

## PECULIARITY OF FORMATION OF ZINC CATALYSTS FOR VINYL ACETATE SYNTHESIS ON THE BASE OF MODIFIED ACTIVATED CARBON SUPPORTS

Hoang Kim Bong, Hoang Huu Binh, N.T. Kartel\*, O.N. Temkin

*M.V. Lomonosov Moscow State Academy of Fine Chemical Technology*

*Pr. Vernadskogo 86, 117571 Moscow, Russia, E-mail: hoang46@mail.ru*

*\*O.O. Chuiko Institute of Surface Chemistry of National Academy of Sciences of Ukraine*

*General Naumov Str. 17, 03164 Kiev, Ukraine, E-mail: nikar@kartel.kiev.ua*

*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.*

### Introduction

The activity and stability of supported catalysts depends on conditions of stirring during application of salts [1]. For example, the catalysts prepared by stirring of the support in solution is more active and stable in vinyl acetate synthesis than catalysts prepared by simple immersion of support in solution [2]. The ultrasonic treatment of the solution-supported system during application of salt further increases the activity of the resulting catalysts in vinyl acetate synthesis. Thus, the adsorption (generally sorption) is the key step in preparing active and stable catalysts for vinyl acetate synthesis.

Along with stirring conditions and sorption temperature, important affecting the salt distribution are the texture of support and chemical composition of the support surface. It is known that in activated carbons the volume of micropores virtually not involved in catalysis is 46 – 50 % of the total pore volume [3]. We found that industrial activated carbons (AGN-2, AGN-3 and ARD) this value is high as 50 %. In applying salt components, some micropores are plugged with salt during drying of the catalyst and, as result, are not involved in catalysis. Only mesopores playing a leading role in catalysis are accessible for adsorption of salts and larger colloid particles from solutions. In this connection, modification of the porous structure of carbon is the great importance. Oxidizing agents are known to change the texture and chemical composition of the carbon surface [4]. Nitric acid may even completely decompose the carbon structure, oxidize humic acid, and yield aromatic polycarboxylic acid. Controlled oxidation of carbon with nitric acid increases the number of surface proton-donor groups and may change the carbon porosity. Furthermore, natural impurities or industrial additives (metal oxides) sorbed on the surface of carbon crystallites are dissolved in nitric acid.

Taking into account the above consideration, we studied in this work the sorption of zinc acetate during forced circulation of its solution through a bed of AGN-2, carbons treated with nitric acid. The solution was fed in reaction vessel in two ways: from the top down (hereinafter referred to as fixed bed) and from bottom upwards (hereinafter referred to as fluidized bed). The impregnation is the key step in preparation of sorption catalysts.

### Experimental

Carbon treated with nitric acid was placed in a 350 ml cylindrical glass vessel 45 mm in diameter, equipped with a jacket. To prevent loss of carbon from the reaction zone, the carbon bed was fixed at both ends with filters.

The sorption was studied at temperatures from 0 to 85 °C under static conditions or with circulation of an aqueous solution of  $\text{Zn}(\text{CH}_3\text{COO})_2$  with various flow velocities through

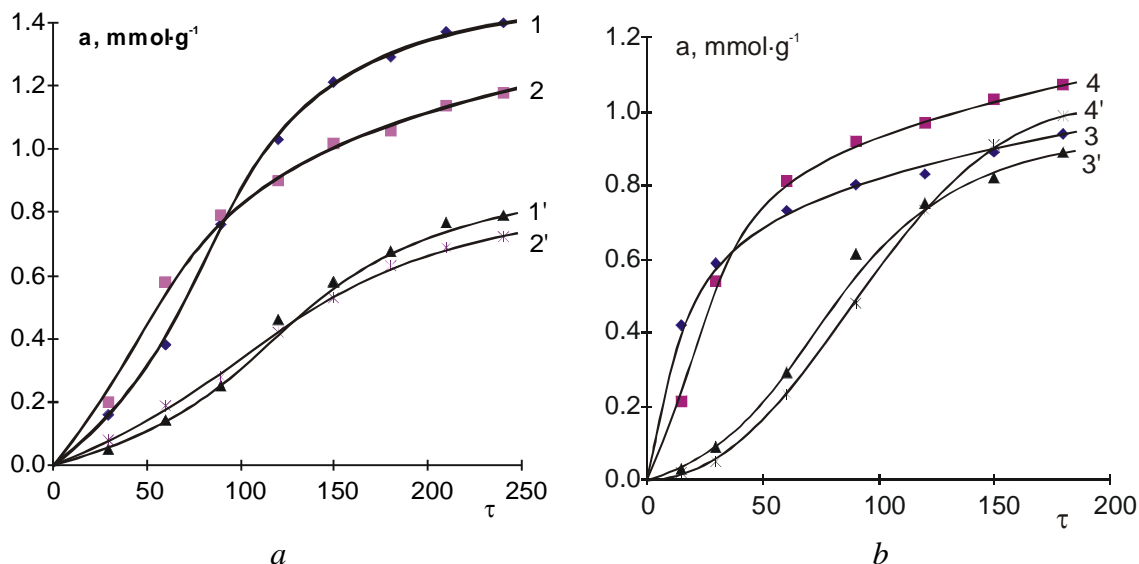
fixed and fluidized carbon beds for 7 – 8 h until a constant  $\text{Zn}(\text{CH}_3\text{COO})_2$  concentration in solution was attained. In all experiments the solution to activated carbon volume ratio was 10:1. The total content of the salt in carbon was determined from the difference between the salt concentration in solution prior to attainment of the sorption equilibrium and the equilibrium concentration. The  $\text{Zn}(\text{CH}_3\text{COO})_2$  concentration was determined by titration with 0.05 M solution of  $\text{Na}_2\text{EDTA}$  and by interferometer. The accuracy of determination of the salt content in the carbon phase was  $\pm 0.013 \text{ mmol g}^{-1}$ . The relative difference between the concentrations determined by both methods did not exceed 6.5 %. 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.

The activity of catalysts was measured at 175, 205, and 230 °C in flow-through unit at  $4.2 \text{ g l}^{-1} \text{ h}^{-1}$  constant space velocity of a  $\text{C}_2\text{H}_2:\text{CH}_3\text{COOH}:\text{N}_2$  (4:4:1) mixture. The unit was described in detail in [4].

## Results and discussion

By the example of AGN-2 we demonstrate that the specific surface area and porosity of carbon considerably change after treatment. The volumes of meso- and macropores increase by a factor 1.5, and the micropores volume decreases by 14 %. Thus, the chemical treatment resulting in oxidation of humic acids and polycondensed structures and dissolution of oxide impurities on the carbon surface changes the pore distribution and decreases the specific surface area to 160-180  $\text{cm}^2\cdot\text{g}^{-1}$ , owing to enlargement of micropores. The total concentration of acid groups is 1.2 in g-equivalent NaOH [3].

Comparison of kinetic curves of  $\text{Zn}(\text{CH}_3\text{COO})_2$  sorption on initial carbons and carbons treated with nitric acid at 50 °C from solutions with 15 and 19 wt % of the salt shows (Fig. 1, *a*) that sorption rate of the treated carbons increases about 2.8 times within the first 1.5 h. The total amount of sorption increases about 1.75 times (19 % solution, 4 h). After performing, sorption the surface area of the treated and initial samples decreases from 690 to 80 – 90 and from 870 to 194  $\text{m}^2\cdot\text{g}^{-1}$  respectively.



**Fig. 1.** Kinetic curves of  $\text{Zn}(\text{CH}_3\text{COO})_2$  sorption from aqueous on AGN-2 carbon. (*a*) Sorption ( $\text{mmol}\cdot\text{g}^{-1}$ ) and ( $\tau$ ) time (min); (*a*) AGN-2: (1, 2) treated with nitric acid and (1', 2') initial. (*b*) carbon bed: (3, 4) fluidized and (3', 4') fixed. Solution temperature 50 °C. Concentration of solution  $c_{\text{eq}}$  (wt %): (1, 1') 19, (2, 2') 15, (3, 3') 12 and (4, 4') 25.

The stirring condition also have a strong effect on the sorption rate (Fig. 1b) and, as further studies showed, on activity and stability of the catalysts in vinyl acetate synthesis. It should be noted that even at continuous circulation of a solution with  $12.1 \text{ cm s}^{-1}$  flow velocity through the carbon bed the sorption rate in fluidized bed increases 5-6 times within first 30 min as compared with fixed bed. In all subsequent experiments the zinc acetate sorption was studied in fluidized bed.

Varying the circulation flow velocity of zinc acetate solution in the range from 7 to  $20 \text{ cm}\cdot\text{s}^{-1}$  showed the optimal flow velocity is  $12\text{-}15 \text{ cm}\cdot\text{s}^{-1}$ . Increasing the circulation flow velocity reduces the catalytic activity (Table 1).

**Table 1.** Activity of catalysts prepared at various flow velocities of circulating  $\text{Zn}(\text{CH}_3\text{COO})_2$  solution ( $c_0 \approx 19 \text{ wt } \%$ ,  $T=50 \text{ }^\circ\text{C}$ )

Sample*	V, $\text{cm}\cdot\text{sec}^{-1}$	Catalytic activity at $230 \text{ }^\circ\text{C}$ , $\text{g}\cdot\text{l}^{-1}\cdot\text{h}^{-1}$
K8	6.8	82.0
K10	9.0	95.9
K12	12.2	105.9
K14	15.0	107.7
K16	17.4	97.4
K18	20.3	85.8

\* The content of the zinc acetate in all catalysts was 24-25 wt%

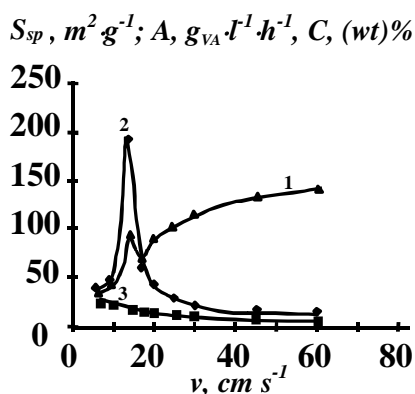
The circulation rate of the solution in the interval  $V = 7\text{-}60 \text{ cm}\cdot\text{sec}^{-1}$  [2] has a very noticeable influence upon catalyst. The maximum activity was reached at  $V = 15\text{...}18 \text{ cm}\cdot\text{sec}^{-1}$  ( $195 \text{ g}\cdot\text{l}^{-1}\cdot\text{h}^{-1}$  at  $230 \text{ }^\circ\text{C}$ ) (Fig. 2).

Extremes are observed on the curve  $S_{\text{sp}}\text{-}V$  too. The circulation velocity influences the distribution of pores volume on radii and the value of pore volumes.

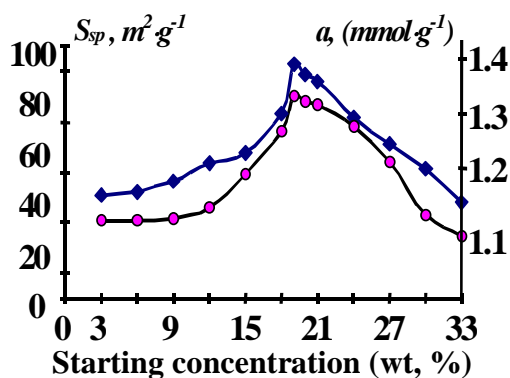
The sorption of zinc acetate differs from that of  $\text{HgCl}_2$  [5] in a higher pH of the solution and the appearance of maxima in the  $\alpha\text{-}\tau$  curves. As is seen from Fig. 3, the maximal amount of sorption is the higher and attained the faster, the higher the pH of the initial solution. In the 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  $4.9\pm 0.1$ . 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. At large volume excess of the circulating solution with respect to the catalyst (10:1) the maximal amount of sorption  $a_{\text{max}}$  is almost independent of the equilibrium salt concentration on the solution  $c_{\text{eq}}$  over entire range of the tested initial concentration of  $\text{Zn}(\text{CH}_3\text{COO})_2$ . It should also be noted that sorption under static conditions (without stirring) is described by ordinary Langmuir isotherms without maxima [3].

Variation of the initial concentration of zinc acetate showed that at  $50 \text{ }^\circ\text{C}$  the dependence of the catalytic activity of the treated catalysts on  $c_0$  (at one and the same content of the salt in the catalyst) passes through maximum at the initial concentration 19 – 20 wt %. Further increase of the initial concentration reduces the catalytic activity by 30 – 40%. Dependence of  $S_{\text{sp}}$  and amount of adsorbed salt ( $a$ ) upon initial concentration in the interval 3-33 (wt %) looks unusual as well (Fig. 4).

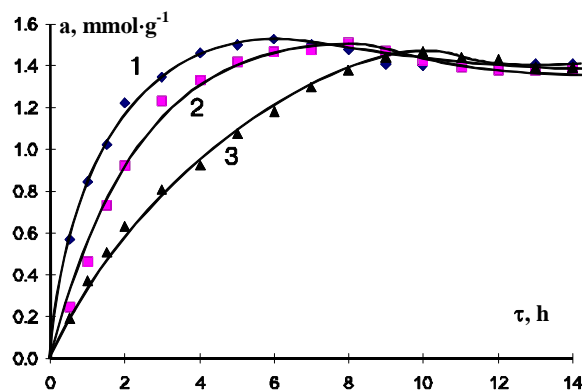
When temperature of deposition is changed in the interval of  $0\text{--}80 \text{ }^\circ\text{C}$  ( $T_{\text{max}} = 50 \text{ }^\circ\text{C}$ ) initial adsorption rates and the amount of supported salt (in 1, 2, 3 hours) become sharply dependent upon it (Fig. 5). Catalyst activity in vinyl acetate synthesis passes through maximum values at  $50 \text{ }^\circ\text{C}$  too. There is observed an extreme change of  $S_{\text{sp}}$  at  $20\text{-}80 \text{ }^\circ\text{C}$  ( $49 \text{ m}^2$  at  $20 \text{ }^\circ\text{C}$ ,  $90 \text{ m}^2$  at  $50 \text{ }^\circ\text{C}$  and  $37 \text{ m}^2$  at  $80 \text{ }^\circ\text{C}$ ) as well.



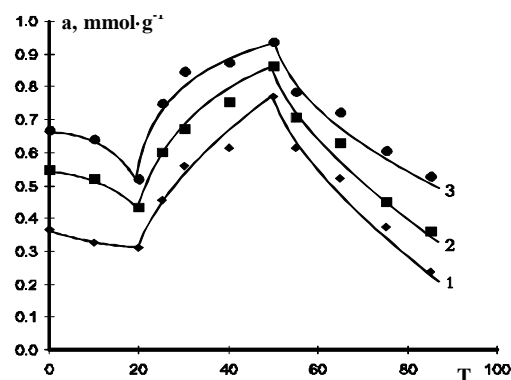
**Fig. 2.** Dependence of the catalysts characteristics from circulation flow velocity. (1)-Surface (S), (2)-Catalytic activity (A), (3) -amount of  $\text{Zn}(\text{OAc})_2$  in catalyst, (C).



**Fig. 4.** Dependence of the catalyst characteristics  $\text{Zn}(\text{OAc})_2/\text{C}$  on starting salt concentration in aqueous solution.



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

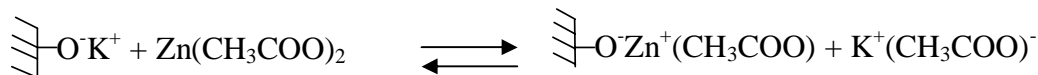


**Fig. 5.** Dependence of amount of zinc acetate adsorbed on activated carbon treated with nitric acid vs. temperature  $T$  ( $^\circ\text{C}$ ). Adsorption duration (min): (1) 60, (2) 120 and (3) 180.

In accordance with these dependences it is evident that the process of  $\text{Zn}(\text{OAc})_2$  deposition is a complex process involving  $\text{Zn}(\text{OAc})_2$  adsorption and ion exchange of different forms of Zinc salts (exothermic and endothermic steps, changing of pH during adsorption) on oxidized AC surface.

The well pronounced extremes found for the temperatures dependences of the sorption rate and the amount of sorption of zinc acetate were also found for the dependence of catalytic activity on the temperature of application of zinc acetate (Table 2). The catalysts prepared at  $50^\circ\text{C}$  are highly active.

The acceleration of the sorption with increasing pH of initial solution after addition of KOH is likely to be due to partial neutralization of acidic functional groups to form  $\text{K}^+$ -substituted groups, which actively exchange  $\text{K}^+$  with zinc acetate by the reaction



**Table 2.** Catalytic activity of zinc acetate catalysts prepared at various temperatures ( $V = 15 \text{ cm}^3 \cdot \text{s}^{-1}$ ,  $c_0$  19.5 wt%)

Sample	T, °C	Catalytic activity at 230 °C, $\text{g} \cdot \text{l}^{-1} \cdot \text{h}^{-1}$
K8	20	68.3
K10a	30	79.5
K12a	40	99.7
K14	50	107.2
K16a	55	89.8
K18a	65	74.2

The second reaction is the more active sorption of partially hydrolyzed mono- and polynuclear compounds containing  $-\text{Zn}-\text{OH}$  group. The increase in pH during sorption can be explained by binding to the carbon surface of acetic acid formed in reaction of  $\text{Zn}(\text{CH}_3\text{COO})_2$  with strongly acidic carboxyl groups or with water (hydrolysis).

The appearance of maxima on the kinetic curves obtained in the case of intense hydrodynamic application of the salt can be explained by the fact that the sorption rate under these conditions is higher than the rate of attainment of particular equilibria on the surface (ion exchange, oligomerization and hydrolysis of zinc acetate, and sorption of acetic acid). As a result in the first steps the sorbent becomes supersaturated with zinc acetate and only then the sorption equilibrium is attained. Under static conditions (without stirring) the sorption of zinc acetate monotonically increases up to the equilibrium value.

Thus, the sorption of zinc acetate from aqueous solution on the carbon surface (which we term as adsorption) involves adsorption of zinc acetate in various forms (including the hydrolysis products) and probably ion-exchange process.

Probably, in concentrated solutions of zinc acetate, different forms of zinc acetate are adsorbed on oxidized activated carbons by different mechanisms.

We suggest that the sorption equilibrium is attained via the following endothermic and exothermic stages: (1) dehydration of hydrated zinc acetate molecules ( $\Delta H > 0$ ); (2) dehydration of the surface, i.e., rupture of hydrogen bonds between water molecules and the surface (especially surface functional groups,  $\Delta H > 0$ ); (3) sorption of zinc acetate molecules ( $\Delta H < 0$ ); (4) dimerization and oligomerization of zinc acetate on the surface to form bridging acetate groups ( $\Delta H < 0$ ); and (5) ion exchange of zinc acetate with  $\text{—OH}$  and  $\text{—O}^-\text{K}^+$  groups (may be both exothermic and endothermic).

If several zinc acetate species are immobilized on the surface by sorption ion exchange mechanisms (including oligomerization), this is sufficient for a combination of exothermic and endothermic processes to result in extremal dependences.

### Conclusions:

Thus the most active catalysts can be prepared under the following conditions: concentration of the initial solution 19-20 wt%; flow velocity of circulating solution  $12\text{-}15 \text{ cm} \cdot \text{s}^{-1}$ ; tenfold volume excess of the solution temperature  $50^\circ\text{C}$ .

The condition of oxidation of activated carbon and hydrodynamic parameters of circulation will be refined in further publications.

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## **ОСОБЕННОСТИ ФОРМИРОВАНИЯ ЦИНКОВЫХ КАТАЛИЗАТОРОВ СИНТЕЗА ВИНИЛАЦЕТАТА НА ОСНОВЕ НОСИТЕЛЕЙ ИЗ МОДИФИЦИРОВАННОГО АКТИВНОГО УГЛЯ**

**Хоанг Ким Бонг, Хоанг Хю Бинх, Н.Т.Картель\* и О.Н.Тёмкин**

*Московская государственная академия тонкой химической  
технологии им. М.В. Ломоносова*

*пр. Вернадского 86, 117571 Москва, Россия, E-mail: hoang46@mail.ru*

*\*Институт химии поверхности им. А.А. Чуйко Национальной академии наук Украины  
ул. Генерала Наумова 17, 03164 Киев, E-mail: nikar@kartel.kiev.ua*

*Изучена адсорбция ацетата цинка из водных растворов на активированных углях (АГН-2, АГН-3 и АРД), обработанных азотной кислотой, при разных гидродинамических условиях и температурах. Определены адсорбционные условия для приготовления активных катализаторов синтеза винилацетата.*

## **ОСОБЛИВОСТІ ФОРМУВАННЯ ЦИНКОВИХ КАТАЛІЗАТОРІВ СИНТЕЗУ ВІНІЛАЦЕТАТУ НА ОСНОВІ НОСІЇВ З МОДИФІКОВАНОГО АКТИВНОГО ВУГІЛЛЯ**

**Хоанг Кім Бонг, Хоанг Хю Бінх, М.Т.Картель\* и О.М.Тьомкін**

*Московська державна академія тонкої хімічної технології ім. М.В. Ломоносова  
пр. Вернадського 86, 117571 Москва, Росія, E-mail: hoang46@mail.ru*

*\*Інститут хімії поверхні ім. О.О. Чуйка Національної академії наук України  
вул. Генерала Наумова 17, 03164 Київ, Україна, E-mail: nikar@kartel.kiev.ua*

*Вивчена адсорбція ацетату цинку з водних розчинів на активованих вуглях (АГН-2, АГН-3 та АРД), оброблених азотною кислотою, при різних гідродинамічних умовах та температурах. Визначені адсорбційні умови для приготування активних каталізаторів синтезу вінілацетату.*