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Loss Mechanism and Loss Rate of Zinc Acetate from the Surface of the Activated Carbon in the Reaction Process

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Abstract: In the reaction process of synthesizing vinyl acetate, the loss of the active species $Zn(OAc)_2$ from the surface of activated carbon results from $Zn(OAc)_2$ sublimating of gas phase and the blocking inside micropores with condensation products. The sublimation mechanism is that the reaction product vinyl acetate acts with $Zn(OAc)_2$ to produce a volatilizable complex, then sublimates to gas phase. The overall loss ratio(LR) can be described as the equation $LR = 1 - \exp(-kvt)$, which is extensive application of the sublimation rate equation, where v is the flow rate of gas stream, t is reaction time, and k is loss rate constant.

Key words: activated carbon; deactivation of catalyst; synthesis of vinyl acetate; zinc acetate

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Introduction

The catalyst $Zn(OAc)_2$ supported on activated carbon is used in the industrial process of the synthesis of vinyl acetate(VAc) from acetylene(C_2H_2) and acetic acid(HOAc). A distinguishing characteristic of the catalyst is that the catalytic activity decays continually in the applied process. In order to study the deactivation of the catalyst, the physicochemical properties of the fresh catalysts as well as the spent ones are determined and contrasted. It is shown that the decreasing of active species is one of the common characteristics of all consumed catalysts. For example, Czamy[1] reported that the content of $Zn(OAc)_2$ in a fresh catalyst was 39.65% by weight, but 27.68% in a deactivated one; Romanchuck[2] reported that was 27% by weight in a fresh catalyst, but only 18% ~ 22% in a deactivated one. Therefore, studying the loss mechanism and the effect of reaction conditions on loss rate of $Zn(OAc)_2$ in the catalysts is a foundational work for the research of deactivation of the catalyst. But up till now. there is no reports of monographic study on this aspect. The purpose of this paper is to take a step further in studying the loss mechanism and the overall loss rate of Zn $(OAc)_2$ from the surface of the catalyst, which is on the basis of some related researches of the deactivation catalysts. In recent years, we have reported the study of the loss mechanism and the loss rate by sublimation of active species I_2[3], $HgCl_2$[4] and MoO_3[5,6] from the surface of catalysts. This paper is a new advance in our serial study.

1 Industrial Catalyst Samples and Their Physicochemical Properties

The fresh catalyst is prepared with immersion method. The activated carbon used for preparing the catalyst is the same kind as the support of I_2 – activated carbon[3]. Its particle diameter is 0.453 mm(30 ~ 40 mush). The content of $Zn(OAc)_2$ in the fresh catalyst is about 30% by weight. No crystal peak of $Zn(OAc)_2$ was found in the fresh catalyst determined with XRD, which was consistent with the result reported in literature[1,2]. Thus, $Zn(OAc)_2$ is dispersed in a monolayer on the surface of the activated carbon in this catalyst. The fresh catalyst was put in industrial fluidized reactor. As the reaction time was extended, the reaction

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temperature rose gradually. The catalyst sample were taken out from the reactor when the reaction temperature is 177 ℃, 187 ℃ and 202 ℃ respectively.

The specific surface and pore volume of the catalyst samples were determined with nitrogen absorption method . The results are listed in Table 1.

Table 1　The pore diameter and specific surface of the catalyst

feature	active carbon/%	new catalygt/%	the decayed datalyst/%		
			I	II	III
probable diameter/nm	< 1.0	< 1.0	2.1	2.1	2.1
specific surface/(m^2/g)	1459	375	19.4	13.4	7.4
($Zn(OAc)_2$)/(catalyst)/(kg/100 kg)	0	31.10	25.69	18.22	10.20
bulk density/(kg/m^3)	–	565.7	–	–	759.4

The data in Table 1 shows that as the reaction time extends, the amount of carbonaceous deposit increased the micropores smaller than 1.0 nm were blocked with condensation product, the specfic surface was decreased rapidly and the bulk density was increased. At the same time the content of $Zn(OAc)_2$ was decreasing continceously because of loss by sublimation. In literature, nitrogen[3,4,6] or water[5] was replaced by the reaction gas to determine the loss rate of active species (such as I_2, $HgCl_2$ or MoO_3) from the surface of catalysts. In those process, the surface of catalyst is not full of carbonaceous deposit. Their surface is clean. Because the loss process of $Zn(OAc)_2$ is accompanied with the carbonaceous disposit, to study the loss kinetics of $Zn(OAc)_2$ will be a new work in this field. Obviously, this work has great value for deactivation of catalysts.

2　Experiment Method

2 ~ 4 g of fresh catalyst was put into a flow recycle reactor which had been used for studying the loss of $HgCl_2$ from activated carbon. Gas stream passed through the reactor with a constant flow rate. Acetylene gas had been purified. Acetic acid was carried with gas stream into the reactor after the molar ratio had been determined. After a period of time, the catalyst was taken out, weighted and analyzed, then the loss ratio(LR) of $Zn(OAc)_2$ was calculated as following:

$$LR = \frac{W_B C_B - W_A C_A}{W_B C_B}, \qquad (1)$$

As the amount of activated carbon is constant before and after the reaction, 1kg activated carbon is taken as a basis of calculation. The flow rate of gas stream indicated was v [m^3 C_2H_2 (or N_2)/kg Carbon · h]. The amount(W_C) of activated carbon put into reactor can be calculated from the amount of the catalyst.

$$W_C = W_B(1 - C_B).$$

Analysis method: Put the catalyst sample 1.5 ~ 2 g, 2 ml 1∶1 HCl and 80 ml distilled water into a Erlenmeyer flask, boil slowly for 30 minutes, regulate pH = 5 ~ 6 with HOAc – NaOAc, Titrate with standard solution of EDTA. The content of Zinc is indicated in the form of $Zn(OAc)_2$.

3　Result and Discussion

3.1　Loss mechanism and reaction mechanism

The loss by sublimation of active species is actually the desorption of it from the surface of support into the gas phase and carried away with the reaction gas stream. The sublimation mechanism can be divided into two kinds, physical loss and chemical loss[5]. In the process of physical loss, the loss rate is independent of the component of reaction gas. It is a process of physical desorption. Thus, the nitrogen can be used as a substitute for reaction gas to determine the loss rate. In the chemical loss process, one of the component in reaction gas react with the active species to produce a complex which is more volatile than the active species itself, so the loss rate will be accelerated. In order to examine the loss mechanism of $Zn(OAc)_2$, the experiments were carried out as follows.

After nitrogen, acetylene and 25% HOAc – 75% N_2 mixture gas stream passed through the fresh catalyst at 200 ℃ and v = 5.4 m^3/(kg · h) for 8 h respectively, it was found that the amount of $Zn(OAc)_2$ in the catalyst did not change and LR were all zero . But when 40% VAc – 60% N_2 mixture gas stream passed through the fresh catalyst, the amount of $Zn(OAc)_2$ in the catalyst decreased and LR = 4.7%. Obviously, the loss experiment should only be done under the reaction condi-

tion, in which the product VAc is formed. Thus, the loss of $Zn(OAc)_2$ in catalyst was due to the interaction of VAc and $Zn(OAc)_2$, which belonged to chemical loss mechanism. Then acetylene and acetic acid mixture gas stream passed through the fresh catalyst at 200 ℃ for 8 hours, while *MR* was 40, 15 and 2.88 respectively. It was found that the amount of Zn $(OAc)_2$ in the catalyst were all decreased. The *LR* is the maximum when *MR* = 15. The results are shown in table 2.

Table 2 The loss ratio in various *MR* reaction temperature 200 ℃, reaction time 8 h

No.	*MR*	W_B/g	W_A/g	C_B/%	C_A/%	v/(m^3/(kg·h))	*LR*/%
1	40	1.9230	1.9586	29.8	28.3	2.8301	3.3
2	15	2.2324	2.5324	29.8%	18.0%	2.6813	31.3
3	2.88	3.4581	3.9704	32.1	26.2	3.0180	6.3

The relationship between *MR* and *LR* can be interpreted with reaction kinetics. Cornelism[7] pointed out that HOAc absorption on the surface of catalyst is much stronger then C_2H_2. In the region of $P_{HOAc} < 0.05 \times 10^3$ Pa, as the P_{HOAc} is raised the reaction rate increase. In the region of $P_{HOAc} > 0.12$, the reaction rate varies directly as the P_{HOAc}. In the region of $P_{HOAc} = 0.05 \sim 0.12$, the reaction rate is maximum. In our experiment date in Table 2, when *MR* = 40, P_{HOAc} (= 0.024) is lower than 0.05, the reaction rate is lower because the HOAc is gas phase is too low. When *MR* = 15, P_{HOAc} (0.0625) just belongs in the region of maximum reaction rate. Because the reaction rate is faster, the produced VAc is bigger, which will result in *LR* bigger. When *MR* = 2.88, the C_2H_2 in gas phase is lower, the produced rate of VAc is slower, so the *LR* will be smaller, therefore, the relationship between *MR* and *LR* is an evandanle for the chemical loss mechanism is this process.

3.2 Loss Rate

The effect of reaction time and temperature on the loss rate of $Zn(OAc)_2$ was carried out with *MR* = 15 at which the *LR* is the maximum. The experimental results are listed in Table 3.

Table 3 Effect of reaction time and temperature on *LR*, *MR* = 15, C_B = 31.1%

No.	Temperature/℃	W_B/g	W_A/g	v/(m^3/(kg·h))	C_A/%	T/h	*LR*/%
4	200	2.3248	2.6113	2.6231	22.0	4	19.8
5	200	2.3449	2.7312	2.4359	24.5	2	8.2
6	225	2.2716	2.6238	2.7496	18.3	2	31.9
7	210	2.1493	2.2904	2.8436	25.5	7/6	12.4
8	180	2.3077	2.4184	2.6423	28.1	4	5.3

After arranging the data of *MR* = 15 in Table 2 and 3, we found that these data can be fitted as an experience equation as following:

$$1 - LR = \exp(-kvt); \quad (2)$$

$$\ln k = 24.073 - 13276.3/T, \quad (3)$$

the comparison of calculated and experiment values are listed in Table 4.

Table 4 Comparison between calculated and experiment values of *LR*; *MR* = 15

No.	2	4	5	6	7	8
LR(cal)/%	32.6	17.6	8.6	33.9	10.3	5.4
LR(exp.)/%	31.3	19.8	8.2	31.9	12.3	5.3

We have suggested a sublimation rate equation (4) to fit data of loss by sublimation of active species $HgCl_2$[4], I_2[3] and MoO_3[5].

$$\frac{dC_s}{dt} = kvC_s^n, \quad (4)$$

if $n = 1$, its integral equation is

$$\frac{C_s}{C_{s0}} = \exp(-kvt), \quad (5)$$

where C_{S0} and C_S (kg active species/kg carbon) are content of active species before and after reaction. C_S/C_{S0} is mass ratio of active species after and before reaction. thus,

$$\frac{C_s}{C_{s0}} = 1 - LR, \quad (6)$$

Substituting Eq. (6) to Eq. (5), Eq. (2) is obtained. That is to say, Eq. (2) is experience extension of sublimation rate equation. The sublimation rate equation includes loss by sublimation only. But, the former (Eq. (4)) includes the factor of micropores blocking

besides the factor of sublimation.

4 Conclusion

The loss ratio of $Zn(OAc)_2$ from the surface of activated carbon was determined in nitrogen, C_2H_2, HOAc and VAc atmosphere respectively. It is found that the loss rate is accelerated with the reaction product VAc. Compare the loss rate with the reaction rate, and this mechanism is further proved.

It is found that the sublimation rate equation can be applied to this loss process. The sublimation rate order $n = 1$.

Nomenclature:

C—the content of $Zn(OAc)_2$ in the gas phase, kg/m^3;
C_A—the content of $Zn(OAc)_2$ in the catalyst after reaction, wt.%;
C_B—the content of $Zn(OAc)_2$ in the catalyst before reaction, wt.%;
C_s—the content of active species after reaction, kg active species/kg carbon;
C_{s0}—the content of active species before reaction, kg active species/kg carbon;
k—constant in reaction rate equation;
LR—the loss rate of $Zn(OAc)_2$;
MR—the molar ratio of C_2H_2 and HOAc;
n—sublimation order;
P—partial pressure;
t—reaction time, h;
T—reaction temperature, K;
v—the flow rate of gas stream, m^3 gas/kg activated carbon;
W_A—the catalyst weight after reaction, g;
W_B—the catalyst weight before reaction, g;
W_C—the amount of support activated carbon of the catalyst put in the reactor.

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醋酸锌自催化剂表面上的流失机理和流失速度

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摘　要：乙炔和醋酸合成醋酸乙烯的反应过程中，催化剂的失活，是由催化剂中的醋酸锌 $Zn(OAc)_2$ 从活性炭表面上升华到气相中以及被凝聚物堵在微孔内部而引起的. 升华机理是反应产物与 $Zn(OAc)_2$ 作用生成挥发性络合物再升华到气相中去. 总流失速度可用 $LR = 1 - \exp(-kvt)$ 来描述，这是升华速度方程式的应用推广. 式中 v 为气流速度，t 为反应时间，k 为速度常数.

关键词：活性炭；醋酸乙烯合成；催化剂失活；醋酸锌