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TEMPERATURE-PROGRAMMED DESORPTION OF ORGANIC BASES ON NaY ZEOLITE UNDER CHROMATOGRAPHIC CONDITIONS

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SUMMARY

Temperature programmed desorption (TPD) of pyridine, 2,6-dimethylpyridine, piperidine, quinoline and *n*-butylamine on NaY zeolite has been studied under chromatographic conditions at temperatures ranging from 353 to 623°K using gas chromatography. The shape and width of the TPD chromatograms and the dependence of the initial temperature of desorption on the initial concentration of adsorbed base indicate a broad site energy distribution on the zeolite. The extent of irreversible adsorption of these bases in NaY at 623°K follows the order:

pyridine < 2,6-dimethylpyridine < *n*-butylamine < piperidine < quinoline

Pyridine is not adsorbed irreversibly ta 623°K on NaY but it is adsorbed strongly at lower temperatures. All the other bases are adsorbed strongly at or below 623°K. Since NaY has neither Lewis not protonic acid centres, the results indicate that these bases (except pyridine at > 623°K) are adsorbed strongly on the non-acidic sites at or below 623°K.

INTRODUCTION

Temperature-programmed desorption (TPD) or flash desorption[1-3] is one of the most important techniques employed for studying adsorption, surface heterogeneity and active sites on solid catalysts and adsorbents. By using gas chromatography (GC)[4,5] with a long chromatographic column packed with the catalyst or adsorbent as the desorption reactor it is possible to measure *in situ* the initial surface coverage (or the intitial concentration of adsorbed gas or vapour), adsorption and other physicochemical properties[6], in a simple and rapid manner.

In the present paper GC technique for studying TPD under chromatographic conditions is described. The technique has been employed to study TPD of pyridine, 2,6-dimethylpyridine (2,6-DMPy), piperidine, quinoline and *n*-butylamine on NaY zeolite in the temperature range 353–623°K. These bases are commonly used[7,8] for characterizing the acidic properties of solid catalysts and adsorbents. NaY zeolite contains neither Lewis nor protonic acid sites[7]. It is a starting material for a number of partially cation-exchanged zeolite catalysts. The study of the adsorption (or in-

teraction) of the above bases on non-acidic sites of the zeolite is therefore of great interest from the point of view of using these bases for measuring the acidic properties of zeolite catalysts in general.

The GC method consists of introducing a pulse of a known amount of adsorbate into a stream of inert carrier gas flowing over the catalyst packed in a chromatographic column. After sufficient time has been allowed for the redistribution of adsorbed species, the temperature of the GC oven is increased at a programmed linear rate and the concentration of desorbed adsorbate is measured continuously with a detector. When the final temperature of the temperature programme has been attained, the desorption is allowed to continue isothermally to desorb completely the reversibly adsorbed species. The above procedure is then repeated for at different initial surface coverages. The initial surface coverage can be varied simply by changing the pulse size, *i.e.*, by injecting different amounts of the adsorbate at the initial temperature of TPD. This simplifies the experimental procedure and enables rapid studies of TPD on heterogeneous surfaces.

In the present case, when an adsorbate is injected in the adsorbent column at the initial temperature of TPD it is adsorbed first on the active sites of the initial portion of adsorbent, *i.e.*, it is not distributed uniformly on the highly active sites. As the temperature is increased the adsorbate on the less active sites is desorbed due to weakening of the chemisorptive bond and moves along the column until it finds more favourable adsorption sites. The adsorbate is thus made to undergo a number of adsorption–desorption cycles during TPD before it emerges from the column.

EXPERIMENTAL

TPD data were obtained using a conventional gas chromatograph (Perkin-Elmer Sigma 1) with a flame ionization detector (FID). Nitrogen (99.996%, further dried over activated molecular sieve) was used as the carrier gas [flow-rate: 9.5 cm^3 (at NTP)/min].

Reagents and NaY column

Pyridine ($>$ 99.5%; E. Merck, Darmstadt, G.F.R.), 2,6-DMP$_y$, (99%), piperidine ($>$ 99%), quinoline (99%) and *n*-butylamine ($>$ 99%; all from Fluka, Buchs, Switzerland) were used without further purification.

NaY zeolite was obtained from Union Carbide (New York, NY, U.S.A.). It was pressed binder-free at 300 kg/cm^2 and crushed to get particles of 0.2–0.3 mm in size.

The column was prepared by packing about 0.3 g of NaY zeolite (particle size: 0.2–0.3 mm) in a stainless-steel tube (3.0 mm O.D., 2.0 mm I.D. $\times$ 15 cm). One end of the column was directly connected to the detector. A 50 cm long capillary tube (1.5 mm O.D., 0.6–0.7 mm I.D.) was fitted between the other end of the column and the injection port so that the adsorbate vapour could be heated to the required temperature before entering the column.

Procedure

After connection the adsorbent column to the GC oven, the NaY zeolite was calcined, *in situ*, at 623°K for 5 h in a flow of nitrogen [9.5 cm^3 (at NTP)/min]. The

oven was heated at a programmed linear rate of $10°K/min$ until this temperature was reached. After calcination, the GC oven temperature was decreased to $353°K$, the initial temperature of TPD. A known amount of base was injected into the column and after waiting for 1 min to allow redistribution of adsorbed species in the column, TPD was started at a linear heating rate of $10°K/min$ in the flow of nitrogen [9.5 cm^3 (at NTP)/min]. The final temperature chosen for the TPD run was $623°K$. When this was reached the desorption of the reversibly adsorbed base was allowed to continue isothermally at $623°K$ for 1 h. Almost all the base reversibly adsorbed on the zeolite at $623°K$ was desorbed during this period. After recording the first TPD chromatogram, the GC oven temperature was again reduced to $353°K$ and the above procedure was repeated to obtain TPD chromatograms at other initial adsorbate concentrations, θ_i, on the zeolite.

The amount of base adsorbed irreversibly at $623°K$ was determined from the first TPD chromatogram (obtained with fresh adsorbent) using the relation

$$q_{i(base,\ 623°K)} = \left[X - \frac{A}{S} \right] / W \tag{1}$$

where $q_{i(base,\ 623°K)}$ is the amount of base adsorbed irreversibly at $623°K$; X the amount of base injected, A the area under the TPD chromatogram; S the detector sensitivity and W the weight of catalyst.

The initial concentration of adsorbed base, θ_i, was calculated as follows. For the first chromatogram (obtained with fresh adsorbent)

$$\theta_i = X/W$$

while for subsequent TPD chromatograms

$$\theta_i = q_{i(base,\ 623°K)} + (X/W) \tag{3}$$

since the adsorbent was saturated with the irreversibly adsorbed base after the first adsorbed base after the first adsorption–desorption experiment carried out at $623°K$.

TPD data were obtained for pyridine, 2,6-DMP$_y$, piperidine, quinoline and n-butaylamine at different initial base concentrations, θ_i. For each base, fresh NaY zeolite was used. The reproducibility of the TPD chromatograms was very good for pyridine and quinoline, good for 2,6-DMP$_y$, but poorer for n-butylamine and piperidine.

RESULTS

Irreversible adsorption of bases

Data on the irreversible adsorption of the bases at $623°K$ are given in Table I. In the present study the irreversible adsorption at $623°K$ is defined as the amount of base retained by the presaturated NaY after it had been swept with pure nitrogen

TABLE I

IRREVERSIBLE ADSORPTION OF ORGANIC BASES ON NaY ZEOLITE AT 623°K

Base	Irreversible adsorption at 623°K	
	mmol/g	No. of base molecules per supercage
Pyridine	0.00	0.00
2,6-DMP$_y$	0.073	0.16
n-Butylamine	0.263	0.57
Piperdine	0.490	1.06
Quinoline	0.623	1.35

for a period of 60 min at that temperature. This period was sufficient to desorb almost all the reversibly adsorbed base on NaY at 623°K. The results (Table I) indicate that the amount of pyridine irreversibly adsorbed on NaY at 623°K is close to zero, while that of the other bases follows the order:

$$2,6\text{-DMP}_y\,(0.16) < n\text{-butylamine}\,(0.57) < \text{piperidine}\,(1.06) < \text{quinoline}\,(1.35)$$

The numbers in parentheses indicate the number of base molecules adsorbed irreversibly per supercage of NaY zeolite, obtained by dividing q_i by the supercage density. For NaY, the supercage density is the reciprocal of the formula weight of a sodalite unit[9].

TPD of bases on NaY

The TPD chromatograms for pyridine, 2,6-DMP$_y$, quinoline, piperidine and n-butylamine on NaY are shown in Figs. 1–4.

For all the bases, the TPD chromatograms have the following common features. The chromatograms are very broad (particularly at higher values of θ_i) and have two maxima, the first in the low temperature region and second in the high temperature region. The start of desorption is very sharp. The desorption edges of the superimposed chromatograms are almost coincident for the TPD of pyridine and quinoline. In the case of the other bases a small deviation is observed due to a small change in the surface properties resulting from a reaction of these bases on the NaY. After TPD experiments, the reolite showed a small change in colour from white to greyish black when n-butylamine, piperidine and 2,6-DMP$_y$ were used as adsorbates.

The dependence of the initial desorption temperature, T_D, on θ_i in the TPD of the bases on NaY is shown in Fig. 5. It is seen that T_D decreases with increasing θ_i.

DISCUSSION

A TPD spectrum for a heterogeneous surface with a broad site energy distribution is expected[2] to be broad. The shape and width of the TPD chromatograms (Figs. 1–4) for all the bases indicate that NaY has such a broad distribution. This
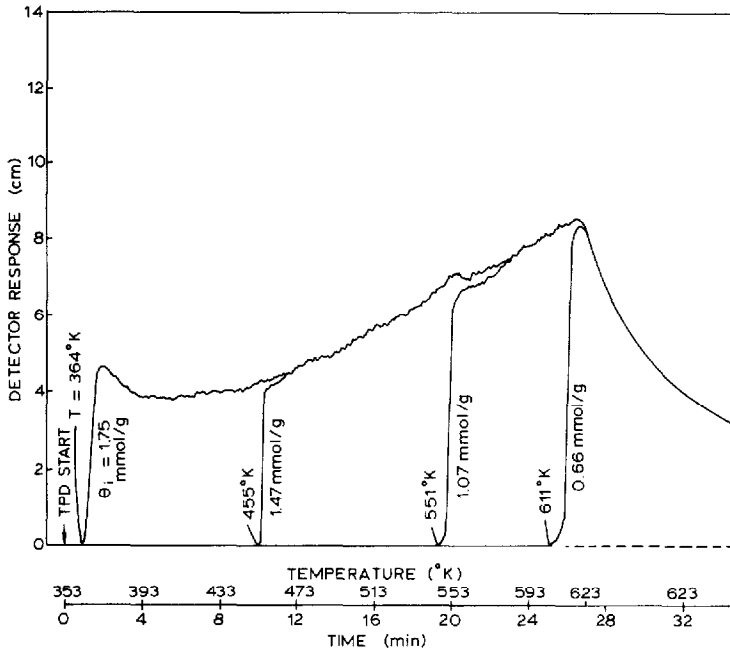
Fig. 1. TPD chromatograms of pyridine on NaY (0.301 g) under chromatographic conditions at different initial concentrations, θ_i. q_i for pyridine at 623°K $\approx$ 0.00 mmol/g.
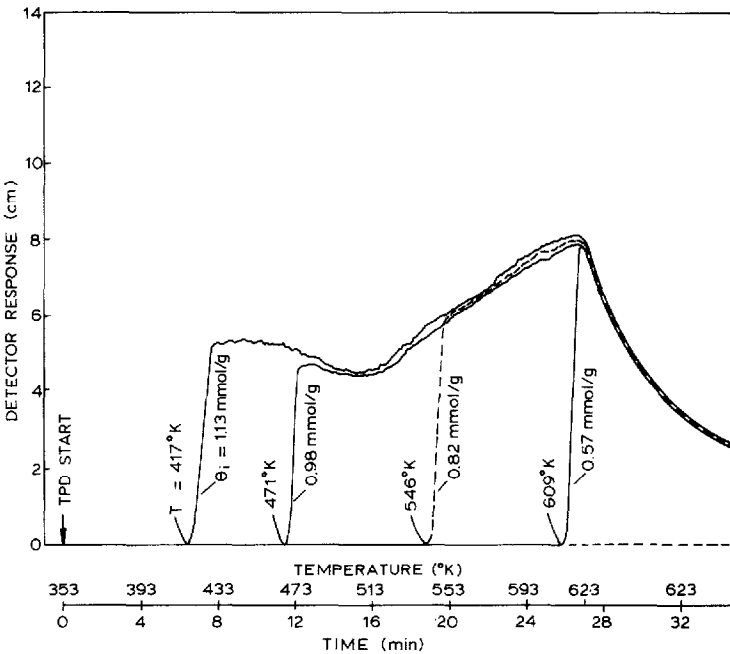

Fig. 2. TPD chromatograms of 2,6-DMP$_y$ on NaY (0.302 g) under chromatographic conditions at different initial concentrations, θ_i. q_i for 2,6-DMP$_y$ at 623°K = 0.07 mmol/g.
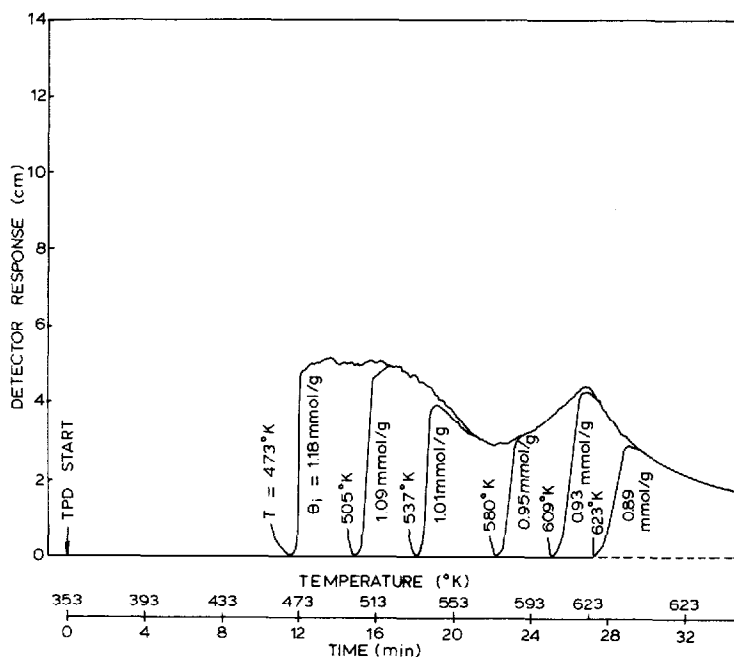
Fig. 3. TPD chromatograms of quinoline on NaY (0.273 g) under chromatographic conditions at different initial concentrations, θ_i. q_i for quinoline at 623°K $= 0.62$ mmol/g.
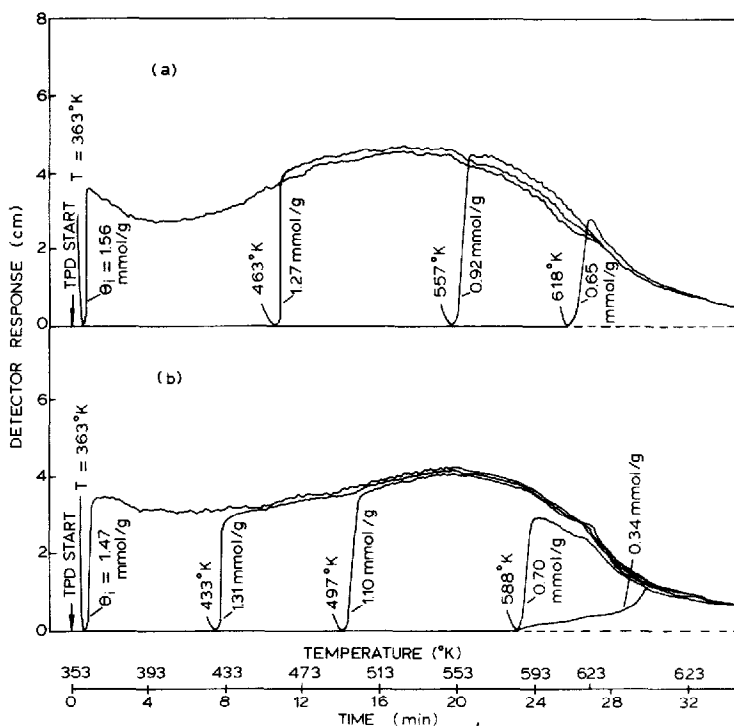

Fig. 4. TPD chromatograms of piperidine (a) on NaY (0.284 g) and n-butylamine (b) on NaY (0.301 g) under chromatographic conditions at different initial concentrations, θ_i. q_i at 623°K $= 0.263$ mmol/g for n-butylamine and 0.49 mmol/g for piperidine.
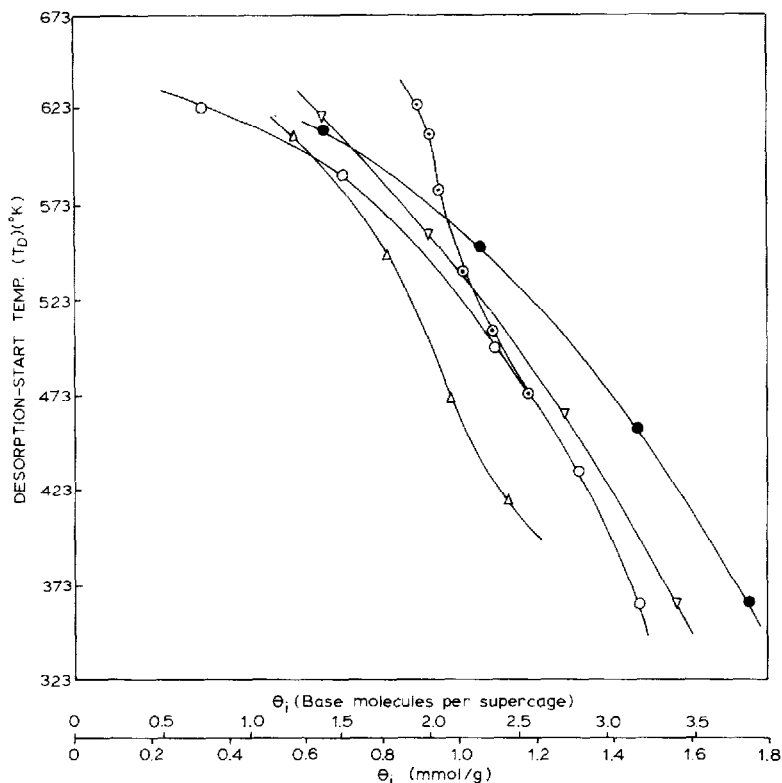
Fig. 5. Dependence of initial temperature of desorption T_D, on initial concentration of adsorbed base, θ_i, on NaY zeolite. Bases: pyridine (●); 2,6-DMP$_y$ (△); quinoline (☉); piperidine (▽); n-bytylamine (○).

conclusion is supported by the fact that T_D increases with decreasing θ_i (Fig. 5), which indicates that increasing energy is required for the desorption of chemisorbed base from sites with increasing strengths. The initial temperature of desorption, T_D, in TPD may be taken as a measure of the relative site strength. When all other conditions are kept constant, T_D depends on the initial concentration of adsorbed species, θ_i. The curve of T_D vs. θ_i therefore reflects the site energy distribution and gives qualitative, information about this distribution on solid surfaces.

The irreversible adsorption of the bases at 623°K (Table I) and the T_D vs. θ_i curves (Fig. 5) show that all the bases except pyridine at $\leqslant$ 623°K are adsorbed very strongly on NaY at or below this temperature. The probable chemisorption sites are Na$^+$ because NaY has neither Lewis nor protonic acid sites[7]. IR spectroscopic studies[7] of adsorbed pyridine on NaY have indicated that this base is adsorbed weakly by coordination to alkali metal ions. However, the present work shows that pyridine is adsorbed strongly on NaY at tempertures below 623°K.

n-Butylamine is commonly used[7,8] in the non-aqueous titration method for determining surface acidity and acid strength at room temperature. The other bases are frequently used at higher temperatures for measuring surface acidity and as selective poisons for determining acidic sites in catalytic titrations[7]. All these

methods for measuring the acidity distribution of solid catalysts are based on the assumption that the bases are chemisorbed selectively on the acidic sites. However, the present investigation indicates that these bases are also adsorbed very strongly on the non-acidic sites. Hence, care must be exercised when using these bases as acid probes in the measurement of the acidity of solid catalysts and adsorbents, particularly those containing alkali metal ions, *e.g.*, partially cation-exchanged NaY. In this respect, pyridine appears to be a better choice when it is employed in titrations at higher temperatures. Selective poisoning of the more strongly acidic sites of CeNaY, HNaY and HNaZSM-5 zeolites[10-12] in the order of their increasing acid strength by irreversible adsorption of pyridine at different temperatures has also indicated that only the acidic sites that can adsorb pyridine irreversibly at temperatures $> 570°$K are involved in catalytic cracking and isomerization reactions.

CONCLUSIONS

A gas chromatographic technique was employed for studying TPD of organic bases (commonly employed in surface acidity measurements) on NaY under chromatographic conditions. This is a very simple and rapid technique for investigating the site energy distribution on a solid surface. The TPD studies lead to the following important conclusions.

NaY has a broad site energy distribution. Pyridine, 2,6-DMP$_y$, piperidine, quinoline and *n*-butylamine are adsorbed strongly on NaY, which contains neither Lewis nor protonic acid sites. This fact should be taken into account when using these bases for characterizing acidic sites of solid catalysts and adsorbents. Pyridine is not adsorbed irreversibly on NaY at higher temperatures ($\leqslant 623°$K), hence it seems to be quite suitable for measuring the acidity of solid catalysts at such temperatures.

REFERENCES

1 R. J. Cvetanovic and Y. Amenomiya, *Advan. Catal.* 17 (1967) 103.
2 R. J. Cvetanovic and Y. Amenomiya, *Catal. Rev.*, 6 (1972) 21.
3 M. Smutak, S. Cerny and F. Buzek, *Advan. Catal.*, 24 (1975) 343.
4 V. R. Choudhary, *J. Chromatogr.*, 157 (1978) 391.
5 V. R. Choudhary and S. D. Sansare, *J. Chromatogr.*, 192 (1980) 420.
6 V. R. Choudhary and L. K. Doraiswamy, *Ind. Eng. Chem., Product. Res. Develop.*, 10 (1971) 218.
7 H. A. Benesi and B. H. C. Winquist, *Advan. Catal.*, 27 (1978) 97.
8 L. Forni, *Catal. Rev.*, 8 (1973) 65.
9 M. S. Goldstein and T. R. Morgen, *J. Catal.*, 16 (1970) 232.
10 V. R. Choudhary, unpublished results.
11 V. S. Nayak and V. R. Choudhary, *J. Catal.*, in press.
12 V. S. Nayak, *Ph. D. Thesis*, University of Poona, Poona, 1982.