

## CHARACTERIZATION OF ACIDITY TYPES AND STRENGTH ON H-NaY ZEOLITES BY TA \*

LIU JINXIANG \*\*, YANG LIXIN, LIU MIN and GAO XIUYING

*Dalian Institute of Chemical Physics, Chinese Academy of Sciences,  
Dalian (People's Republic of China)*

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### ABSTRACT

The conversion temperature of B–L acid centers on H–NaY zeolites has been examined and the ratio of B/L acid centers was established as 2:1 by TG. Then in order to characterize acid strength desorption, active energy was determined by DTG using  $\text{NH}_3$  as adsorbate. Finally, taking the cracking reaction of n-hexane as a probe reaction, the influence of the acid type and acid strength on the selectivity of zeolite catalysts for the conversion of n-hexane to lower carbon olefins has also been studied.

### INTRODUCTION

As the acidity of zeolite catalyst surfaces is related to the activity or selectivity of reaction, measurements of the acidity of zeolite catalyst surfaces have been of interest in catalytical research. Spectrophotometric methods and the adsorption of gaseous basic substances were commonly applied [1]. The former determined not only the acid density and the acid strength, but also the acid type. However, using this method it is not possible to make acidity determinations in the real working conditions of the catalyst. The latter method cannot distinguish between Brønsted and Lewis acid centers, particularly determinate acting acid centers, although the acidity measurements can be made in the real working conditions of the catalyst, because it is difficult to find an adsorbate having selective adsorption [2].

In the work reported here we initiated an investigation to examine the conversion temperature of B–L acid centers and established the ratio of B/L acid centers as 2:1 by TG. Then desorption active energy was also determined in order to characterize acid strength. Finally, we used the cracking reaction of n-hexane as a probe reaction. The influence of the acid

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\*\* To whom all correspondence should be addressed.

type and acid strength on the selectivity of zeolite catalysts for the conversion of n-hexane to lower carbon olefins has also been studied.

## EXPERIMENTAL

### *H-NaY zeolite catalysts*

H(77)-NaY; H(64)-NaY; H(46)-NaY; H(20)-NaY; H(15)-NaY.

All catalysts were prepared by the dissociation of  $\text{NH}_3$  from  $\text{NH}_4\text{-NaY}$  zeolites.

### *Acidity determination*

#### *Experimental equipment*

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

#### *Experimental conditions*

Detection range, 5 mg; heating rate, 10, 15 and  $20^\circ\text{C min}^{-1}$ ; atmosphere,  $\text{N}_2$ .

#### *Experimental procedure*

$\text{NH}_4\text{-NaY}$  zeolite was put in a small basket made of quartz and suspended at the center of the reaction tube, and then balanced with weights. Carrying gas is divided into two paths: one goes into the balance box and another goes through the reactor.

First the zeolite catalyst was heated in a temperature programmed mode up to  $550^\circ\text{C}$ . This temperature was maintained for 30 min in order to eliminate physically adsorbed water and ammonia. Then the sample was cooled to  $150^\circ\text{C}$ . After this, ammonia was brought to the reactor by the carrying gas at a speed of  $30\text{--}40\text{ ml min}^{-1}$ . When adsorption reached equilibrium, the ammonia was turned off. Physically adsorbed ammonia was purged by means of  $\text{N}_2$  gas flow, then desorption was performed in a temperature programmed mode. The temperature and the amount of deammoniation were recorded.

## RESULTS AND DISCUSSION

### *Thermal behavior of $\text{NH}_4\text{-NaY}$ zeolites*

The TG-DTG curves of 77% exchanged  $\text{NH}_4\text{-NaY}$  zeolites in  $\text{N}_2$  atmosphere are shown in Fig. 1. One can see that there are four peaks in the

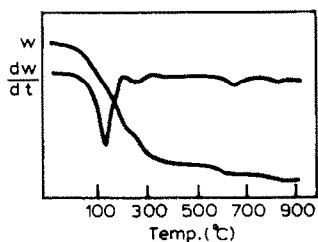


Fig. 1. TG-DTG curve of  $\text{NH}_4\text{-NaY}$  zeolite in  $\text{N}_2$ .

DTG curve and a corresponding weight-loss step in the TG curve. We have assigned the peaks as follows

*peak 1:* Ranging from 28 to 255°C, desorption of physically adsorbed water.

*peak 2:* Ranging from 255 to 396°C, dissociation of  $\text{NH}_3$  from  $\text{NH}_4\text{-NaY}$ .

*peak 3:* Ranging from 618 to 700°C, dehydroxylation of  $\text{H-NaY}$ .

*peak 4:* Ranging from 732 to 890°C, dehydroxylation of  $\text{Si-OH}$  from the surface of the zeolite.

A plot of the deammoniation amount vs. exchange degree is shown in Fig. 2. It is evident that the amount of deammoniation from  $\text{H-NaY}$  zeolite increases as the exchange degree increases. This is probably due to the fact that  $\text{H}^+$  from the dissociation of  $\text{NH}_4^+$  remains near the  $\text{Al}_4^-$  tetrahedron, and neutralized one negative charge on it, so that formed a B acid center. Usually, the higher the  $\text{NH}_4^+$  exchange degree, the more ( $\text{H}^+$ ) proton numbers are produced and the more B acid centers are formed.

#### Determination of the B/L acid centers ratio on $\text{H-NaY}$ zeolites

The conversion of B/L acid centers on  $\text{H-NaY}$  zeolites is represented by the equation

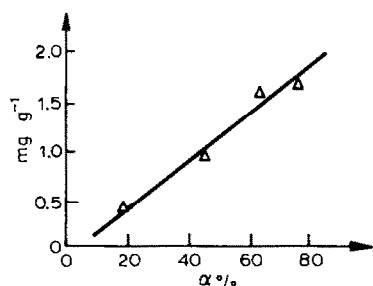
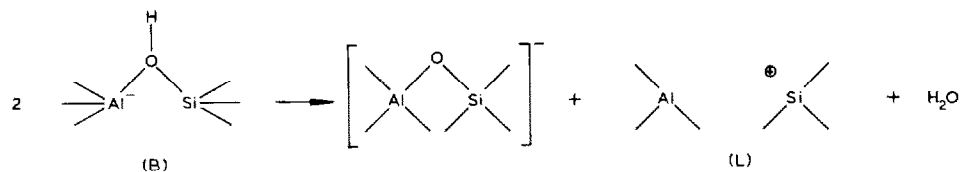


Fig. 2. Deammoniation amounts vs. exchange degree ( $\alpha\%$ ).

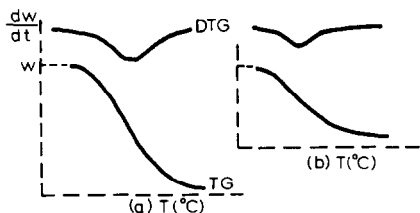


Fig. 3. The deammoniation TG-DTG curve for 77% exchanged  $\text{NH}_4$ -NaY zeolite (a) before dehydroxylation; (b) after dehydroxylation.

It is clear that the conversion process of B-L acid centers is essentially the dehydroxylation process of H-NaY zeolites, i.e., two B acid centers become one L acid center. In order to demonstrate this ratio relation, we took  $\text{NH}_3$  as adsorbate and measured the amount of deammoniation for H-NaY zeolites having various degrees of exchange.

The deammoniation TG-DTG curves for 77% exchanged  $\text{NH}_4$ -NaY zeolites before and after dehydroxylation are shown in Fig. 3 and results presented in Table 1.

We can see from Fig. 3(a) that only one weight-loss step appeared in the TG curve and there were two corresponding peaks without clear limit in the DTG curve. They correspond to strong and weak B acid centers respectively. Figure 3(b) also shows one weight-loss step in the TG curve and one corresponding dilatory peak in the DTG curve.

The deammoniation amounts of zeolites which did or did not dehydroxylate show that the ratio of B/L acid centers is basically 2:1. These results are in agreement with those of IR measurements by Datka [3]. The only difference is that TG measurements are performed under real working conditions.

According to the chemical composition of zeolites, the theoretical B acid center number is  $4.38 \text{ mmol g}^{-1}$ . Experimental results calculated from deammoniation amounts are reported in Table 2.

From the comparison shown in Table 2, we know that the number of both B and L acid centers adsorbed on H-NaY zeolite increases with the increase in exchange degree, and total numbers of adsorbed centers are on the whole

TABLE 1

The results of measurement by TG-DTG

Acid types	DTG		TG	
	Temp. range	Peak temp.	mg	ratio
$B_1$	205-295	257		
$B_2$	295-445	375	1.16	2
L	210-440	270	0.52	1

TABLE 2

The comparison of acid center numbers

Zeolites	Sample weight (mg)	Adsorption numbers (mmol g <sup>-1</sup> )		Theoretical numbers (mmol g <sup>-1</sup> )	
		B	L	B	L
NH <sub>4</sub> (77)-NaY	22.2	2.94	1.46	3.06	1.53
NH <sub>4</sub> (64)-NaY	22.3	2.85	1.40	2.80	1.40
NH <sub>4</sub> (46)-NaY	22.2	1.56	0.79	2.01	1.00
NH <sub>4</sub> (15)-NaY	23.7	0.50	0.30	0.87	0.32

consistent with the theoretical value. This reveals that the NH<sub>3</sub> adsorbed type on H-NaY zeolites is single center adsorption: (i.e., one NH<sub>3</sub> molecule was adsorbed by one acid center.)

*Characterization of acid strength by means of deammoniation activation energy*

The activation energy of deammoniation ( $E_d$ ) can be calculated from the temperature of the peak maxima of deammoniation ( $T_m$ ) in the DTG curve at various heating rates. We can calculate  $E_d$  from the Kissinger equation

$$\frac{d \ln(\Phi/T_m^2)}{d(1/T_m)} = -\frac{E_d}{R}$$

where  $R$  is the gas constant. The temperature of the peak maxima in the DTG curve at various heating rates are shown in Table 3. Figure 4 is a plot of  $\ln(\Phi/T_m^2)$  vs.  $1/T_m$ .

It can be seen that the plot of  $\ln\Phi/T_m^2$  vs  $1/T_m$  is a straight line. The activation energy of deammoniation can be obtained from the slope of the straight line. The calculated activation energy of both acid centers for variously exchanged H-NaY zeolites are shown in Table 4, a plot of activation energy vs. exchange degree is reported in Fig. 5.

The results in Table 4 and Fig. 5 show that both the strong and weak B acid centers could be distinguished by deammoniation peak temperature  $T_m$  in the DTG curve for NH<sub>4</sub>-NaY zeolites having a higher exchange degree (over 60%). Therefore, the deammoniation activation energy of strong and

TABLE 3

The temperatures of the peak maxima  $T_m$ , at various heating rates

Heating rate (°C min <sup>-1</sup> )	$T_m$ (°C)		
	B <sub>1</sub>	B <sub>2</sub>	L
10	257	375	270
15	274	380	280
20	284	390	282

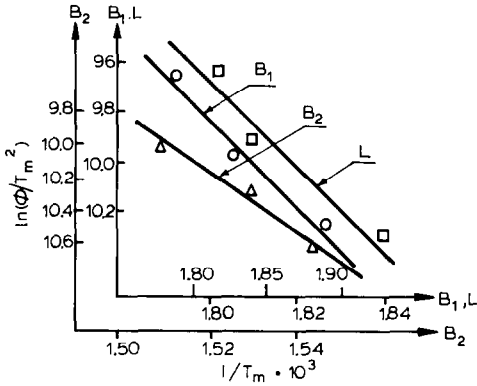


Fig. 4.  $\ln(\Phi/T_m^2)$  vs.  $1/T_m$ .

TABLE 4

Calculated values of desorption activation energy  $E_d$

Catalyst	$E_d$ (kcal mol <sup>-1</sup> )		
	B <sub>1</sub>	B <sub>2</sub>	L
NH <sub>4</sub> (77)-NaY	15.90	35.19	38.38
NH <sub>4</sub> (64)-NaY	16.91	38.10	23.76
NH <sub>4</sub> (46)-NaY	-	23.84	18.38
NH <sub>4</sub> (20)-NaY	-	12.36	10.57

weak centers could be obtained from  $T_m$ . However, the deammoniation peak temperatures of B<sub>1</sub> centers are not clear for NH<sub>4</sub>-NaY zeolites having a lower exchange degree. Thus, we can only calculate the activation energy for B<sub>2</sub> centers.

The results in Table 4 show that B<sub>2</sub> acid centers have higher deammoniation energy than the B<sub>1</sub> acid centers. This suggests that the desorption of adsorbed ammonia for the B<sub>2</sub> acid center is more difficult than for the B<sub>1</sub> acid center, i.e., B<sub>2</sub> acid strength is greater than that of B<sub>1</sub>. It has also been found from deammoniation energy data that B acid centers have greater

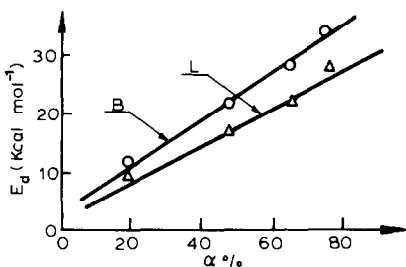


Fig. 5. Deammoniation activation energy vs.  $\alpha$ %.

TABLE 5

Evaluated values of activity and selectivity of catalysts

Set	Catalysts		Reaction temperature (°C)	Products distribution (wt%)		Conversion (%)	Selectivity C <sub>2-4</sub> <sup>=</sup> (%)
	Calcination temperature (°C)	Acid type		C <sub>1-5</sub> <sup>0</sup>	C <sub>2-4</sub> <sup>=</sup>		
1	700	B	525	3.56	3.90	7.70	52.70
		L	550	2.17	3.63	5.80	62.69
2	700	B	550	6.34	7.35	14.11	52.09
		L	580	6.07	8.64	14.70	56.53

acid strength than L acid centers, and that deammoniation activation energy on both acid centers increases as the degree of exchange increases. This is probably due to the fact that the hydroxy numbers in the supercage increase with increase in degree of exchange.

#### *Influence of both acid types on the selectivity of zeolites catalyst*

We took the cracking reaction of n-hexane as a probe reaction and used H-NaY zeolites before and after dehydroxylation as catalysts having acid centers of B and L types. The influence of both acid types on selectivity of reaction for the conversion of n-hexane to lower olefins has been examined by means of GC. The results are shown in Table 5.

It is evident that the olefins' selectivity for catalysts having an L acid center is always higher than for those having a B acid center, under condition of near conversion, no matter what their extent of conversion. It is obvious from conversion per unit that the L acid centers also have higher olefins selectivity than B acid centers at the same reaction temperature. Therefore, we can say that L acid centers have a higher olefins selectivity than B acid centers for the cracking reaction of n-hexane.

#### CONCLUSIONS

1. The results of TG and DTG measurements show that the thermal behavior of NH<sub>4</sub>-NaY zeolites is as follows: (a) desorption of physically adsorbed water before 225°C; (b) dissociation of NH<sub>3</sub> from NH<sub>4</sub>-NaY at 225-396°C; (c) dehydroxylation of H-NaY from 618 to 700°C; (d) dehydroxylation of Si-OH on out-surfaces of the zeolite from 732 to 890°C.

2. The experimental results show that the ratio of B/L acid centers is basically 2:1.

3. The deammoniation temperature peak maxima in the DTG curve can be taken as a qualitative criterion of characterization of acidity strength.

Using DTG maxima peak temperature at different heating rates, the activation energy of deammoniation from the Kissinger equation can be used as a quantitative criterion.

4. Taking n-hexane as a cracking probe reaction, pulse mic-reaction experimental results show that the L acid center has an obviously higher selectivity for low carbon olefins than do B acid centers.

#### REFERENCES

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