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KINETICS AND MECHANISM OF THE VAPOR-PHASE SYNTHESIS OF VINYL ACETATE FROM ETHYLENE

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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%CH3COOK/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%.
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.

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).

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

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complex catalyst. The process consists of two stages. Catalyst for catalyst preparation was hydrothermally treated at 200 °C 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.

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 °C, 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 °C, 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.

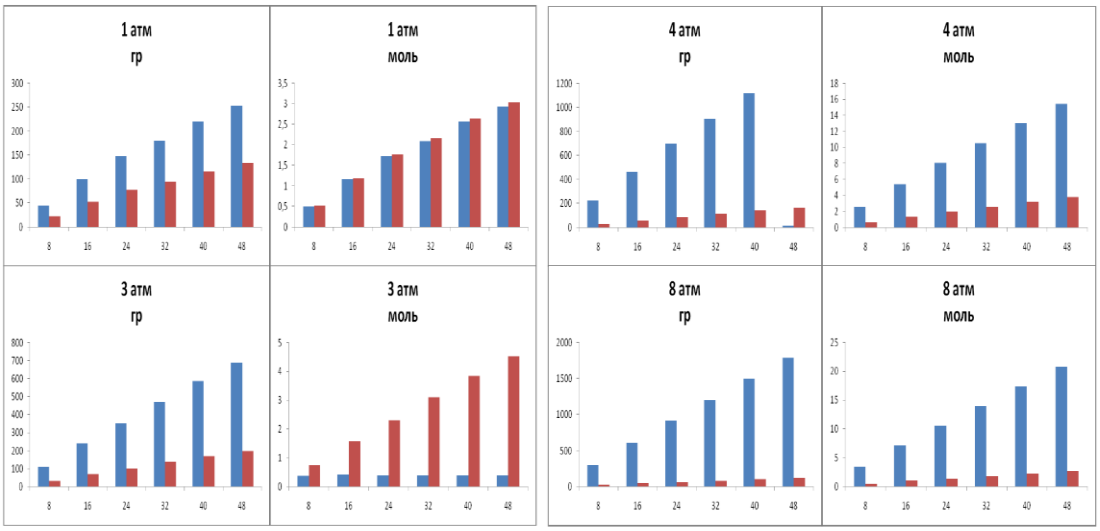

Figure 1. Influence of process pressure

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 °C, 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 Table 1.

Table 1

Influence of oxygen concentration in VGM

Reaction time, hours	Vinyl acetate release, g mol	CO_2 formation, g mol	Selectivity and conversion (CH_3COOH) (C_2H_4)

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$[O_2]$=1%					
8	48	0,56	2,978	0,067	0,943 (1,06) (0,28)
16	112	1,30	6,915	0,157	
24	168	1,95	10,372	0,235	
32	208	2,42	12,87	0,293	
40	256	2,97	15,79	0,339	
48	288	3,35	17,82	0,405	
$[O_2]$=3%					
8	152	1,77	9,065	0,206	0,945 (3,25) (0,86)
16	320	3,72	19,05	0,433	
24	464	5,39	27,61	0,627	
32	624	7,25	37,13	0,849	
40	760	8,84	45,27	1,029	
48	904	10,50	53,77	1,222	
$[O_2]$=5%					
8	224	2,61	13,11	0,297	0,945 (4,84) (1,28)
16	464	5,39	27,07	0,615	
24	696	8,09	40,64	0,924	
32	912	10,60	53,25	1,210	
40	1136	13,21	66,36	1,508	
48	1344	15,63	78,51	1,784	
$[O_2]$=5%					
8	328	3,81	21,41	0,486	0,946 (6,9) (1,84)
16	680	7,91	44,39	1,009	
24	1016	11,81	66,34	1,508	
32	1328	15,44	86,72	1,971	
40	1648	19,16	107,62	2,446	
48	1960	22,79	128,01	2,909	

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 - 2000 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 Table 2. The output of VA and the formation of CO_2 are nonlinear. The rates of formation of reaction products by processing them were calculated.

Table 2

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

Reaction time,	Vinyl acetate release,	CO_2 formation, g mol	Selectivity and conversion (CH_3COOH) (C_2H_4)

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hours	g mol				
$[C_2H_4]$:$[CH_3COOH]$=2:1					
8	128	1,49	7,78	0,177	
16	272	3,16	16,49	0,375	
24	424	4,93	25,77	0,585	0,944
32	552	6,42	33,51	0,762	(3,0) (0,83)
40	664	7,72	40,31	0,916	
48	744	8,65	45,16	1,026	
$[C_2H_4]$:$[CH_3COOH]$=3:1					
8	224	2,61	14,39	0,327	
16	488	5,61	31,284	0,711	
24	736	8,56	47,23	1,073	0,941
32	944	10,98	60,58	1,377	(4,8) (1,333)
40	1144	13,31	73,44	1,669	
48	1328	15,44	85,19	1,936	
$[C_2H_4]$:$[CH_3COOH]$=4:1					
8	296	3,44	20,01	0,455	
16	608	7,07	41,12	0,935	
24	896	10,42	60,61	1,377	0,938
32	1200	13,95	81,14	1,844	(5,85) (1,57)
40	1480	17,21	100,11	2,275	
48	1752	20,37	118,48	2,693	
$[C_2H_4]$:$[CH_3COOH]$=6:1					
8	304	3,53	33,75	0,767	
16	632	7,35	70,27	1,597	
24	944	10,98	104,97	2,386	0,902
32	1232	14,33	137,01	3,114	(5,98) (1,59)
40	1528	17,77	169,89	3,861	
48	1808	21,02	200,97	4,567	
$[C_2H_4]$:$[CH_3COOH]$=8:1					
8	296	3,44	32,15	0,730	
16	608	7,07	66,07	1,502	
24	912	10,61	99,15	2,254	0,904
32	1200	13,95	130,36	2,963	(5,612) (12,49)
40	1496	17,39	162,54	3,694	
48	1768	20,56	192,14	4,367	

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.

As can be seen from the given data, the increase in the amount of oxygen leads to a linear

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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.

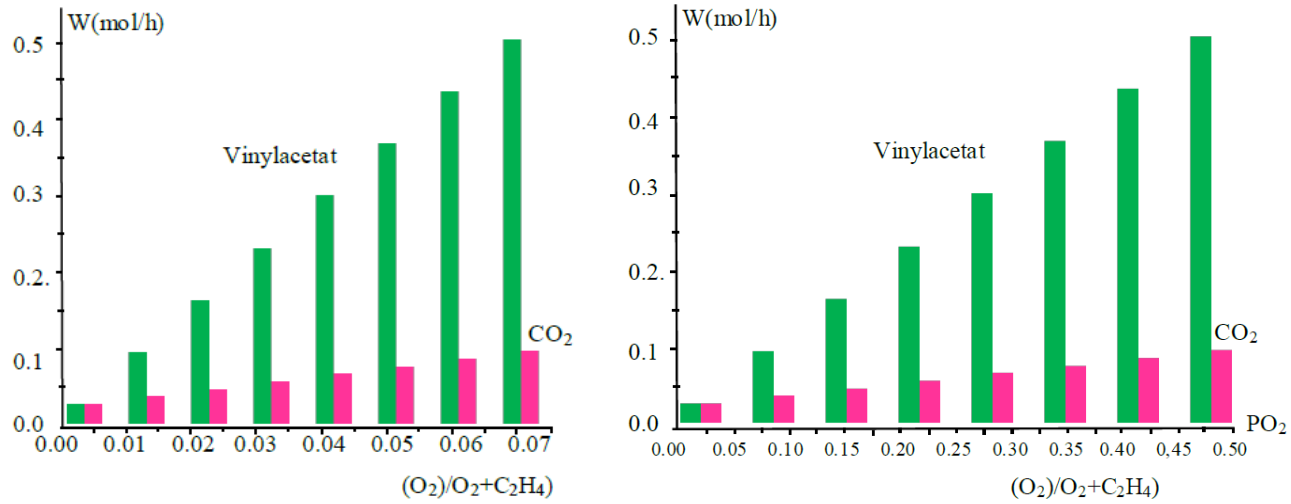

Figure 2. Graphs of changes in the rates of formation of reaction products depending on the amount of oxygen in ethylene: the mole fraction of O_2 in ethylene at a total pressure of 4 atm and the partial pressure of oxygen in VGM, P (O_2) atm.

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.

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,

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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 of 4 atm to 4: 1 and oxygen content 7%.

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