

## 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

©Fayzullayev N., ORCID: 0000-0001-5838-3743, Dr habil., Samarkand State University, Samarkand, Uzbekistan, f-normurot@samdu.uz

©Buronov F., ORCID: 0000-0003-3241-3849, Karshi Engineering Economics Institute, Karshi, Uzbekistan, firdavsiy.buronov@mail.ru

©Musulmonov N., ORCID: 0000-0002-2092-3115, Ph.D., Samarkand State University, Samarkand, Uzbekistan, noryigit1977@gmail.com

©Qodirov O., Ph.D., Samarkand State University, Samarkand, Uzbekistan, oqsh@bk.ru

©Toshboyev F., Samarkand State University, Samarkand, Uzbekistan, toshboyevferuz54@gmail.com

## ВЛИЯНИЕ КОЛИЧЕСТВА АКТИВНЫХ КОМПОНЕНТОВ КАТАЛИЗАТОРА НА ВЫХОД ПРОДУКТА ПРИ СИНТЕЗЕ ВИНИЛАЦЕТАТА ИЗ ЭТИЛЕНА И УКСУСНОЙ КИСЛОТЫ

©Файзуллаев Н. И., ORCID: 0000-0001-5838-3743, д-р техн. наук, Самаркандский государственный университет, г. Самарканд, Узбекистан, f-normurot@samdu.uz

©Буронов Ф. Э., ORCID: 0000-0003-3241-3849, Каршинский инженерно-экономический институт, г. Карши, Узбекистан, firdavsiy.buronov@mail.ru

©Мусулмонов Н. Х., ORCID: 0000-0002-2092-3115, канд. техн. наук, Самаркандский государственный университет, г. Самарканд, Узбекистан, noryigit1977@gmail.com

©Кодиров О. Ш., канд. фармацевт. наук, Самаркандский государственный университет, г. Самарканд, Узбекистан,

©Тошбоев Ф. Н., Самаркандский государственный университет, oqsh@bk.ru  
г. Самарканд, Узбекистан, toshboyevferuz54@gmail.com

*Abstract.* The development of active and selective catalysts for the synthesis of vinyl acetate from ethylene and acetic acid, the effect of the amount and ratio of individual components of the catalyst to control the catalytic properties of the introduced components were studied. In vinyl acetate synthesis, the effects of each component were studied to describe the effect of catalyst constituents on its properties, and empirical one-factor mathematical dependencies were obtained. Their generalized mathematical relationships of the activities of the catalysts, defined as the rates of the reactions of the formation of vinyl acetate and CO<sub>2</sub>, have been proposed. As a result of the research, a mathematical model was proposed to select the most optimal composition of the catalyst. The activity of the catalyst containing 0.4%Pd+4%Cu+7%CH<sub>3</sub>COOK/HSZ averaged 700 g VA/(1×cat×h) at 93–97% selectivity of ethylene-vinyl acetate formation.

*Аннотация.* При разработке активных и селективных катализаторов синтеза винилацетата из этилена и уксусной кислоты изучалось влияние количества и соотношения отдельных компонентов катализатора с целью контроля каталитических свойств вводимых компонентов. При синтезе винилацетата влияние каждого компонента было изучено для описания влияния компонентов катализатора на его свойства. Были получены эмпирические однофакторные математические зависимости. Предложены обобщенные математические зависимости активностей катализаторов, которые определяются как скорости реакций

образования винилацетата и CO<sub>2</sub>. В результате исследований была предложена математическая модель для выбора наиболее оптимального состава катализатора. Активность катализатора, содержащего 0,4%Pd+4%Cu+7%CH<sub>3</sub>COOK/ВКЦ, составляла в среднем 700 г ВА/(л×кат×ч) при селективности образования винилацетата по этилену 93–97%.

*Keywords:* vinyl acetate, acetic acid, exothermic process, catalyst preparation methods.

*Ключевые слова:* винилацетат, уксусная кислота, экзотермический процесс, способы получения катализаторов.

### Introduction

Vinyl acetate (VA) is one of the important monomers, the production of which is growing rapidly worldwide. Vinyl acetate is a raw material for the production of polyvinyl acetate, which is used as a binder in the manufacture of polymer concrete, as a base for adhesives, as a film former in the production of emulsion varnishes and paints, in the form of aqueous dispersions for the production of polyvinyl alcohol and polyvinyl acetates [1–2]. With acidic or alkaline alcoholysis of polyvinyl acetate, polyvinyl alcohol is obtained, which is widely used as an emulsifier in the polymerization of fibres, as well as in the production of medicines, blood substitutes and plasma substitutes. Also, vinyl chloride, ethylene, acrylic acid esters, styrene-vinyl acetate copolymers are widely used [3–4]. At present (2000–2003)) the world consumption of vinyl acetate is 4.0–4.5 million tons per year. As in Russia, and several other countries, the industrial production of vinyl acetate is carried out in two ways:

1. Based on acetylene and acetic acid [5–7];
2. Based on ethylene, acetic acid and oxygen.

The advantage of the second method over the first is the lower cost of ethylene compared to acetylene.

The oxidation process of C<sub>2</sub>H<sub>4</sub> ethylene to vinyl acetate (Moiseev's reaction) [8] is based on the following reaction:



This previously unknown reaction is carried out in a homogeneous catalytic system based on palladium and copper compounds [9] and a heterogeneous catalyst containing palladium [10]. In industry, the process of producing vinyl acetate from ethylene [11] is carried out as follows: a gas mixture consisting of oxygen, acetic acid and an excess of ethylene is passed over the catalyst at a temperature of 150–170 °C and a pressure of about 5 MPa (the catalyst contains an oxidation-resistant carrier, for example, palladium, which is dipped in spherical silicon oxide with a particle of 4–5 mm in diameter). To increase catalytic activity and reduce oxidation, a few per cent of Na is added to the catalyst (1% potassium acetate increases the process rate by about 10 times, however, a positive place can be occupied by the content of potassium acetate up to 2–3%, a further increase of which leads to a decrease in the rate of the process). The process is considered a very powerful exothermic process; therefore, it is carried out in a tubular reactor with an internal diameter of about 25 mm using boiling water as a heat carrier.

Ethylene conversion is about 10–20% at 60–70% oxygen consumption in one pass.

The selectivity of this process is quite high: 91–94% is accounted for by ethylene, which has entered into a chemical reaction. About 1% of ethylene is consumed in the formation of acetaldehyde, and the rest is converted to carbon dioxide. Many publications provide methods for preparing catalysts for producing vinyl acetate in a heterogeneous form by oxidative acetoxylation of ethylene [12–20]. In all these works, the catalyst contains palladium and its compounds, compounds of alkali metals, as well as gold or cadmium and their compounds in the carrier. In [12], it is also proposed to change the composition of the carriers. Currently, more than 90% of all vinyl acetate is obtained by gas-phase acetoxylation of ethylene in the presence of modified heterogeneous catalysts:



In 1996, about 88% of vinyl acetate was obtained by oxidative acetoxylation of ethylene. Synthesis of vinyl acetate by gas-phase acetoxylation of ethylene, the main active component of which is Pd or is precipitated in various porous and acetic acid-resistant adsorbents (aluminium oxide, silica gel, zeolites, coal, pumice, aluminosilicates), its salts in a finely dispersed state are carried out in the presence of catalysts included in the mixture. The Pd content in the catalysts is from 0.1 to 10%. In addition to Pd and its salts, the catalyst retains alkali metal acetates (from 1 to 30%) as modifying additives, without which the reaction with the formation of vinyl acetate practically does not take place. The most active catalysts are based on potassium acetate (PA).

Often modifying additives are offered to increase catalyst activity, selectivity, and performance stability. We studied the effect of ethylene on the volumetric velocity of the vapour-gas mixture in the acetylation reaction in the vapour phase, the total pressure in the reactor, the oxygen concentration in the vapour-gas mixture, the ratio of ethylene and acetic acid concentrations, the synthesis temperature, and the rate and selectivity of hydrothermal processes. The process takes place under the following conditions: temperature around 165 °C, pressure 0.4 MPa, catalyst: 0.4%Pd+4%Cu+7%CH<sub>3</sub>COOK/HSZ were administered by ingestion of potassium acetate with a vapour-gas mixture at a rate of 2000 h<sup>-1</sup> volume of the vapour-gas mixture and a volume of oxygen with ethylene in the mixture at 7 vol.%. During 2000 hours of operation, the catalyst activity was 95–97% selectivity at 370–350 g of vinyl acetate/1×cat×hours.

This work aims to study the effect of changes in the chemical composition of the catalyst containing 0.4%Pd+4%Cu+7%CH<sub>3</sub>COOK/HSZ on its activity, selectivity and service life.

### *Experimental Part*

The process of synthesis of vinyl acetate was carried out at a temperature of 145–200 °C (temperature rises slowly depending on the activity of the catalyst), pressure 0.4 MPa, volumetric rate of delivery of the vapour-gas mixture (MGM) at 2000 h<sup>-1</sup>. 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%. Vinyl acetate synthesis is accomplished by the 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%. Vinyl acetate synthesis is carried out in an experimental device for the preparation of a complex catalyst. The process consists of two stages.

*Preparation of a catalytic base for the introduction of metals.* The required amount of distilled water is poured into the autoclave, on the surface of which, for example, in the sieve is placed the calculated amount of silica gel sample selected as the future holder of the catalytic complex. The

autoclave is closed, the heating is switched on, and the silica gel is subjected to a hydrothermal action in the chamber at a temperature of 200–320 °C for a calculated number of hours. The autoclave heating is then turned off, the pressure removed, and the holding air left to cool. The cooled, hydrothermal prepared holder is emptied, its porosity and specific surface area are checked, and if it is not suitable, it is used to prepare the catalyst. The radius and size of the pores are controlled by a P-5M mercury parametric device based on the amount of mercury squeezed into the pores. The comparative surface is carried out on the Color-800 chromatograph by the method of low-temperature adsorption of inert gas argon. The pile density is calculated as the ratio of the mass of the weighed particles to the measured volume of the mass weighed in the measuring cylinder. Addition of the required amount of active substance: palladium, copper and metal acetates to the surface of the catalytic base is carried out as follows.

The calculated amount of chemically pure sodium tetrachloropalladate salt is dissolved in distilled water, then the required amount of evaporated holder prepared in an autoclave (in litres) is added, then the water is evaporated in a rotor evaporator, then the catalyst is dried in hot air at a temperature not exceeding 100–120 °C. After drying, the semi-finished product of the catalyst is placed in a bath with an aqueous solution of sodium hydroxide and kept for 24–28 hours. During this time, the transition of the palladium chloride salt to water-insoluble palladium hydroxide is completed. The semi-finished product of the catalyst is then placed in a bath containing an aqueous solution of 7% hydrazine hydrate and held for a calculated time. This is necessary to return the active component to the metallic state. The described mode of absorption and retention allows obtaining a ready-made catalyst. On the cross-sectional surface of the granules, the thickness of the palladium layer 0.1–3.0 mm, located at a depth of 3–5 mm from the surface, is visible. After the metal catalyst is returned, it is placed in a bath and the hydrazine is washed thoroughly with distilled water from the hydrate and chloride ions. The end of the washing process is the absence of traces of hydrazine hydrate and chloride ions in the washed water. Then the finished semi-finished product of the catalyst should be dried with hot air at a temperature not exceeding 120 °C. Copper insertion technology is similar to palladium insertion. The starting material here is a catalytic base with a palladium insert and a chemically pure hydrogen copper chloride  $\text{HCuCl}_4 \times 4\text{H}_2\text{O}$  acid. To add potassium acetate to the holding surface, the calculated amount of potassium acetate salt is dissolved in a vessel of distilled water and the appropriate amount of prepared palladium or copper-palladium catalyst is added to the solution (in litres). The solution is then evaporated in a rotary evaporator at a temperature of 100 °C to a residual humidity not exceeding 2.0%. The finished catalyst is then discharged and used as intended.

The concentrations of palladium and copper in the finished catalyst are monitored as follows on a spectrophotometer. First, the rare metals are transferred to a hydrochloric acid solution, then the solution is sprayed into a flammable acetylene flame in the air, and the adsorption of copper and palladium atoms is measured. Their amount is determined for resonance lines: copper — 242.8 nm, palladium — 247.8 nm on a pre-formed calibration line for control solutions with a given concentration of metals. Hollow cathode lamps for copper and palladium are sources of resonant radiation. Potassium acetate concentration is monitored on a PAZh-1 (*Plammeno-fotometricheskii Analizator Zhidkosti — Flame Photometric Liquid Analyzer*) flame photometer by the spectrophotometric method. The essence of the method is to compare the intensity of the resonance lines of potassium and the control solution, which are analyzed in the combustion flame of propane-butane mixtures in air.

HSZ (high silica zeolite) with 200 °C hydrothermal treatment for 6 hours, the specific surface area of 150 m<sup>2</sup>/g, pore density of 54 g/cm<sup>3</sup>, the pore size of 0.78 cm<sup>3</sup>/g and particle diameter of

4.5–5.0 mm were used as catalyst preparation. Absorbed with an aqueous solution of sodium tetrachloropalladate with a moisture content of not more than 4.0%, and in the presence of copper in the catalyst — with a mixture of sodium tetrachloropalladate and hydrogen monochloride acid, the amount of solution corresponded to the moisture content of the holder. The absorbed precipitate was dried with hot air at 120 and then treated with an aqueous solution of NaOH to convert the precious metal chlorides to their water-insoluble hydroxides. After 23–25 hours of storage, the precious metals from the salts were returned with a hydrazine-hydrate solution. The catalyst was then washed with distilled water until it did not contain  $\text{Cl}^-$  ions in the wash water and dried with hot air. The dried semi-finished product of the catalyst was ingested with an appropriate amount of aqueous solution of  $\text{CH}_3\text{COOK}$  and dried with hot air at  $\leq 120$  °C. The catalysts were tested in a 20 mm diameter, 900 mm high (heated oil to dissipate the heat of the exothermic reaction to the formation of vinyl acetate and  $\text{CO}_2$ ) in a tube-reactor in a demonstration device of vinyl acetate synthesis.

Each of the catalyst samples was tested for 36-40 hours at a load of  $100 \text{ cm}^3$  of catalyst in the reactor, and the optimal process parameters found experimentally for this device were: 165 °C, 0.4 MPa, ethylene: acetic acid ratio 4:1, volumetric rate  $6000 \text{ h}^{-1}$ , the amount of oxygen in the dry gas is 7.0 volume %. Under the specified conditions, the reaction of the formation of vinyl acetate and  $\text{CO}_2$  proceeds with a slight effect of diffusion in the kinetic field, which begins to manifest only with an increase in the time of the vapor-gas mixture in the reactor — at a volumetric velocity of  $3000 \text{ h}^{-1}$ . The composition of the vinyl acetate feedstock and gas mixture was determined by the chromatographic method after the reactor. Catalyst performance criteria — its activity  $g \text{ VA} / (1 \text{ cat} \times \text{h})$  and selectivity for the formation of vinyl acetate on ethylene, the reaction rate was calculated for  $100 \text{ cm}^3$  of the total mass of the catalyst in the reactor.

### Results and Discussion

The observed changes (decrease) in catalyst activity and  $\text{CO}_2$  formation over time (main by-product) are not linear in the presence of different catalyst samples and can be described by the following equations:

$$n_{\text{VA}} = n_{0\text{VA}} \tau \cdot \exp(-\gamma \tau), \quad (1)$$

$$n_{\text{CO}_2} = n_{0\text{CO}_2} \tau \cdot \exp(-\gamma \tau), \quad (2)$$

Here  $\tau$  is the operating time of the device,  $\gamma$  is the instability coefficient of the catalyst over time,  $n_0$  is the time-independent constants, the equivalent output velocities,  $\exp(-\gamma \tau)$  is the product of the functional dependence of the catalyst activity (instability) over time. A series of one-factor experiments were set up to develop a general mathematical model showing the activity and selectivity of the catalyst, in which the amount of Pd,  $\text{CH}_3\text{COOK}$ , and the second modifier — Cu was changed over as wide a range as possible.

As can be seen from the data obtained (Table 1), the change (decrease) in catalyst activity over time for different quantitative catalysts of Pd in the samples is not linear, indicating unstable catalyst performance (among these experiments the catalyst retained 7%  $\text{CH}_3\text{COOK}$ ). In this case, the degree of decontamination depends on the amount of Pd. We observe the same relationship between the formation of vinyl acetate and the change in catalyst activity for the combustion reactions of ethylene. The obtained mathematical dependencies are given in Table 2. The nature of the dependence of the catalyst activity on the amount of Pd can be explained by the fact that the reaction takes place in different active centres of the catalyst. The main contribution is when it consists of individual metal atoms. As the Pd concentration increases, clusters of the less active

[...Pd-Pd-Pd..] type are formed. Using the obtained equations, it is possible to determine the concentration of Pd, in which the greatest selectivity is observed.

Table 1.

THE NUMBER OF PRODUCTS FORMED (N) OVER TIME,  
 DEPENDING ON THE COMPOSITION OF THE CATALYST

Content, %	n	Time, h, and amounts, mol, of the VA and CO <sub>2</sub> products formed during the time, h								
		4	8	12	16	20	24	28	32	36
<i>Pd % 7% CH<sub>3</sub>COOK</i>										
1.0	VA	0.49	0.95	1.39	1.82	2.24	2.64	2.99	3.33	3.65
	CO <sub>2</sub>	0.19	38	55	0.72	0.89	1.04	1.18	1.14	1.44
2.0	VA	0.80	1.69	2.37	3.03	3.57	4.09	4.54	4.91	5.25
	CO <sub>2</sub>	0.16	30	0.42	54	0.64	0.73	0.81	0.88	0.94
3.0	VA	1.21	2.38	3.52	4.62	5.68	6.72	7.72	8.68	9.62
	CO <sub>2</sub>	0.26	52	0.76	1.00	1.23	1.46	1.68	1.89	2.09
0.4	VA	1.72	3.41	7.04	6.58	8.09	9.39	10.69	11.82	12.8
	CO <sub>2</sub>	39	0.71	1.16	1.51	1.86	2.16	2.46	2.72	2.94
0.2	VA	1.3	2.56	3.78	4.49	6.06	7.14	8.17	9.15	10.08
	CO <sub>2</sub>	0.41	0.81	1.19	1.56	1.91	2.25	2.57	2.88	3.17
0.1	VA	0.91	1.64	2.29	2.95	3.53	4.01	4.4	4.68	-
	CO <sub>2</sub>	0.4	0.61	0.85	1.01	1.32	1.49	1.64	1.74	-
<i>CH<sub>3</sub>COOK % 0.4 % Pd</i>										
	VA	1.25	2.46	3.72	7.02	6.23	7.49	8.79	10.05	11.26
	CO <sub>2</sub>	37	0.74	1.11	1.51	1.86	2.24	2.63	3.03	3.36
15	VA	1.49	2.93	4.42	5.86	7.39	8.84	133	11.72	13.21
	CO <sub>2</sub>	37	0.72	1.09	1.45	1.83	2.19	2.55	2.89	3.26
10	VA	1.63	3.30	4.88	6.51	8.19	9.72	11.30	12.93	14.51
	CO <sub>2</sub>	31	0.63	0.93	1.24	1.56	1.85	2.15	2.46	2.76
7	VA	1.61	3.24	4.89	6.47	8.01	9.61	11.24	12.82	14.35
6	VA	1.61	3.26	4.88	6.42	8.02	9.61	11.23	12.82	14.35
5	VA	1.58	3.21	4.79	6.33	7.91	9.44	11.07	12.65	14.17
3	VA	1.16	2.28	3.49	4.74	5.91	7.02	8.18	9.31	137
2	VA	37	0.79	1.26	1.63	1.95	2.23	2.61	2.93	3.21
<i>Cu % 0.4 % Pd+7% CH<sub>3</sub>COOK</i>										
0.00	VA	0.86	1.69	2.20	3.18	3.72	4.06	4.44	4.76	7.00
	CO <sub>2</sub>	0.28	55	0.79	1.04	1.21	1.32	1.45	1.55	1.63
0.1	VA	0.91	1.86	2.74	3.61	4.25	4.67	4.95	5.21	5.49
	CO <sub>2</sub>	0.29	0.61	0.89	1.18	1.38	1.52	1.61	1.69	1.79
0.5	VA	1.28	2.42	3.49	4.49	5.53	6.32	7.02	7.65	8.16
	VA	35	0.66	0.95	1.23	1.51	1.72	1.92	2.09	2.23
1	VA	1.65	3.09	4.39	5.77	7.16	8.51	9.95	11.30	12.69
	CO <sub>2</sub>	33	54	0.76	1.14	1.42	1.48	1.73	2.24	2.511
2	VA	1.69	3.27	4.86	6.35	7.86	9.35	10.86	12.35	13.81
	CO <sub>2</sub>	38	0.73	1.08	1.41	1.75	2.08	2.41	2.74	3.07
4.0	VA	1.74	3.46	5.14	6.81	8.58	137	11.91	13.56	15.14
	CO <sub>2</sub>	0.43	0.85	1.27	1.68	2.12	2.56	2.94	3.35	3.74
6	VA	1.74	3.63	5.56	7.39	9.25	11.21	13.18	17.05	16.84
	CO <sub>2</sub>	0.47	39	1.52	2.02	2.52	3.06	3.59	4.12	5.49

The dependence of the change in catalyst activity overtime on the amount of CH<sub>3</sub>COOK in the range of 5 to 20% turned out to be almost linear (in this series of experiments, the catalyst retained 0.4% Pd). The observed decrease in activity for samples with CH<sub>3</sub>COOK ≈3% is adequately described by the equation  $\gamma = 0.001$ . A decrease in the amount of this modifier additive increases the instability of the catalyst and increases the instability coefficient  $\gamma$  to 0.008. An increase in the amount of CH<sub>3</sub>COOK to 5–6 ms % increases the activity, but with its subsequent increase, the reaction rate begins to decrease. The rate of oxidation of ethylene to CO<sub>2</sub> also increases with the amount of CH<sub>3</sub>COOK but changes little when it reaches a maximum.

Therefore, the amount of CH<sub>3</sub>COOK in the primary catalyst should be 5–6%, taking into account its leakage from the catalyst surface during operation. This explains the low rate of vinyl acetate formation in the amount of acetate additive <2%. In this case, it is necessary to carry out the process by continuously injecting the CH<sub>3</sub>COOK solution into the vapor-gas mixture entering the reactor to maintain the required speed. The obtained dependencies are given in Table 2.

Table 2.

MATHEMATICAL DEPENDENCE OF THE SPEED OF THE PROCESS  
 IN A SERIES OF SINGLE-FACTOR EXPERIMENTS

A series of experiments	Content in the catalyst, %			W <sub>VA</sub> moll/h	W <sub>CO2</sub> moll/h
	Pd	PA	Cu		
1	3–3.0	7.0	0	(35[Pd])/(1+0.05[Pd] <sup>4</sup> )	(0.08[Pd])/(1+0.065[Pd] <sup>3</sup> )
2	0.6	2,0–20,0	0	(0.1(1+[KA]))/(1.0+0.0133[KA] <sup>2</sup> )	0.04+0.0043[KA]
3	0.6	7.0	0.05–3.0	(0.24+0.47[Cu])/(1+1.75[Cu])	0.075+0.018[Cu]
CH <sub>3</sub> COOK- (PA)					

In the last step, the effect of copper addition on the catalyst activity and the selectivity of vinyl acetate formation on ethylene was studied (in this series of experiments, the catalyst retained 0.4% Pd and 7% CH<sub>3</sub>COOK). The rate of formation of vinyl acetate is described by the fractional-linear equation. It is important to study the dependence of the change in the rate of CO<sub>2</sub> formation when the amount of Cu in the sample changes. The oxidation rate of ethylene turned out to be linearly related to the amount of Cu in the catalyst and is represented by a linear function. It has been shown that the addition of 3–5% Cu to the catalyst allows to obtain a time-stable catalyst and increase its activity by ≈30%, almost without increasing the rate of combustion of ethylene. The physical meaning of the given dependencies reflects the assumption that the total rate of reactions is proportional to the amount of modified and unmodified Pd active centres but at different levels.

In an abundant amount of the modifier, some of the active sites become blocked and the reaction rate decreases. In the figure, the magnitudes are proportional to all active sites, and in the denominator to -Pd-Pd-Pd- palladium inactive cluster aggregates and single-atom Pd-centers inhibited by excess Cu and CH<sub>3</sub>COOK. It should be noted that the difference in the equations of velocity formation of vinyl acetate and SO<sub>2</sub> testifies to the fact that these reactions take place in different active centres of the catalyst.

Empirical dependencies are in the simplest variant:

$$WVA = [Pd](C_1 + C_2[CH_3COOK] + C_3[Cu]) / (1 + C_4[Pd]^4 + C_5[CH_3COOK]^2 + C_6[Cu]), \quad (3)$$

$$(4)$$

$$W_{CO_2} = [Pd](C'_1 + C'_2[CH_3COOK] + C'_3[Cu]) / (1 + C'_4[Cu]^3)$$

The numerical values of  $C_1$ - $C$  and  $S$   $C_1$ - $C_6$  и  $C'_1$ - $C'_6$  coefficients that support the multi regression method are obtained. Generalized mathematical dependencies, which allow calculating the optimal composition of the catalyst, are defined as Vinylacetate and  $CO_2$  formation speeds:

$$WVA = [Pd](35+38[CH_3COOK]+4.2[Cu]):(1+0.05(1+80[Pd]^4+0.01[CH_3COOK]^2+1.1[Cu]) \quad (5)$$

$$W_{CO_2} = [Pd](0.09 + 0.024[CH_3COOK]+0.1[Cu])/(1 + 0,07(1 + 20[CH_3COOK])[Pd]^3) \quad (6)$$

In all series of experiments, the rates of the vinyl acetate formation reaction obtained, and the calculated values have a good correlation with these dependencies.

Formation reaction rates Correlation rates vinyl acetate — 0.98,  $CO_2$  — 0.92. Using the dependences of the catalyst activity on the stored components in it (Pd,  $CH_3COOK$  and Cu), their optimal amount was determined to achieve both high activity and selectivity of vinyl acetate formation. The data obtained showed that their activity and selectivity were stable over time. The activity of the catalysts was 340–290, 550–480, 750–670 g VA/(1×cat×h), respectively, at 95–92% selectivity of vinyl acetate formation on ethylene.

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#### Conclusion

The development of active and selective catalysts for the synthesis of vinyl acetate from ethylene and acetic acid, the effect of the amount and ratio of individual components of the catalyst was studied to control the catalytic properties of the introduced components. In vinyl acetate synthesis, the effects of each component were studied to describe the effect of catalyst constituents on its properties, and empirical one-factor mathematical dependencies were obtained. The generalized mathematical dependences of the catalyst activities, defined as the rates of the reactions of the formation of vinyl acetate and  $CO_2$ , have been proposed. As a result of the research, a mathematical model was proposed to select the most optimal composition of the catalyst. The activity of the catalyst containing 0.4%Pd+4%Cu+7% $CH_3COOK$ /HSZ averaged 700 g VA/(1×cat×h) at 93–97% selectivity of vinyl acetate formation on ethylene.

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