

Highly active catalyst for vinyl acetate synthesis by modified activated carbon

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Abstract

A new zinc acetate catalyst which was prepared from modified activated carbon exhibited extreme activity towards the synthesis of vinyl acetate. The activated carbon was modified by nitric acid, vitriol and peroxyacetic acid (PAA). The effect on specific area, structure, pH and surface acidity groups of carriers by modification was discussed. Amount of carbonyl and carboxyl groups in activated carbon was increased by peroxyacetic acid treatment. The productivity of the new catalyst was 14.58% higher than that of catalyst prepared using untreated activated carbon. The relationship between amount of carbonyl and carboxyl groups (m) and catalyst productivity (P) was $P = 1.83 + 2.26 \times 10^{-3} * e^{3.17m}$. Reaction mechanism was proposed.

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Keywords: Surface acidic groups; Peroxyacetic acid; Activated carbon; Catalyst for vinyl acetate synthesis

A well-known industrial process of vinyl acetate synthesis by acetylene was still given considerable attention by researchers who develop commercial catalysts. An increase in activity and service life of catalyst makes this industrial process competitive with the oxidative esterification of ethylene. Temkin et al. [1] found that a change in the procedure of activated carbon impregnation with a zinc acetate solution, the use of oxidized activated carbons and the addition of organic solvents to the aqueous solution of zinc acetate during impregnation made it possible to obtain a highly active catalyst of vinyl acetate synthesis. Sichuan Vinylon Works [2] and Chengdu Institute of Organic Chemistry developed a catalyst (mass ratio of AC:Zn(Ac)₂:(BiO)₂CO₃ = 100:27–40:0.026) with high activity and long lifetime. Chen et al. [3] treated the activated carbon by HNO₃ and activity of the catalyst was 5.36% higher than that of activated carbon without being treated. The relationship between surface groups of treated activated carbon and activity of catalyst was discussed, too.

Our experience in improving catalyst for vinyl acetate [2] synthesis shows that there is still potential room to increase activity and lifetime of Zn(OAc)₂/C catalyst while maintaining selectivity. Carbon surface modification was paid more and more attentions by reason of its important effects on improving the catalyst [4–6]. As far as we know, this is the first report that the activity of catalyst for vinyl acetate synthesis was improved as increasing amounts of carbonyl and carboxyl groups in activated carbon. A highly active catalyst was obtained from the modification of

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Table 1
Effect of acid treatment on activated carbon and catalysts' activity.

Sample	S_{BET} (m ² /g)	V_s (cm ³ /g)	R (Å)	pH _{pzc}	A (mmol/g)						P (g mL ⁻¹ d ⁻¹)
					-COOH	-OH	-COOR	C=O	m	Total	
1	1093	0.64	10.9	9.13	0.16	0.00	0.07	1.27	1.43	1.50	1.92
2	1164	0.69	11.2	6.69	0.29	0.00	0.08	1.32	1.61	1.69	2.20
3	1100	0.67	11.2	6.23	0.01	0.29	0.38	1.06	1.07	1.74	1.88
4	1156	0.69	11.0	6.10	0.00	0.23	0.25	1.30	1.30	1.78	1.90

¹AC; ²AC modified by PPA; ³AC modified by nitric acid; ⁴AC modified by vitriol. P is on a vinyl acetate content basis, content of vinyl acetate 50%–56%; acetic acid 42.5%–48.5%, acetaldehyde 1.5% over all samples during vinyl acetate synthesis.

activated carbon by peroxyacetic acid. The relationship between amount of surface groups in activated carbon and catalyst productivity was discussed and the reaction mechanism was proposed.

Table 1 lists the pore structure, surface acidity groups and catalyst's productivity variations of the untreated and acid-treated activated carbon samples. BET surface area, pore volume and average pore radius were slightly enhanced due to acid treatment, which had almost no impact on the catalyst's productivity. Acid treatment also enhanced pH and total acid of activated carbons. PAA treatment can increase amount of carbonyl and carboxyl groups in activated carbon, nitric acid and vitriol treatment resulted in increase of lactones and single hydroxyl groups. The catalyst's productivity was increased by PAA treatment. In addition, the carboxyl groups were absent in sample 3 and sample 4. The existence of carboxyl group is almost inevitable after treatment by nitric acid and vitriol acid. However, the carboxyl group was thermally unstable and easy to be eliminated by high temperature heating [4,5,7]. Samples 3 and 4 were more difficult to be washed to neutral and dried to constant weight than sample 2 on account of the strong acidity of the nitric acid and vitriol acid. Higher drying microwave power and longer drying time caused the absence of the carboxyl groups in samples 3 and 4.

Fig. 1 was the relation dot graph between sum of carboxyl and carbonyl groups and the productivity of catalysts whose carriers were treated by peroxyacetic acid. The curve fit analysis showed the equation was $P = 1.83 + 2.26 \times 10^{-3} * e^{3.17m}$. It shows that the productivity of the catalysts is a monotone increasing function of sum of carboxyl and carbonyl groups and its value can be used as a quantitative index for activity of the catalyst. According to the equation the productivity of the catalyst will increase with the increasing of the concentration of carboxyl and carbonyl groups. The productivity of catalyst was 2.20 g d⁻¹ mL⁻¹ when the sum of carboxyl and carbonyl groups was 1.61 mmol/g modified by 10 wt% PAA at 90 °C for 3 h. In addition, the activity of catalyst was 14.58% higher than that of activated carbon without being treated and three times higher than the activity of KO45 [1] at same reaction condition. The content of zinc in fresh catalysts which were prepared by samples 1–4 were respectively 11.64%, 13.22%, 11.50%, 11.55%. It seems that the carboxyl and carbonyl groups in activated carbon absorbs more zinc acetate and makes the catalysts more efficient. The amount of the carboxyl and carbonyl groups in carrier is a key factor influencing the activity of the catalyst.

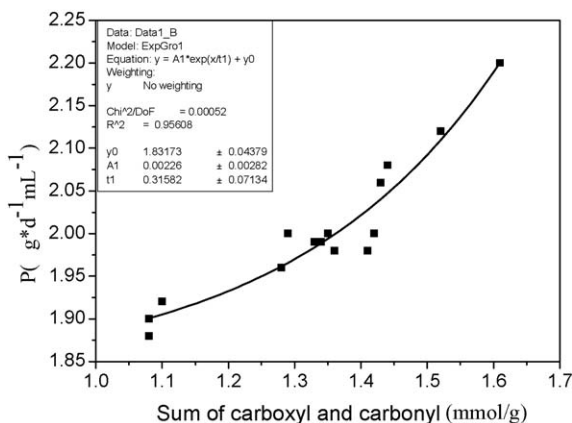
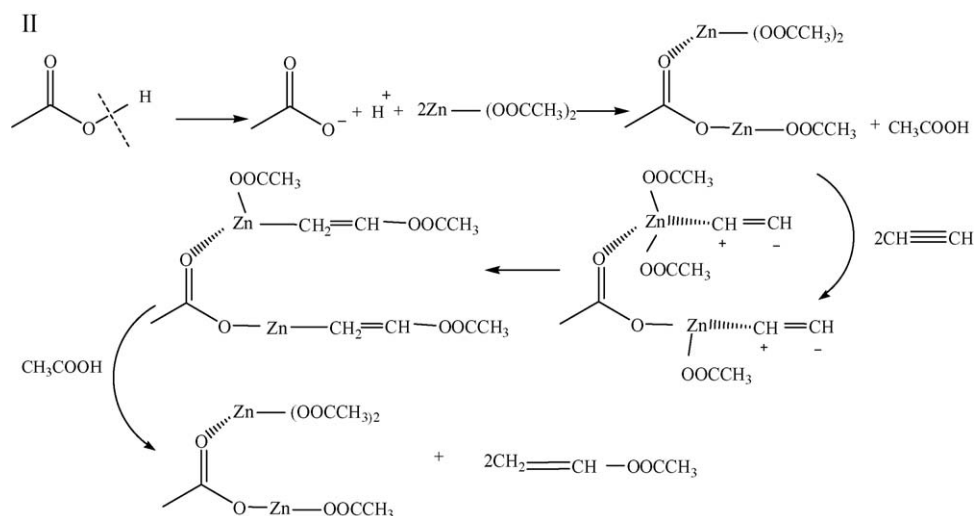
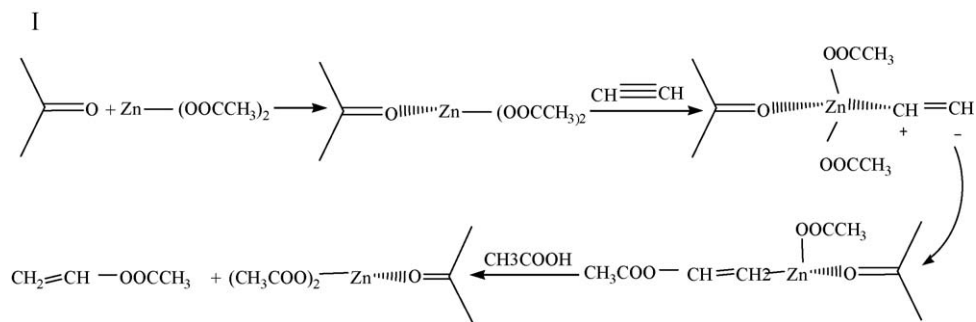


Fig. 1. Relation between sum of carboxyl and carbonyl groups and productivity of catalysts.

Commonly believed by scholars is that the adsorption of C_2H_2 on zinc acetate is the rate-determining step of the vinyl acetate synthesis reaction [8,9]. Some researchers believed that zinc acetate was absorbed by lactones in activated carbon [3], others believed that it is the carbonyl groups in activated carbon that absorb zinc acetate [9]. New mechanisms different from the old ones were proposed according to the above study on the relation between the carboxyl and carbonyl groups in the activated carbon and the activity of catalysts for vinyl acetate synthesis. There are two possible adsorption mechanisms: carboxyl-involved path I and carbonyl-involved path II.

Bonds between carbon and its three attached atoms are formed by overlap of the three sp^2 orbitals with orbitals of the attached atoms. The overlapped atomic orbitals thus form molecular orbitals with oxygen atom, which constitute sigma bonds. The unhybrid p orbitals form anti bonding molecular orbital with oxygen atom, which constitute pi bond. The carbon–oxygen double bonds exert a stronger pull on the electrons than does the carbon–oxygen bond. The electronic structure of lactones was more stable comparing to carbonyl groups and difficult to provide electrons to bind with Zn^{2+} . As a result, Zn^{2+} preferred binding carbonyl oxygen to binding lactones. It is known that the carboxyl hydrogen is more active than the hydroxyl hydrogen. The removal of proton H has increased the negative charge on carboxyl oxygen which is easier to be attacked by Zn^{2+} to reform a new O–Zn bond relative to the hydroxyl groups. Acetylene form π complex with zinc acetate which binds carboxyl and carbonyl groups in the activated carbon. The π complex converted to σ complex to achieve target products due to the conjugative effect.



In summary, PAA treatment can increase carboxyl and carbonyl groups in activated carbon which adsorb more zinc acetate and improve activity of the catalyst for vinyl acetate synthesis.

1. Experimental

1.1. Preparation of activated carbon and catalysts

Yinchuan activated carbon was modified by nitric acid, vitriol and peroxyacetic acid. The treated activated carbon was washed to neutral and dried by microwave oven. Modified activated carbons were impregnated in zinc acetate solution for 1 h, dried by microwave oven to obtain zinc acetate catalysts. Activities of the catalysts were measured in a self-made fixed-bed reactor.

1.2. Measurement of catalysts' activity

Activities of the catalysts were measured in a self-made fixed-bed reactor. The stainless steel reaction tube was filled with 40 mL ϕ 2–3 mm columnar catalyst. The mole ratio of C_2H_2 and HAc was 6:1 by controlling the evaporating temperature of HAc. The reaction temperature was 175 °C and the space velocity was 300 h⁻¹. The reaction mixture left the reactor and passed through a condenser, after which liquid product was timing sampled and analyzed by gas chromatography. The gaseous product was metered and emptied. Activity of the catalyst was measured by the index of productivity (P g d⁻¹ mL⁻¹). The formula for calculating the P value is $P = 24 \text{ h} \sum m_{1/2\text{h}} \text{VAC wt \%} / T_{\text{total}} V_{\text{cat}}$ where $m_{1/2\text{h}}$ is the product weight per 30 min, VAC wt % is the mass fraction of vinyl acetate of product, T_{total} (h) is the total reaction time and V_{cat} is the volume of the catalyst.

Content of zinc in the fresh catalysts was measured using ICP-AES (Thermo IRIS 1000).

1.3. Characterizations of activated carbons

The functional groups in the activated carbon surface, mainly including carboxyl groups, lactones, single hydroxyl groups and carbonyl groups were determined by linked-alkali titration method [10]. The pH_{pzc} of the activated carbons was obtained by mixing 2 g of carbon with 50 mL 0.1 mol/L NaNO_3 solution [11]. The textural structure was determined by N_2 adsorption/desorption at -196 °C which was conducted using a gas sorption analyzer (Builder SSA-4200).

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