrightarrow}} \mathrm{CH}_2 = CH - Pd \ + \ PdH$$

$$\mathbf{C}_2\mathrm{H}_4 + 2\mathrm{Pd} \underset{K1}{\overset{K1K}{\Leftrightarrow}} \mathrm{CH} = CH - Pd \ + \ PdH$$

$$\mathrm{O}_2 + 2\mathrm{Pd} \underset{\mathrm{K}_2}{\overset{K2K2}{\Leftrightarrow}} 2\mathrm{Pd} - \mathrm{O}$$

$$CH_3COOH \ + Pd \underset{\mathrm{K}_3}{\overset{\mathrm{K}_3\mathrm{K}_3}{\Leftrightarrow}} 2\mathrm{Pd} - \mathrm{CH}_3\mathrm{COOH}_{ads}$$

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

IJDIAS International Journal of Discoveries and Innovations in Applied Sciences
| e-ISSN: 2792-3983 | www.openaccessjournals.eu | Volume: 2 Issue: 3

$$Pd-CH_3COOH_{ads}+PdO \overset{K_4K_4}{\underset{K_4}{\Leftrightarrow}} PdOCOCH_3+PdOH$$

$$PdOCOCH_3+CH_2=CH\cdot Pd \overset{K_5K_5}{\underset{K_5}{\Leftrightarrow}} Pd-CH_2=CHOCOCH_{3ads}+Pd$$

$$Pd-CH_2=CHOCOCH_{3ads} \overset{K_6K_6}{\underset{K_6}{\Leftrightarrow}} Pd+CH_2=CHOCOCH_3$$

$$PdOH+PdH \overset{K_7K_7}{\underset{K_7}{\Leftrightarrow}} Pd-H_2O_{ads}; Pd-H_2O_{ads} \overset{K_8K_8}{\underset{K_8}{\Leftrightarrow}} Pd+H_2O$$

Additional (lateral) reactions:

$$CH_2=CH-Pd+PdO \overset{K_9K_9}{\underset{K_9}{\Leftrightarrow}} Pd-CO_{2ads}+Pd-H_2O_{ads}$$

$$Pd-CO_{2ads} \overset{K_{10}K_{10}}{\underset{K_{10}}{\Leftrightarrow}} Pd+CO_2$$

$$Pd-H_2O_{ads} \overset{K_{11}K_{11}}{\underset{K_{11}}{\Leftrightarrow}} Pd+H_2O$$

The interaction between the dissociatively adsorbed ethylene and acetic acid is the limiting phase. The kinetic equation for the formation of VA is written as follows:

$$W_{VA}=\frac{K_5K_1K_2^{0.5}K_3K_4P_{C2H4}\cdot P_{O2}^{0.5}P_{acetic\ acid}}{(1+K_1P_{C2H4}+(K_2P_{O2})^{0.5}+K_3P_{acetic\ acid})^2}$$

W_{VA} -catalyst activity, g/(l cat.*c); P- pressure, atm

Conclusion

Thus, the process of obtaining VA by catalytic oxidation of ethylene in the vapor phase was studied in detail in a catalyst containing 0,4%Pd + 4%Cu + 7%CH_3COOK/HSZ. It was found that the total rate of the reaction was proportional to the amount of unmodified and modified active sites of palladium (not clusters). Excessive amounts of the modifier (both potassium acetate and copper) have been shown to block active sites, reducing catalyst efficiency. As a result of the study, the following optimal conditions were selected for the reaction: at a temperature of 165 °C in the middle zone of the reactor, volume rate - 2000 h^{-1}, the ratio of ethylene to acetic acid at a pressure

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

of 4 atm to 4: 1 and oxygen content 7%. Under these optimal conditions, the activation energies of VA formation and ethylene oxidation reactions are as follows:

$$E_{a(VA)} = 8{,}17 kcal/(mol-K) \; and E_{a(CO_2)} = 19.61 \, kcal/(mol-K).$$

A reaction mechanism for the formation of VA from ethylene and acetic acid in the presence of a palladium catalyst has been proposed. Based on the results obtained, the kinetic equation of the reaction to obtain VA by oxidation of ethylene acetylene was proposed.

References

1. N.S.Sarimsakova, N.I. Fayzullaev, N.X.Musulmonov, S.T. Atamirzayeva, M.N.Ibodullayeva. Kinetics and Mechanism of Reaction for Producing Ethyl Acetate from Acetic Acid.Control Autom [Internet]2020 Apr 13; 13(02):373–82.
2. Firdavsiy, B. (2021). Influence of the Nature of the Retainer (Carrier) on the Catalytic Activity of the Catalyst in the Gas-Phase Synthesis of Vinyl Acetate from Ethylene. Turkish Journal of Computer and Mathematics Education (TURCOMAT), 12(10), 2262-2270.
3. Buronov, F.E., &Fayzullayev, N.I., Optimization of vinyl acetate production process. International scientific journal GRAIL OF SCIENCE № 4 May 2021 (Vienna, Austria). (pp 187-191). ISSN: 2710–3056 DOI 10.36074/grail-of-science.07.05.2021.035
4. Buronov F., Salohiddinov F. Mathematical model of the efficiency of the catalyst in the synthesis of vinyl acetate // Universum: технические науки : электрон. научн. журн. 2021. 5(86). (pp 82-86). URL: https://7universum.com/ru/tech/archive/item/11845
5. Normurot, F., & Firdavsiy, B. (2021). The Effect of Catalytic Activity of Catalyst (Carrier) Nature in the Synthesis of Vinyl Acetate.// https://journals.researchparks.org/index.php/IJHCS e-ISSN: 2615-8159 | p-ISSN: 2615-1898. Volume: 03 Issue: 10 |Dec 2021.
6. Abanto-Chavez H.J. Novaja tehnologija prigotovlenija cinkacetatnyh katalizatorov i kineticheskie modeli sinteza vinilacetata. [Doctoral dissertation], Mosk. akad. tonkoj himicheskoj tehnologii). (in Russian).
7. Ashpina, O. Vinyl acetate is a deficient product [Text]. The Chemical Journal. May 2016; 44-47.
8. Arapov D.V., Skrypnikov A.V., Denisenko V.V., Chernyshova E.V. Mathematical modelling of ethylene acetoxylation process on a domestic catalyst. Bulletin of the Voronezh State University of Engineering Technologies. 2018; 80 (1 (75)):124-128.
9. Voskanyan P.S. Influence of the nature of the support on the catalytic activity of a palladium catalyst for the synthesis of vinyl acetate by gas-phase acetoxylation of ethylene. Catalysis in industry. 2014 Nov 20; (4): 33-41.
10. Voskanyan P.S. Influence of the content and ratio of active components on the activity and selectivity of the catalyst for the synthesis of vinyl acetate by gas-phase acetoxylation of ethylene. Catalysis in industry. 2010; (2): 43-9.
11. Patent. 2132325 (Russia). Process in a fluidized bed for ethylene acetoxylation to obtain vinyl acetateю N.K. Benkalovich, P.R. Blum, L.M. Sirjak, M.F. Lemanski, K. Paparizos, M.E. Pepera, D.R. Wagner. 1999.

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022

12. Fayzullayev, N.I., Umirzakov, R.R., Pardaeva, S.B. Study of acetylating reaction of acetylene by gas chromatographic method. ACS National Meeting Book of Abstracts, 2005; 229(2).
13. Fajzullaev, N.I., Muradov, K.M. Investigation of reaction of catalytic vapor-phase synthesis of vinyl acetate on applied catalyst. Khimicheskaya Promyshlennost', 2004; (3): 136–139.
14. Файзуллаев, Н., & Буронов, Ф. (2021). Исследование каталитической активности катализатора в синтезе винилатцетата из этилена при различных носительях. Збірник наукових праць ΛΌΓΟΣ. DOI 10.36074/logos-30.04.2021.v1.44
15. Буронов, Ф. (2021). Винилацетат синтезида катализатор самарадорлигининг математик модели. Збірник наукових праць SCIENTIA. May 21, 2021 | Singapore, Republic of Singapore | Collection of scientific papers «SCIENTIA».
16. Buronov F., & Fayzullaev N. Active catalysts for producing vinyl acetate monomers // Universum: технические науки : электрон. научн. журн. 2021. 5(86).). (pp 79-82). URL: https://7universum.com/ru/tech/archive/item/11684
17. Fayzullayev, N. Buronov, F., Musulmonov, N., Qodirov, O., & Toshboyev, F. Effect of the Number of Active Components of the Catalyst on the Yield of the Product During the Synthesis of Vinyl Acetate From Ethylene and Acetic Acid. Bulletin of Science and Practice, (2021; 7(4):301-311. https://doi.org/10.33619/2414-2948/65/34

ISSN 2792-3983 (online), Published under Volume: 2 Issue: 3 in March-2022