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STUDY OF THE SURFACE ACIDITY BEFORE AND AFTER HEAT OR STEAM TREATMENT FOR P OR Mg MODIFIED ZSM-5 ZEOLITES

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ABSTRACT

The method of adsorption of vapor of basic substance ($C_2H_5NH_2$) was employed to determine acidity of ZSM-5 catalyst. Effects of heat or steam treatment on acidity of modified ZSM-5 catalysts have been studied by TG-DTG and de-ethylamination activation energy was obtained by Broid method from TG data. Also, effects of heat and steam treatment on selectivity of modified ZSM-5 catalysts were examined.

INTRODUCTION

The conversion of methanol to lower olefines is an acid-base reaction. Methanol can be converted to hydrocarbons on many solid acid catalysts. One of the best catalysts is ZSM-5 type zeolites because the ZSM-5 zeolites have high Si/Al ratio and specific pore structure. They not only have a good stability for heat and steam treatment but they are suitable to catalyze several reactions through changing their acidity and pore size.

It is reported that a moderate acidity can improve selectivity of ZSM-5 zeolite catalysts. Results show that the selectivity for lower olefines in methanol conversion was enhanced by the modification of ZSM-5 catalysts. But it is also necessary to study effects of heat and steam on acidity and selectivity for modified ZSM-5 catalysts because higher reaction temperature was employed and there is a large amount of water formed in methanol conversion.

In this paper the adsorption of vapor of basic substance ($C_2H_5NH_2$) was employed to determine number of acid centers for modified ZSM-5 catalysts by TG-DTG. De-ethylamination activation energy was obtained by Broid method effects of heat and steam treatment on acidity and selectivity for lower olefines in methanol conversion were also examined.

EXPERIMENTAL

Modified ZSM-5 zeolite catalysts

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P-ZSM-5 ; Mg-ZSM-5

Acidity determination

Experimental equipment

All thermal analyses were performed on the Shimazu DT-20B Thermal Analyzer

Experimental conditions

TG : Detection range, 2 mg; heating rate, 10°C min^{-1} ; atmosphere, N_2

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

Experimental procedure

The same as in reference(1) .

RESULTS AND DISCUSSION

1. Thermal behavior and determination of number of acid centers on P-ZSM-5 and Mg-ZSM-5 zeolites

P-ZSM-5 and Mg-ZSM-5 zeolites have similar de-ethylamination TG-DTG curve. The de-ethylamination TG-DTG curve of P-ZSM-5 zeolite in air is shown in Fig.1.

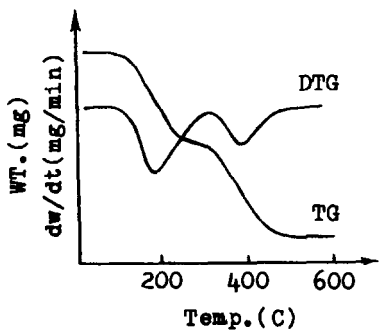

Fig.1. TG-DTG curve of de-ethylamination for P-ZSM-5 zeolite

We can see that the TG curve shows two weight-loss steps in the temperature ranges of 160-310°C and 392-498°C, and there is also a corresponding peak in the DTG curve. This suggests that there are two adsorption centers or acid centers in the surface of P-ZSM-5 zeolite. According to the desorption temperature the former was assigned to the weak acid centers and the latter to the strong acid centers. Number of acid centers or amount of acid and acid strength were characterized by the amount of desorbed ethylamine and by

temperature of peak maxima T_p in the DTG curve respectively. The results of measurement by TG-DTG are shown in Table 1.

Table 1. Results of de-ethylamination TG-DTG for ZSM-5 catalysts before treatment

Zeolite	Sample weight (mg)	Wt loss by dehydration (mg)	TG		DTG Tp.	
			Weak site (%)	Strong site (%)	Weak site (℃)	Strong site (℃)
H-ZSM-5	51.50	2.85	1.40	1.94	225	423
P-ZSM-5	51.45	0.92	0.68	0.34	216	440
Mg-ZSM-5	32.10	3.10	1.93	1.52	200	402

Number of hydrogen proton calculated from Al/Si ratio is taken to be the number of theoretical acid centers. Suppose that one ethylamine molecule was adsorbed on one acid center, comparison of number of acid centers on strong and weak sites calculated from the amount of desorbed ethylamine with theoretical values is reported in Table 2 .

Table 2. The comparison of acid center number

Zeolite	$\frac{SiO_2}{Al_2O_3}$	M_H %	Number of adsorption center(10^{17}/g.cat)			Number of theoretical acid center (10^{20}/g.cal)
			Weak site	Strong site	total	
H-ZSM-5	48	6.7	1840	2540	4380	4.04
P-ZSM-5	60	5.4	0.9	0.45	1.35	10.60
Mg-ZSM-5	60	5.4	2.6	2.00	4.60	6.10

We can find that the number of acid centers from experiment is close to the theoretical numbers for H-ZSM-5 zeolite. It is shown that almost one ethylamine molecule was adsorbed on one acid center in such a case while for modified ZSM-5 zeolites the number of acid centers is lower than the theoretical values. This may be due to the fact that a part of the acid centers occupied by modification element. If T_p in the DTG curve is taken as a measure of acid strength, we can see from data in Table 1 that effects of P and Mg on acid strength are not completely the same. Acid strength on weak acid sites was decreased for both elements, while on strong acid sites it was increased for P and decreased for Mg.

2. Effects of heat and steam treatment on number of acid centers and acid strength on P-ZSM-5 zeolite

P-ZSM-5 before and after heat or steam treatment have similar de-ethylamination TG-DTG curve. Relationship between temperature of treatment and the decrease in number of acid centers on strong acid sites for P-ZSM-5 is shown Fig. 2.

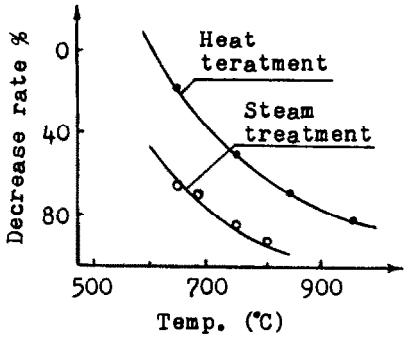

Fig.2. Relationship between temperature of treatment and decrease rate of number of acid centers on strong acid sites for P-ZSM-5 zeolite

Results indicate that with the increase of temperature of heat or steam treatment number of acid centers on strong and weak acid sites for P-ZSM-5 is decreased. Decrease rate of number of acid centers on strong acid sites is faster than that on weak acid sites. But according to T_p in the DTG curve acid strength on strong and weak acid sites does not change obviously.

We can see from Fig. 2. that decrease rate of number of acid centers on strong acid sites after heat and steam treatment is nearly the same. But number of acid centers after steam treatment decreases obviously faster than that after heat treatment at the same temperatune. The results of ESCA indicate that Al and P increase on surface after steam treatment. This may be due to accelerated hydrolysis of skeleton Al by steam thus resulting in migration of Al, i.e. acid centers was decreased. Thus, in order to obtain the same weaker acidity, temperature of treatment by steam should be 100-150°C lower than that by heat.

3. Effects of steam treatment on number of acid centers and acid strength on Mg-ZSM-5 zeolite

Relationship between temperature of steam treatment and decrease rate of number of acid centers on strong acid site is shown in Fig.3.

We can find that, with the increase of temperature of steam treatment, change of number of acid centers on strong and weak acid

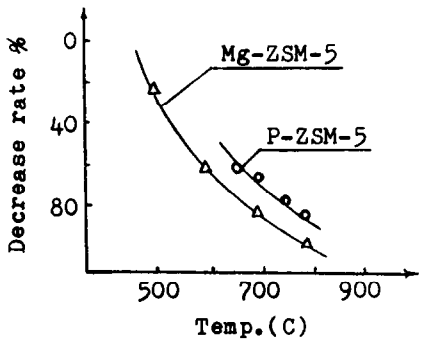

Fig.3. Relationship between temperature of steam treatment and decrease rate of number of acid centers on strong acid sites for modified ZSM-5 zeolites

sites for Mg-ZSM-5 has the same rule with that for P-ZSM-5. But the T_p values in the DTG curve change slightly, i.e. acid strength on strong acid sites does not change obviously, while acid strength on weak acid sites decreased.

We can also find from Fig.3 that decrease rate of number of acid centers for Mg-ZSM-5 is faster than that for P-ZSM-5 at the same temperature. Therefore, in order to obtain the same weaker acidity temperature of treatment by steam for Mg-ZSM-5 is 100 °C lower than that for P-ZSM-5.

4. Characterization of acid strength by means of de-ethylamination activation energy

The de-ethylamination activation energy can be calculated from de-ethylamination TG data by Broid method. The linearized equation of this method is as follows

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

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

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

The reaction order can be calculated from de-ethylamination DTG data by Kissinger equation

$$S = 0.63\ n^2$$

Where S stands for shape index.

Relationship between temperature of treatment and de-ethylamination activation energy on strong acid sites for modified ZSM-5

is illustrated in Fig. 4 .

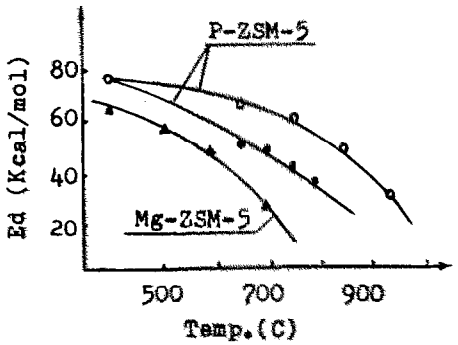

Fig.4 Relationship between temperature of treatment and de-ethylamination activation energy Ed on strong acid sites for modified ZSM-5 catalysts

o — Heat treatment

• — Steam treatment

We can see that with the increase of temperature of treatment de-ethylamination activation energy on strong acid sites decreased. i.e. acid strength decreased. The decrease rate of acid strength for P-ZSM-5 treated by steam is faster than that by heat. Therefore in order to obtain the same weaker acid strength, temperature of treatment by steam is 150°C lower than that by heat. When modified ZSM-5 treated only by steam, Mg-ZSM-5 is 100-150°C lower than P-ZSM -5. It can be seen that in order to decrease acid strength using steam treatment is more effective than using heat treatment.

5. Effects of heat or steam treatment on selectivity for lower olefines in methanol conversion for modified ZSM-5 catalysts

Acidity of modified ZSM-5 directly affects the selectivity of methanol conversion to lower olefines. The results show that when P-ZSM-5 was taken for catalyst, methanol conversion and selectivity of ethylene obviously decreased with increase of temperature of heat or steam treatment. This is probably because of decreasing acidity on strong acid sites for P-ZSM-5 catalyst. But yield of propylene and butylene increased. When Mg-ZSM-5 was taken for catalyst, selectivity of propylene remained constant, while activity of methanol conversion decreased.

REFERENCE

1. Liu Jinxiang et al. Thermochimica Acta, 123(1988) 113-120 .