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TEXTURE CHARACTERISTICS OF ZINC ACETATE CATALYST

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Abstract. *In the article, for the first time, the properties of carbon sorbents obtained on the basis of FC modified with acetic acid or hydrogen peroxide as carriers for zinc acetate catalysts of vinyl acetate synthesis were systematically studied. It was found that the adsorption process on modified coals strongly depends on hydrodynamic regimes, adsorption transfer temperature, initial salt concentration and initial value of pH solution. Adsorption isotherms were obtained on the modified FC surface, which is of the Langmuir type of adsorption isotherms. Optimum conditions of zinc acetate immobilization compatible with catalytic activity were established on the surface of modified sorbents (T=50°C, solution circulation speed 15,2±0,2 cm/sec, initial values pH=5,5÷6,0 and =20% by mass). The purpose of the work is to study the textural characteristics of zinc acetate catalyst prepared by soaking in activated carbon in different ways.*

Keywords: *activated carbon, zinc acetate, surface area, Dubinin-Radushkevich equation, vapor adsorption.*

ТЕКСТУРНЫЕ ХАРАКТЕРИСТИКИ КАТАЛИЗАТОРА АЦЕТАТА ЦИНКА

Аннотация. *В статье впервые систематически изучены свойства углеродных сорбентов, полученных на основе ТЦ, модифицированных уксусной кислотой или перекисью водорода, в качестве носителей для цинкацетатных катализаторов синтеза винилацетата. Установлено, что процесс адсорбции на модифицированных углях сильно зависит от гидродинамических режимов, температуры адсорбционного переноса, исходной концентрации солей и исходного значения pH раствора. Изотермы адсорбции получены на модифицированной поверхности ТЦ, которая относится к ленгмюровскому типу изотерм адсорбции. На поверхности модифицированных сорбентов установлены оптимальные условия иммобилизации ацетата цинка, совместимые с каталитической активностью (T=50°C, скорость циркуляции раствора 15,2±0,2 см/сек, исходные значения pH=5,5÷6,0 и = 20% по массе). Цель работы – исследование текстурных характеристик катализатора из ацетата цинка, приготовленного пропиткой в активированном угле разными способами.*

Ключевые слова: *активированный уголь, ацетат цинка, площадь поверхности, уравнение Дубинина-Радушкевича, адсорбция паров.*

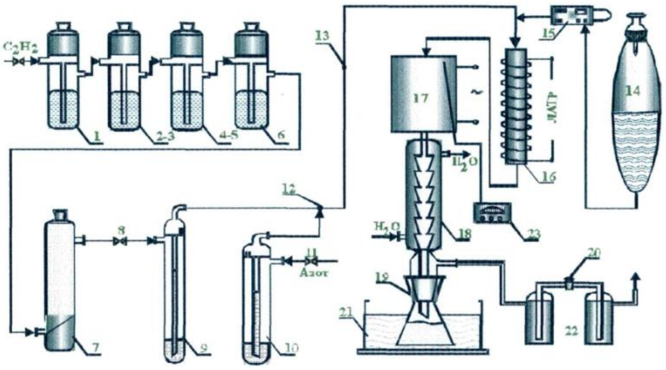
INTRODUCTION

In recent years, one of the trends in the development of catalysts for the acetylation reaction of acetylene with acetic acid is the preparation of catalysts with high catalytic activity and productivity using carbon as a carrier. [1-6]. Carbon materials have several important advantages: they have a large surface area, the ability to regulate the size distribution of pores, and the ability to recover active metals from spent catalysts by burning carbon. An important advantage of carbon as a catalyst carrier is the immobility of the surface, which excludes the occurrence of unwanted side reactions [7-12]. Carbon catalysts are resistant to coke layer [13]. Carbon materials used as carriers are different in nature. They can be activated carbons, technical carbon and compositions based on it. The advantages of compositions based on technical carbon, for example, Sibunit [14], are chemical purity compared to activated carbons (the content of C is not less than 99.5%), high strength and the spherical shape of the granules. [15]. Creation of materials with hierarchical porosity is one of the fastest growing areas of materials science today. Due to the improved transport properties of the porous structure, such materials are widely used as carriers of sorbents and catalysts. The template method for the preparation of hierarchical porous materials, among other approaches to creating hierarchical structures, is distinguished by its simplicity, versatility compared to the previous ones used, and the ability to strictly control the textural properties, and as a result, the resulting material is mechanically strong. In this work, the use of polymer microspheres as a template was preferred due to their inexpensive and easy-to-scale method for their synthesis, as well as the ability to precisely set the particle diameter from 50 nm to 1000 nm. It should be noted that monodisperse polymer microspheres with different functional groups and sizes of 5 μm are a valuable research object for themselves [16-17]. Up to a quarter of a billion tons of hydrocarbons, including heavy hydrocarbons, are mined in our country every year, but the depth of their processing is about 70%. The creation of a stable hierarchical texture prevents the "overgrowth" of transport channels, thereby increasing the capacity and service life of such sorbents [19-20].

MATERIALS AND METHODS

The general scheme of the laboratory setup for the synthesis of vinyl acetate is shown in Figure 6.

Acetylene passes through a cleaning system consisting of six scrubbers from the cylinder. 1 scrubber is filled with a saturated solution of hydroxylamine for cleaning from acetone (300 ml. water, 225 g. hydroxylamine. 15 g. 20% potassium hydroxide solution); Scrubbers 2 and 3 are filled with potassium bichromate solution (300 ml. water, 30 ml. sulfuric acid, 15 g for cleaning from and), 4 and 5 scrubbers are filled with copper sulfate solution (93.6 g., 250 ml. water, 30 ml of sulfuric acid) for additional cleaning from sulfur and phosphorus compounds. 6 scrubber filled with alkali solution. After purification, the acetylene passes through the scrubber 7 filled with potassium hydroxide for drying, and after that it goes through the mixer 12 to the vaporizer 16, where it is mixed with the nitrogen coming from the cylinder. Gases are measured using rheometers 9 and 10. Acetic acid flows from the measuring burette 14 to the medical dispenser 15, which controls its consumption, and then to the vaporizer 16. In the evaporator, acetic acid vapors are mixed with a gaseous mixture of acetylene and nitrogen and heated to the reaction temperature, and then enter the reactor 17. The temperature in the evaporator is maintained by. The reactor has 18 coolers for rapid condensation of contact gases. The condensate is collected in receiver 19 for chromatographic analysis. After analysis, exhaust gases are removed from the system through 22 glasses.



1-6 scrubbers
7-cylinders for drying
8.11. – cranes
9.10.- rheometers
12- mixer
13,20- gas tests
14- UK burette
15- UK dispenser
16- vaporizer
17- reactor
18- refrigerator
19- condenser receiver
21- cooling chambers
22- output glasses
23- thermocouple

Figure 1**.** Laboratory apparatus for the synthesis of vinylacetate

RESULTS

Activity and stability studies of zinc acetate catalyst samples are conducted in a flow reactor made of heat-resistant glass. The reactor is a silicone oil-filled tube with a length of 130 mm and an inner diameter of 11 mm, equipped with a jacket for heating. The temperature in the reactor is maintained using a relay and a contact thermometer. In the reaction zone, there is a channel for a thermocouple for more accurate temperature measurement. Accuracy of temperature measurement is +1°C.

The quality control of the prepared catalysts was carried out in cyclic mode, the essence of which is to repeat the activity measurement at three temperatures of catalysis many times.

Experiments are carried out at 175 °C, 205 °C and 230°C with no more than 50% acetic acid turnover. The transfer rate of the mixture of gases is 722c-1. Ratio. The catalyst activity on vinyl acetate is calculated according to the following formula [29-37]:

$$\eta = \mathrm{X} \cdot \frac{\mathrm{m}}{V_k} \cdot t \qquad g/l \cdot hour$$

Here: X – mass content of vinyl acetate (VA) in the sample;

m – sample mass, g;

$\mathrm{v_k}$ – catalyst volume, l; $\mathrm{v_k} = 6\ \text{см}^3$

t – sampling time interval, hours.

After condensation, contact gases were checked for vinyl acetate content. The stability of the catalysts' performance was observed during 8-10 cycles of experiments in the cyclic change of the synthesis temperature of 175-205-230°C. At each temperature, the process is carried out in stationary mode for 1.5 hours.

Chromatographic analysis was used for quantitative determination of synthesis products of vinyl acetate. The accuracy of such an analysis of the material balance is within 3-5%. The selectivity for acetic acid is 95% and more. To compare activity and stability, one of the best foreign catalysts - MAVC catalyst from Montecatini (Italy) was used as a catalyst.

Analysis of the main and auxiliary products of vinyl acetate synthesis. Chromatographic analysis is used to determine the amount of products obtained. Table 1 and Figures 2 show the values of chromatographic coefficients for the investigated substances and typical chromatograms for liquid and gas samples.

Table 1.

Chromatographic coefficients

	A calonium	B calonium
Acetylene	242	0,35
Nitrogen	1	---
Acetaldehyde	---	0,28
Acetone	---	0,25

Vinyl acetate	---	0,45
Acetic acid	---	1

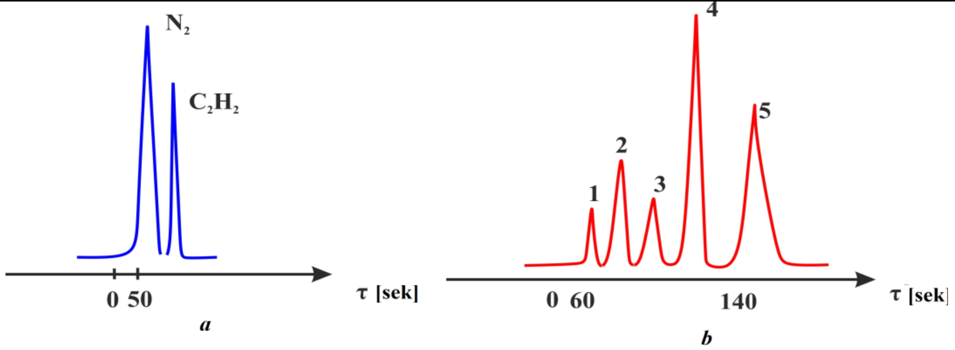


Figure 2. a) Typical chromatogram of a gas sample (colu*mn A);*

б) A typical chromatogram of a condensate sample (column B);

here: peak 1-C_2H_2 (scale.32), peak 2-CH_3CHO (scale.32), peak 3–CH_3COCH_3 (scale.4), peak 4-CH_2CHOAc (scale.64), peak 5-CH_3COOH (scale.64).

Parameters of macropores. The main parameters of the macroporous structure of activated carbons are the size of the macropores, their specific surface area and the distribution of the size of the pores.

Coal macropore volume Vmax (cm^3/g) is found from the difference between the total pore volume and the maximum volume of adsorbed standard vapor (benzene):

$$V_{max} = V_{\Sigma} - V_S$$

here: V_{Σ} - total coal pore volume, sm^3/g

V_S– adsorption volume (adsorption value at saturated vapor concentration of benzene, = $a_s \cdot V^*$ is equal to) sm^3/g

V^* - molar volume of standard - (benzene), cm^3/g

The size distribution of macropores can be determined by the mercury intrusion method, which is based on measuring the volumes of mercury that fill the pores at different hydrostatic pressures.

S_{max} the relative surface area of the macropores can be determined by graphical integration of the experimental curve. value (in cm^2/g) can also be approximated by the equation:

$$S_{max} = 2V_{max} / r_m$$

Here: – the radius of the pores corresponding to the maximum of the distribution curve, cm.

Permeable pore parameters. The volume of the passing pores is determined by the standard volume sorption isotherm of benzene as the maximum volume of the substance sorbed as a result of capillary condensation up to a relative pressure of 0.95-0.98; where if the pore surface is very large (more than 50m^2/g), then the adsorption on the pore surface will be modified until capillary condensation begins. The formula for determining the volume of permeable pores (in cm^3/g) is:

$$V_n = (a_S - a_0 + \alpha_0 S_n) v$$

here: a_S – mmol/g, the final magnitude of sorption at an equilibrium relative pressure equal to one;

a_0 – 0,17 (represents the sum of the final value of adsorption responsible for filling the micropores and the value of adsorption on the surface of the permeable pores) the amount of adsorption for the starting point of hysteresis corresponding to the relative pressure in mmol/g;

α_0 – 0,0047 The magnitude of benzene adsorption for blackberry at a relative pressure of 0.17 mmol/m^2

$S_п$ – the size of the permeable pore surface, m^2 g;

v - mole volume of benzene (20^{0}C да 0,088 cm^3/mmol).

The specific surface area of the passing pores can be assumed to be equal to the specific surface area of the adsorbing film at the surface (cm^2/g) determined by the desorption network in the area of vapor pressures that characterizes capillary condensation:

$$S_a = 1/\sigma \int_{a_S}^{a_0} A da$$

here: σ - surface tension of the adsorption film;

A – The differential molar work of adsorption, erg/mol, is equal to:

$$A = RT \ln(P_S/P)$$

R = 8,31107 эrg/mol. level

T – experimental temperature, ºК

P_S - saturated vapor pressure;

P- equilibrium vapor pressure.

For benzene and an experimental temperature of 20°C, this equation becomes:

$$A = 5{,}6 \cdot 10^{10} \lg(P_S/P)$$

S_a integral is found graphically, in which a table is made according to the differential molar adsorption from the sorption magnitude in the interval from the point of hysteresis to the maximum magnitude of sorption at a relative pressure equal to one.

Parameters of micropores. The main parameters of the microporous structure are the volume of micropores and V and the equation of the volume filling theory of micropores (Dubinin-Radushkevich equation). constant is the final size of the adsorption space. At small values of V, the magnitude of the constant is close to the volume of micropores. The constant V describes the dimensions of the micropores. An increase in V indicates an increase in micropore size.

$V_{мик}$, В ва W_0 parameters are located in the experimental isotherm of standard vapor (benzene or acetic acid) adsorption.

$V_{мик}$ (cm^3/g) micropore volume is expressed by the following equation:

$$V_{мик} \ (a_0 - \alpha_0 S_п)v$$

here a_0 – 0,17 The magnitude of adsorption for the starting point of hysteresis corresponding to the relative pressure of benzene equal to mmol/g:

α_0 – 0,0047 The amount of benzene adsorption on the surface of the charcoal at a relative pressure of 0.17 mmol/m;

$S_{\text{п}}$ – specific surface of passing pores, m^2/g;

v - molar volume of benzene (0,088 cm3/mmol at 20°C).

The method of deducting structure constants V and Wo depends on the microporous structure of activated carbon. All currently known coals are divided into two groups according to the characteristics of the micropore structure: coals with a narrow distribution of micropores and activated carbons with a wide distribution of micropores.

According to the theory of volume filling of micropores, the benzene adsorption isotherm for activated carbons with a narrow distribution of micropores has the following form:

$$a = (W_0/v)[-\exp BT^2(\lg(P_S/P))^2]$$

here: a – p the equilibrium size of adsorption at pressure is mmol/g;

T – experimental temperature, °K

Using the previous equation in linear form to determine the constants V and W at experimental points:

$$\lg a = C - D[\lg(P_S/P)]^2$$

here: $C = \lg(W_0/v),\ D = 0{,}434\ BT^2$.

After that, a correlation table is drawn up and the constants V and Wo are found using the above equations in terms of the parameters S (the segment intersected by a straight line on the ordinate axis) and D (the tangent of the angle of inclination of the line to the axis of the abscissas).

In the case of activated carbon with a wide distribution of micropores, the equation of the benzene adsorption isotherm has the following form: $a = W_{01}/v[-\exp B_1T^2(\lg(P_S/P))^2 + W_0/v[-\exp B_2T^2(-\exp B_2T^2(P_S/P))^2]]$

When using the equation of the adsorption isotherm for activated carbons with a narrow distribution of micropores of this type, a linear dependence is observed only in the area up to 10-5. Thus, it is characterized by the presence of two independent structures with a wide distribution of micropores and parameters.

W_{01}, and constants describe the first component of the structure found in coordinates from along a straight line corresponding to the adsorption of smaller micropores.

To calculate the parameters of the larger micropores (the second component of the structure), the difference Δα between the experimental values of adsorption and the values of adsorption corresponding to a straight line relationship is used. Then a correlation table is drawn from and the parameters of the obtained straight line and are found.

DISCUSSION

All obtained adsorption isotherms are presented in the coordinates of the Dubinin-Radushkevich equation, which is used to calculate the structural parameters of the pores. An example of the calculation according to the Dubinin-Radushkevich equation is shown in Fig.3.

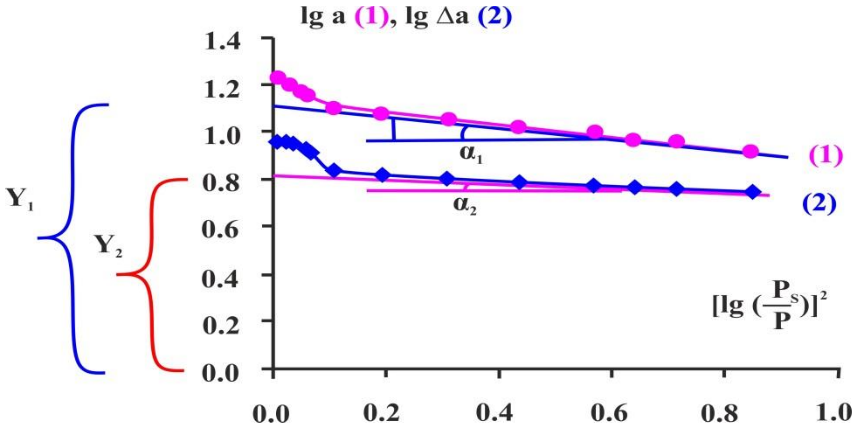


Figure 3. Vapor adsorption isotherms in the coordinates of the Dubinin-Radushkevich equation.

Specific features of measuring vapor adsorption differential heats. Adsorption heats of vapor can be determined from vapor adsorption isotherms, but reliable determination of isosteric heats of adsorption from isotherms is possible only if the isotherms are thermodynamically equal and reversible. Such isotherms belong to "adsorbate-adsorbent" systems characterized by weak interaction. Even if the interaction occurs due to the formation of hydrogen bonds, it is not possible to obtain a complete reversible isotherm at the experimental temperature. In such cases, adsorption calorimetry is the only tool that gives a clear picture of the number and quality of centers of different energy of adsorption on the carrier surface.

In our work, the DAK-1 calorimeter manufactured at the Chernogolovka EZNP plant was used to determine the heat of adsorption of benzene and water vapor on activated carbon. DAK-1 has a high sensitivity (about 1,10-19 s/mm of scale) and a sufficiently large capacity of calorimetric cells (about 6 cm^3 each), so it is suitable for measuring the heats of adsorption from the series of instruments currently in mass production. However, to study the differential heats of adsorption of vapors of substances according to the surface concentration and temperature, in order to more fully realize its potential, the vapor dosing precision system of the adsorbed substance; lack of temperature gradients, symmetry of steam transport paths to the measuring and comparison cells of the calorimeter, proportional thermoregulation is required for continuous 1-3 weeks. Such strictness of the technical specifications means that the adsorption calorimeter is able to exchange mass and heat with the environment while measuring the differential heats of adsorption. Detailed technical data of DAK-1 and the method of measuring vapor adsorption heats are described in.

Different forms of salt component adsorption and different mechanisms of sorption in U can be represented by the following scheme. Adsorption takes place on a flat surface with ZN sour centers (after treatment with acetic acid) under conditions of independence of equilibrium constants according to the degree of saturation of the surface with the salt component. We consider the adsorption of only mononuclears on Zn at one surface center.

a) $Zn(OAc)_2 + ZH \xleftrightarrow{b_1} ZH[Zn(OAc)\,](X_1)$

Chemosorption in acidic $H[Zn(OAc)_3]_{ads}$ center or forming $AsOH_{ads}$ $AcOH_{ads}$. to form a complex with

We accept, for step (a). $\Delta H_{адс.} < 0$.

b) $Zn(OAc)_2 + ZH \xleftrightarrow{b_2} Z[Zn(OAc)_2](X_2) + HOAc$

ion exchange process, $\Delta H_{\text{и·о}} > 0$.

v) $Zn(OAc)_2 + H_2O \xleftrightarrow{K_1} Zn(OH) + HOAc$

Hydrolysis in solution, $\Delta Hr >> 0$.

g) $Zn(OH)(OAc) + ZH \xleftrightarrow{b_3} Z[Zn(OAc)](X_3) + H_2O$

Surface neutralization, $\Delta H_{\text{Н}} < 0$.

d) $Zn(OH)(OAc) + ZH \xleftrightarrow{b_4} Z[Zn(OH)](X_4)$

Adsorption of hydroxyacetate in sour center, $\Delta H_{\text{А,Г}} < 0$.

The total amount of adsorbed salt component is written by the following equation according to mechanisms a, b, g and d

$$a = n_{X1} + n_{X2} + n_{X3} + n_{X4} = b_1Cp[ZH] + b_2Cp\frac{[ZH]}{[AcOH]} + b_3K_1Cp\frac{[ZH]}{[AcOH]} + b_4K_1Cp[ZH]\frac{[H_2O]}{[AcOH]} \quad 1*$$

$$G = [ZH]_\Sigma = [ZH] = n_{X1} + n_{X2} + n_{X3} + n_{X4} \qquad (2*)$$

$$[ZH] = \frac{G}{1 + \left(b_1 + \frac{b_2}{[AcOH]}\right)Cp + (b_3 + b_4[H_2O])K_1\frac{Cp}{[AcOH]}} \qquad (3*)$$

Here we get from (1*) and (3*).

$$a = \frac{\left\{b_1 + \frac{b_2}{[AcOH]} + (b_3 + b_4[H_2O])\frac{K_1}{[AcOH]}\right\}CpG}{1 + \left\{b_1 + \frac{b_2}{[AcOH]} + (b_3 + b_4[H_2O])\frac{K_1}{[AcOH]}\right\}Cp} \qquad (4*)$$

(4*) the equation corresponds in form to Langmuir's isotherm equation with magnitude.

$$b = \left\{b_1 + \frac{b_2}{[AcOH]} + (b_3 + b_4[H_2O])\frac{K_1}{[AcOH]}\right\} \quad \text{ва} \quad a_\infty = G$$

It follows from the equation that for the constants b1, b3, b4 and b2, K1, at different values of ΔN, the probability of extreme dependence of a r on T is high and can be a complex dependence from pH. At pH.>7, there is a possibility of adsorption of more hydrolyzed forms of salt and neutralization of ZH centers

$$ZH + OH^- \leftrightarrow Z^- + H_2O$$

In zinc acetate associates (Sr.>0.7-1 mol.l-1) the real situation is likely to have a more complex description due to the formation of polynuclear hydrocomplexes and multicenter adsorptions.

The porous structure of the catalysts was determined by adsorption of benzene vapors and acetic acid vapors. Acetic acid vapor isotherms (Fig. 28a) and benzene vapor adsorption isotherms on catalysts treated with hydrogen peroxide belong to the Langmuir type of isotherms. This also applies to the acetic acid vapor adsorption isotherm on the acetic acid-treated catalyst. On other catalysts treated with acetic acid, isotherms belonging to the IV type of adsorption isotherms were obtained. The obtained results show that the obtained catalysts are characterized by relatively large size of micropores, mesopores and high adsorption capacity for acetic acid.

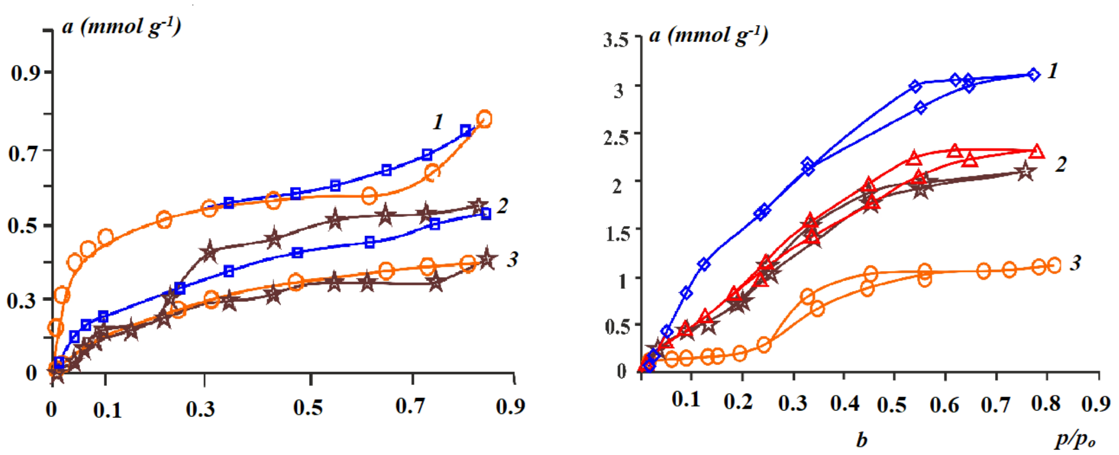


Figure 4. Benzene vapor adsorption isotherms at T=25°C on hydrogen peroxide-treated (a) and acetic acid-treated catalysts.

As can be seen from Fig. 4, the dependence of the specific surface area on the temperature of the discharge of zinc acetate from aqueous solutions passes through T≈500°C in activated carbons.

All hydrogen peroxide-treated and acetic acid-treated catalysts described above were dried at 150-160°C for 3 hours after zinc acetate was added. It is known that the drying mode significantly affects the salt component distribution and can be reflected in the catalyst activity. To determine the effect of drying mode, we varied the rate of temperature rise (0.3°C per minute) with subsequent drying at 150°C for 2 hours.

Thus, comparing the dispersed structures of the considered catalysts shows the dominant influence of the method and conditions of formation on the state of the salt component in their composition.

The presented results of X-ray studies of catalysts are in agreement with SEM and RMA data. Electron microphotographs taken at the maximum magnification for this method (x20000) show only the morphological structure of activated carbons with a well-branched system of carriers-pores. Particles of activated carbons have a corpuscular structure formed by irregular polygons and a globular structure belonging to amorphous carbon. The structure of the salt component is not visible at these magnifications.

Quantitative analysis of the lateral and internal surfaces of the catalyst samples was carried out to obtain information about the characteristics of the distribution of the salt component.

CONCLUSIONS

1. For the first time, the properties of carbon sorbents based on FC modified with acetic acid or hydrogen peroxide as carriers for zinc acetate catalysts of vinyl acetate synthesis were systematically studied..

2. It was found that the adsorption process on modified coals strongly depends on hydrodynamic regimes, adsorption transfer temperature, initial salt concentration and initial value of pH solution.

3. Adsorption isotherms on the modified FC surface, which belong to the Langmuir type of adsorption isotherms, were obtained.

4. Optimum conditions of zinc acetate immobilization compatible with catalytic activity were established on the surface of modified sorbents (T=50°C, solution circulation speed 15±2 cm/sec, initial values pH=5,5÷6,0 and =20% by mass).

5. The resulting catalysts were studied by small-angle X-ray scattering, scanning electron microscopy, and X-ray microanalysis.

REFERENCES

1. Gaffney T. R., Curr O. Solid State Mater //Sci. – 1996. – Т. 1. – №. 1. – С. 69-75.
2. Fuertes A. B., Centeno T. A. Carbon molecular sieve membranes from polyetherimide //Microporous and mesoporous materials. – 1998. – Т. 26. – №. 1-3. – С. 23-26.
3. Wahby A. CO_2 adsorption on carbon molecular sieves //Microporous and Mesoporous Materials. – 2012. – Т. 164. – С. 280-287.
4. Toda Y., Yuki N., Toyoda S. Change in pore structure of active carbon with heat-treatment //Carbon. – 1972. – Т. 10. – №. 1. – С. 13-18.
5. Palchikov V. A. Morfoliny. Sintez i biologicheskaia aktivnost //Zhurn. org. himii. – 2013. – Т. 49. – С. 807..
6. Jasieńko-Hałat M., Kędzior K. Comparison of molecular sieve properties in microporous chars from low-rank bituminous coal activated by steam and carbon dioxide //Carbon. – 2005. – Т. 43. – №. 5. – С. 944-953.
7. Henning K. D., Schäfer S. Impregnated activated carbon for environmental protection //Gas separation & purification. – 1993. – Т. 7. – №. 4. – С. 235-240.
8. Тарковская И.А. Сто профессий активного угля. - Киев: Наукова Думка, 1990. - 200 с.
9. Azat S. et al. Applications of activated carbon sorbents based on greek walnut //Applied Mechanics and Materials. – Trans Tech Publications Ltd, 2014. – Т. 467. – С. 49-51..
10. Lenghaus K. et al. Controlling carbon microporosity: the structure of carbons obtained from different phenolic resin precursors //Carbon. – 2002. – Т. 40. – №. 5. – С. 743-749.
11. Yue Z., Economy J., Bordson G. Preparation and characterization of NaOH-activated carbons from phenolic resin //Journal of Materials Chemistry. – 2006. – Т. 16. – №. 15. – С. 1456-1461.
12. Wang Y. X. et al. Preparation of porous carbon derived from mixtures of furfuryl resin and glycol with controlled pore size distribution //Carbon. – 2003. – Т. 41. – №. 11. – С. 2065-2072.
13. Tamai H., Kouzu M., Yasuda H. Preparation of highly mesoporous and high surface area activated carbons from vinylidene chloride copolymer containing yttrium acetylacetonate //Carbon (New York, NY). – 2003. – Т. 41. – №. 8. – С. 1678-1681.
14. Huang J. M., Wang I. J., Wang C. H. Preparation and adsorptive properties of cellulose-based activated carbon tows from cellulose filaments //Journal of Polymer Research. – 2001. – Т. 8. – №. 3. – С. 201-207..
15. Tanaike O. et al. Preparation and pore control of highly mesoporous carbon from defluorinated PTFE //Carbon. – 2003. – Т. 41. – №. 9. – С. 1759-1764.
16. Li W. et al. Honeycomb carbon foams with tunable pore structures prepared from liquefied larch sawdust by self-foaming //Industrial Crops and Products. – 2015. – Т. 64. – С. 215-223.

17. Zhu Z. et al. Preparation and characterization of polymer-based spherical activated carbons //Chinese Journal of Polymer Science. – 2008. – T. 26. – №. 05. – C. 645-651.
18. Li A. et al. Adsorption of phenolic compounds from aqueous solutions by a water-compatible hypercrosslinked polymeric adsorbent //Chemosphere. – 2002. – T. 47. – №. 9. – C. 981-989.
19. Tsubota T. et al. Spherical activated carbon derived from spherical cellulose and its performance as EDLC electrode //Journal of Applied Polymer Science. – 2014. – T. 131. – №. 20.
20. Boudou J. P., Martinez-Alonzo A., Tascon J. M. D. Introduction of acidic groups at the surface of activated carbon by microwave-induced oxygen plasma at low pressure //Carbon. – 2000. – T. 38. – №. 7. – C. 1021-1029.
21. Chen J. P., Wu S., Chong K. H. Surface modification of a granular activated carbon by citric acid for enhancement of copper adsorption //Carbon. – 2003. – T. 41. – №. 10. – C. 1979-1986..