Mathematical modeling of ethylene oxidative acetylation process

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Abstract. In the article, the kinetic laws, kinetics, and mechanism of the oxidative acetylation reaction of ethylene in the vapor phase were studied in detail in the 0.4%Rd+4%Cu+7%CH_3 COOK/YuKTs catalyst . As a result of the research, the following optimal conditions for the reaction were selected: in the middle zone of the reactor at a temperature of 165 °C, a volume velocity of 2000 h^{-1}, a pressure of 4 atm, a ratio of ethylene to acetic acid of 4:1 and an oxygen content of 7% by volume. Under these optimal conditions, the activation energies of the reactions of vinyl acetate formation and ethylene oxidation are respectively equal to: $E_{a(VA)}$ = 8.17 kcal/(mol·K) and $E_{a(SO2)}$ = 19.61 kcal/(mol· K). It was found that the rate of oxidation of ethylene is higher than the rate of formation of vinyl acetate when the temperature exceeds 220°C. The reaction mechanism of vinylacetate formation from ethylene and acetic acid in the presence of a palladium catalyst was proposed.

1 Introduction

Despite the fact that the process of obtaining vinylacetate by oxidative acetylation of ethylene has been developed to a high degree, interest in this reaction has not faded until now. In works [1-3], the nature of the retainers in the gas-phase oxidative acetylation reaction of ethylene, the effect of their processing regimes and methods on the properties of heterogeneous palladium catalysts synthesized on their basis were described. The equation for the oxidative acetylation reaction of ethylene:

$$C_2H_4 + CH_3COOH + 1/2O_2 \rightarrow CH_2=CHOOCCH_3 + H_2O \quad (1)$$

The oxidative acetylation reaction of ethylene is carried out in the presence of palladium catalysts modified with potassium acetate and finely dispersed gold (with Au salts that do not retain halogen ions) under the following optimal conditions: ethylene:acetic acid ratio 4:1, pressure 0.4 MPa, temperature 165°C, according to raw materials volumetric speed 2000-8000 hours $^{-1}$.

In the work, heat transfer parameters were studied in the reactor of oxidative acetylation of ethylene to vinylacetate with a fixed layer of porous cylindrical particles of the catalyst,

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and in [4-10] the process of oxidative acetylation of ethylene in a boiling bed at a temperature of 100-250°C and at high pressure was described, where the catalysts were Pd, Au, Cd, Bi, Cu, Fe, Co, Ce, U compounds, as well as alkali metals and their mixtures in silicon dioxide were used. The reaction mixture entering the reactor contains 30-70 volume % ethylene, 10-25 % acetic acid and 8-25 % oxygen.

Synthesis of vinylacetate based on ethylene is carried out by passing acetic acid and oxygen through the catalyst bed of the vapor-gas mixture of the initial reagents at a temperature of 140-200 °C and a pressure of 0.8 MPa. The chemistry of the process is approximated by the gross-reactions of the formation of target by-products [8-12]:

$$C_2H_4 + CH_3COOH \backslash / 2O_2 \rightarrow CH_3COOCH = CH_2 + H_2O \quad (2)$$

$$C_2H_4 + 3\ O_2\ 2CO_2 + 2\ H_2O \quad (3)$$

Over time, the catalytic complex wears out and its activity decreases. In order to maintain the constant activity of the catalyst, the vinyl acetate synthesis process is carried out with a slow temperature increase from 140 to 200°C for 1 year. Service life of imported catalyst is 1 year.

Today, world scientists are very interested in syntheses based on methane, ethylene and acetylene. It is especially important to obtain ethylene from methane and vinyl acetate from acetylene in one step. Ethylene is not only obtained by one-step oxycondensation of methane, but also obtained from methanol and dimethyl ether. Creating a catalyst with high efficiency according to this method is an urgent issue today. At the same time, extraction of aromatic hydrocarbons from the propane-butane fraction and petroleum gases is the only way to dispose of the propane-butane fraction and petroleum gases [10-20].

2 Materials and methods

The VA synthesis process was conducted at a temperature of 145-200°C (the temperature rises slowly depending on the activity of the catalyst), a pressure of 0.4 MPa, and a volume rate of steam-gas mixture (BGA) injection at 2000 h^{-1}. The molar ratio of ethylene to acetic acid is 4:1, and the volume concentration of oxygen in dry gas (without acetic acid) is 7%. VA synthesis is carried out with incomplete conversion of starting substances. Unreacted ethylene, oxygen and acetic acid are purified and returned to the steam-gas mixture preparation node.

The conversion level is average in one transfer: for ethylene – 8%, for acetic acid – 18%, for oxygen – 47%. The synthesis of VA is carried out in a pilot plant for the preparation of a complex catalyst. The process consists of two stages.

It was hydrothermally treated at 200°C for 6 hours as a holder for the preparation of a catalyst, with a specific surface area of 150 m^2/g,a bulk density of 54 g/cm^3 , a pore size of 0.78 cm^3/g and a particle diameter of 4.5-5 mm. YuKTs (high silica zeolite) was used.

Catalysts were tested in a 20 mm diameter, 900 mm high tube-reactor (heated oil is fed to dissipate the heat of the exothermic reaction of VA and SO_2 formation) in a demonstration unit of VA synthesis.

Each of the catalyst samples was tested for 36-40 hours at a reactor loading of 100 cm 3 of catalyst, and the optimal process parameters for this device were found experimentally: 165°C, 0.4 MPa, ethylene:acetic acid ratio 4:1, volumetric rate 2000 $hours^{-1}$, the oxygen content in dry gas is 7.0% by volume. Under these conditions , the reaction of formation of VA and SO_2 proceeds with a slight effect of diffusion in the kinetic field, which begins to manifest only with an increase in the time of steam-gas mixture in the reactor - at a volume rate of steam-gas mixture injection of 2,000 h^{-1}.

3 Results and Discussion

Initial components – effect of ratio of ethylene to acetic acid. The molar ratio of ethylene to acetic acid was varied between 2:1 and 8:1. The experiments were conducted under the following conditions: the middle zone of the reactor T=165°C, R=4 atm, volume velocity – 2000 h^{-1}. The amount of oxygen in the mixture with ethylene is 7%. The amount of catalyst is 100 cm^3. The data of the experiments are presented in Table 1. Vinyl acetate release and SO_2 formation are not linear. By processing them, the rates of formation of reaction products were calculated.

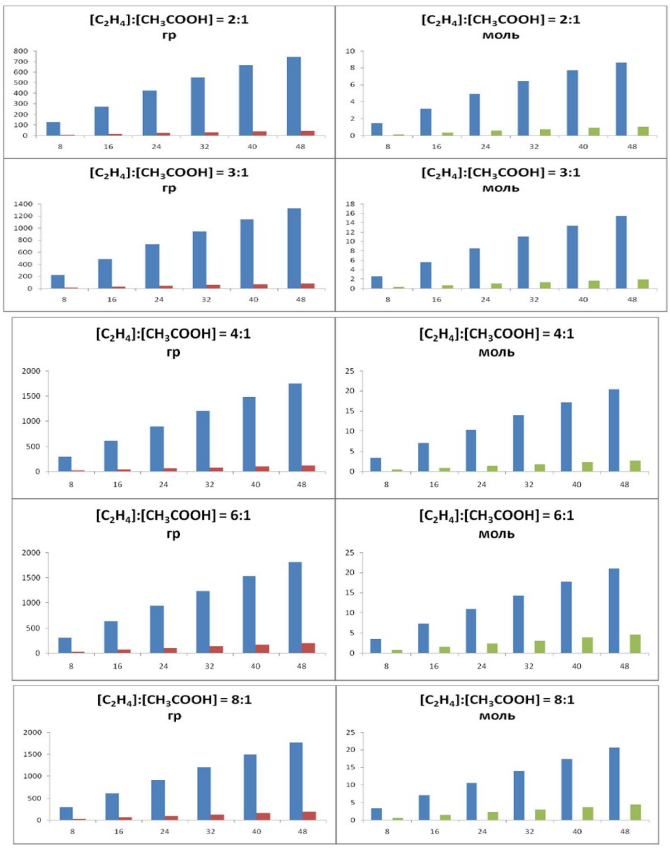

Fig. 1. Effect of ratio of primary components – ethylene to acetic acid.

Results in a nonlinear increase in the rates of vinyl acetate formation and ethylene oxidation to SO_2. The growth of the reaction rate stops when the ratio reaches ≈ 5. In this series of experiments, the concentrations of all reagents are varied, which makes it much more difficult to find functional dependences of the rates of vinyl acetate and SO_2 formation on the $[C_2H_4]$/[Acetic acid] ratio and their partial pressures.

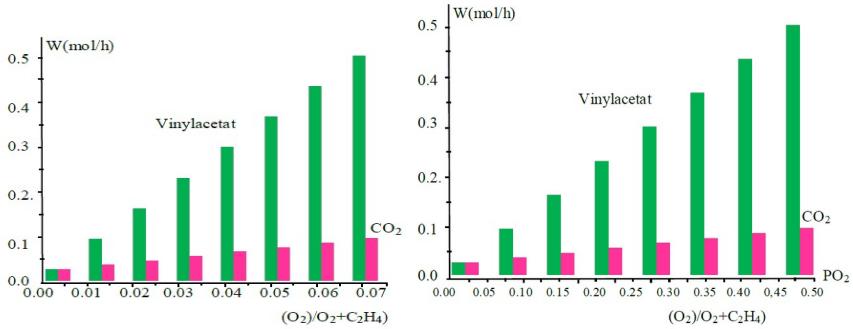

Fig. 2. Graphs of changes in the rate of formation of reaction products depending on the amount of air oxygen in ethylene: per mole fraction of O_2 in ethylene at a total pressure of 4 atm ; and to the partial pressure of oxygen in the vapor-gas mixture, $R(O_2)$ atm.

$CC_2H_4/C_{CH3COOH}$ to look for the relationships you want with an increase in the ratio, that is, taking into account the increase in the partial pressure of ethylene (R(et)), the series of results obtained on the effect of changes in the total pressure and partial pressure of oxygen in the system were analyzed. From the series of experiments mentioned above, we came to the conclusion that the first results can be described by fractional-linear functions. Thus, the rate of vinylacetate formation is a function of $R(O_2)\times R(et)$, whereas the rate of ethylene formation is only proportional to $R(O_2)$. In general, these speeds look like this:

$$W_{VA} = \frac{P(O_2) * X_{et}}{C_1 + C_2 * P + C_3 * P * P}, \text{ mol/hours}$$

$$W_{CO_2} = \frac{P_{(et)}}{C_4 + C_5 * P * P} \text{ mol/hours}$$

Here, C_1-S_5 : ethylene and CH_3COOH are functions of sorption coefficients on the catalyst, which may depend on the ratio of reagents. The appearance of terms with S_2 refers to the monosorption of ethylene and/or acetic acid, and the appearance of terms with S_3 and S_5 refers to the quadratic sorption of these reagents in the active centers of the catalyst. Taking into account the partial pressure of the components can be expressed in the form of the following functions:

$$P_{etilen} = \frac{X * P_o}{1 + X + Y * X} \text{ mol/hours}$$

$$P_{O_2} = \frac{Y * X * P_o}{1 + X + Y * X} \text{ mol/hours}$$

$$P_{CH_3COOH} = \frac{P_o}{1 + X + Y * X} \text{ mol/hours}$$

Here P_0 is the total pressure in the system, X is the ratio of $[C_2H_4]/[CH_3COOH]$, Y is the ratio of $[O_2]/[C_2H_4]$, the desired relationships of reaction rates should look like this:

$$W_{VA} = \frac{X*X}{C_1' + C_2'*X + C_2'*X*X} \text{ mol/hours}$$

$$W_{CO_2} = \frac{X*(X+YX)}{C_4' + C_5'*X + C_6'*X*X} \text{ mol/hours}$$

The nonlinear regression method, these functions were determined:

$$W_{VA} = \frac{X*X}{6,36 + 1,57*X + 1,88*X*X} \text{ mol/hours}$$

$$W_{CO_2} = \frac{X*(X+YX)}{230 + 3,06*X + 7,35*X*X} \text{ mol/hours}$$

They adequately describe the experimental data.

Effect of synthesis temperature. The temperature was changed from 140 to 200°C. The series of experiments was conducted under the following parameters: R = 4 atm, BGA volume velocity 2000 h^{-1}, ethylene to acetic acid ratio 4:1, and oxygen content 7% v/v. The data of the experiments are presented in Figure 3. Vinyl acetate output and SO_2 formation is linear. Formation rates of reaction products were calculated from the constructed kinetic curves.

Formation of vinyl acetate:

$$W_{BA} = \exp(8.63)\cdot\exp(-4086/T°K) \text{ mol/hours}$$

$$W_{SO2} = \exp(20.1)\cdot\exp(-9810/T°K) \text{ mol/hours}$$

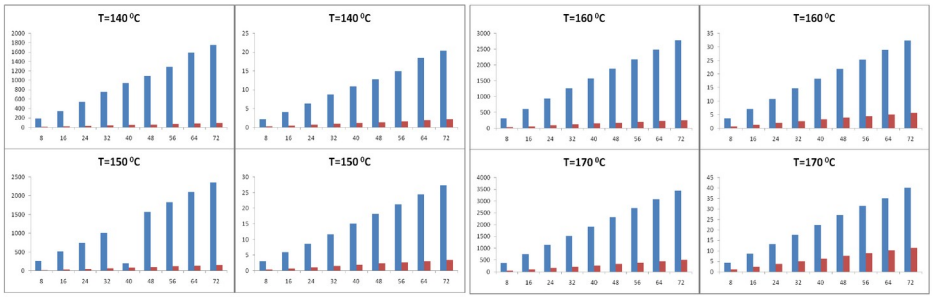

Fig. 3. The effect of reaction temperature on the yield of products in the catalytic oxidative oxyacetylation reaction of ethylene with acetic acid in the presence of atmospheric oxygen.

The relationship between the yield of vinylacetate obtained as a result of the cross-oxidation catalytic oxyacetalation reaction of ethylene with air oxygen in the presence of acetic acid with the help of catalysts in the vapor phase and the formation of carbon dioxide is linear. Formation rates of reaction products were calculated from the constructed kinetic curves.

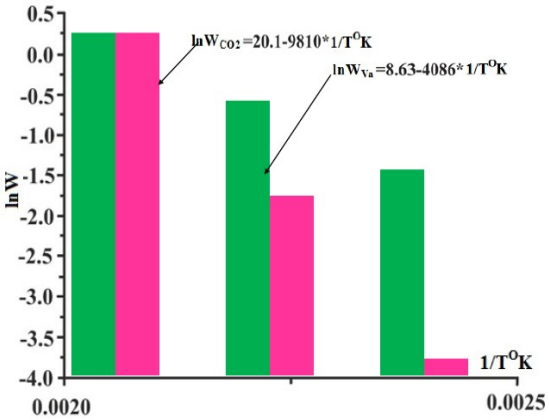

Fig. 4. Inverse temperature dependence of the logarithms of the rates of vinylacetate and carbon dioxide formation obtained as a result of the catalytic oxyacetalation reaction of ethylene with atmospheric oxygen in the presence of acetic acid in the vapor phase.

4 Conclusion

Thus, the process of obtaining vinylacetate by catalytic oxidation acetylation of ethylene in the vapor phase was thoroughly studied in the catalyst with 0.4%Rd+4%Cu+7%CH_3 COOK/YuKTs. The overall reaction rate was found to be proportional to the amount of unmodified and modified active centers of palladium (not clusters). Excess amounts of modifier (both potassium acetate and copper) have been shown to block active sites, reducing catalyst efficiency. As a result of the research, the following optimal conditions for the reaction were selected: in the middle zone of the reactor at a temperature of 165 °C, a volume velocity - 2000 h^{-1}, a pressure of 4 atm, a ratio of ethylene to acetic acid of 4:1 and an oxygen content of 7 vol.%. Under these optimal conditions, the activation energies of the reactions of vinylacetate formation and ethylene oxidation are respectively equal to: $E_a(VA) = 8.17$ kcal/(mol·K) and $E\ a(SO_2) = 19.61$ kcal/(mol·K). The reaction mechanism of vinylacetate formation from ethylene and acetic acid in the presence of a palladium catalyst was proposed. On the basis of the obtained results, the following kinetic equation of the reaction of obtaining vinyl acetate by oxidative acetylation of ethylene was proposed.

$$W_{VA} = \frac{K_5 K_1 K_2^{0.5} K_2 K_4 P_{C_2H_4} * P_{0.2}^{0.5} P}{(1 + K_1 P_{C_2H_4} + (K_2 P_{O_2})^{0.5} + K_2 P}, \text{mol/hours}$$

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

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