



VINYL ACETATE PRODUCTION TECHNOLOGY

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ABSTRACT

In this paper, we consider the texture characteristics of the developed highly active catalyst $(ZnO)_x \cdot (CdO)_y \cdot (ZrO_2)_z$ for the catalytic acetylation of acetylene based on the Sol-Tel technology, and also study the influence of some parameters (temperature, volumetric rate, C_2H_2 molar ratio : CH_3COOH , catalyst preparation procedure) for the course of this process.

KEY WORDS: acetylene, acetic acid, vinyl acetate, catalyst, sol-gel technology, material balance, technological scheme.

INTRODUCTION

The annual demand of vinyl acetate in the world is about 5 million tons, and the annual demand for the Republic of Uzbekistan is 30 thousand tons. Today, the bulk of vinyl acetate is obtained from ethylene through its oxidative combination with acetic acid on gold-palladium catalysts, but the alternative method for producing vinyl acetate from acetic acid and acetylene also remains important [1-3].

Due to the low cost of ethylene compared to acetylene, the first method is more common. At present, cheaper sources of acetylene production are found as an additional product of new production processes. Therefore, the production process of vinyl acetate from acetylene remains relevant.

The problem of vapor-phase catalytic synthesis of VA has been the subject of a large number of works [1-5]. The process is carried out in the presence of zinc acetate on activated carbon at temperatures of 170-230 ° C, molar ratios of acetylene: acetic acid from 2: 1 to 10: 1 and pressures close to atmospheric. Partial or complete replacement of zinc acetate with cadmium acetate can increase the activity of the catalyst [6-7]. An important factor affecting the VA yield and increasing the catalyst service life is the choice of carrier [8]. On an industrial zinc acetate catalyst supported on activated carbon, under conditions of a 3-4-fold excess of acetylene and the conversion of acetic acid 50-70%, the selectivity for acetylene is 95-99%, for acetic acid 50-70%. By-products of this reaction are mainly acetaldehyde, acetone and crotonic aldehyde. The reaction rate constant at low concentrations of zinc

acetate is proportional to its content, and ceases to depend with an increase and even decreases slightly. The upper boundary of the linear dependence (the critical content of zinc acetate - Scr) increases with an increase in the fraction of carrier micropores and can reach 40 wt. % [9]. Under the conditions of an industrial process, the reaction rate is directly proportional to the concentration of acetylene and either does not depend on the concentration of acetic acid or is slightly inhibited by the latter. Similar patterns are also observed on the cadmium acetate catalyst [10]. In the industrial synthesis of vinyl acetate, both tubular reactors and fluidized-bed reactors are used. The advantage of the latter is the convenience of unloading the catalyst, which is essential since its service life is measured in tens of days. The disadvantage of the process is the relatively rapid deactivation of the catalyst, the average life of the catalyst in the fluidized bed is approximately 60 days [11], and in a motionless one, depending on the process conditions, 80 - 120. To maintain activity at the required level, the temperature is gradually increased from 160 ° C to 240 ° C, after which the catalyst is replaced.

Industrial zinc acetate catalysts for the synthesis of VA are obtained by impregnating activated carbon with salt solutions. The activity and stability of the supported catalysts depends on the mixing conditions during the deposition of zinc acetate on the carrier. A comparison of two modes of deposition of zinc acetate showed that the use of a method involving mixing a solution and a carrier, as compared to simple immersion of a carrier in a solution, leads to an increase in the activity and

stability of the catalyst. An even more noticeable effect in increasing the activity of the catalyst is observed if the deposition process occurs under the influence of ultrasound on the solution – carrier system. Salt catalysts supported on activated carbon are predominantly adsorption. Therefore, it is the adsorption process (in the general case of sorption) that is crucial for the preparation of active and stable catalysts for the synthesis of VA.

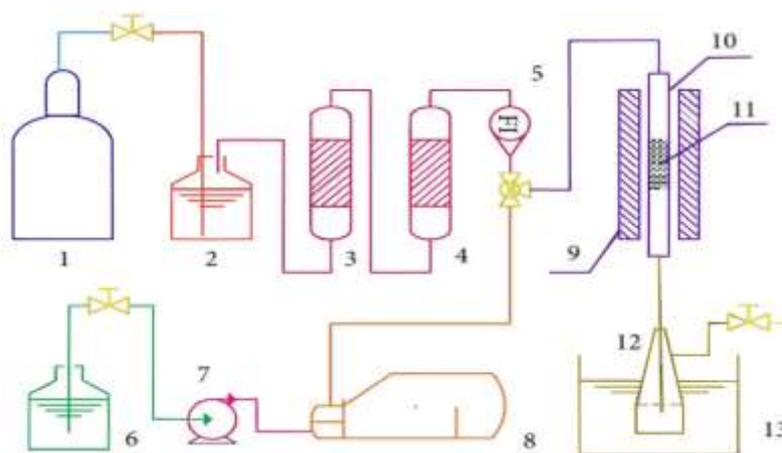
Based on the foregoing, the production of vinyl acetate is one of the main tasks of creating new, economic, waste-free methods in technology, as well as the development of effective catalysts with high selectivity, activity and productivity of modeling technological and operating parameters of the process.

EXPERIMENTAL PART

The catalytic acetylation reaction of acetylene was carried out in a flow reactor under the following optimal conditions: $t = 1800\text{C}$, C_2H_2 : $\text{CH}_3\text{COOH} = 4: 1$, $V_{\text{c}_2\text{n}_2} = 280 \text{ h}^{-1}$.

The reaction products were analyzed by a flame-ionization detector using gas-liquid chromatography under the following optimal conditions: a stationary liquid phase with a particle size of 0.250-0.315 mm in Tsvetochrom -545, 15% nimlestosil, glass column 1000C, the flow rate of the incoming gas - nitrogen 30 ml / min.

Qualitative analysis of "witnesses" and the retention time of parameter values is based on a comparison method; and quantitative analysis is calculated based on the method of internal normalization.



1-acetylene gas; 2-20% NaOH solution; 3-silica gel; 4-activated carbon; 5-gas flow meter; 6-acetic acid; 7-piston metering pump; 8-gasifier; 9-heating device; 10-reaction tube; 11-layer catalyst; 12-collector; 13th ice bath.

Fig. 1. Schematic diagram of the synthesis of vinyl acetate

The texture characteristics of the intermediate materials and finished samples of expanded clay carriers were studied by low-temperature nitrogen adsorption on a FISIONS Carlo Erba complex installation, including the Soptomatic-1900 adsorption device. When determining the specific surface of ABET (m^2 / g), 10–12 experimentally measured equilibrium values of nitrogen adsorption at 77 K in the relative pressure range $P / P_0 = 0.05–0.33$ were used. The total pore volume V_{Σ} (cm^3 / g) was calculated from the adsorbed amount of adsorbate in the saturation region of the adsorption branch of the isotherm ($P / P_s > 0.992$), expressed as the volume of liquid. The micropore volume V_{mic} (cm^3 / g) was calculated from the experimental data from the Dubinin-Radushkevich equation.

The data on the texture characteristics of the samples were obtained on an ASAP 2010M device in a stream of liquid nitrogen at 77.35 K by low-temperature adsorption. Before analysis, the samples were dried

at 1200°C for 4 hours and burned at 5500°C for 6 hours. The comparable surface was determined by the BET method. The total surface volume was calculated based on the amount of nitrogen adsorbed at maximum saturation. Sponge size distributions were determined by the BJH method.

The phase composition was studied on a DRON-3 diffractometer ($\text{CuK}\alpha$ radiation) by X-ray diffraction. The dispersion properties of the catalyst were checked in a scanning electron microscope (JSM - 6510 LV). The catalytic activity of the obtained sample was studied in acetylene acetylation reaction.

One of the important factors affecting the yield of vinyl acetate and increasing the life of the catalyst is the choice of the main indigenous substance (carrier). Therefore, we considered it advisable to use domestic ceramics instead of activated carbon and based on it we created a nanocatalyst with high catalytic activity and



performance using the sol-gel technology. Using the sol-gel technology to prepare the catalyst allows one to obtain nanosized particles that differ from the usual method of absorption of a substance into the core. This method has an advantage in a number of ways, such as the simple equipment used, profitability, environmental safety and technology flexibility.

Nanocatalysts exhibit high catalytic activity, selectivity, stability (stability). It is known that in catalytic processes, mainly mesoporous catalysts have high catalytic activity. The most effective method for producing mesoporous catalysts is the sol-gel method, which allows one to control the particle size, comparative surface, and porous structure of the catalyst at any stage.

EXPERIMENT RESULTS AND DISCUSSION

To obtain vinyl acetate from acetylene and acetic acid, solutions of zinc acetate, cadmium acetate and zirconium oxynitrate in microspherical nanoporous expanded clay, the size of which is 200-300 μm, were introduced.

The catalysts were prepared under the following conditions: solutions of a 5–25% solution of zirconium oxy nitrate by adsorption at 600 ° C were absorbed onto a microspherical nanoporous retention agent (expanded clay). The salt absorption time varied within 60-90 minutes.

The substance is the carrier expanded clay: the solution was taken in the range of ratios 1: 3 - 1: 8.5. After the absorption process, the catalyst was dried at room temperature for 24 hours, then in an oven at 100 - 1300 ° C (with a temperature increase of 100 ° C every 1 hour). The amount of zinc acetate in the catalyst was 11-30%.

The catalyst, the volume of which was 9 cm³, was lowered into a flow reactor and the system was washed in a stream of nitrogen at a speed of 10 l / h for 15 minutes. The synthesis of vinyl acetate from acetylene was carried out at normal atmospheric pressure at 180°C. Under the above conditions, the life of the catalyst was 2000 hours.

The synthesis of vinyl acetate in the vapor phase has been published in many works, the absorption process is carried out on activated carbon in the presence of zinc acetate at 170-2300C, the process was carried out at atmospheric pressure in the range of the molar ratio of acetylene: acetic acid from 2: 1 to 10: 1. Partial or complete replacement of zinc acetate with cadmium acetate leads to an increase in catalyst activity. K₂Cr₂O₇ (2% compared with the weight of the catalyst) is used as a promoter additive. For the first time in the catalytic acetylation reaction in the vapor phase of acetylene, we studied the catalytic activity of catalysts made from salts of d - elements obtained by the sol-gel method (Table 1).

Table 1. The effect of primary substances on the activity of the catalyst in the catalytic acetylation of acetylene. (T = 453K, C₂H₂: CH₃COOH = 4: 1, V c₂n₂ = 280 hr⁻¹, promoter: 1.8% K₂Cr₂O₇)

№	Catalyst Structure	Conversion CH ₃ COOH, %		Selectivity S %
		General	According to vinyl acetate	
1	ZnO/keramzite	60.0	43.0	71.1
2	ZnO:CdO/keramzite	80.6	73.5	91.2
3	ZnO:ZrO ₂ /keramzite	51.4	38.2	74.3
4	ZnO:CdO:ZrO ₂ /keramzite	85.4	79.8	93.4
5	ZnO:Cr ₂ O ₃ /keramzite	46.2	30.6	66.2
6	Cr ₂ O ₃ :CdO:ZrO ₂ /keramzite	67.8	49.2	72.5
7	ZnO:Cr ₂ O ₃ :ZrO ₂ /keramzite	72.1	51.9	72.0
8	ZnO:Fe ₂ O ₃ :Cr ₂ O ₃ /keramzite	70.9	48.0	67.7

As can be seen from table 1, the catalyst (No. 4) containing oxides of zinc, cadmium, zirconium has a high yield and selectivity. The table shows that the total conversion of acetic acid is 95.4%, with respect to the conversion of vinyl acetate is 79.8%.

The results of the study of the influence of the composition of the catalyst on the productivity and selectivity of the process with respect to vinyl acetate are presented in table 2.



Table 2. The effect of the composition of the catalyst on the performance and selectivity in relation to vinyl acetate

№	Amount (ZnO) _x ·(CdO) _y ·(ZrO ₂) _z , % mass	Productivity on vinyl acetate, kg (m ³ ·h ⁻¹)			Selectivity S %,	Resistance for abrasion, %
		170°C	200°C	220°C		
1	10.3:2.6:0.4	41	180	315	>98	97
2	9.6:2.2:0.5	35	183	314	>98	97
3	12.0:2.6:0.3	55	177	295	>98	98
4	11.3:2.1:0.6	38	163	313	>98	97
5	11.8:2.5:0.2	50	130	240	>98	97
6	9.2:2.0:0.1	37	160	315	>98	98
7	9.0:2.5:0.5	47	170	305	>98	97
8	8.5:1.5:0.2	31	150	300	>98	97
9	10.8:3.0:0.4	57	166	305	>98	98
10	8.8:2.2:0.25	55	141	300	>98	97
11	9.5:1.5:0.3	57	200	327	>98	97
12	10.2:1.86:0.4	44	168	300	>98	98
13	11.5:2.4:0.6	52	182	323	>98	98
14	16.7:2.1:0.3	30	174	290	>98	97

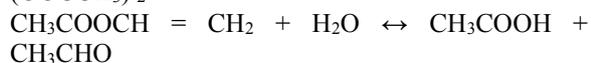
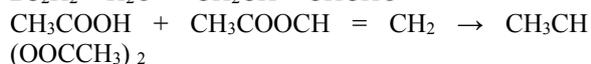
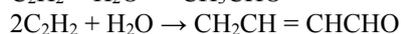
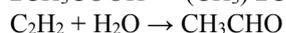
There are some problems in the processes of catalytic conversion of acetylene; these problems have not yet been solved. Under the conditions of vinyl acetate production, acetylation of acetylene by catalytic, forming a croton - aldehyde resin reduces the activity of the catalyst. The degree of frequency of the extracted vinyl acetate adversely affects its polymerization rate and the quality of the forming polymer. For example, if vinyl acetate contains 0.005% crotonaldehyde, its polymerization is reduced to 15%, if 0.2%, then 40%. The polymerization is 100% terminated in the presence of 1.3 * 10⁻² mol of crotonic aldehyde in 100 g of vinyl acetate. Therefore, the creation of catalysts with high catalytic activity, as well as the improvement of existing technologies are relevant.

The deactivation of the catalyst is explained by the decomposition of zinc acetate from the core according to the following reaction:

During the formation of zinc oxide, the main reaction is inactive. After a while, with an excess of acetic acid, the activity increases with the formation of lead acetate.



In the synthesis of vinyl acetate proceed according to this reaction



To prevent such reactions, the process is carried out in excess of acetylene.

CONCLUSIONS

1. Based on the sol-gel technology for the catalytic acetylene acetylation reaction, a catalyst was created — a nanocatalyst with high catalytic activity (ZnO)_x·(CdO)_y·(ZrO₂)_z / expanded clay.
2. The influence of various factors (temperature, space velocity, molar ratios C₂H₂: CH₃COOH, catalyst preparation method, etc.) on the yield of the target product in the acetylene acetylation reaction was studied.

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