UNEXPECTED EFFECT OF ADSORPTION OF ZINC ACETATE ON MODIFIED ACTIVATED CARBON FROM AQUEOUS PHASE.

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Introduction

Adsorption of zinc acetate from aqueous solution on activated carbons (AGN-2, AGN-3 and ARD) treated with nitric acid was studied in relation to the hydrodynamic conditions and temperature. The adsorption conditions for preparing active catalysts for vinyl acetate synthesis were determined.

Experimental

The sorption was studied at temperatures from 0 to 85?C with circulation of an aqueous solution of $Zn(CH_3COO)_2$ with various flow velocities through fluidized carbon beds for 7-8 h until a constant $Zn(CH_3COO)_2$ concentration in solution was attained. In all experiments the solution to activated carbon volume ratio was 10:1. The total content of the salt in carbon was determined from the difference between the salt concentration in solution prior to attainment of the sorption equilibrium and the equilibrium concentration. The $Zn(CH_3COO)_2$ concentration was determined by interferometry. After impregnation, carbon was filtered off and dried at 175-180?C in hot nitrogen flow. The surface area, porosity, and activity of the resulting catalyst were measured.

Results and Discution

Zinc Acetate catalyst for Vinyl Acetate synthesis (VA) was prepared by the immobilization of Zinc Acetate from aqueous solutions on the surface of oxidized by HNO_3 (15% solution) activated carbon (AC). AGH-2 the characteristics of AC: S_{sp} - 690 $m^2.g^{-1}$, pores volume:V_{mac}=1,425 $cm^3.g^{-1}$, V_{mes}=0,065 $cm^3.g^{-1}$, V_{mic}=0,27 $cm^3.g^{-1}$, and total volume:0,76 $cm^3.g^{-1}$. Total concentration of acid groups in g? equivalent NaOH is 1,2 [1].

Study of Zinc Acetate (ZnA) adsorption on oxidated and nonoxidated activated carbons in the conditions of intensive circulation of solution through support bed showed that ZnA adsorption rate on oxidized AC increases 2,5-3 times and the total ZnA amount increases 1,7 times . The catalyst surface on oxidized AC is approximately 100 $m^2.g^{-1}$ lower, while the amount of supported salt is the same.

When temperature of immobilization is changed in the interval of 0-80?C (Tmax=50?C) initial adsorption rates and the amount of supported salt (in 1, 2, 3 hours) become sharply dependent upon it (Fig. 1) Catalyst activity in Vinyl Acetate synthesis passes through maximum values at 50?C too. There's observed an extreme change of S_{sp} at 20-80?C (49 $m^2.g^{-1}$ at 20?C, 90 $m^2.g^{-1}$ at 50?C and 37 $m^2.g^{-1}$ at 80?C) as well.

In accordance with these dependences is evident that the process of ZnA immobilization is complex enclosing ZnA adsorption and ion exchange of different forms of Zinc salts (exothermic and endothermic steps, changing of pH during adsorption) on oxidated AC surface.

The sorption of zinc acetate differs from that of $HgCl_2$ [3] in a higher pH of the solution and the appearance of maximal in the a? ? curves. As seen from fig. 2, the maximal amount of sorption is the higher andattained the faster, the higher the pH of the initial solution. In this case the equilibrium amount of sorption remains virtually constant, irrespective of the pH of the initial solution, and the pH of the equilibrium solutions is 4.9 ? 0.1. In all cases the pH of the solution increases during the sorption and at the maximal amount of sorption slightly exceeds the pH of the equilibrium solution.

Dependence of Ssp and amount of adsorbed salt (a) upon initial salt concentration in the interval 3-33% (mass) looks unusual as well (Fig. 3).

Circulation rate of the solution in the interval V=7-60 cm.sec^{-1} [2] has a very noticiable influence upon catalyst. The maximum activity was reached at V=15-18 cm.sec^{-1} (195 g?l^{-1}?h^{-1} at 230?C) (Fig. 4). Extremes are observed on the curve Ssp-V too. Circulation velocity influences distribution of pores volume on radiuses and the value of pores volumes.

Thus catalytic activity of ZnA on AC is determined by Zn concentration (C), S_{sp} value and the conditious T of immobilization, initial concentration and circulation rate) under which these values namely of S_{sp} and C, have been obtained.

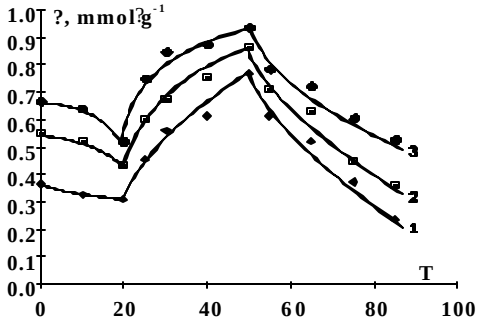

Fig. 1 Dependence sorption amount of zinc acetate sorbed on activated carbon treated with nitric acid at temperature T (?C). Sorption duration (min): (1) 60, (2) 120, and (3) 180.

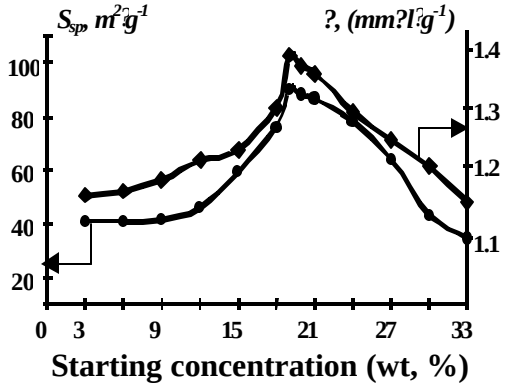

Fig.3 Dependence of the catalyst characteristics Zn(OAc)$_2$/C on starting salt concentration in aqueous solution

Reference

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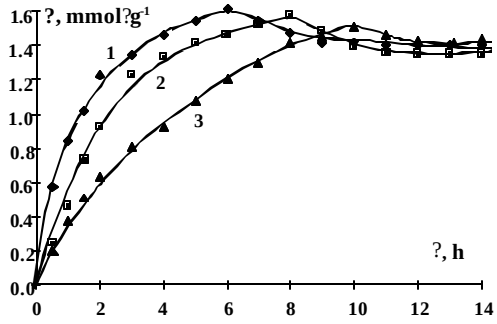

Fig. 2. Sorption of Zn(CH$_3$COO)$_2$ from its 19% aqueous solution on activated carbon at T=50?C as a function of pH of the initial solution. (a) Sorption (mmol?g^{-1}) and (?) time (h). pH: (1) 5.05, (2) 4.00 and (3) 2.95.

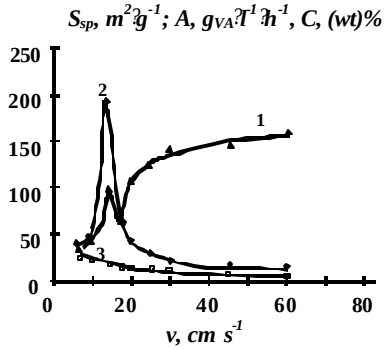

Fig. 4 Dependence of the catalysts characteristics from circulation flow velocity. (1)-Surface (S), (2)-Catalytic activity(A), (3) -amount of Zn(OAc)$_2$ in catalyst, (C).