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## GAS CHROMATOGRAPHIC ADSORPTION–DESORPTION TECHNIQUES FOR MEASURING ACID STRENGTH DISTRIBUTION ON SOLID CATALYSTS

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### SUMMARY

Two simple and rapid gas chromatographic techniques based on adsorption and thermal desorption of pyridine, *viz.*, stepwise thermal desorption and temperature-programmed desorption under chromatographic conditions, for measuring the acid strength distribution on solid catalysts at temperatures close to those employed in catalytic reactions are described. These methods have been employed to carry out such measurements on CeY zeolite in the temperature range 353–623°K. The results obtained from the two techniques indicate that the CeY has a broad acid strength distribution.

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### INTRODUCTION

Zeolites are important catalysts employed in a number of hydrocarbon conversion reactions (*e.g.*, cracking, isomerization and alkylation). The high activity of these catalysts is attributed to their high acidity, particularly proton acidity. A knowledge of the acidity distribution (*i.e.*, the number and strength of acid sites) is therefore essential for understanding the catalytic phenomena over zeolites. The acid strength distribution of solid catalysts, including zeolites, is measured experimentally by two principal methods<sup>1–3</sup>: (1) non-aqueous *n*-butylamine titration using indicators of varying  $pK_a$  and (2) adsorption–desorption of gaseous bases (*e.g.*, ammonia, pyridine). The latter method has the advantage that the adsorption can be measured at or close to temperatures at which the catalytic processes occur.

Gas chromatography (GC) provides simple and rapid methods<sup>4</sup> for determining the surface properties of solid catalysts under reaction conditions. With zeolites, GC methods have a high potential for the measurement of acidity distributions but they have so far not been fully utilized for this purpose<sup>2</sup>.

In this paper, two simple and rapid GC methods for measuring acid strength distributions on solid catalysts are described: the first is based on the stepwise thermal desorption (STD) of pyridine and the second on the temperature-programmed desorption (TPD) of pyridine under chromatographic conditions. The application of these methods is illustrated by describing in detail the study of acidity distribution on CeY zeolite.

## EXPERIMENTAL

GC adsorption, desorption and TPD data were collected using a Perkin-Elmer Sigma 1 gas chromatograph fitted with a flame-ionization detector. Nitrogen (99.996%) was passed over activated molecular sieve to remove traces of moisture and used as a carrier gas at a flow-rate of 9.5 cm<sup>3</sup> (at NTP)/min in all the experiments. Pyridine (>99.5%, GC grade) (E. Merck) was used without further purification.

The catalyst CeY (with a degree of cation exchange of 97.5%) was prepared by the procedure described by Weitkamp<sup>5</sup>.

A 15-cm GC column was prepared by packing 0.32 g of CeY zeolite (particle size 0.2–0.3 mm) in a stainless-steel tube (O.D. 3 mm, I.D. 2 mm). In order to minimize the dead volume, one end of the column was directly connected to the detector and the other end to the injector through a 50-cm stainless-steel capillary (about 1.5 mm O.D. and 0.7 mm I.D.), which acted as a pre-heater. The catalyst was calcined, *in situ*, by heating it in a flow of nitrogen from 353 to 623°K at a linear heating rate of 10°K/min and further at 623°K for 5 h.

*Stepwise thermal desorption (STD)*

In this method, pyridine, adsorbed irreversibly on a catalyst at the lowest temperature chosen for the STD, was thermally desorbed in a number of temperature steps (each of 30–50°K, depending on the temperature range covered) and the pyridine desorbed in each step was measured quantitatively with a detector. After the maximum temperature of each step had been attained, sufficient time was allowed for the desorption of reversibly adsorbed base. The amount of base desorbed in a particular step gave the number of sites having an acid strength designated by the temperature limits of the desorption step. Here, the desorption temperature was taken as a measure of acid strength.

The amount of pyridine desorbed in a step in which the increase in temperature was from  $T_1$  to  $T_2$  is obtained from the equation

$$(q_d)_{T_1}^{T_2} = A_d/SW \quad (1)$$

where  $(q_d)_{T_1}^{T_2}$  is the amount of pyridine desorbed when the temperature was increased from  $T_1$  to  $T_2$ ,  $A_d$  is the area of the desorption chromatogram,  $S$  is the molar response of the detector for pyridine and  $W$  is the weight of the catalyst.

The amount of pyridine adsorbed irreversibly at different temperatures [ $q_i(T)$ ] can be obtained from the STD data as follows:

$$q_i(T) = q_i(T_m) + (q_d)_T^{T_m} \quad (2)$$

$q_i(T_m)$ , which is the amount of pyridine adsorbed irreversibly at the maximum temperature,  $T_m$ , chosen for the STD, can be determined by the GC pulse technique<sup>6,7</sup>.

The STD of pyridine irreversibly adsorbed at 353°K on the CeY zeolite was carried out by raising the temperature of the catalyst from 353 to 623°K in seven discrete temperature steps. The temperature corresponding to each step was attained at a linear heating rate of 10°K/min. When the maximum temperature of the step had

been attained, 1 h was allowed to elapse for the desorption of the reversibly adsorbed base from the catalyst at that temperature.

The irreversible adsorption of pyridine on the zeolite at 623°K was determined as follows. A number of pulses (each of 3.0  $\mu$ l) of the base were injected, at intervals of 10 min, into the catalyst column at 623°K until an elution chromatogram was recorded on the chart indicating that all the irreversible adsorption sites on the catalyst had been saturated. The elution of the base was continued for 1 h to desorb the base reversibly adsorbed at that temperature. The amount of irreversibly adsorbed base ( $q_i$ ) was calculated from the equation

$$q_i = (X - A/S)/W \quad (3)$$

where  $X$  is the total amount of base injected and  $A$  is the area under the elution chromatogram.

The value of  $q_{i(623^\circ\text{K})}$  obtained by the above pulse method was 0.418 mmol/g, which is very close to that (0.424 mmol/g) obtained by the GC pulse method<sup>7</sup> based on TPD under chromatographic conditions.

In this study, the irreversible adsorption ( $q_i$ ) is defined as the amount of base retained by the presaturated catalyst after it had been swept with pure nitrogen for a period of 1 h at the temperature of study. The quantity  $q$  (eqns. 1–3) represents the amount of pyridine adsorbed/desorbed per unit mass of the catalyst. The experimental error in the measurement is less than 3%.

#### *TPD under chromatographic conditions*

The initial temperature chosen for the TPD run was 353°K. After the calcination of the catalyst, the oven temperature was decreased to 353°K and a known amount of pyridine (less than that required to saturate the chemisorption sites of the catalyst at 353°K) was injected into the catalyst column. A period of 1 min was allowed to elapse for the redistribution of the base on the catalyst sites and the TPD was started in a flow of nitrogen [9.5 cm<sup>3</sup> (at NTP)/min] at a known linear heating rate. When the final temperature chosen for the TPD (623°K) had been reached, desorption of the reversibly adsorbed base was allowed to continue isothermally for 1 h at that temperature. At the end of the TPD, the catalyst retained only irreversibly adsorbed pyridine at 623°K. After recording the first TPD chromatogram, the catalyst temperature was again reduced to 353°K and the above procedure was repeated to record a second TPD chromatogram at a different initial surface concentration of pyridine ( $\theta_i$ ), and so on.  $\theta_i$  was varied by injecting different amounts of pyridine into the catalyst column before starting the TPD at 353°K.

The initial surface concentrations of pyridine ( $\theta_i$ ) were calculated as follows. For the TPD experiment on the fresh catalyst:

$$\theta_i = x/W \quad (4)$$

For the subsequent TPD experiments on the catalyst saturated with irreversibly adsorbed pyridine at 623°K:

$$\theta_i = q_{i(623^\circ\text{K})} + x/W \quad (5)$$

where  $x$  is the amount of pyridine injected before starting the TPD.

TPD data were collected for pyridine on the catalyst for different values of  $\theta_i$  at linear heating rates of 5, 10 and 20°K./min. The reproducibility of the TPD chromatograms was excellent. The adsorption of pyridine on the column walls was negligibly small. The number of molecules per supercage of the zeolite was obtained from a knowledge of the supercage density, which is a reciprocal of the formula weight of the sodalite unit in the CeY zeolite<sup>8</sup>.

## RESULTS

### Acidity distribution from STD of pyridine

The distribution of the sites of different acid strengths obtained from the STD studies on the zeolite, shown by the shaded columns, and the temperature dependence of the irreversible adsorption of pyridine ( $q_i$  versus  $T$  curve) are presented in Fig. 1.

The first column of the distribution represents the total number of acid sites having acid strengths of  $353^\circ\text{K} < T_d \leq T_d^*$  (where  $T_d$  is the desorption temperature and  $T_d^*$  the temperature at which the base irreversibly adsorbed on the strongest acid sites is desorbed) and the other columns show the strength distribution of the total acid sites. The sites of acid strengths of  $353^\circ\text{K} < T_d \leq T_d^*$  and  $623^\circ\text{K} < T_d \leq T_d^*$  were obtained from the amounts of pyridine adsorbed irreversibly at 353 and 623°K, respectively. The sites of acid strengths of  $T_1 < T_d \leq T_2$  were obtained from  $(q_d)_{T_1}^{T_2}$  (i.e. from the amount of pyridine that was initially adsorbed irreversibly at  $T_1$  but desorbed when the temperature was increased from  $T_1$  to  $T_2$ ).

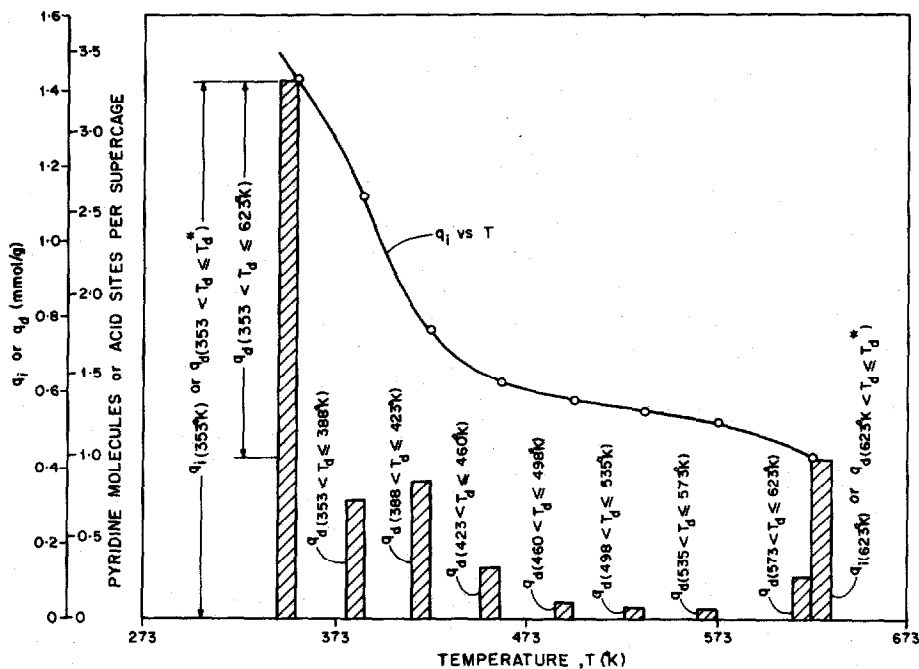


Fig. 1. Acid strength distribution of CeY zeolite.

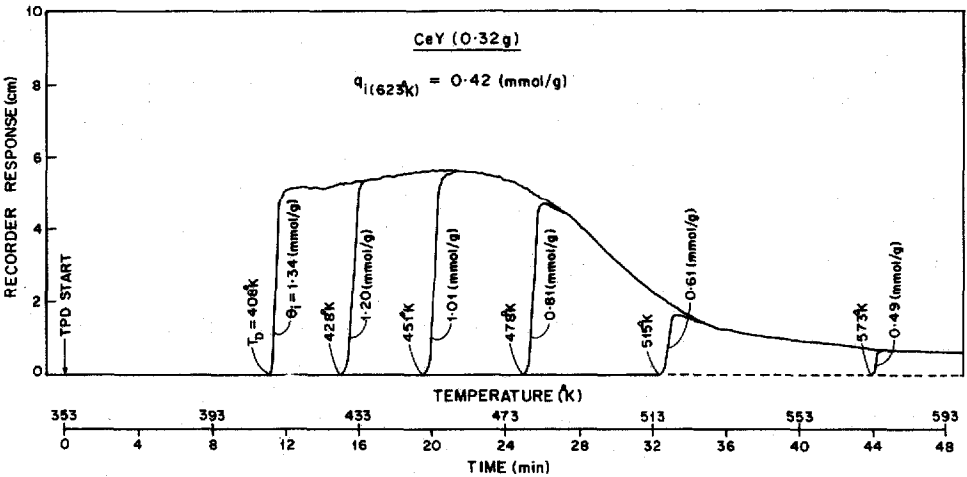
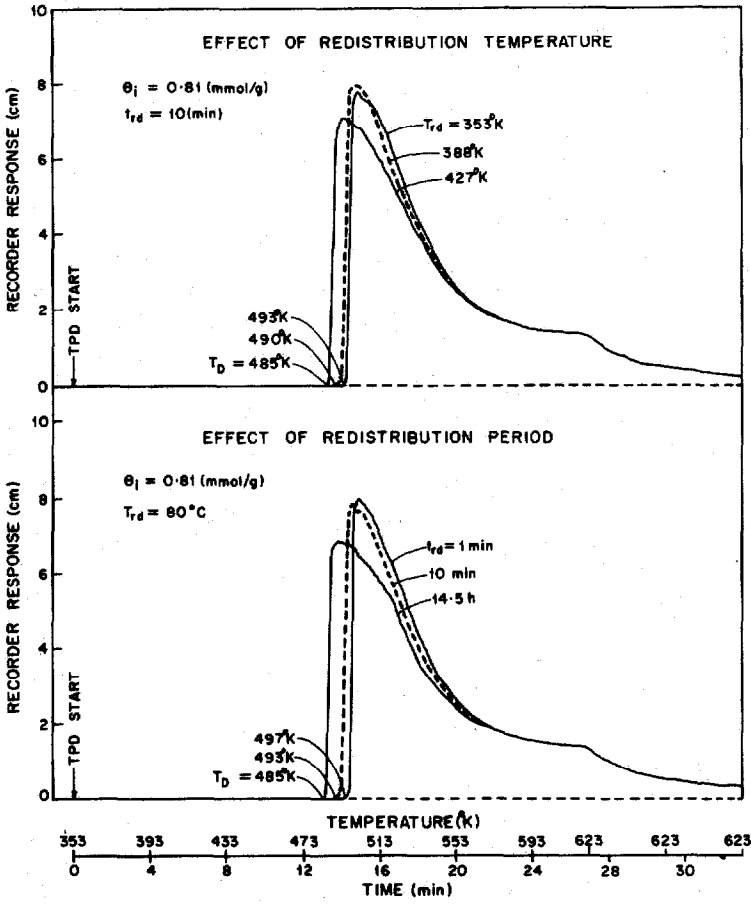


Fig. 2. TPD chromatograms of pyridine on CeY showing effect of redistribution temperature ( $T_{rd}$ ) and redistribution period ( $t_{rd}$ ) on the TPD.

Fig. 3. TPD chromatograms of pyridine on CeY at a linear heating rate of  $5^{\circ}\text{K}/\text{min}$  for different initial concentrations of the base ( $\theta_i$ ).

In the adsorption of a base on an acidic solid, the strength of the chemisorption bond between the base molecule and the acid site is proportional to the acid strength of the site<sup>1</sup>. When the temperature of the catalyst pre-saturated with the irreversibly adsorbed base at low temperature is increased, the irreversibly adsorbed base molecules are desorbed successively from the sites of increasing acid strength owing to the weakening of the acid site-base chemisorption bonds. Hence, it is possible to obtain the distribution of sites of different acid strengths by measuring the amount of pyridine (which was adsorbed irreversibly at 353°K) desorbed from 353 to 623°K in the seven steps, and expressing the acid strength in terms of the range of desorption temperature. The pyridine adsorbed on the sites possessing acid strengths of  $T_1 < T_d \leq T_2$  (expressed in terms of a range of desorption temperatures) is not desorbed at temperatures less than  $T_1$ , but these sites cannot adsorb pyridine irreversibly at temperatures greater than  $T_2$ . Hence all the irreversibly adsorbed pyridine on these sites is desorbed when the temperature is raised from  $T_1$  to  $T_2$ .

The  $q_i$  versus  $T$  curve also indicates a type of acid strength distribution in which the number of acid sites is expressed in terms of the amount of the base adsorbed irreversibly as a function of the adsorption temperature, this temperature being a measure of the strength of acid sites involved in the irreversible adsorption.

The results in Fig. 1 reveal that the CeY zeolite has a very broad acid strength distribution.

#### *Acidity distribution from TPD of pyridine under chromatographic conditions*

The effect of the redistribution time ( $t_{rd}$ ) (*i.e.*, the time that is allowed to pass between the injection of pyridine and the start of the TPD to ensure the distribution of the adsorbed pyridine on the zeolite) and the redistribution temperature ( $T_{rd}$ ) (*i.e.*, the temperature at which the redistribution of the adsorbed base was allowed to occur for a definite period of time after the injection of base into the catalyst column) on the TPD of pyridine from the zeolite at a linear heating rate of 10°K/min is shown in Fig. 2, which indicates that the effect of the variation of  $t_{rd}$  or  $T_{rd}$  on the TPD is not very significant.

The TPD chromatograms of pyridine on the CeY zeolite for different values of  $\theta_i$  at linear heating rates of 5, 10 and 20°K/min are given in Figs. 3, 4 and 5, respectively. The dependence of desorption start temperature ( $T_D$ ) on  $\theta_i$  is shown in Fig. 6.

It is clear from Figs. 3-5 that the TPD chromatograms, particularly at higher  $\theta_i$  values, are broad, the start of desorption is very sharp, the desorption edges of the superimposed TPD chromatograms obtained at the different values of  $\theta_i$  fall on the same desorption curve, and  $T_D$  increases with decrease in  $\theta_i$ .

With solids that have a broad site energy distribution, the TPD chromatogram is expected to be broad<sup>9</sup> and the temperature corresponding to the peak maximum to increase with decrease in the initial surface coverage<sup>10</sup>. The shape and width of the TPD chromatograms and the dependence of  $T_D$  and the peak maximum temperature on  $\theta_i$  indicate that the CeY zeolite has a broad acid strength distribution.

This TPD method differs from the earlier GC TPD methods<sup>11,12</sup>. In the present study, it is suggested that the TPD occurs under chromatographic conditions as follows. When the base is injected into the catalyst column, it is chemisorbed at the initial temperature of the TPD first on the acid sites of the initial portion of the catalyst and is not distributed uniformly on the strong acid sites. As the temperature

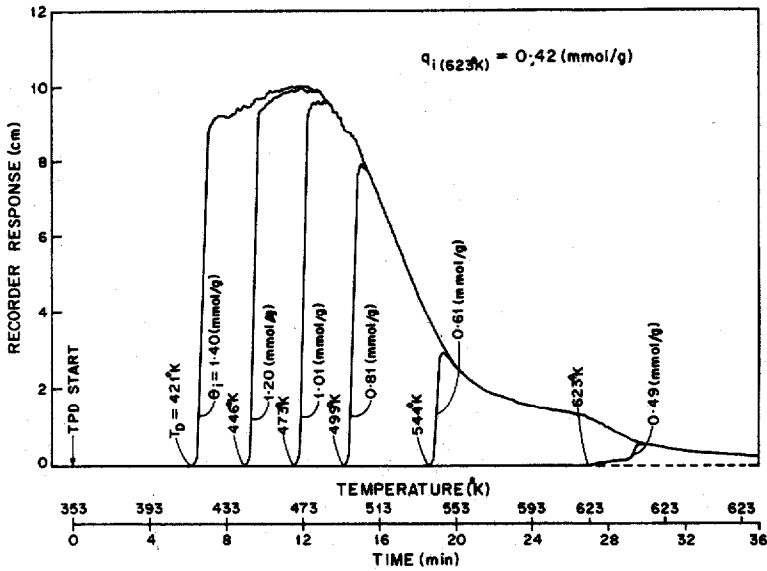


Fig. 4. TPD chromatograms of pyridine on CeY at a linear heating rate of 10°K/min for different values of  $\theta_1$ .

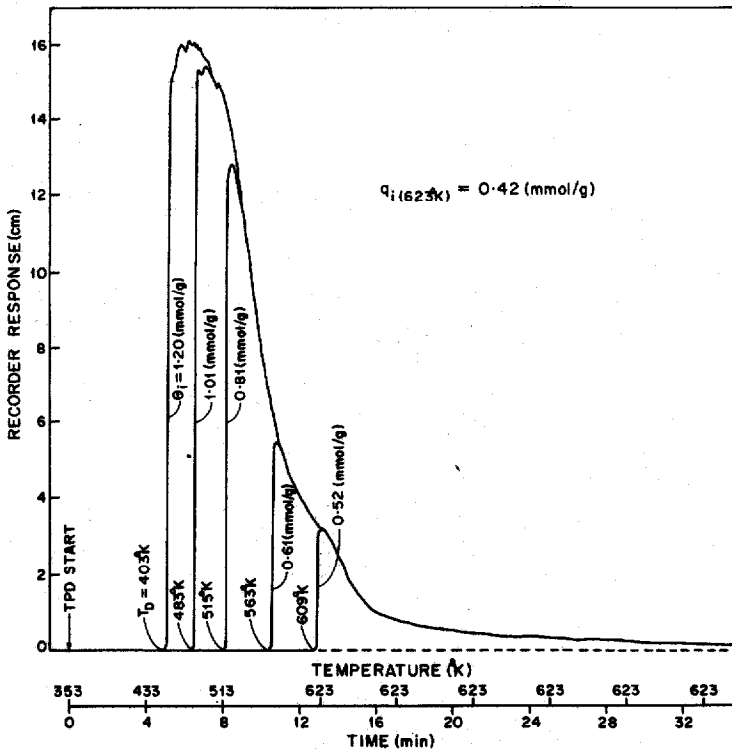


Fig. 5. TPD chromatograms of pyridine on CeY at a linear heating rate of 20°K/min for different values of  $\theta_1$ .

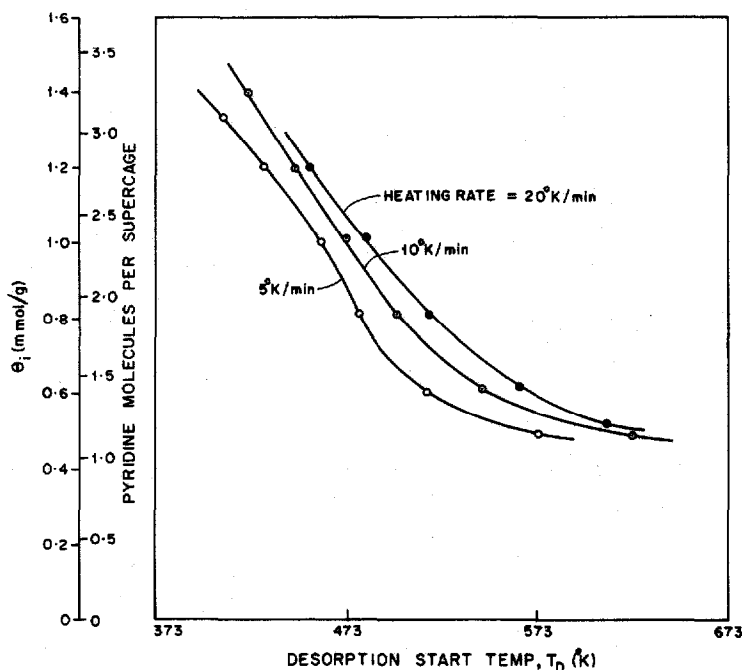


Fig. 6. Dependence of desorption start temperature ( $T_D$ ) on  $\theta_i$  in TPD of pyridine on CeY under chromatographic conditions.

increases after the start of TPD, the base chemisorbed on the weaker acid sites is desorbed owing to weakening of the chemisorption bond and moves along the column until it finds stronger adsorption sites. Thus the base undergoes a number of adsorption-desorption cycles during the TPD before it emerges from the catalyst column and is detected.

The temperature at which the base begins to emerge from the catalyst column ( $T_D$ ) depends on both  $\theta_i$  and the linear heating rate (Fig. 6); it is higher for a higher heating rate for the same  $\theta_i$ . Here,  $T_D$  may be taken as a measure of relative acid strength. In the present case, as the start of desorption in TPD is very sharp and the edges of the chromatograms match each other exactly point to point when superimposed, the  $\theta_i$  versus  $T_D$  curve (Fig. 6) may be regarded as an acid strength distribution curve.

A comparison of Fig. 6 with Fig. 1 reveals that the  $\theta_i$  versus  $T_D$  plot for a heating rate of 5°K/min and the  $q_i$  versus  $T$  plot have nearly the same trend. The lower the heating rate the closer the similarity is between the two.

## DISCUSSION

### *Critique of earlier methods for determining acid strength distribution on solid catalysts*

The *n*-butylamine titration method<sup>13-15</sup> for measuring acid strength distributions on zeolites and other solid catalysts has a number of severe limitations<sup>16</sup>. Deeba and Hall<sup>17</sup> showed that the dependability of the acidity distribution obtained



by this method is highly questionable. They suggested an alternative method<sup>17</sup> which involves an irreversible adsorption of a series of bases of varying  $pK_a$  from their solutions using a suitable solvent. However, it also suffers from the disadvantage that the acidity data are obtained under conditions far removed from those employed in catalytic processes, relative adsorption of solvent and non-selective irreversible adsorption of bases on the acid sites at lower temperatures.

Calorimetric methods based on the measurement of differential heats of adsorption of *n*-butylamine<sup>18-20</sup> from solution and of ammonia<sup>16,21-23</sup> from the gas phase on acid sites at different degrees of surface coverage have also been extensively employed for measuring acidity distributions on zeolites and other catalysts. The variation of the heat of adsorption of a base with surface loading is expected to give the acid strength distribution on solids, provided the base is adsorbed preferentially on the stronger acid sites (that is, the base is adsorbed on the acid sites in the order of their strengths, the strongest being occupied first) when the surface loading is increased by introducing the base in small doses. However, this condition is not satisfied. The preferential adsorption of base at a particular temperature on the stronger acid sites cannot be taken for granted as the probability of the base being irreversibly adsorbed on the sites is the same for all the sites, which can adsorb the base irreversibly at that temperature.

Topchieva and co-workers<sup>24-26</sup> employed a GC method based on the determination of the activation energy of ammonia desorption at different degrees of surface coverage with the base. However, with a catalyst having a broad acid strength distribution, the acid sites available for reversible adsorption or desorption of base are not the same at different temperatures as the amount of base adsorbed irreversibly depends strongly on the temperature. Hence, the temperature dependence of the desorption rates is expected to give only an apparent value of activation energy of desorption.

#### *Present methods*

The STD method provides precise data on the irreversible adsorption of the base at different temperatures and also the distribution of acid sites of different strengths in terms of the amount of base desorbed in the different temperature steps. It is difficult to obtain these data with the same precision by carrying out the adsorption measurement separately at different temperatures. The strength of the acid sites is expressed in terms of either the maximum temperature at which the base is adsorbed irreversibly on these sites or the range of temperatures in which the base initially adsorbed irreversibly at the lowest temperature of the range is desorbed from these sites.

In the TPD method, the shape and width of the TPD chromatograms and the variation of the temperature at which desorption of the base starts with the initial surface loading give a fair idea of the strength distribution of the acid sites. However, the results obtained are qualitative in nature.

Both the STD and TPD methods have the following attractive features:

(1) No serious assumption is involved in the methods. The only assumption made is that the irreversible adsorption of pyridine occurs selectively on the acid sites, and this is reasonably true at higher temperatures.

(2) The methods allow the determination of acidity distribution under con-

ditions close to those employed in catalytic processes. It is therefore possible to relate the acidity to the catalytic activity and selectivity.

(3) The methods are very simple and are faster than any of the earlier methods discussed above. The acid strength distribution can be obtained in just less than 10 h (excluding the period required for the catalyst pre-treatment) by either of the methods. Further, no special equipment is required; a conventional gas chromatograph (with temperature programming facility) which is commonly available in most catalysis laboratories is adequate for collecting the acidity data.

The STD method is particularly suitable when quantitative results are required for relating the acidity to the catalytic activity or selectivity, while the TPD method can be employed when a large number of catalysts are required to be compared for their relative acid strength distributions.

The reliability of both methods was tested by employing them to measure the acidity distributions on a number of catalytically important zeolites (CeNaY, HNaY, PtCeNaY, CeNaX, HM and HNaZSM-5 zeolites)<sup>27,28</sup> and to study the effects of the Si:Al ratio and degree of H<sup>+</sup> exchange<sup>28,29</sup>, deammoniation conditions<sup>28,30</sup> and hydrothermal treatments<sup>28,31</sup> on the acidity distribution of H-ZSM-5 zeolite. The acidity (*i.e.*, strong acid sites measured in terms of pyridine irreversibly adsorbed at 673°K) of H-ZSM-5 correlated well with the catalytic activity in cumene cracking, xylene isomerization and ethanol- and methanol-to-aromatics conversion reactions<sup>28,30-32</sup>; the correlation in the case of *o*-xylene isomerization at low conversions was linear. The STD method has also been employed in catalyst poisoning studies<sup>28,31,32</sup> for selectively blocking stronger acid sites, in the order of their strengths, by irreversible adsorption of pyridine at different temperatures (573-773°K).

*Choice of the base.* Pyridine was chosen as the base for the acidity measurements as it has an intermediate basicity ( $pK_a \approx 5.2$ ) and high thermal stability. It was found not to react or decompose on the zeolites (*e.g.*, CeY, HY and HZSM-5) at high temperatures ( $\leq 773^\circ\text{K}$ ) and an excellent reproducibility of results were obtained with it. On the other hand, when 2,6-dimethylpyridine (which has the advantage of being preferentially chemisorbed on protonic sites<sup>3</sup>) was used, it was found to have decomposed to a small extent at 623°K, as confirmed by the change in the colour of the catalyst to greyish black. Also, it was impossible to obtain results with a reproducibility comparable to that of the results with pyridine. However, 2,6-dimethylpyridine may still be used for this method, particularly when the catalyst has both protonic and Lewis acid sites. Nevertheless, when only one type of acidity exists or predominates, pyridine is preferable to 2,6-dimethylpyridine. In general, the number of acid sites measured by pyridine may be taken as the upper limit of the protonic acid sites present on the catalyst.

The study of the adsorption of pyridine, 2,6-dimethylpyridine, piperidine, quinoline and *n*-butylamine on NaY<sup>33</sup> at 623°K has shown that, whereas pyridine is not irreversibly adsorbed on the zeolite containing non-acid sites, the others are irreversibly adsorbed and in the order 2,6-dimethylpyridine < *n*-butylamine < piperidine < quinoline. This supports the choice of pyridine as the base for acidity measurements.

*Limitations.* The major limitation of the STD and TPD methods is that it may not be possible to measure the strength distribution of very strong acid sites which

adsorb pyridine irreversibly at temperatures greater than 773°K because of the problems associated with the stability or reaction of pyridine on the catalyst at these temperatures. In this investigation the maximum temperature employed was 623°K because of the limitation imposed by the calcination of the catalyst. These methods may be employed at temperatures higher than 773°K by using ammonia instead of pyridine but it is a poor choice<sup>3</sup> when protonic acidity is to be measured and the simplicity of the methods will be reduced, as it will be necessary to use a thermal conductivity detector and a high-temperature oven for the measurements.

As pointed out earlier<sup>9,10</sup>, the TPD methods show promise in the measurement of site energy distribution on solid catalysts. However, although efforts have been made<sup>34,35</sup>, so far this promise remains unrealized because of the insufficient progress made in the interpretation of the TPD data on heterogeneous surfaces. When the theoretical basis of this interpretation has been fully developed, the quantitative analysis of TPD data to obtain the site energy distribution may become a reality.

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