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THERMOANALYSIS OF ZINC ACETATE-ACTIVE CARBON CATALYSTS

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ABSTRACT

TG measurements were carried out for the catalysts made of active carbon with a zinc acetate content of 11.1 – 38.72% and thermoanalyses were made on the active carbon, and a crystallized and anhydrous zinc acetate. There was a good linear relationship between the first weight loss percentage of catalyst y(%) and its zinc acetate content x(%), $y = 1.9308X-0.2535$. This method can be used to determine the zinc acetate content x(%) in the catalysts. Thermoanalyses were made for two kinds of dry mixed catalysts.

INTRODUCTION

Zinc acetate-active carbon catalyst was used for the commercial synthesis of vinyl acetate from acetylene and acetic acid. Its zinc acetate content had great influence on the activity of catalyst [1.2]. The use of the catalyst had lacked a quick and easy quantitative analysis method in the past. In this paper, TG measurements for catalysts of different zinc acetate content with apricot stone active carbon as carrier were carried out. In addition, thermoanalyses for apricot stone active carbon, crystallized and anhydrous zinc acetate were made. Within specific temperature regions, a linear relationship was found between weight loss percent and zinc acetate content of the catalyst. Thus a quick and feasible testing method for determination of the zinc acetate content of commercial catalyst was developed.

Comparative thermoanalyses were made for the dry mixed catalysts before and after the synthesis of vinyl acetate. It was found that the TG-DTA curve of the dry mixed catalysts before the synthetic reaction was similar to that of active carbon, but differed from those of impregnated catalysts. After the synthetic reaction proceeded for several hours, the thermoanalytical curve of dry mixed catalysts exhibited the characteristics of the impregnated catalysts. Activity measurement proves that the dry mixed catalysts possess fairly good activities.

EXPERIMENTAL

1. The preparation of impregnated catalysts

Active carbon used as carrier was GH-11 apricot stone carbon produced by the Beijing Guonghua woodcraft factory. Its granularity was of 28-42 mesh, after baking in oven at 130°C for two hours.

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The zinc acetate used was the second class reagent produced by Beijing Chemical Works. Its formula was $Zn(CH_3COO)_2.2H_2O$.

The preparation of catalysts was through absorbing impregnation, the crystallized zinc acetate was weighed according to a nominal concentration and dissolved by deionized water, then poured onto active carbon whilst it was hot. The impregnation temperature was 60°-80°C. The catalysts were then put into oven and dried slowly by baking for at least four hours at 130°C. Finally the catalysts were preserved in a desiccator before use.

Chemical analysis results of active component content of catalysts are listed in table 1.

TABLE 1

Unit	Content No	1	2	8	3	7	4	5	6
Nominal Content $Zn(OAc)_2.2H_2O$/100g catalyst		15	30	38	45	50	60	70	80
Content determined by chemical analysis	$Zn(OAc)_2$/100g catalyst	11.1	19.54	22.8	26.13	27.59	32.94	34.18	38.72
	$Zn(OAc)_2$/100g active carbon	12.48	24.29	29.53	35.38	38.08	49.13	51.92	63.20
	$Zn(OAc)_2.2H_2O$ /100g active carbon	14.94	29.06	35.33	42.33	45.57	58.78	62.12	75.61

Because the nominal concentration of catalyst was calculated on the basis of including two waters of crystallization (water content 16.44%), and also because there was a white zinc acetate residue in the vessel after impregnating and drying, the actual zinc acetate content of the catalysts was lower than the nominal concentration. The concentrations listed in the bottom three lines of table 1. were determined by chemical analyses by the method of commercial catalyst.

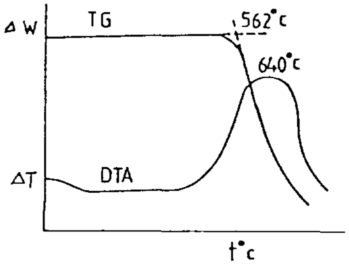


Fig. 1. TG-DTA curves of apricot stone active carbon sample: 5.85 mg. TG range: 10 mg, DTA range: ± 100 μv, heating rate: 20k min^{-1}

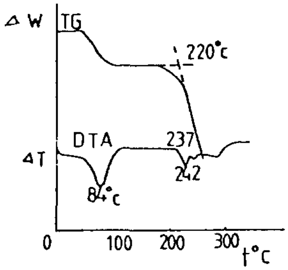


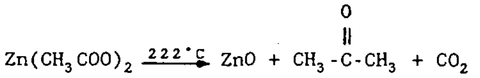
Fig. 2. TG-DTA curves of crystallized zinc acetate sample: 4.40 mg, TG range: 5 mg. DTA range: ± 100 μV, heating rate: 10k min^{-1}

From figure 1 it can be seen that the extrapolated initial temperature Te on the TG curve of apricot stone active carbon was 562°C, and almost no weight loss occurs under 500°C (refer to dried active carbon). The exothermic peak temperature of DTA was cir 640°C, which agreed with Skowronski's experimental result.[3] Figure 2. shows the TG-DTA curves for crystallized zinc acetate, in which the extrapolated initial temperature Te of the first weight loss began at 68°C, and ended at 88°C. The weight loss (16.0%) basically agreed with the theoretical weight loss percent (16.44%) calculated from the loss of two water of crystallization, so can be attributed to the dehydration. The DTA endothermal peak temperature of dehydration was 84°C. The extrapolated initial temperature Te of the second weight loss began at 222°C and ended at 290°C. The three corresponding endothermic peaks on the DTA curve were:

(a) first endothermic peak, (extrapolated initial temperature Te - 237°C) was the melting peak of zinc acetate (the melting point found in reference handbook was 237°C) and the temperature at the maximum was 242°C;

(b) second endothermic peak temperature was 262°C;

(c) third endothermic peak temperature was 290°C which it is suggested corresponds to the thermal effect of the decomposition of zinc acetate. The decomposition reaction is:



$$Zn(CH_3COO)_2 \xrightarrow{222^\circ C} ZnO + CH_3-\overset{\overset{O}{\|}}{C}-CH_3 + CO_2 \qquad (1)$$

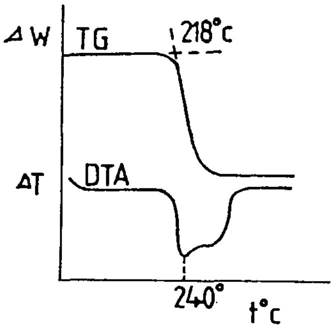


Fig.3. TG-DTA curves of anhydrous zinc acetate sample: 4.40 mg, TG range: 5 mg. DTA range: ± 100 μv, heating rate: 20k min^{-1}

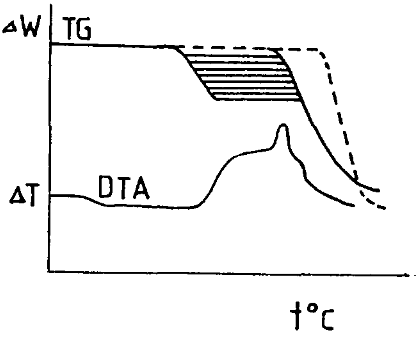


Fig. 4. TG-DTA curves of (different content) Zinc acetate-active carbon catalysts sample: 3.5-4.6 mg. TG range: 5 mg. DTA range: ± 100 μv, heating rate: 20k min^{-1}.

Figure 3. is the TG-DTA curves of anhydrous zinc acetate which was prepared by baking crystallized zinc acetate at 150°C in oven for 24 hours. The extrapolated initial temperature began at 218°C and ended at 282°C, corresponding to an endothermic shoulder peak. Weight losses of two replicates were 55.68%

and 56.09% respectively, in basic agreement with the theoretical weight loss 55.61% calculated from equation (1).

Figure 4. shows the TG-DTA curves of impregnated catalysts of eight different zinc acetate contents. It could be seen that the first weight loss rate on the TG curve increased with the increase of zinc acetate concentration of the catalysts. There were differences among the extrapolated initial temperature in the beginning of weight losses, which, at low concentration, was obviously higher than the decomposition temperature of zinc acetate, and at high concentration, which was similar to the decomposition temperature of anhydrous zinc acetate. This reflected the interaction between the active component zinc acetate of the catalyst and its active carbon carrier. The first weight loss on TG curve characterized the decomposition of anhydrous zinc acetate, because during preparation, the catalysts had been baked at 130°C for four hours. The absence of absorbed or crystallized water was noted. The second weight loss of the catalysts with different zinc acetate content corresponded to the oxidation of carbon. Their extrapolated initial temperatures fell between 448°-520°C, which were 42°-114°C lower than the temperature of oxidation of pure active carbon, and 50°-150°C lower than that of the exothermic maximum . The main tendency of the extrapolated initial temperatures was that of a decrease with increasing concentration of zinc acetate.This was explained in that the presence of metal ions was beneficial to the oxidation of carbon. This explanation agreed with both the conclusions reached by Jones et al [4], and the work done earlier by the author [5]. The relevant data are listed in table 2. The fourth line in the table 2 was the determination value y(%) by chemical analysis with the method of commercial catalyst; the seventh line was the first weight loss percentage x(%) of the corresponding catalyst in thermoanalysis. Plotting y against x, Fig. 5 was obtained.

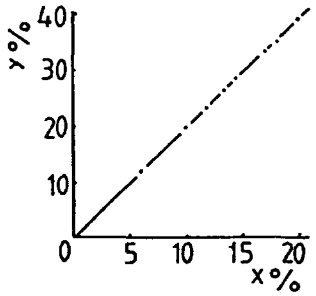


Fig. 5. The relationship between the weight losses percentage x(%) with the contents of the corresponding catalysts.

Table 2. Thermoanalytical data of zinc acetate-active carbon catalysts

Test No	Catalysts No	Zinc Acetate Content (%)		sample (mg)	decomposition of zinc acetate			Oxidation of active carbon	
		nominal value	determined value*		extrapolated initial temperature Te(°C)	weight loss amount (mg)	weight loss rate (%)	extrapolated initial temperature Te(°C)	peak temperature Tm(°C)
1	pure active carbon	0	0	5.85	-	-	-	-	640
2	1#	15	11.10	4.05	244	0.25	6.17	520	588
3	2#	30	19.54	4.60	237	0.465	10.11	500	588
4	8#	38	22.80	4.07	236	0.485	11.92	488	572
5	3#	45	26.13	3.50	236	0.475	13.57	484	560
6	7#	50	27.59	4.60	224	0.665	14.46	476	548
7	4#	60	32.94	4.10	223	0.705	17.16	452	532
8	5#	70	34.18	4.25	220	0.815	18.23	454	530
9	6#	80	38.72	4.10	220	0.815	19.88	448	520
10	anhydrous zinc acetate	-	(100)	4.40	218	2.45	55.68	-	-
11	DM 1A	-	-	2.35	-	-	-	536	580
12	DM 2A	-	-	4.05	-	-	-	544	586
13	DM 1B	-	(26.43)	3.80	220	0.575	13.82	488	572
14	DM 2B	-	(27.78)	3.10	224	0.450	14.52	480	576

* This value is determined by chemical analysis with the method of commercial catalyst by Prof. Li Guoying and Mr Wang Wenhai in Department of Chem., Peking University.

The above-mentioned data of y(%) and x(%) can be obtained through one-place linear regression with a programming calculator:

$y = a + bx$

regression coefficient $a = -0.2535$, $b = 1.9308$

correlative coefficient $r = 0.9994$

ie $y = 1.9308\,x - 0.2535$

The linear relationship was good and so provided the basis for deriving the concentration of zinc acetate through the amount of the first weight loss from the catalyst. On the other hand a linear regression for weight loss percentage x and nominal content y, gave:

$a = 6.7049$, $b = 4.0210$, $r = 0.9853$.

3. The preparation of dry mixed catalysts and their thermoanalyses

Based on the phase analysis with X-ray diffraction, Xie Youchang and Tong Youqi et al.[6] concluded that certain kinds of salts or oxides, such as zinc acetate, copper chloride etc., after being mixed with a carrier of high specific surface, and baked for a long time at temperatures far below their melting point, the salt molecules will enter the pores of the carrier and form a mono-layer coverage. For this reason dry mixed catalysts 1A and 2A were prepared based on the formula of impregnated catalyst No. 2 (nominal concentration 30%), whilst the baking temperature and heating time were varied. The crystallized zinc acetate was first ground, mixed with active carbon (granularity 0.28 - 0.45 mm), and baked at the temperature conditions listed in table 3 (activity is expressed as reaction rate γ under 200°C).

TG tests were made on prepared dry mixed catalysts 1A and 2A respectively. Little weight loss occurred below 540°C, and the TG curve was similar to that of active carbon. The results of activity measurement in a gradientless reactor with outer-circulation are listed in table 3.

Table 3. Preparation and activity data of dry mixed catalysts.

Catalysts	Preparing conditions	Reaction rate $r \times 10^3$ mol/g(cat)hr
DM 1A	115°C baking 24 hrs and 150°C baking 48 hrs	1.389
DM 2A	115°C baking 24 hrs and 150°C baking 48 hrs and 170°C baking 42 hrs	1.407
IP 2	Impregnate catalyst nominal concentration 30%	1.607

Comparing with impregnated catalysts No 2 of nominal concentration 30%, the activity dropped by only about 12%. After reaction, the colours of catalyst 1A and 2A turned black just like the impregnated catalyst. After baking for two hours at 120°C to removed acetic acid and vinyl acetate, these catalysts were designated as dry mixed 1B and 2B respectively. The thermoanalyses for these catalysts exhibited the characteristic curve of typical impregnated catalysts (see Fig. 6).

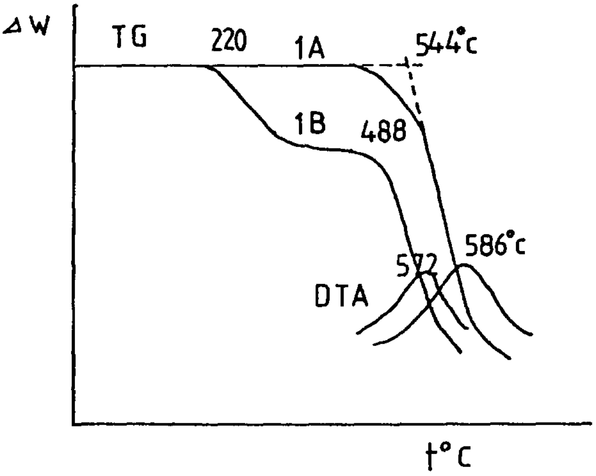


Fig. 6. TG-DTA curves of dry mixed catalyst before and after synthesis reaction.

The first weight loss of dry mixed catalyst 1B began at 220°C and the second weight loss at 480°C. The exothermic peak temperature of oxidation was 576°C, similar to that of the impregnated catalysts. The data are shown in table 2. The zinc acetate contents derived from the first weight loss are listed in parentheses on the third line of table 2; the values obviously deviated. This may be caused by the reactant and product retained on catalysts and desorbed at high temperatures.

RESULTS AND DISCUSSION

1. A new method for determining zinc acetate content of zinc acetate-active carbon catalyst has been developed. The method is quick (the test lasts about an hour), no sample treatment is needed, it is free from residual chemical agent.
2. Through the thermal analysis of catalysts with different zinc acetate content, the author found that the variation of decomposition temperature (heat stability) was regular, which supported the viewpoints of Xie Youchang and Tong Youqi that there was a strong active force between the large

amounts of polar groups and unsaturated site of valence bonds on the active carbon surface and the ions of $Zn(Ac)_2$. The heat stability of catalysts with low zinc acetate concentration was markedly higher than that of catalysts with high zinc acetate concentration. This was because the active carbon surface affected the mono-layer molecules of zinc acetate more strongly than multi-layer molecules of that salt.

3. Pure zinc acetate and pure active carbon have no catalytic effect on the gas phase synthesis of vinyl acetate from acetylene and acetic acid. After mixing zinc acetate powder with active carbon granules, the dry-mixed catalysts formed through baking under 115°-170°C for scores of hours possess fairly good catalytic activity for the synthesis of vinyl acetate. This proved the mix prepared in this way was catalytically active and the thermal analysis curve obtained from the sample after reaction exhibited characteristics of that of the impregnated catalysts. These two points have not yet been confirmed by Xie Younchang and Tong Youqi with X-ray diffraction [6]. This proved that the active component, zinc acetate, can enter the inner surface of the porous carrier, active carbon, at temperatures much lower than its melting point and showed the tendency to a mono-layer self-distribution.

4. Thermoanalytical tests of the newly prepared and unreacted dry mixed catalysts exhibited no characteristic of that of impregnated catalysts, i.e. no first weight loss occurred at 220°C-290°C. It is considered that this was due not only to $Zn(Ac)_2$, but also to ZnO, distributed on the surface, for the latter will not decompose and lose weight; but ZnO will still turn into $Zn(Ac)_2$ when reacted with acetic acid. Of course this conclusion needs further proof.

   As to the relationship between structure and activity of zinc acetate-active carbon catalysts, the hypothesis of mono-layer distribution of zinc acetate on the active carbon surface, these topics have been dealt with in another paper [7].

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