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Research Article

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

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Abstract: The article examines the effect of γ-Al_2O_3, high-silicon zeolite (HSZ), bentonite, expanded clay, the nature of bentonites, their porous structure, methods of preparation and modes on the activity of the catalyst consisting of palladium, copper and potassium acetate for the vapour phase synthesis of ethylene-vinyl acetate. IR spectra of the synthesized samples were recorded in the reflection mode in the range 400–4000 cm^{-1} using a Nexus Nicolet Fourier transform IR spectrometer (Thermo Scientific). Thermal studies (TG/DTG-DTA) were carried out on an STA-1500H thermal balance. The specific surface area was determined by the method of low-temperature nitrogen adsorption using a Quantachrome Autosorb-6B instrument. X-ray structural analysis (XRD) was investigated in the range 5–80° 2θ on a DRON 3M diffractometer using a CuK_α (λ=1,54178 ̊A) radiation source. X-ray photoelectron spectra were recorded on a SERIES 800XPS Kratos photoelectron spectrometer. Transmission electron microscopy (TEM) photomicrographs were obtained using a JEM100CX-II electron microscope.The specific surface area was determined by low-temperature argon adsorption on a Crystallux-4000M gas chromatograph. The size and radius of the pores were determined using mercury porometry directly on the amount of mercury compressed in them in a mercury porometric device that allows the measurement of the size of the pores. Vinyl acetate synthesis in a pilot device on a catalyst containing 0,4%Pd+4%Cu+7%CH_3COOK/HSZ for 2000 hours at a temperature of 165 °C, a pressure of 0.1 MPa, a vapour-gas mixture at a volumetric rate of 2000 h^{-1} and the amount of oxygen in the mixture with ethylene Performed when 7 vol.%. During 2000 hours of operation, the catalyst activity was 95-97% selectivity at 370-350 g of vinyl acetate/l. cat. hours.

Keywords: ethylene, acetic acid, acetoxylation, vinyl acetate, carrier, selectivity.

1. Introduction

Vinyl acetate (VA) is one of the most important monomers in the plastics industry and serves as the main raw material for the synthesis of polymers of complex vinyl esters of carbonic acids. Polyvinyl acetate is a complex ester of polyvinyl alcohol, as well as derivatives of polyvinyl alcohol and polyvinyl alcohol - polyvinyl acetals, in particular polyvinyl butyral, polyvinyl formal and others [1].

Acetylene, ethylene, acetaldehyde, methanol and ethylidene diacetate are used as the main raw materials in the production of vinyl acetate. Until 1967, in industry, vinyl acetate was produced only from acetylene and acetic acid by the vapour-phase method. By the mid-1980s, two-thirds of the vinyl acetate produced was derived from ethylene, acetic acid, and oxygen. In recent years, there has been great interest in the processes of obtaining vinyl acetate by methanol-based methyl acetate and ethylidene diacetate, a much cheaper and more commonly inexpensive raw material [2].

Currently, most industrial plants in the world produce vinyl acetate from ethylene by gas-phase acetoxidation. The main manufacturers of vinyl acetate monomer in the world market are Celanese, Lyondell Basell, Dow Chemical, Du Pont (USA), Ineos (UK), Wacker Chemie (Germany), Acetex Chimie. (France).

In the former Soviet Union, Stavrolen LLC (Russia) is intended for the production of ethylene and vinyl acetate on the basis of Nevinnomysskiy Nitrogen (Russia) and SSME Nitrogen Association (Ukraine) - acetylene. The production capacity of vinyl acetate at Stavrolen LLC is 50,000. t/year. The synthesis of vinyl acetate is carried out in the gas phase in the immobile layer of a heterogeneous catalyst, the spherical particles of aluminosilicate containing finely dispersed palladium, copper and potassium acetate act as a catalyst. The activity of the catalyst is 270-300 g of vinyl acetate/*l* cat. h, the selectivity for the formation of vinyl acetate on ethylene is 89-91%. The service life of the catalyst is at least 1 year.

Acetylene-based vinyl acetate production unit capacity is 20-25 thousand tons per year. In this process, zinc acetate absorbed into activated carbon acts as a catalyst [3-7]. The activity of the catalyst is 50-60 g VA/l cat. h, service life - no more than 4 months. Today, the annual growth of the global market for vinyl acetate production averages 5% per year, and the expected growth rates in Asian countries are expected primarily in China [8].

Synthesis of vinyl acetate from ethylene is carried out at a pressure of 0.8 MPa and a slow rise in temperature from 145 to 200 °C to maintain the specified activity of the catalyst throughout the year; the volumetric velocity of the gas mixture is 2000 h^{-1}, the proportion of oxygen in relation to ethylene to dry gas is 7.0% by volume, which is limited by the explosive limit of the mixture of ethylene with oxygen. It should be noted that the synthesis of vinyl acetate is carried out by incomplete conversion of the primary reagents - ethylene, acetic acid, and oxygen (~ 8; 18 and 45%, respectively). After proper purification, the initial components that did not react are returned to the vinyl acetate synthesis reactor node. Therefore, the problems remain relevant on the basis of research, including palladium and its compounds, aimed at accelerating the synthesis of vinyl acetate from ethylene and finding new catalytic systems [9].

In addition to the search for more active catalysts based on the optimization of the chemical composition of the catalyst and the methods of its preparation, the study of the nature and effectiveness of the inorganic carrier as an important component of the catalyst is of great interest. Relatively inexpensive and common inorganic materials are activated carbon, pumice, alumina, asbestos, silicon carbide, zeolites, aluminosilicate gel, silica gel [10-18] and other materials resistant to acetic acid as catalyst holders in the synthesis of vinyl acetate. Despite the large selection of materials available, most of the published work, based on experimental data, states that alumina and silica gel-based carriers are preferred [19-28].

In this article, we studied the effect of γ-Al_2O_3, high-silicon zeolite (HSZ), Claydite, nature of bentonites, porous structure, methods and modes of their preparation on the activity of the catalyst consisting of palladium, copper and potassium acetate for the synthesis of ethylene-vinyl acetate in the vapour phase.

2. Experimental part

The content of Pd and Cu in the catalytic composition was determined by the X-ray spectral fluorescence method on a VR A-30 analyser with an X-ray tube Cr anode. The texture properties of the coatings (specific surface area and pore volume) were studied by low-temperature nitrogen adsorption on an ASAP 2400 Micro metrics setup at 77 K. The morphological properties of the coatings were studied by scanning electron microscopy (SEM) using a JSM 6460LV microscope (JEOL, Japan) and transmission electron microscopy (TEM) using a JEM-2010 microscope (JEOL, Japan). The local elemental composition of the catalyst surface was studied by energy dispersive X-ray analysis using an EDA X (EDA X Co) energy dispersive X-ray spectrometer. The activity of the catalysts in the ethylene acetoxylation reaction was measured in a flow-through reactor at a space velocity of 1000 h^{-1}.

The synthesis of a colloidal solution of palladium nanoparticles was carried out according to the procedures [33–35]. Weighed portions of polyvinylpyrrolidone and sodium hydroxide were dissolved in ethylene glycol with constant vigorous stirring and heating under reflux. The resulting reaction mixture was heated to 120 °C and aqueous solutions of $PdCl_2$ and $CuCl_2$ were slowly added dropwise.

The resulting solution was kept at 120 °C for 60 min and cooled to room temperature. The resulting colloid containing palladium nanoparticles stabilized by polyvinylpyrrolidone was precipitated with acetone with stirring, followed by redispersion of the precipitated precipitate in ethyl alcohol.

Catalysts supported with palladium nanoparticles on a high-silica (HSZ) support were prepared as follows. The required volume of colloidal solution was added to the high-silica supports pre-dried at 200 °C, based on the content of 0.4% Pd and 4% Cu in the finished catalyst, and dried, stirring occasionally, at 75-80 °C, preventing the solution from boiling, with further drying at 160 °C for 4 h. The deposition of palladium and copper nanoparticles on HSZ was carried out as follows. The carrier was preliminarily crushed, a 0.25-0.5 mm fraction was selected, and calcined at 650 °C in a muffle furnace. The cooled HSZ was mixed with an appropriate amount of palladium colloid to obtain 0,4%Pd+4%Cu+7%CH_3COOK/HSZ and evaporated at 85 °C with periodic stirring until the catalyst was completely dry. The resulting mass was dried at 130 °C for 4 h. Samples for obtaining TEM (Transmission electron microscopy) images were prepared by applying a drop of a colloidal solution of nanoparticles in ethanol onto a copper grid covered with a thin carbon film. A sample of 600-800 particles was used to construct particle size distribution diagrams.

Samples of 0,4%Pd+4%Cu+7%CH_3COOK/HSZ were ground in an agate mortar to a powdery state and dispersed in ethanol, after which TEM images were obtained in a similar manner. The content and concentration of acid sites were determined by the Boehm method. A weighed portion of the sample was kept in a 0.05 N NaOH solution for a day, after which the sample was filtered and a given volume of hydrochloric acid was added to the filtrate. The resulting sample was titrated potentiometrically with 0.05N sodium hydroxide solution.

According to the TEM data (Figure 1), the initial sample (calcined at 630 °C) contains palladium in the form of $PdCl_2$ chloride nanoparticles with a size of 2-4 nm. Thermal ageing of the sample at 1000 °C leads to significant particle agglomeration. The size of the formed agglomerates, according to TEM data, is 150-200 nm.

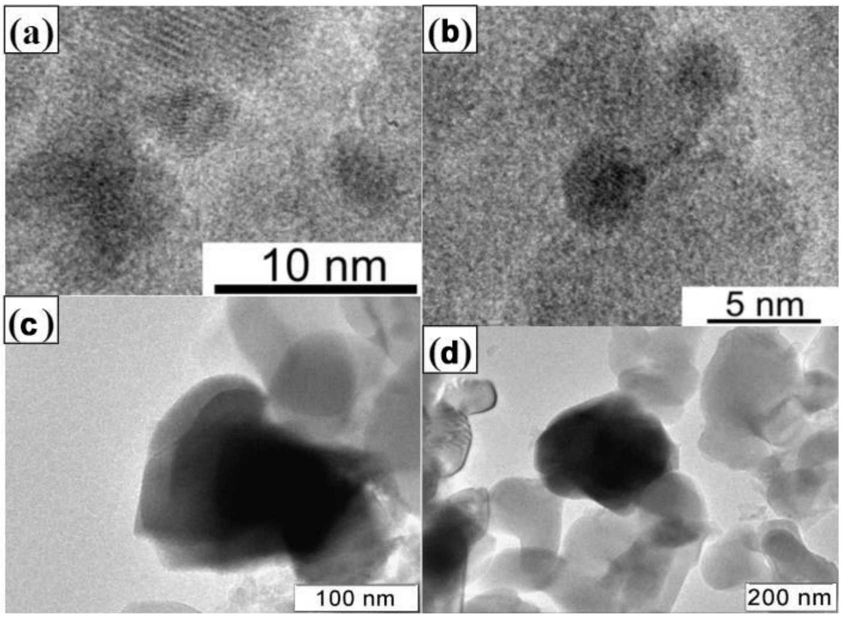
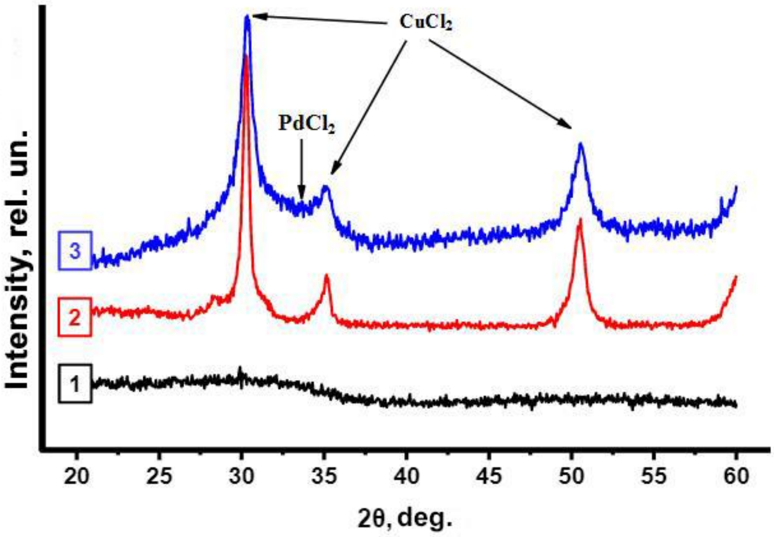


Figure 1. TEM micrographs of the catalyst 0,4%Pd+4%Cu+7%CH_3COOK/HSZ calcined at 630 °C (a, b) and 1000 °C (c, d).

A sample of 0,4%Pd+4%Cu+7%CH_3COOK/HSZ containing palladium was examined by the XRF method (X-ray fluorescence analysis). Figure 2 shows the diffractograms for this sample as well as for the carrier. It can be seen that, as a result of calcination, the formation of the HSZ crystal structure occurs, which corresponds to the appearance of the corresponding reflections in the diffractogram. The diffractogram for the palladium-containing catalyst also clearly shows an enlarged region in the region of 33°, related to the dispersed phase of $PdCl_2$. It should be noted that for other samples with lower metal content, similar changes in the diffractograms of relatively pure support were not observed.



(1) HSZ (not processed); (2) HSZ (after calcination at 1100 °C);
(3) 0,4%Pd+4%Cu+7%CH_3COOK/HSZ (after calcination at 1100 °C)

Figure 2. XRF diffraction patterns of the HSZ support (untreated and calcined at 1100 °C) and the 0,4%Pd+4%Cu+7%CH_3COOK/HSZ catalyst.

IR spectra of the synthesized samples were recorded in the reflection mode in the range 400–4000 cm^{-1} using a Nexus Nicolet Fourier transform IR spectrometer (Thermo Scientific). Thermal studies (TG / DTG-DTA) were carried out on an STA-1500 H thermal balance. The specific surface area was determined by the method of low-temperature nitrogen adsorption using a Quantachrome Autosorb-6B instrument. X-ray structural analysis (XRD) was investigated in the range 5–80° 2θ on a DRON 3 M diffractometer using a CuK_α radiation source (λ= 1,54178 Å). X-ray photoelectron spectra were recorded on a SERIES 800XPS Kratos photoelectron spectrometer.

Industrial and experimental carriers γ-Al_2O_3, expanded clay, bentonite and HSZ were used for the preparation of catalyst samples. The characteristics of the carriers are shown in Table 1. In studying the effect of the nature of carriers on catalytic activity, their initial samples were pre-treated. Thus, γ-Al_2O_3 - based carriers (cylindrical particles with a height of 4 to 25 mm, diameter 4–6 mm) are heated in air at 1000 °C and expanded clay (a sphere with a diameter of 5 ± 0.2 mm) at 1050 °C. processed. HSZ carrier samples (5-6 mm diameter spherical medium-porous) were processed in an autoclave at hydrothermal and equilibrium vapour pressures for a certain period at temperatures from 200 to 300 °C (see Table 1). The specific surface area of these carriers was determined by low-temperature argon adsorption on a Crystallux-4000M gas chromatograph. The size and radius of the pores were determined using mercury porometry directly on the amount of mercury compressed in them in a mercury porometric device that allows the size of the pores to be measured. The pile density of the holder was determined as the ratio of the total mass of the particles measured in the measuring cylinder to the total mass of the sample.

Table 1. Characteristics of carriers

№	Carrier Name	Method of processing	Density, g/cm^3	Comparable surface area, m^2/g	Volume of pores, cm^3/g	Average radius of pores, nm
1	γ-Al_2O_3	Not processed	0.4-0.58	200-220	0.8-0.9	r_1=800 r_2=40000
2	γ-Al_2O_3	Thermally treated at 1100 °C	0.65	13	0.6	r_1=6000 r_2=78000
3	Claydite	Not processed	0.86	120	0.5	200
4	Claydite	Thermally treated at 1050 °C	0.98	17	0.45	6000
5	Bentonite	Not processed	0.58	380	0.92	600
6	HSZ	Not processed	0.57	580	0.89	376
7	HSZ-1	6 hours hydrothermal at 200 °C	0.59	180	0.86	1440
8	HSZ-2	10 hours hydrothermal at 300 °C	0.58	147	0.84	1400
9	HSZ-3	6 hours hydrothermal at 250 °C	0.59	160	0.81	1700
10	HSZ-4	4 hours hydrothermal at 00 °C	0.57	190	0.84	920

3. Results and discussion

In the first stage, a comparison of the efficiency of aluminium oxide carriers (γ-Al_2O_3 and expanded clay) and catalysts prepared on the basis of spherical large-porous and medium-porous silica gels (bentonite and expanded clay, respectively) was carried out. For this purpose, catalysts used in carrier samples containing 1-6 (Table 1) were prepared: mass content: 0,4%Pd+4%Cu+7%CH_3COOK/HSZ. Catalysts were tested in the equipment at a temperature of 165 °C, pressure 0.1 MPa, ethylene: acetic acid ratio 4:1, total process duration 48 hours, 18-hour periodicity of analysis. Test results showing changes in the amount of vinyl acetate and CO_2 in samples with different carriers over time are shown in Table 2.

Table 2. Changes in the selectivity of the product (n) formed over time and the formation of vinyl acetate on ethylene, depending on the type of carrier

Carrier	Indicator	Mole content of vinyl acetate and CO_2 and selectivity for vinyl acetate, % over time, hours					
		8	16	24	32	40	48
γ-Al_2O_3	N_{VA}	2.32	4.19	5.58	6.98	7.72	8.19
	n_{CO2}	1.55	3.09	3.92	5.16	6.01	6.69
	S	75	73	74	73	72	71
γ-Al_2O_3. 1100 °C	N_{VA}	2.98	5.68	8.19	10.51	12.75	14.98
	n_{CO2}	0.59	0.99	1.82	2.34	3.15	4.48
	S	91	92	90	90	89	87
Claydite	n_{BA}	1.12	2.14	3.07	4.0	4.93	5.86
	n_{CO2}	2.22	4.44	6.23	8.31	10.48	13.04
	S	50	49	49	49	48	47
Claydite, 1050 °C	n_{BA}	3.07	5.95	8.56	11.08	13.3	15.35
	n_{CO2}	0.46	1.17	1.49	2.46	2.96	3.79
	S	93	91	92	90	90	89
Bentonite	n_{BA}	0.33	1.67	2.33	2.79	3.26	3.72
	n_{CO2}	0.31	0.49	0.76	0.98	1.34	1.63
	S	89	87	86	85	83	82
HSZ	n_{BA}	0.74	1.44	2.09	2.74	3.3	3.86
	n_{CO2}	0.22	0.51	0.68	0.89	1.26	1,69
	S	87	85	86	86	84	82
Correction. Mass composition of the catalyst: 0.4%Pd+4%Cu+7%CH_3COOK/HSZ							

It follows from these data that catalysts in γ-Al_2O_3 carriers are more active than primary and processed silica gels. However, samples in primary γ-Al_2O_3 carriers (γ-Al_2O_3, expanded clay) are significantly lower in selectivity than bentonite and HSZ. Significant increase in the rate of formation of vinyl acetate and the formation of a by-product-CO_2, resulting in a sharp increase in the selectivity of catalysts on vinyl acetate. However, heat treatment did not improve the stability of the catalysts: in almost all cases, changes in activity over time are nonlinear and indicate decrease inactivity. Mathematically considered contradictions, the activity and selectivity of the catalyst during operation can be described by the exponential equations of the same form:

$$n_{VA} = n_{0VA} \bullet \tau \ exp\left(-\gamma \bullet t\right), \tag{1}$$

$$n_{CO2} = n_{0CO2} \bullet \tau \ exp\left(-\gamma \bullet t\right), \tag{2}$$

Where τ is the current operating time of the catalyst;

γ is the instability coefficient of catalyst operation over time;

n_0 is the equivalent rate constant of time-independent product formation;

exp(-γ•t) is the product of the functional dependence of the catalyst activity drop over time.

Catalysts based on heat-treated bentonite and HSZ showed high selectivity at very low activity compared to similar catalysts in heat-treated carriers (Table 2).

The nature of the changes in activity is that the catalysts also have a gradual decrease in activity over time, but are more stable in the catalyst-based HSZ carrier. It is therefore important to take into account the time factor when selecting a carrier, i.e. how the catalytic characteristics change over time.

The selectivity (S) for the formation of vinyl acetate on ethylene was selected as the solvent characteristic, and its variation during continuous operation of the device was considered for 48 and 200 h.

The numerical values of the time-independent constants n_0 and the instability coefficients g of the catalyst with respect to the formation of vinyl acetate and CO_2 are given in Table 3.

Table 3. Depending on the nature of the carrier, the time-independent constant n0 for the formation of vinyl acetate and CO_2 and the instability coefficients (g) of the catalyst.

Carrier	Carrier processing	Constant n_0, mol/hour		Catalyst instability coefficient, γ, $hour^{-1}$	
		n_{0VA}	n_{0CO2}	VA	CO_2

γ-Al_2O_3	t/i1100	0.40	0.07	γ-Al_2O_3	t/i1100
Claydite	t/i1050	0.40	0.06	Керамзит	t/i1050
HSZ	Not processed	0.10	0.030	HSZ	Not processed
HSZ-2	hydro-t/i	0.300	0.043	HSZ-2	hydro-t/i

By varying the temperature and processing time, modified samples of YuKTs with different porous structures were produced. At the same time, it was found that the specific surface area decreases and the radius of the pores increase with increasing duration of hydrothermal treatment at 300 °C. Increasing the duration of hydrothermal treatment allows a uniform distribution along the radius of the pores. From the results obtained, carrier samples for subsequent experiments for the preparation of mixed palladium catalysts were selected based on porous structure and mechanical strength. Catalyst samples with a mass of 0,4%Pd+4%Cu+7%CH_3COOK/HSZ were prepared in these carriers and the carriers were tested under similar conditions to catalysts of the same composition prepared in the samples 1-6 (see Table 1). The test results are given in Table 4.

Table 4. Changes in the selectivity (C,%) of the formation of vinyl acetate on ethylene over time, depending on the appearance of modified HSZ and the amount of products formed

Carrier	Indicator	Mole content of vinyl acetate and CO_2 and selectivity for vinyl acetate,% over time, hours					
		16	32	48	64	80	96
HSZ-1	n_{VA}	3.35	6.67	9.97	13.32	16.63	19.93
	n_{CO2}	0.38	1.01	1.50	2.32	2.89	3.94
	S	94	93	93	92	91	91
HSZ-2	n_{VA}	1.30	2.42	3.26	4.00	4.74	5.39
	n_{CO2}	0.08	0.15	0.97	0.33	0.50	0.69
	S	97	97	96	96	95	94
HSZ-3	n_{VA}	2.33	4.37	6.23	8.09	9.58	10.88
	n_{CO2}	0.33	0.76	1.38	1.6	2.13	2.69
	S	93	92	90	91	90	89
HSZ-4	n_{VA}	0.56	1.20	1.58	2.00	2.37	2.74
	n_{CO2}	0.26	0.59	0.89	1.13	1.49	1.73
	S	81	80	78	78	76	76
Correction. Mass composition of the catalyst:0.4%Pd+4%Cu+7%CH_3COOK/HSZ							

It follows that hydrothermal treatment of carriers has a significant effect on the rate of formation of reaction products. In hydrothermally treated silica gel samples, the activity of the catalyst HSZ-1 and HSZ-2 can be compared (or increased) with analogues for catalysts in thermally treated carriers. However, the selectivity of the process decreases over time as before, indicating instability in catalyst performance. The results of a comparative prediction of the performance stability of catalysts in modified silica gel carriers over time are presented in Table 5.

Table 5. Variation of experimental and calculated values of selectivity for the formation of vinyl acetate on ethylene over time, depending on the nature of the carrier.

Carrier	ΔS	Change in selectivity over time (hours),%								
		8	16	24	32	40	48	96	144	200
HSZ-1	exp.	0.91	0.92	0.90	0.90	0.89	0.87	-	-	-
	account.	0.91	0.90	0.89	0.89	0.88	0.87	0.83	0.71	0.59

HSZ-2	exp.	0.93	0.91	0.92	0.90	0.90	0.89	0.76	0.61	0.52
	account.	0.92	0.91	0.90	0.89	0.88	0.87	0.74	0.65	0.50
HSZ-3	exp.	0.89	0.87	0.86	0.85	0.83	0.82	-	-	-
	account.	0.89	0.87	0.86	0.85	0.83	0.81	0.66	0.42	0.3
HSZ-4	exp.	0.87	0.85	0.86	0.86	0.84	0.82	0.76	0.74	0.64
	account.	0.86	0.85	0.84	0.84	0.83	0.82	0.75	0.70	0.62

It follows from the data in Table 5 that the calculated values of the ΔS selectivity changes over time are consistent with the experimental values. From this, it can be concluded that the proposed description allows predicting the performance of catalysts for the long-term operation of the device even in this case. Graphical correlations of experimental data on the activity, selectivity and the amount of vinyl acetate formed over time are expanded clay (t / i 1050 ℃), HSZ, HSZ-1 (t / i 200 ℃, 6 hours) and HSZ-2 (t/i 300). ℃, 10 h) are shown in Figures 3 and 4 for the 4 most active catalysts based on the carriers.

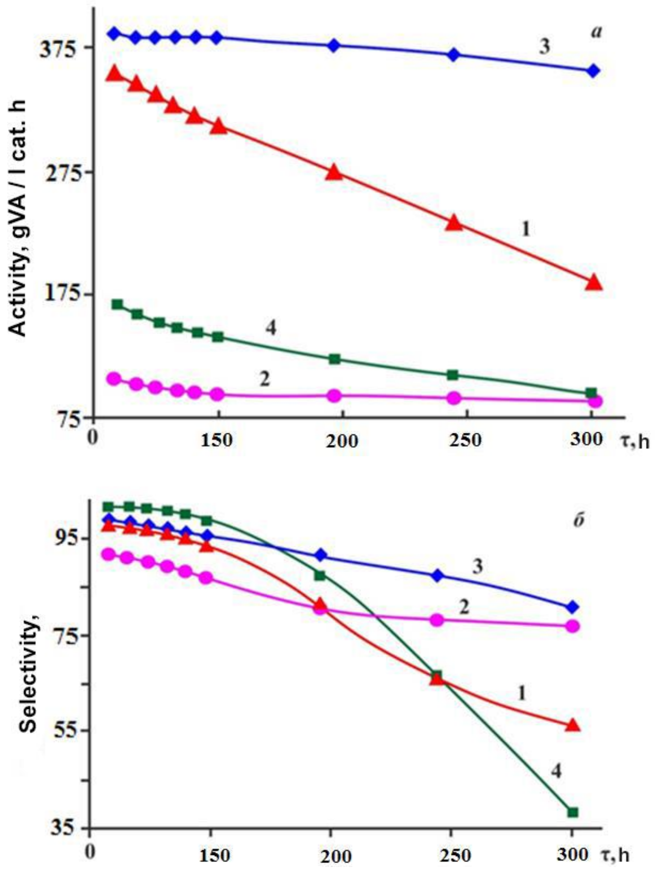


Figure 3. Claydite (1); HSZ (2); HSZ-1 (3); For catalysts based on HSZ-2 (4), the change in activity (a) and the selectivity of vinyl acetate formation (b) during 300 hours of operation.

Test results of 4 catalyst samples over 300 hours showed that the formation of vinyl acetate on ethylene shows the greatest activity, selectivity and stability over time HSZ-1-based catalyst. Thermally treated expanded clay-based catalysts have high initial activity and selectivity, but within 300 hours they are reduced by about 50%.

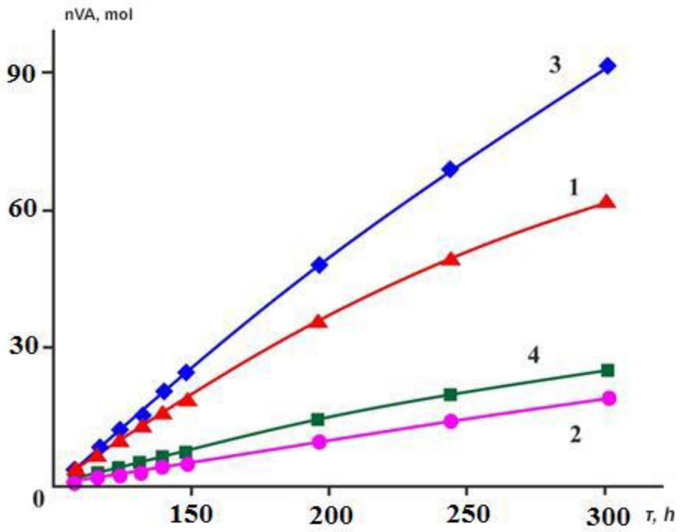


Figure 4. Claydite (1); HSZ (2); HSZ-1 (3); Correlation between the operating time of catalysts prepared on the basis of HSZ-2 (4) and the amount of vinyl acetate formation.

4. Conclusion

The study of catalysts for the gas-phase synthesis of vinyl acetate by oxidative acetylation of ethylene showed that the nature of the carrier and the porous structure have a significant effect on the parameters of the catalytic process of vinyl acetate synthesis.

The nature of the change in the amount of vinyl acetate (n_0) generated over time indicates a decrease in the activity of the catalysts over time, but the time dependence of n for the catalyst in the HSZ-1 carrier is almost linear, indicating stable catalyst performance.

To confirm this conclusion, an experimental test of the stability of 1 dm3 of catalyst performance per reactor on an HSZ-1 carrier containing 0,4%Pd+4%Cu+7%CH_3COOK/HSZ was performed on a vinyl acetate synthesis pilot device. The test was performed by ingestion of potassium acetate with a vapour-gas mixture at a temperature of 165 ℃, a pressure of 0.1 MPa for 2000 h, a volumetric velocity of 2000 h^{-1} and a volume of oxygen with ethylene in the mixture at 7 vol.%. During 2000 hours of operation, the catalyst activity is 370-350 g of vinyl acetate / l.cat. hours at 95-97% selectivity.

A catalyst batch of 100 l of similar composition was then produced under industrial conditions and loaded into 20 (5 *l* each) tubes (tubes) of the industrial reactor. The catalyst was operated at a temperature of 145–165 ℃ for about 6 months and, after removal, was tested in a pilot device: its activity was 380–360 g of vinyl acetate/l.cat.hours at 97–95% selectivity, which is 22-27% higher than the values obtained in the industrial catalyst (270-300 g of vinyl acetate/l.cat.hours at 89-91% selectivity of vinyl acetate formation on ethylene).

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