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Sorption of Benzene in CeNaY Zeolite under Catalytic Conditions

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Sorption isotherms of benzene in CeNaY (Ce^{3+}-exchange: 72%) and in the same zeolite with its stronger acid sites poisoned with pyridine were obtained in the temperature range 463–623 K by the gas chromatographic pulse technique using the peak maximum method. The sorption data could be fitted well to the Langmuir type sorption equation. The isosteric heats of sorption at different sorbate loadings were evaluated from the sorption data. The heat of sorption at near zero intracrystalline sorbate concentration was obtained separately by gas chromatographic technique. Temperature-programmed desorption (TPD) of benzene from the zeolite under chromatographic conditions at different initial sorbate loadings were also investigated. The poisoning of the stronger acid sites of the zeolite has resulted in a very significant decrease in the extent of sorption and in the heat of sorption, indicating the involvement of the acid sites in the sorption. The variation of the isosteric heat of sorption with the sorbate loading, the TPD data and the analysis of pressure derivatives of the sorption clearly show the presence of site energy distribution in the zeolite.

INTRODUCTION

Rare earth (particularly Ce and La) exchanged Y-type zeolites are commercially important catalysts used in cracking and alkylation of hydrocarbons (*1–3*). The interaction between aromatic hydrocarbons and the zeolites involving strong sorption occurs in many catalytic reactions, and is therefore of great interest (*4*). The sorption is a result of the interaction of the π-electron system of the benzene ring with the cation or the acidic hydroxyl group of the zeolites (*5–7*). Apart from the chemical interaction, the physical interaction has also been found to be quite significant (*8*). Hence, the study of adsorption of aromatic hydrocarbons in the zeolites under catalytic conditions is of great interest. However, aromatic hydrocarbons (except benzene) undergo catalytic conversion reactions (viz. dealkylation, isomerization, and disproportionation) at higher temperatures and this makes the measurement of their sorption very difficult.

Only a few studies (*8, 9*) have been reported on the sorption of aromatics in the rare earth exchanged Y-type zeolites. A detailed investigation of the sorption of benzene in Ce-exchanged, particularly under catalytic conditions, has not been carried out so far. Also, a knowledge of the effect of poisoning of the zeolite on its sorption properties would prove very useful for understanding the sites involved in the sorption. The present investigation was therefore undertaken with the objective of studying in detail the sorption of benzene under catalytic conditions in CeNaY (Ce^{3+}-exchanged: 72%) zeolite and on the same zeolite with its stronger acid sites blocked with pyridine, using gas chromatographic techniques.

CeNaY ZEOLITE

The CeNaY zeolite (Si/Al = 2.43 and Ce^{3+}-exchange = 72%) was provided by Dr. J. Weitkamp of the Engler-Bunte Institute, University of Karlsruhe, West Germany. The zeolite powder was pelletted binder-free and crushed to particles of 0.2 mm in size. The crystals of the zeolite were

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examined with a Cambridge Stereoscan Model 150 scanning electron microscope. The average size of the zeolite crystals was found to be about 0.8 μm.

Before carrying out the sorption measurements, the zeolite was calcined *in situ* by heating it in a flow of helium from 353 to 673 K at a heating rate of 10 K $\cdot$ min^{-1} and further at 673 K for 4 h.

The acidity distribution on the zeolite was measured in terms of the pyridine sorbed irreversibly at different temperatures, using the GC method based on stepwise thermal desorption (*10*). The number of protonic acid sites on the zeolite was determined by measuring the irreversible sorption of 2,6-dimethylpyridine at 623 K, using the GC pulse method based on TPD under chromatographic conditions (*11*). The acidity data are given below.

Temperature (K):	353	423	498	573	623
Pyridine sorbed irreversibly (mmol $\cdot$ g^{-1}):	1.48	0.83	0.55	0.48	0.43
2,6-Dimethyl pyridine sorbed irreversibly (mmol.g^{-1}):	—	—	—	—	0.47

The decrease in the irreversible sorption of pyridine with the increase in the temperature indicates a broad acid strength distribution on the zeolite. It may be noted that the acid sites as measured by the irreversible sorption of both pyridine and 2,6-dimethylpyridine (which is expected to be chemisorbed preferentially on protonic acid sites (*1, 12*) at 623 K (0.43 and 0.47 mmol $\cdot$ g^{-1}, respectively) are quite comparable (the higher value for 2,6-dimethylpyridine is probably due to its higher basicity), indicating that the zeolite contains mostly protonic acid sites.

EXPERIMENTAL PROCEDURES

Gas chromatographic adsorption, desorption, and TPD data were collected using a Perkin–Elmer, Sigma 3B gas chromatograph, fitted with a flame ionization detector. Helium (>99.99%) was used as the carrier gas.

A 15-cm GC column was prepared by packing 0.42 g of the zeolite in a stainless-steel tube (3 mm o.d.). 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 preheater.

The irreversible sorption of benzene in the zeolite at 623 K was measured by the GC pulse method (*11*) based on TPD under chromatographic conditions and that at 513–583 K was measured by the stepwise thermal desorption of benzene sorbed irreversibly at 513 K, using the GC sorption/desorption method (*10*). The irreversible sorption in the present study is defined as the amount of sorbate retained by the presaturated zeolite after it was swept with pure helium for a period of 60 min.

The TPD of benzene under chromatographic conditions from 353 to 673 K at different intracrystalline benzene concentrations was studied by the procedure described elsewhere (*10, 13*).

The stronger acid sites on the zeolite were selectively poisoned (*14, 15*) by blocking them with pyridine sorbed irreversibly at 623 K. All the measurements on the poisoned zeolite were performed at temperatures $\leq$583 K so as to ensure that the irreversibly sorbed pyridine was not desorbed.

Isotherms of reversible sorption of benzene in the zeolite before and after poisoning were determined by the GC pulse method (*16*) using helium as the carrier gas (flow rate: 9.0 cm^3 $\cdot$ min$^-$). Benzene pulses of different volumes (0.1 to 10 μl) were injected into the zeolite column at a known temperature and the elution chromatogram of each pulse was recorded until the recorder pen reached the baseline. Detailed experimental procedure for the pulse experiments has been given earlier (*17*).

The adsorption of benzene on the column wall was found to be negligible. The pressure drop across the zeolite bed was negligibly small (<1% of the outlet pressure).

The pulse data on the zeolite were collected in the temperature range 463–623 K, and the data on the zeolite poisoned with pyridine in the range 523–583 K. The pulse data on the zeolite of particle size 0.1 mm were also collected at 463 K for ascertaining the mass transfer limitations on the sorption.

The heat of sorption of benzene in both the unpoisoned and poisoned zeolite at near zero intracrystalline sorbate concentration was determined by the GC pulse method (*18*). The GC retention data were collected at different temperatures (533 to 623 K for the unpoisoned zeolite and 533 to 583 K for the poisoned zeolite) with pulses of benzene vapor diluted with helium (concentration of benzene in the pulse $\simeq$1 mol%). The size of the pulse was 0.5 cm^3. Helium was used as the carrier gas at a flow rate of about 20 $cm^3 \cdot min^{-1}$.

The number of molecules per supercage of the zeolite was obtained from a knowledge of the supercage density, which is the reciprocal of the formula weight of the sodalite unit in the Y zeolite (*19*).

RESULTS

Irreversible Sorption and TPD under Chromatographic Conditions

The variation of irreversible sorption of benzene in the zeolite with temperature is shown in Fig. 1a.

The superimposed chromatograms for the TPD of benzene under chromatographic conditions at different initial concentrations of sorbed benzene (θ_i) in the zeolite are presented in Fig. 2. It may be noted that the TPD chromatograms at higher θ_i values are very broad, the start of desorption is very sharp, and the desorption edges of the chromatograms match each other exactly.

The variation of the desorption starting temperature (T_D) with θ_i for the TPD of benzene is shown in Fig. 1b. It is noteworthy that the trend of the curves in Figs. 1a and b are similar.

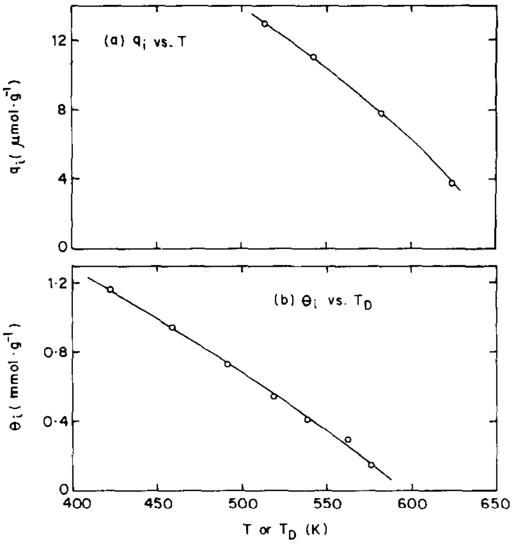

FIG. 1. (a) Temperature dependence of irreversible sorption of benzene in the CeNaY zeolite. (b) Dependence of desorption start temperature (T_D) on initial sorbate concentration (θ_i) in TPD of benzene on the CeNaY zeolite under chromatographic conditions.

Benzene Sorption Isotherms

The desorption edges of the elution curves for benzene on the zeolite at all the temperatures showed a strong dependence on the amount of benzene injected. Therefore, the peak maxima method (*16*) was employed for estimating the sorption isotherm from the pulse data.

The isotherms of sorption of benzene in the unpoisoned and poisoned zeolite are given in Fig. 3. A detailed procedure for the estimation of sorption data from the superimposed elution curves by the pulse maxima method has been given elsewhere (*17*).

A change in the particle size of the zeolite from 0.2 to 0.1 mm has been shown to have no significant effect on the sorption at 463 K, indicating the absence of external (film diffusion) and intercrystalline (macropore) mass transfer limitations on the sorption process. Also, since the size of the zeolite crystals is very small (about 0.8 μm), the

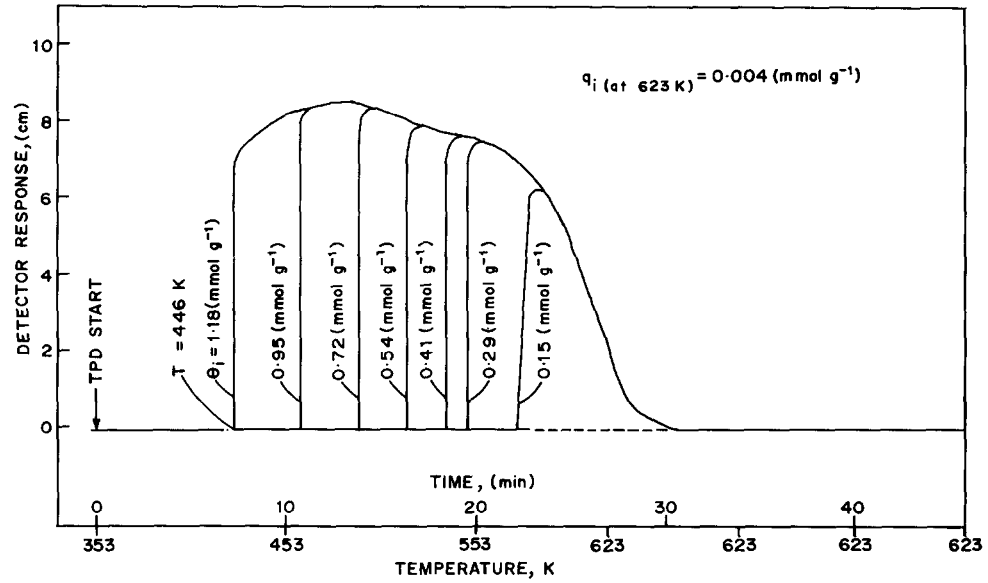

FIG. 2. Chromatograms (superimposed) for TPD of benzene on the CeNaY zeolite under chromatographic conditions at different initial concentrations of sorbed benzene (θ_i).

intracrystalline mass transfer effect is expected to be absent.

Efforts were made to fit the sorption data to the Freundlich, the Dubinin–Polanyi and the Langmuir sorption equations. For both the unpoisoned and poisoned zeolites, the Freundlich plots exhibit a break at all the temperatures indicating that the sorption does not follow the Freundlich isotherm. Although most of the data showed a good fit to the Dubinin–Polanyi equation (*20*), the data could not be represented by a unique temperature independent characteristic curve. This shows that the Dubinin–

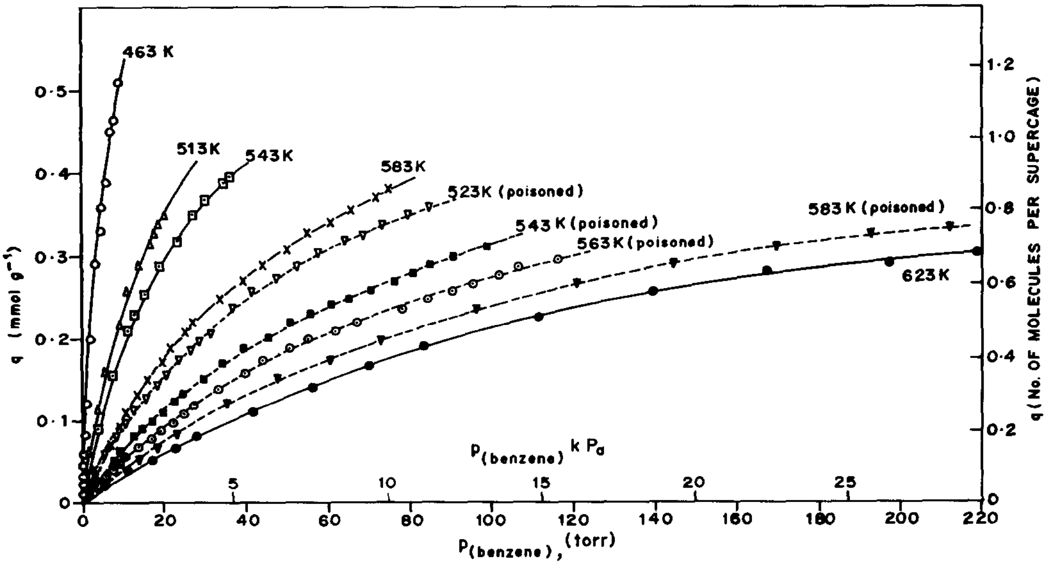

FIG. 3. Sorption isotherms for benzene on the CeNaY zeolite (unpoisoned and poisoned).

Polanyi equation is not strictly valid for the benzene–CeNaY zeolite system, indicating that the sorption does not follow the volume filling mechanism. The data could, however, be fitted very well to the Langmuir type equation.

$$q = q_m[\alpha p/(1 + \alpha p)] \quad (1)$$

where q is the amount adsorbed at pressure p; q_m, the maximum sorption capacity; and α, the sorption constant. The temperature dependence of α and q_m is shown in Fig. 4, which satisfies the Arrhenius type equation.

Isosteric Heat of Sorption (from Sorption Isotherms)

The dependence of the isosteric heat of sorption (Q_a) of benzene in the unpoisoned and poisoned zeolites obtained from the slope of the linear plots of log of the pressure vs the reciprocal of the absolute temperature at a constant sorbate loading by means of the Clausius–Clapeyron equation (*20*) on the sorbate loading in the zeolite is shown in Fig. 5.

It can be noted from Fig. 5 that Q_a decreases with the sorbate loading, the decrease being more pronounced in the case of the poisoned zeolite in the region of lower sorbate loading.

Heat of Sorption by GC Pulse Technique

At the conditions of the pulse experiments (viz. pulse size, 0.5 cm^3; concentration of benzene in pulse, 1 mol%; and temperature, 533–623 K), the retention volume was found to be independent of the carrier gas flow rate. This has indicated that the sorption in the zeolite under the above conditions corresponds to the linear portion of the sorption isotherm. The heat of sorption from the GC retention data was evaluated using the relation (*18*).

$$\log(t_m \cdot v) = A - (\Delta H/2.303R)\,(1/T) \quad (2)$$

where t_m is the retention time of sorbate; v, the volumetric flow rate of carrier gas (corrected for the column conditions); A, the constant; ΔH, the heat of sorption; R, the gas constant; and T, the temperature.

The values of heat of sorption of benzene obtained from the slopes of the linear plots of log ($t_m \cdot v$) vs $1/T$ are 56.8 (for the unpoi-

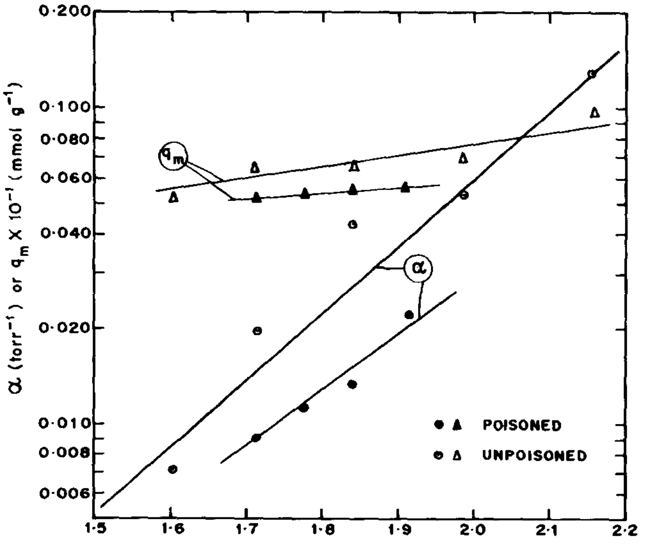

FIG. 4. Temperature dependence of constants of the Langmuir type equation for the sorption of benzene in the CeNaY zeolite (unpoisoned and poisoned with pyridine).

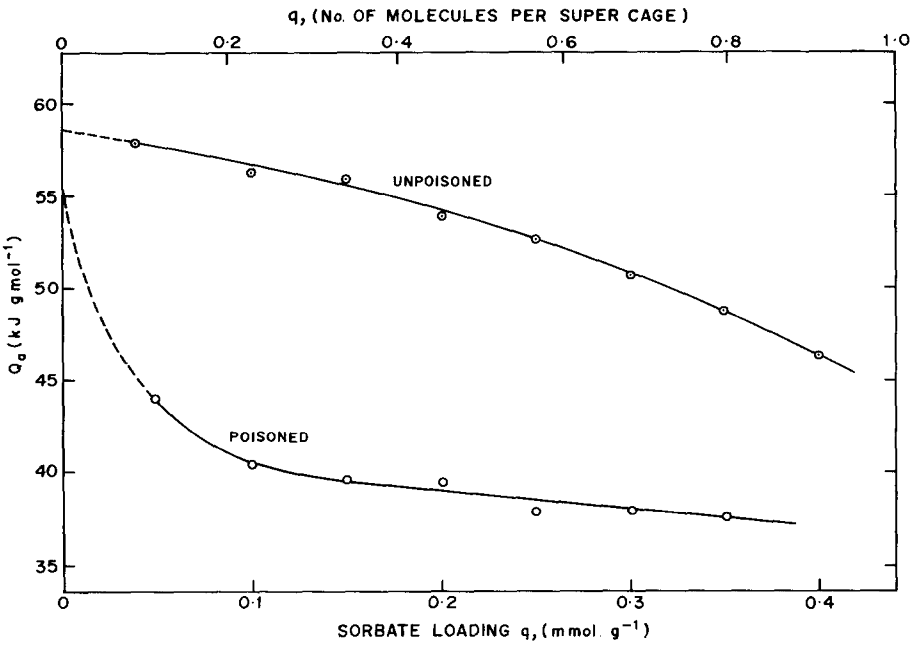

FIG. 5. Variation of isosteric heat of sorption (Q_a) of benzene with the sorbate loading (q) in the CeNaY (unpoisoned and poisoned) zeolite.

soned zeolite) and 54.7 (for the poisoned zeolite) kJ · mol^{-1}.

DISCUSSION

Sorption of Benzene

The irreversible sorption of benzene (Fig. 1a) is very small compared to that of pyridine. This small sorption is expected due to the interaction of benzene mainly with very strong protonic acid sites of the zeolite. The irreversible sorption of pyridine and 2,6-dimethyl pyridine at 623 K has indicated that the acid sites on the zeolite are mostly protonic ones.

The broad shape of the TPD chromatograms (Fig. 2) and the increase in the desorption start temperature with the decrease in the sorbate loading (Fig. 1b) and the decrease in the irreversible sorption with the increase in the temperature indicate the presence of broad site energy distribution on the zeolite.

The benzene sorption isotherms (Fig. 3) were determined by the GC pulse technique based on the peak maxima method (*16*). This method minimizes the effect of longitudinal diffusion, convectional mixing, and mass transfer and hence gives a more accurate estimate of the isotherm than the single injection method.

The evaluation of equilibrium sorption data from transient pulse experiments is evidently based on the assumption that sorption equilibrium is always established locally between the mobile gas phase and the zeolite particles. This assumption is satisfied in the present case as the time required for the establishment of the equilibrium (which is estimated to be of the order of 10^{-6} sec, assuming the heat of sorption of benzene about 58 kJ · mol^{-1}) is very small as compared to the residence time of the sorbate (which is about 1.7 sec) in the zeolite particles. The time constant for the intracrystalline diffusion of benzene (assuming its diffusion coefficient to be of the order of 10^{-7} cm^2 · sec^{-1}) in the zeolite (crystal size: 0.8 μm) has been estimated to be of the order of 10^{-3} sec, which is very small compared to the residence time of the sorbate in the zeolite particles. This indicates the absence of intracrystalline mass transfer limitation on the sorption. The absence of the film diffusional and intercrystalline mass transfer limitation on the sorption was also confirmed by changing the particle size of the zeolite from 0.2 to 0.1 mm. Further, the chromatographic peaks of benzene were found to be very broad as compared to those of methane. This has also indicated (*8*) the absence of mass transfer resistance in the sorption.

The analysis of the sorption isotherms indicated that the sorption does not follow the volume filling mechanism. The data could be fitted very well to the Langmuir type equation. However, it is interesting to note that q_m (maximum sorption capacity) decreases with the sorption temperature (Fig. 4). Also, the values of q_m are lower than what one would expect when the microvoids comprising the supercages in the Y-type zeolite are completely filled by the sorbate. The volume of microvoids accessible to benzene molecules is 0.3 $cm^3 \cdot g^{-1}$. This points to the fact that, in the present case, the sorption is not a physical phenomenon, but is the result of chemical interaction of the sorbate with the sorption sites. The q_m in the present case may be interpreted as the maximum sorption in the zeolite instead of considering it as the filling of microvoids. Also, the variation of q_m with the temperature indicates that the sorption does not strictly follow the Langmuir type adsorption.

Heat of Sorption of Benzene

The isosteric heat of sorption of benzene at the different sorbate loadings in the zeolite (unpoisoned and poisoned) was obtained from the sorption data. The isosteric heat of sorption (Q_a) decreases with the increase in the sorbate loading (Fig. 5). At such a low sorbate loading (<1 benzene molecule per supercage), the interaction between the sorbate molecules are expected to be nonexistent. The decrease in Q_a is, therefore, attributable mainly to the site energy distribution in the zeolite, which is consistent with the observation made from the irreversible sorption of pyridine and benzene and TPD of benzene on the zeolite.

The heat of sorption of benzene at near zero sorbate loading was determined from the GC pulse retention data at the different temperatures. In order to obtain reliable value of heat of adsorption by this method, the condition that the adsorbate concentration falls in the linear portion of the isotherm must be satisfied (*21*). Since zeolites, in general, are known to give nonlinear sorption isotherms even at lower sorbate pressures, it becomes essential to make sure that the above condition is satisfied. This was accomplished in the present study by carrying out the pulse experiments with very dilute sorbate pulses (1 mol% benzene) of smaller size (0.5 cm^3) and finding the effect of flow rate of the carrier gas on the retention volume of the sorbate.

A comparison of the values of isosteric heat of sorption extrapolated to zero sorbate loading (Fig. 5) with the ones at near zero sorbate loading obtained with the GC pulse method shows that there is a very good agreement between the two.

Pressure Derivatives

Recently, Prasad and Doraiswamy (*22, 23*) calculated the pressure derivatives of the mean surface coverage for three well-known site energy distributions, namely, negative exponential, positive exponential, and constant distributions, and predicted that, for these site energy distributions, a plot of the product of surface coverage (θ) and its pressure derivative ($\theta \cdot d\theta/dp$) vs log p should pass through a maximum.

The CeNaY zeolite shows site energy distribution for the sorption of benzene. This system is, therefore, used for testing the validity of the theoretical prediction. For the sorption of benzene in both the unpoisoned and poisoned zeolites at all the temperatures, the plots of $q(dq/dp)$ vs log p were found to pass through a maximum. A few representative plots are shown in Fig. 6. The maximum of the pressure derivative

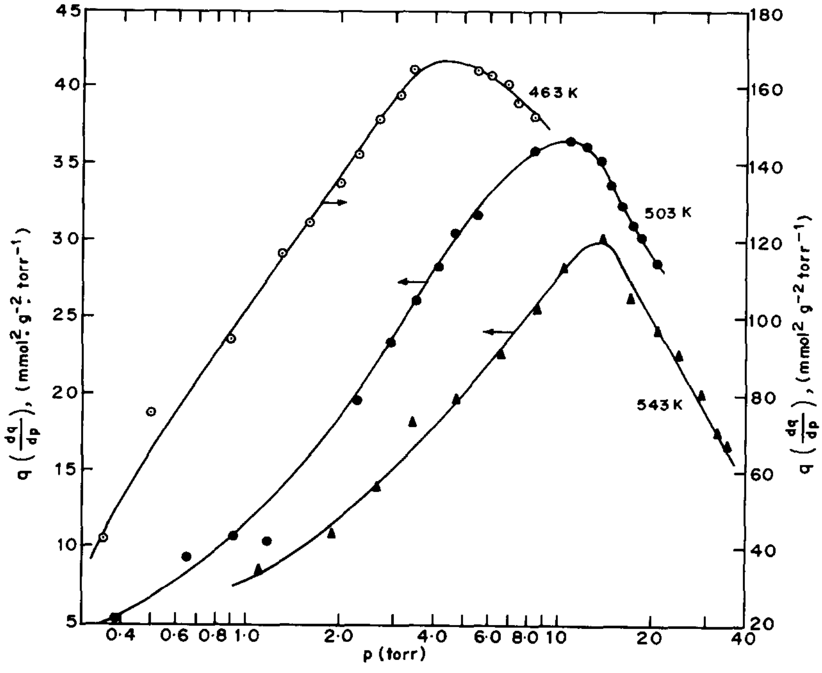

FIG. 6. $q(dq/dp)$ vs log p plots for sorption of benzene in the CeNaY zeolite.

plots is found to shift toward the higher pressure side with the increase in the temperature, as follows

For the unpoisoned zeolite,

Temperature (K):	463	513	543	583	623
p (Torr) at maximum:	4.5	11.0	13.5	25.0	84.0

For the poisoned zeolite,

Temperature (K):	523	543	563	583
p (Torr) at maximum:	28.0	47.0	55.0	70.0

This shift is quite consistent with the prediction by Prasad and Doraiswamy (*24*).

Influence of Poisoning

When the stronger acid sites on the zeolite are selectively blocked by pyridine sorbed irreversibly at 623 K (which correspond to the blockage of about one site per supercage) the sorption of benzene in the zeolite is affected in the following manner. The extent of sorption decreases very considerably (Fig. 3). Also, the values of the Langmuir parameters (sorption constant and the maximum sorption capacity) decrease (Fig. 4). This is to be expected as the blockage of stronger acid sites by pyridine results in a decrease in the sorption sites. This effect of the blockage of the stronger acid sites on the sorption clearly indicates that the protonic acid sites (as the zeolite contains mostly protonic acid sites) are involved in the sorption process.

The isosteric heat of sorption decreases to a significant extent (Fig. 5) because of the stronger acid sites not being available for sorption. This also confirms the involvement of acid sites in the sorption. Further, the shape of the plot of the dependence of Q_a on the sorbate loading changes from convex to concave. This is probably due to the influence of sorbed pyridine on the site energy distribution caused by the blockage of the stronger acid sites and also by the interaction of the base with the other sorption sites.

The difference between the values of heat of sorption at near zero sorbate loading for the unpoisoned and poisoned zeolite is very small. This is probably because of the presence of a small number of stronger acid sites on the poisoned zeolite, which are not blocked by pyridine during the poisoning of the zeolite and/or because they become available due to a slow desorption of pyridine.

Application of GC Techniques to Zeolites

Gas chromatography provides simple and rapid technique (*18*) for measuring adsorption, heat of adsorption, and surface properties of solid catalysts under catalytic conditions. However, with zeolites, the GC techniques have been used mostly for the measurement of acid strength distribution (*1, 10, 25–28*) and heat of sorption (*29–33*).

The present study shows that the GC pulse technique can be conveniently employed for the measurement of equilibrium sorption in Y-type zeolite. The GC approach is particularly useful for studying the sorption and heat of sorption at high temperatures, where the volumetric and gravimetric methods (which are commonly used in the measurement of sorption in zeolites) become inapplicable because of the long contact time involved, which leads to the decomposition of organic sorbate. Besides the simplicity and rapidity with which the sorption and/or heat of sorption data can be collected, a particularly attractive feature of the GC techniques is that the measurements can be made on a large and representative sample of the zeolite at temperatures approaching those of the commercial catalytic processes.

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