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STUDY OF THE DECOKING KINETICS OF DEACTIVATED ZEOLITE CATALYSTS FOR ETHYLATION OF BENZENE BY TA

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ABSTRACT

The decoking behaviour of deactivated ZSM-5 zeolite catalysts for ethylation of benzene has been studied by using TG-DTG. The kinetic parameters of the decoking reaction were obtained by Broid's method from TG data. Also the order of the regeneration capacity of catalysts according to the activation energy of decoking was given. It was shown that the regeneration of catalysts in air was easier than in O_2.

INTRODUCTION

In order to prevent polymerization, cracking, coking and other side reactions in the ethylation of benzene, ZSM-5 type zeolite catalysts have been modified by Zn, Mg and P + Mg so as to adjust the pore structure of the zeolites and their acidity, and enhance the formation of ethylbenzene. The results show that the coking of the modified zeolite catalysts was improved in the process of reaction, but the coking still remained one of the important causes which influenced the stability of the catalysts. Therefore, it is necessary to investigate the regenerating properties to ensure the industrial utilization of these catalysts.

Usually, regeneration of these catalysts was conducted in small size fixed or fluidized bed reactor. And in recent years, regeneration of these catalysts was reported to be studied by TA. This method is easier and faster than the conventional methods, and kinetic parameters of decoking can also be obtained.

In this paper, the thermal behaviour of modified catalysts and the influence of the gas environment on decoking have been investigated by TG-DTG. Meanwhile, kinetic parameters of decoking by the Broid method and order of regenerating capacity of the catalysts according to activation energy of decoking have been obtained. These values are necessary for the design of regeneration reactors.

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EXPERIMENTAL

Deactivated zeolite catalysts

H-ZSM-5 ; Zn-ZSM-5 ; Mg-ZSM-5 ; P,Mg-ZSM-5 .

Determination of decoking amount

Instrument

All experiments were performed on the Shimazu DT-20B thermal analysis equipment.

Experimental conditions

TG: Detection Range, 2mg; heating rate, 10 °C min^{-1} ;
atmosphere, air, O_2 .

DTG: Detection Range 4mv min^{-1} others were the same as in TG .

Procedure

Deactivated zeolite catalyst was put in a small basket made of quartz and suspended at the center of the reaction tube, and then balanced with weights. Then air or oxygen was introduced. The decoking was performed in a temperature-programmed mode. The temperature and the amount of decoking were recorded.

RESULTS AND DISCUSSION

1. Thermal behavior of deactivated zeolite catalyst

The decoking TG-DTG curves in O_2 atmosphere of the deactivated P,Mg-ZSM-5 catalyst are shown in Fig. 1. Tables 1 and 2 summarize the results of determination.

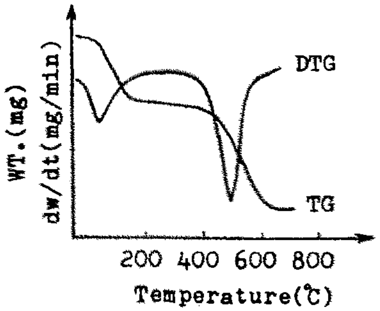


Figure 1. The TG-DTG curve of decoking reaction in O_2 for P,Mg-ZSM-5 catalyst

Table 1. The results of measurement by TG-DTG in air

Zeolites	Sample weight (mg)	TG Temp. range (℃)	Amount of coke removed (mg)		DTG Peak temp. (℃)	Maximum decoking rate mg/min
ZSM-5-H	13.56	349-590	0.72	5.3	491	0.073
ZSM-5-Zn	15.11	319-604	1.08	7.1	497	0.098
ZSM-5-Mg	15.22	445-600	0.22	1.4	512	0.036
ZSM-5-P,Mg	16.41	385-622	0.38	2.3	538	0.023

Table 2. The results of measurement by TG-DTG in O_2

Zeolites	Sample weight (mg)	TG Temp. range (°C)	Amount of coke removed (mg)		DTG Peak temp. (°C)	Maximum decoking rate mg/min
ZSM-5-H	17.29	335-572	0.82	4.7	465	0.092
ZSM-5-Zn	13.76	320-570	0.98	6.7	470	0.102
ZSM-5-Mg	17.64	386-610	0.27	1.5	466	0.044
ZSM-5-P,Mg	17.50	382-570	0.38	2.2	492	0.076

One can see that there are two peaks in the DTG curve and a corresponding weight-loss step in the TG curve. The peak in the temperature range of 30-200°C can be attributed to water-desorption. The peak in the range 382-570 °C is obviously the oxidation peak of coke deposits in catalyst. i.e. the decoking reaction

$$C + O_2 \longrightarrow CO_2\uparrow$$

If the initial decoking temperature is taken as a measure of ease of decoking, then the following sequence can be obtained:

$$\text{Zn-ZSM-5} > \text{H-ZSM-5} > \text{P,Mg-ZSM-5} > \text{Mg-ZSM-5}$$

The sequence was the same as in O_2 atmosphere.

Again, when we take the maximum decoking rate as a measure of decoking, we also get the above sequence in O_2 atmosphere, but coke deposit in Mg-ZSM-5 was more easily removed than that in P,Mg-ZSM-5. We can see from Tables 1 and 2 that initial decoking temperatures of all catalysts in O_2 were lower than that in air except Zn-ZSM-5. Their decoking rate in O_2 was faster than that in air. This can be explained by regeneration of deactivated catalysts being easier in O_2 than in air .

2. Calculation of the decoking kinetic parameters for deactivated catalysts

The Broid method is employed to calculate the kinetic parameters from the TG curves of the decoking reaction. The linearized equation of this method is as follows

$$\mathrm{LnLn}\frac{1}{\alpha} = -\frac{E}{R}\cdot\frac{1}{T} + \text{constant} \qquad n=1$$

$$\mathrm{Ln}\left[\frac{1}{1-n}(1-\alpha^{1-n})\right] = -\frac{E}{R}\cdot\frac{1}{T} + \text{constant} \qquad n\neq 1$$

Where α stands for cyclohexane fraction, n for reaction order, E for reaction activation energy, R for gas constant and T for temperature.

Reaction order can be obtained by trying if the plots of LnLn or $\mathrm{Ln}\left[\frac{1}{1-n}(1-\alpha^{1-n})\right]$ vs. $\frac{1}{T}$ were a straight line, and the activation energy was calculated from the slope of the straight lines. Then the prefactors were obtained from $\frac{1}{T}$ value when $\mathrm{LnLn}\frac{1}{\alpha}$ or $\mathrm{Ln}\left[\frac{1}{1-n}(1-\alpha^{1-n})\right] = 0$.

In order to confirm that the treatment of the TG data obtained in our equipment by the Broid method is justified, we first use this method to treat TG data of the decomposition of calcium carbonate, as the kinetics parameters are known from the literature.

The TG curve of the decomposition of calcium carbonate in air is shown in Fig.2. Procedure of determination of reaction order is illustrated by a plot of the $\mathrm{LnLn}\frac{1}{\alpha}$ or $\mathrm{Ln}\left[\frac{1}{1-n}(1-\alpha^{1-n})\right]$ vs. $\frac{1}{T}$ in Fig.3.

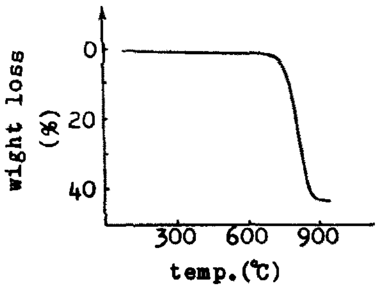
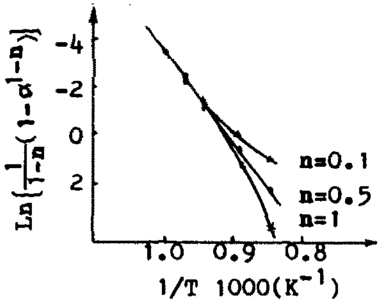


Fig.2. TG curve of decomposition of $CaCO_3$



ig.3. Relationship between $\mathrm{Ln}\left[\frac{1}{1-n}(1-\alpha^{1-n})\right]$ and 1/T

It can be seen that the plot of $\mathrm{LnLn}\frac{1}{\alpha}$ or $\mathrm{Ln}\left(\frac{1}{1-n}(1-\alpha^{1-n})\right)$ vs $\frac{1}{T}$ is a straight line when n is equal to 0.5.

The results of all kinetics parameters were compared with those from the literature as shown in Table 3.

Table 3. Comparison of kinetics of the decomposition of $CaCO_3$

Author	Method	n	E (kcal/mol)	A sec^{-1}
K.M.Caldwell	Freeman- Carroll	0.47	52	$5\cdot10^{8}$
	Coats-Redfern	0.5	51	$3\cdot10^{8}$
	Achar Brindle-Sharp	0.5	54	10^{8}
	Isothermal	0.5	48	10^{8}
This work	Broid	0.5	50.54	$3.5\cdot10^{8}$

From the comparison in Table 3 we can see that the values of the kinetics parameters by treating the TG curve for decomposition of calcium carbonate with the use of the Broid method are consistent with those from literature.

Accordingly, the same procedure was used to treat the TG curves of the decoking reaction of the deactivated catalysts and the results are shown in Tables 4 and 5.

Table 4. Kinetics parameters of decoking reaction in air

Zeolite	n	E (Kcal/mol)	A Sec^{-1}
ZSM-5-H	1	18.52	$5.3\cdot10^{3}$
ZSM-5-Zn	1	19.35	$6.55\cdot10^{3}$
ZSM-5-Mg	2	47.33	$8.49\cdot10^{11}$
ZSM-5-P,Mg	1.5	43.06	$2.07\cdot10^{10}$

These results show that the activation energy of the decoking reaction in air is not the same for catalysts modified with different elements. The Zn-ZSM-5 and H-ZSM-5 catalysts have nearly the same activation energies. Mg-ZSM-5 and P,Mg-ZSM-5 catalysts always have activation energies higher than those of the H-ZSM-5. If the activation energies of the decoking reaction are taken as a measure of

Table 5. Kinetic parameters of decoking reaction in O_2

Zeolite	n	E (Kcal/mol)	A Sec^{-1}
ZSM-5-H	1	24.57	$6.29\cdot10^5$
ZSM-5-Zn	1	24.62	$7.47\cdot10^5$
ZSM-5-Mg	2	50.09	$3.77\cdot10^{13}$
ZSM-5-P,Mg	1.5	46.42	$1.79\cdot10^{12}$

regeneration capacity of catalysts,then the following sequence can be obtained H-ZSM-5 > Zn-ZSM-5 > P,Mg-ZSM-5 >Mg-ZSM-5 .

The sequence was the same as in O_2 and also according to their acidity but is different from that according to initial decoking temperatures or maximum decoking rates. This suggests that the decoking ease was related to the acidity of catalysts. i.e. strong acidity on strong acid sites for H-ZSM-5 catalysts results in formation of polyaromatic compounds which are called hydrocarbon coke and can be easily removed. For modified catalysts the acidity on strong acid sites was weakened by modification and results in formation of graphitic or higher graphitic coke which was difficultly to remove.

In addition, pore size of the ZSM-5 zeolite also has an influence on decoking reaction. The results of adsorption indicate that the degree of adsorption for H-ZSM-5 was 6% of the catalyst. While for modified ZSM-5 it decreased to some extent. The minimum adsorption was 3.4%. This shows that the pore size of ZSM-5 contracted due to modification and it would influence the decoking reaction.

The results also show that the activation energy of the decoking reaction in air was 3-6 kcal/mol lower than in O_2 . This may be related to the effect of cage of the zeolites. i.e. the diffusion of the dioxide formed by combustion of the coke from cage in air is easier than in O_2 and enhances decoking reaction.

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