Sorption of n-Butylamine on Ferric-Exchanged Y-Zeolites

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The sorption of n-butylamine (n-BA) on ferric exchanged Y zeolite catalysts has been studied. Freundlich equation is applicable to the sorption data of ferric-exchanged zeolites. The amount of n-BA retained on zeolites under vacuum at different temperatures has been reported which predicts the trend in the acidic strength. FeNaY (46) zeolite shows maximum number of strong acidic centres. The adsorption data for FeNaY zeolite, activated at 500°C, show migration of ferric ions from supercages to sodalite cages or hexagonal prisms, thereby lowering the acidity of zeolite. The isosteric heats of sorption of n-BA on FeNaY zeolites have been determined which support the heterogeneity of surface and migration of ferric ions after heating at 500°C.

Attempts\(^1\) - 5 have been made to determine the number and strength of acidic centres in supercages of zeolites through the measurements of base adsorption. Ammonia molecules are sorbed in the supercages and slowly migrate into sodalite units, while n-butylamine (n-BA) and pyridine do not enter into sodalite cages of Y-zeolites. The adsorption n-BA is useful in determining the number and strength of acidic centres in supercages of Y-zeolites where the catalytic reactions occur. From the absorption measurements of CO\(_2\) and NH\(_3\) on various modified zeolites, Coughlan and co-workers\(^6\,7\) calculated the thermodynamic quantities and reported the sequence in the strength of adsorbate-absorbent interaction. Steinburg \textit{et al}\(^8\) measured heats of adsorption of some basic molecules on ion exchanged zeolites by calorimetric method. Mishin \textit{et al}\(^9,10\) reported sorption isotherms and heats of sorption of n-BA on dealuminated Y-zeolites. They concluded that the silanol groups formed during dealumination are not strong acidic centres and the number of sorption centres (cations and protonated centres) is reduced due to dealumination. In this paper, we report the results of a systematic study of n-BA sorption on ferric-exchanged Y-zeolites.

\section*{Materials and Methods}

Ferric-exchanged Y-zeolites were prepared by treating Linde NaY zeolite (SK-40, Lot No. 96805000) with aqueous solutions of ferric acetate-acetic acid at about pH 4 and 30°C. After exchange all the samples were washed with hot distilled water until the washings were free from acetate ions. The samples were oven-dried at 120°C overnight and stored in a constant humidity atmosphere over a saturated solution of ammonium chloride. The ferric-exchanged samples were yellow in colour with brownish tinge at higher exchanges. The X-ray diffraction patterns showed that all the samples were crystalline. The chemical compositions of the samples were determined by the conventional gravimetric analysis; sodium by flame photometry and iron by atomic absorption spectroscopy and titration method. The chemical compositions and lattice parameters are given in Table 1. The detailed characterisation data were discussed elsewhere\(^11\). It was observed that the framework structures of FeNaY (61) and FeNaY (75) were distorted during ion exchange.

\section*{Procedure}

The isotherms for the sorption of n-BA were measured in the temperature range of 100-350°C by the gravimetric method using a calibrated silica spring balance. Sample (100 mg) in the form of a pellet was used and activated under high vacuum (~10\(^{-6}\) torr) at 350°C for 4 hr to a constant weight and brought to the desired temperature. The absorbate liquid bulb was rendered air-free and was separately thermostated. The pressure of the absorbate was measured accurately with a cathetometer. The amount sorbed was estimated from change in weight of sample after equilibrium was obtained. The adsorption isotherms were obtained by progressive increase of vapour pressure and noting the extent of adsorption. The reproducibility was checked in some experiments. The amount of adsorbate (n-BA) retained was estimated by evacuating the sample under high vacuum (~10\(^{-5}\) torr) for 2 hr to a constant weight at different temperatures. The rates of sorption at 25°C were obtained and equilibrium n-BA sorption capacities are given in Table 1.
Results and Discussion

Typical families of sorption isotherms of n-butylamine (n-BA) on a series of ferric-exchanged Y-zeolites are presented in Figs 1 and 2. The trend in the number of n-BA molecules sorbed per unit cell at 350°C is NaY > FeNaY (46) > FeNaY (37) > FeNaY (82) > FeNaY (75). The isotherm for NaY showed slower increase in sorption capacity compared to that in FeNaY samples. Due to strong Na+ - n-BA interaction NaY adsorbs larger amount of n-BA. The rearrangement of molecules should take place to achieve the saturation capacity at a particular temperature. On the other hand, in the case of FeNaY samples, the n-BA molecules are sorbed strongly on Fe3+, Na+ and H+. The sorption of n-BA on Fe3+ and H+ is irreversible (up to 350°C) and the sorption on Fe3+ may have specific orientation. The FeNaY (75) absorbs smaller number of n-BA molecules as compared to NaY and FeNaY (46) because of distortion of framework structure as observed from the X-ray diffraction and water sorption studies. The unit cell composition, the lattice parameter representing crystallinity and n-BA sorbed on the catalysts at 25°C and 70 mm Hg of n-BA, are given in Table 1. In the case of FeNaY (46), as a typical example, the number of n-BA molecules sorbed at 25°C is 47.1 molecules per unit cell. As a first approximation, we may consider that the n-BA sorption is localized. The total number of cations in FeNaY (46) is 40.0 (8.4 Fe3+ + 28.6 Na+ + 3H+) per unit cell as given in Table 1. The number of cations in the supercages is 20.6 (~ 6 Fe3+ + 11.6 Na+ + 3H+) per unit cell while ~ 2.4 ferric and 18 sodium ions are in sodalite cages (site I' and II') or hexagonal prisms (site I). The ferric ion being trivalent should be shared by three aluminium tetrahedra. For geometric reasons, this results into Al-tetrahedra having local anionic charges which hydrolyse water molecules to increase the H+ ions, and consequently the Brønsted acidic centres. The infrared studies showed that n-BA molecules interact strongly with cations like sodium in Y-zeolite. The trend in the number of n-BA molecules sorbed at 25°C, i.e. saturation capacity, is as follows: FeNaY (46) > FeNaY (37) > NaY > FeNaY (82) > FeNaY (75) = FeNaY (61). The zeolites FeNaY (61) and FeNaY (75) adsorb smaller number of n-BA or water molecules as compared to NaY or FeNaY (46) because of distortion of zeolite framework structure as observed from the sorption isotherms, XRD patterns and water sorption studies. The framework distortion may be due to the lowering of pH from 4 to ~ 3.7 during the ion-exchange process.

The following sorption equations were tested for the data: Langmuir, Freundlich, Temkin, Sipps and Dubinin equations. Langmuir equation though fits better for the data (Fig. 3b), it is not applicable in principle due to heterogeneity of the surface. A typical Freundlich plot for n-BA sorption on FeNaY (37) is depicted in Fig. 3a. Freundlich equation is applicable to all the ferric-exchanged Y-zeolites. Linear plots with the other sorption equations could not be obtained. The analysis suggests that the n-BA sorption is localized and heterogeneity in the surface potential exists.

Figure 4 shows the amount of n-BA retained on zeolites under high vacuum (~ 10^-5 mm Hg) as a function of temperature. The data indicate the trend in the strength of n-BA interaction with the different samples at various temperatures. At about 200°C, the number of irreversibly sorbed n-BA on NaY and FeNaY (46, 500, 5) decreased than that for FeNaY catalysts. Above 200°C, the trend in the amount of n-BA retained was as follows: FeNaY (46) > FeNaY (82) > FeNaY (75) = FeNaY (61). The zeolites FeNaY (61) and FeNaY (75) absorb smaller number of n-BA or water molecules as compared to NaY or FeNaY (46) because of distortion of zeolite framework structure as observed from the sorption isotherms, XRD patterns and water sorption studies. The framework distortion may be due to the lowering of pH from 4 to ~ 3.7 during the ion-exchange process.

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Fig. 1—Sorption isotherms for n-butylamine on (1) NaY, (2) FeNaY (37), (3) FeNaY (46), (4) FeNaY (75)

Fig. 2—Sorption isotherms for n-butylamine on (1) FeNaY (82), (2) FeNaY (46, 500, 5)

(82) > FeNaY (37) > FeNaY (61) > FeNaY (75) > NaY. This indicates that the interaction of n-BA is stronger with ferric ions and acidic protons available in the supercages than that with sodium ions. The maximum number of strong interacting centres were present in FeNaY (46) among the zeolites under study. The total number of interacting centres responsible for n-BA chemisorption was more in FeNaY (46) and NaY as compared to those in other samples. We may attribute the number of n-BA molecules sorbed approximately corresponds to the number of sorption centres. Comparatively sharp decrease in irreversibly sorbed n-BA on NaY at about 200°C leads to the conclusion that most of n-BA molecules sorbed on sodium ions are desorbed up to 200-250°C.

In order to evaluate the effect of thermal treatment, FeNaY (46) was heated at 500°C for 5 hr in air.
and designated as FeNaY (46, 500, 5). The rate of n-BA sorption and the nature of sorption isotherms for FeNaY (46, 500, 5) were found to be similar to those for untreated FeNaY (46). (Fig. 2). However, the amount of n-BA retained under high vacuum was much lower for FeNaY (46, 500, 5) than that for FeNaY (46) as shown in Fig. 4. This is due to the loss of strong acidic centres by dehydroxylation and migration of ferric ions from supercages to sodalite cages or hexagonal prisms occupying sites inaccessible to n-BA molecules. A comparison of irreversibly sorbed n-BA (Fig. 4) on NaY, FeNaY (46) and FeNaY (46, 500, 5) indicates that the nature of sorption centres is identical in NaY and FeNaY (46, 500, 5) except some more acidic centres are present in FeNaY (46, 500, 5). On the other hand, for FeNaY (46) the irreversibly sorbed n-BA molecules are larger in number, throughout the temperature range up to ~350°C.

Chemical affinity of adsorbed phase

The change in chemical potential of n-BA between gas phase at standard pressure ($P_0 = 760$ Torr) and adsorbed state at equilibrium pressure $P$, is given by

$$
\Delta \mu = \Delta \mu_0 - RT \ln \left( \frac{P}{P_0} \right)
$$

The magnitude of a decrease in chemical potential, $-\Delta \mu$, is a measure of chemical affinity of n-BA for a zeolite sample. Figure 5 shows the plot of $-\Delta \mu$ as a function of coverage of n-BA molecules per unit cell at 200°C. The affinity sequence, throughout temperature range is NaY > FeNaY (46) > FeNaY (46, 500, 5) > FeNaY (37) > FeNaY (82) > FeNaY (61) > FeNaY (75). The trend in affinity is similar throughout the coverage range as that for equilibrium adsorption capacity of the zeolites.

Isosteric heat of adsorption

The isosteric heats of adsorption, $q_{st}$, were obtained by Clausius-Clapeyron equation:

$$
q_{st} = -\Delta H = R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \ln \left( \frac{P_2}{P_1} \right)
$$
The successive adsorption isotherms were used to determine $q_m$. The values of $q_m$ are given in Table 2. In the case of NaY, at coverage of 18 molecules per unit cell, the heat of $n$-BA adsorption is 82.4 kJ mol$^{-1}$, which decreases to 41.8 kJ mol$^{-1}$ at coverage of 35 molecules per unit cell. Due to strong interaction between sodium ion and NH$_2$ group of $n$-BA, the heat of $n$-BA adsorption is higher as compared to those for other hydrocarbons. For FeNaY (37), FeNaY (46) and FeNaY (82) at lower coverages (15-20 molecules per unit cell) $q_m$ is above 170 kJ mol$^{-1}$, which is much higher than that for NaY. The value of $q_m$ for FeNaY (46) at coverage of 20 $n$-BA molecules per unit cell attains a maximum value of 187.4 kJ mol$^{-1}$. In the case of FeNaY (61) and FeNaY (75), the adsorption data and low $q_m$ values indicate that the framework structure is distorted to a great extent during ion exchange and this is also confirmed by X-ray and water adsorption data.

The presence of [Fe(OH)(H$_2$O)$_{2+}$] in supercages has been established for untreated ferric-exchanged Y-zeolites based on spectral and thermal data. After activation at 350°C, the coordinated water molecules are removed and (Fe(OH))$^{2+}$ interacts with the framework at site-II in tetrahedral coordination. At 400°C, dehydroxylation of hydroxyl groups attached to ferric ions takes place and simultaneously, ferric ions migrate to inaccessible sites (sites I, I' and II'). It is also evident that up to 50% ion-exchange, ferric ions preferably occupy site-II in supercages, during ion-exchange.

In the case of thermally treated FeNaY (46, 500, 5) sample, the heat of adsorption is 75-80 kJ mol$^{-1}$ at coverages of 15-25 $n$-BA molecules per unit cell, which decreases to 52 kJ mol$^{-1}$ at coverage of 30 molecules per unit cell. Due to thermal treatment, Brønsted acidic centres are destroyed by dehydroxylation as confirmed by the TG analysis; and ferric ions migrate into sodalite cages or hexagonal prisms, the sites inaccessible to $n$-BA molecules. The $q_m$ values and the amount of $n$-BA retained under vacuum indicate that FeNaY (46) has stronger interacting centres. Migration of ferric ions into sodalite cages and hexagonal prisms is probably an irreversible process with respect to hydration and $n$-BA adsorption, due to the formation of Fe$^{3+}$ - O - Fe$^{3+}$ linkages in sodalite units. The DTA did not give any support for the existence of hexaaquo complex of ferric ion after thermal treatment. The variation in $q_m$ thus helps in understanding the heterogeneity in surface potential.

### Change in entropy of $n$-BA sorption

The entropy changes for $n$-BA sorption on ferric-exchanged Y-zeolites are given in Table 3, as a function of coverage. The values of $\Delta H$ and $\Delta S$ for NaY are approximately constant over a wide range of coverage, indicating the homogeneous nature of the catalytic surface of NaY. The $\Delta S$ values for FeNaY (37), FeNaY (46) and FeNaY (82) are 261.2, 278.0 and 209.3 JK$^{-1}$ mol$^{-1}$ at the coverage of 18-20 $n$-BA molecules per unit cell. The higher values of $\Delta S$ indicate strong and localized chemisorption of $n$-BA.
Table 3—Entropy Changes ($\Delta S \text{ in } \text{JK}^{-1}\text{mol}^{-1}$) of $n$-BA Sorption

<table>
<thead>
<tr>
<th>Zeolite</th>
<th>$S_1$ at $n$-BA coverage (molecules/unit cell)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>18</td>
</tr>
<tr>
<td>NaY</td>
<td>105.1</td>
</tr>
<tr>
<td>FeNaY (37)</td>
<td>261.2</td>
</tr>
<tr>
<td>FeNaY (46)</td>
<td>183.8</td>
</tr>
<tr>
<td>FeNaY (75)</td>
<td>110.1</td>
</tr>
<tr>
<td>FeNaY (82)</td>
<td>209.3</td>
</tr>
<tr>
<td>FeNaY (46, 500, 5)</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The $\Delta S$ values for thermally treated FeNaY (46, 500, 5) zeolite are comparable to those of NaY, and indicate that on thermal treatment, ferric ions migrate to inaccessible sites in the sodalite cages and hexagonal prisms and some Brönsted acidic centres are destroyed. As a result, $n$-BA molecules interact mainly with sodium ions in supercages.

**Conclusion**

Basic molecules like $n$-butylamine ($n$-BA) are chemisorbed on cations (Na$^+$ or Fe$^{III}$) and acidic protons in supercages of Y-zeolites. The equilibrium sorption values show direct proportionality to number of interacting centres, including acidic protons, while retention of $n$-BA sorption under vacuum and heats of sorption data indicate the trend in the strength of sorbate-sorbent interactions. Among the ferric-exchanged Y-zeolites, FeNaY (46) has the maximum number of strong active centres including acidic protons and is thermally stable. The retention of $n$-BA under vacuum support ferric ion migration into sodalite cages and reduced acidity after heating FeNaY (46) sample at 500°C for 5 hr in air.

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**References**
