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Quantitative Infrared Spectroscopy of Amines in Synthetic Zeolites X and Y

II. Adsorption of Amines on Na–Hydrogen Zeolites X and Y

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Different amines have been adsorbed on Na–hydrogen zeolites X and Y. The decrease of the OH stretching bands of the zeolites and the formation of ∂NH^+ bands of the alkyl-ammonium ions have been followed quantitatively.

The adsorption involves the following mechanisms: (i) reaction with the acidic hydroxyls, (ii) coordination to residual sodium ions, (iii) adsorption on dehydroxylated sites.

The adsorption of amines has a dehydroxylating effect which is especially pronounced for pyridine.

INTRODUCTION

The hydroxyl groups in hydrogen zeolites Y act as Brønsted acids when bases are adsorbed. Therefore the hydroxyls are generally considered as the active sites for hydrocarbon cracking reactions. Consequently, a lot of infrared studies were performed to clarify the location of the hydroxyl groups in the framework, to determine their accessibility and acidity with respect to bases of different strength such as ammonia, piperidine, pyridine, olefins and alkanes. Reviews on these subjects are available (*1–4*).

Adsorption of ammonia (*5, 6*) and piperidine (*7*) on hydrogen zeolites shows that the hydroxyl groups involved in the bands at 3650 (HF) and at 3550 cm^{-1} (LF) protonate the strong bases. Pyridine, being a weaker base, is protonated readily by the HF hydroxyls (*7–10*), but with the LF hydroxyl groups only a hydrogen-bond interaction is claimed to occur at low temperatures (*10*). Olefin adsorption results only in an interaction with the HF hydroxyls (*9, 11*).

A study of the dealkylation of cumene was performed by Ward (*12*) on an HY sample mounted in the infrared spectrometer. It was concluded that at 250°C only the hydroxyls of the HF band acted as Brønsted acids. Higher temperatures were required to promote the hydroxyls of the LF band into active centers.

All these data cannot be interpreted in terms of differences in acidity. Considering only the force constant reflected in the frequency, the hydroxyls of the LF band would be slightly more acidic than those involved in the HF band. Location at sites with different accessibilities and the possibility of proton migration could well explain the behavior of the hydroxyls involved in the LF band with respect to adsorbed bases and upon heating. This was assumed by Hughes and White (*7*) and also by Schoonheydt and Uytterhoeven (*13*).

In this work different aliphatic amines, straight-chain and branched, and also pyridine and piperidine have been adsorbed

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on two different samples. The X sample was only partially exchanged with NH_4^+ so that deammoniation resulted only in the formation of one type of hydroxyl reflected in the HF band. In the Y sample both HF and LF hydroxyls were present. The behavior of the infrared bands will be interpreted quantitatively, in order to resolve an apparent inconsistency between integrated absorption coefficients obtained by Hughes and White (*7*) and by us (*6*). Selectivities of interaction with HF and LF hydroxyls is discussed below.

EXPERIMENTAL METHODS

The Na^+ form of the zeolites was supplied by the Linde Co. Lot No. 1340080 (SK20) was an X type zeolite; lot No. 5135 (SK40) was a Y zeolite. Two samples have been prepared by exchanging the Na^+ with NH_4^+ ions using solutions containing different proportions of NH_4^+ and Na^+ ions. In this way samples with the following anhydrous unit cell composition were obtained:

$$X40 = (Na)_{51}(NH_4)_{34}(AlO_2)_{85}(SiO_2)_{107},$$

$$Y70 = (Na)_{16.5}(NH_4)_{38.5}(AlO_2)_{55}(SiO_2)_{137}.$$

The samples were dried at 50°C and stored over a saturated NH_4Cl solution. The amines used were analytical reagents. Ethylamine (E1) was purchased from Fluka; piperidine (PI) and diethylamine (E2) from E. Merck A.G.; isopropylamine (IP) from J. T. Baker; butylamine (B1), pyridine (PY), triethylamine (E3) from U.C.B. They were distilled *in vacuo* over a silica gel drying train, and the heart cut was retained for spectroscopic use. The reagents were introduced in the vacuum system over a drying train with type 5A Linde molecular sieve.

For the infrared experiments samples of the zeolite were pressed into films without binder between two steel plates under a load of 900 kg/cm^2 of film. Films of 2 × 2 cm, containing 5 to 8 mg of zeolite/cm^2, were introduced in the sample holder of an infrared cell. Small amounts of gas (1 to 2 μmole) could be introduced in the vacuum cell through a calibrated volume. Greaseless stopcocks were used.

The spectra were recorded on a Beckman IR 12 grating spectrometer, in the bending zone between 1300 and 1700 cm^{-1}, and in the stretching region between 2600 and 3800 cm^{-1}. For the spectra taken at room temperature the slit, energy and scanning conditions were chosen so as to obtain a resolution better than 2 cm^{-1} in the bending region, and better than 4 cm^{-1} in the stretching region. The photometric error and the error in peak absorbance did not exceed 1% for the narrowest band. The spectra at higher temperatures were recorded in somewhat less favorable conditions. To correct for sample emission at temperatures above 70°C the second chopper of the instrument was stopped. In this way the modulation and detection of thermally emitted radiation from the sample was avoided. To obtain suitable transmission during the adsorption experiments higher gain settings were needed. We checked that the resolution was better than 5 and 3 cm^{-1} in the stretching and bending regions, respectively.

The X40 and Y70 samples were vacuum deammoniated at 275 and 350°C, respectively. The rate of heating was about 10°C min^{-1}. This temperature was maintained for 1 hr. The samples were cooled and a spectrum was taken at room temperature. Accurately known increments of adsorbate were added. The spectrum was recorded again after equilibration during 30 min. The equilibration time was selected after careful preliminary experiments. For some amines the room temperature runs were repeated at 75 and 150°C. The nature of the adsorbed species and the temperature at which the spectra were taken are incorporated in the sample indications as follows: E2-11, E2-75 denote adsorption of diethylamine and spectra taken at 11 and 75°C, respectively.

Band areas were used for quantitative measurements. The procedure used to measure and interpret the band areas is extensively described in (*22*). Apparent integrated intensities (AI) were determined by adding accurately known doses of NH_3 or amines and by plotting the decrease of the OH band area as a function of the amount of amine adsorbed. The integrated form of Beer's law was used as described by Hughes and White (7). The AI values for the LF band were obtained by the same method as used previously in NH_3 adsorption experiments (6). On each sample several adsorption runs have been repeated on fresh films. In this way linear plots with at least 15 points are obtained. Least square treatments pointed out that the error on the correlation coefficient was smaller than ±3%. Adsorption isotherms were also carried out in a conventional all glass apparatus in conditions similar to those adopted for the ir experiments, using a McLeod gauge for the low pressure readings.

RESULTS

Sample X40

At room temperature the spectrum of the vacuum deammoniated X40 sample had a single hydroxyl stretching vibration at 3662 cm^{-1} with a half band width of 27 cm^{-1}. The apparent integrated absorption intensity (AI) of this band was determined by adsorbing known doses of ammonia, and plotting the decrease of the OH band intensity against the amount of ammonia adsorbed. The method was developed in an earlier work (6). The AI of the HF band was found to be 5.28 cm $\mu mole^{-1}$. The intensity of the 3662 cm^{-1} peak was converted into absolute concentration units, using this AI value. The pretreatment provokes a stoichiometric deammoniation since 34 ± 1 hydroxyls/unit cell were obtained in agreement with the composition of the sample. Before any adsorption of amines it was always checked carefully that the hydrogen X40 was really stoichiometric and not dehydroxylated.

The adsorption of amines was carried out by determining the decrease of the OH band area in a way similar to that applied for NH_3. This requires an emphasis of the following underlying assumptions. It was assumed that all the molecules introduced into the cell were also adsorbed on the zeolite, and that the hydroxyl groups are the only adsorption sites reacting in a 1:1 stoichiometry. These assumptions were perfectly valid for the adsorption of ammonia. The first assumption was checked for the amines by determining the adsorption isotherms, examples of which are given in Fig. 1. Except for piperidine, a large amount of amine is always adsorbed before any residual pressure is built up. The upper adsorption limit used for the ir spectra is indicated in Fig. 1 by an arrow. This confirms that the first assumption is valid except for piperidine. Adsorption of piperidine at 11°C did not produce a progressive decrease in band intensity: the band disappears at once when several doses of piperidine were introduced into the cell. However, at 150°C the hydroxyl band decreases linearly with the amount of piperidine adsorbed. The assumption of homogeneity of adsorption sites is not always fulfilled in the case of amines as discussed below.

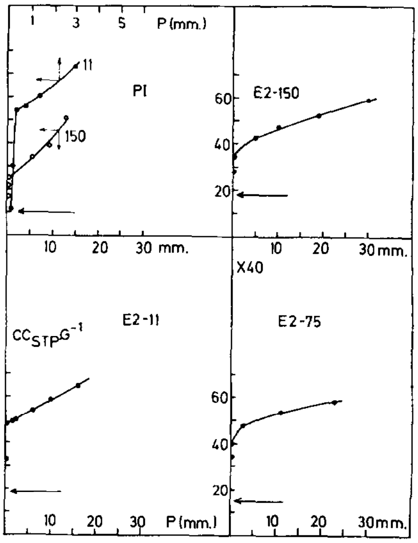

FIG. 1. Adsorption isotherms of different amines on X40.

In Table 1 the AI values are collected for different amines adsorbed at 11, at 75 and at 150°C (column a). The maximum amount of amine adsorbed is given in column b: these values correspond to the arrows on the isotherms. All the data in columns a and b are average values from at least three runs. At 11°C it is seen that all the AI values are lower than the value for NH_3 indicating that the reaction with the hydroxyls is not the only adsorption mechanism. Similar results were obtained

TABLE 1
ABSORPTION OF AMINES ON X40

Adsorbate	(a) Apparent integration intensity (AI; cm μmole^{-1}) of the HF hydroxyl band	(b) Max. amount of amine adsorbed in % of the OH content	(c) Apparent number of amine molecules adsorbed/disappearing OH group[a]	(d) % Dehydroxylation after amine adsorption[b]	(e) % Reversibility of deamination at 430°C	(f) Excess amine adsorbed/unit cell[c]
NH_3-11	5.28	—	1	—	—	—
E1-11	3.53 ± 0.03	32	1.50	3.0	96	17.0
E2-11	3.18 ± 0.04	45	1.66	8.5	90	22.0
E2-75	3.58 ± 0.04	36	1.67	15.0	90	23.0
E2-150	3.85 ± 0.03	43	1.37	25.0	78	13.0
E3-11	3.04 ± 0.03	53	1.74	19.0	83	25.2
IP-11	3.78 ± 0.04	80	1.39	30.0	75	13.3
B1-11	2.77 ± 0.03	36	1.91	25.0	80	31.0
B1-75	3.91 ± 0.04	25	1.35	30.0	80	12.0
B1-150	4.78 ± 0.05	27	1.11	35.0	70	4.0
PY-11	3.34 ± 0.03	50	1.58	—	90	20.0
PY-150	10.36 ± 0.08	45	0.51	—	—	—
PI-150	3.04 ± 0.02	24	1.74	—	95	25

[a] NH_3-11 is used as the reference system.

[b] After adsorption of the amount indicated in column (b).

[c] These values refer to the amount amine adsorbed above the amount needed for neutralization of the OH groups and are obtained by extrapolation to the point of complete neutralization.

at higher temperatures except for the adsorption of pyridine at 150°C. The apparent number of amine molecules adsorbed per OH group that has disappeared is listed in column c.

Apparently pyridine represents a special case. From pyridine adsorption experiments at 150°C Hughes and White (*7*) derived an integrated absorption coefficient 12.23 ± 0.9 cm μmole^{-1} for the HF band in HY. We found in similar conditions an AI value of 10.36 ± 0.08. The slight difference between these two values may be due to the different techniques for estimating the band intensity. This value implies also that the 1:1 stoichiometry is not realized in the reaction between hydroxyls and adsorbed pyridine, and that a side-reaction occurs which consumes hydroxyl groups. It was shown in Part I (*22*) that heating a pyridinium zeolite, even at 150°C, produced a decomposition of the pyridinium ions and a dehydroxylation together with an adsorption of pyridine at the dehydroxylated sites. These facts may explain the behavior of the X40 sample upon adsorption of pyridine at 150°C.

Spectra of the sample X40, loaded with different amounts of pyridine are shown in Fig. 2 (curves e, f, g and h). Pyridinium ions are characterized by typical bands around 1545 and 1635 cm^{-1}. Several authors (*7, 9, 10*) assigned bands at 1445 and 1595 cm^{-1} to pyridine coordinately bonded to residual Na$^+$ ions. Pyridine strongly held at dehydroxylated sites gives bands at 1445 (ν_{19b}) and at 1623 cm^{-1} (ν_{8a}).

In this work (Fig. 2, curves g and h) the bands typical for pyridinium are strong at 11°C, but there is also evidence for the presence of pyridine bonded to Na$^+$ ions with bands at 1445 and at 1590 cm^{-1}. The concentration of dehydroxylated sites is small, according to the weak intensity of the components at 1455 and 1620 cm^{-1}. At 150°C (curves e and f), there is still an appreciable amount of pyridinium formed: the amount of pyridine bonded to Na$^+$ ions

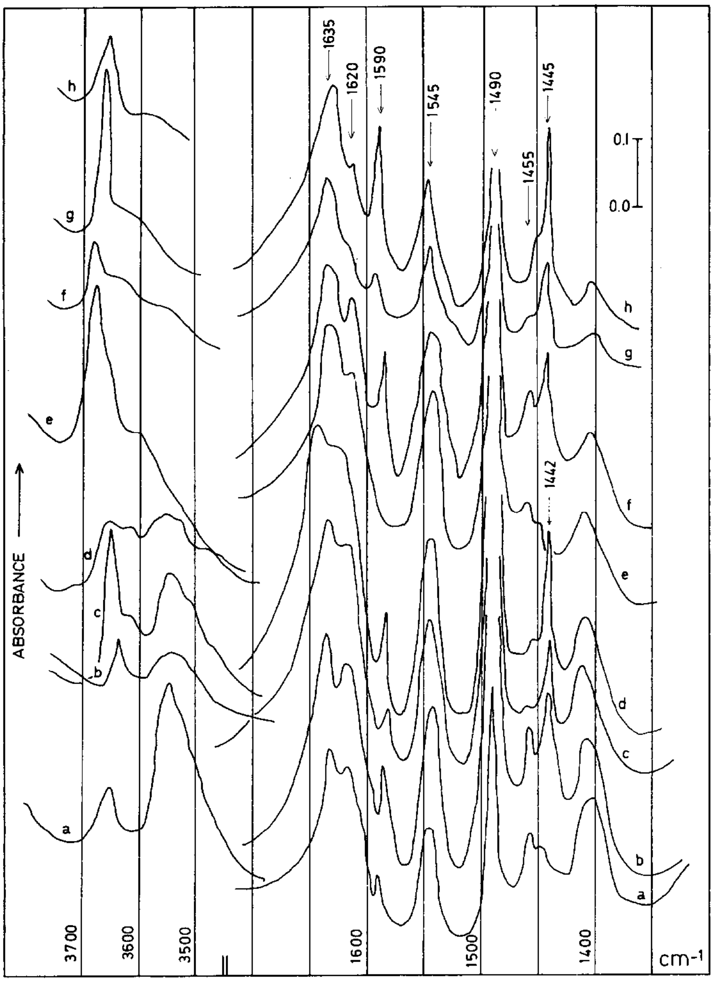

FIG. 2. Infrared spectra of pyridine adsorbed on X40 and Y70. (a, b) increasing amounts PY on Y70 at 150°C; (c, d) on Y70 at 11°C; (e, f) on X40 at 150°C; (g, h) on X40 at 11°C.

decreases in favor of the pyridine on dehydroxylated sites. The relatively important intensity of the 1455 cm^{-1} peak at 150°C illustrates the dehydroxylating action of the adsorbed pyridine. This is in complete agreement with the observations described previously (*22*). It explains the high AI value obtained with pyridine at 150°C, although the stoichiometry of the dehydroxylation mechanism cannot be derived from our results.

In Part I (*22*) it was described that the heat treatment of zeolites saturated with secondary and teritiary alkylammonium ions resulted also in a dehydroxylation. This was clearly confirmed in the present study by the observations made on pyridine adsorption, but the adsorption of other amines also resulted in a dehydroxylation. A quantitative estimation of the extent of dehydroxylation could be made at each stage of the adsorption. To do this the decrease of the hydroxyl band and the increase of the alkylammonium bands were transformed into concentration values using the appropriate absorption coefficients for νOH and ∂N^+H_x, respectively. The difference between these two values was made (Table 1d). The samples were then outgassed at 430°C and the intensity of the hydroxyl band was measured again to check the reversibility of the amine adsorption (Table 1e). The results are expressed in percentage of the initial OH concentration. Within the limits of accuracy the data of columns d and e add up to 100%. It is remarkable that the extent of dehydroxylation increases with the temperature, but even at room temperature dehydroxylation already occurs. Another observation, in contrast with previous data (*22*) is in fact that the dehydroxylation upon outgassing at 430°C is less pronounced compared to the experiments starting from the alkylammonium exchanged materials. Two explanations for this fact are possible: (i) the vacuum deammoniation of the initial X40 sample may have a stabilizing effect on the hydroxyl groups (*6*), and (ii) the amount of organic material is far less here than in the experiments with the alkylammonium zeolites. Also at variance with the previous data (*22*) is the dehydroxylating effect on butylamine adsorption.

The low values of the AI figures obtained with all the amines (except pyridine at 150°C) is ascribed to the adsorption of a large fraction of the amines at sites other than the hydroxyls. The amount of amine adsorbed physically above the amount needed for neutralization of the OH groups at each point can then be calculated (Table 1f). For some amines the correctness of these assumptions has been verified experimentally.

There is clear spectroscopic evidence for the presence of neutral amine molecules after each adsorption step. Indeed, for the primary amines there was a considerable broadening of the ∂NH_3^+ asymmetric vibration and a shoulder at the low frequency side of this band which was not present on the corresponding alkylammonium zeolites. This is probably the NH_2 scissoring of the neutral amine. In order to test this hypothesis, isopropylamine was adsorbed on a NaX and on a NaY zeolite at 11, 75 and 150°C. Amine was indeed adsorbed at these temperatures and the NH_2 scissoring was observed at a frequency which explains the broadening of the ∂NH_3^+ band mentioned above.

Residual Na ions and dehydroxylated spots can be considered to be probable adsorption sites for neutral amines. There is no experimental way to distinguish between the two possible types of coordinately bonded amines. In any case, the amount of adsorbed amines in excess over the alkylammonium ions exceeds the extent of dehydroxylation. Taking the data with pyridine as a comparison we believe that dehydroxylated places are the strongest sites and adsorb preferentially the amines, especially at high temperatures.

Sample Y70

The sample X40 was studied to detect separately the behavior of one type of hydroxyl, those involved in the HF band. In the thoroughly exchanged Y70 sample, after a flash pretreatment at high temperature, OH bands are well developed at 3650 and at 3550 cm^{-1} (respectively, HF and LF band). Flash heating results in practically stoichiometric HY samples: this was checked before each adsorption experiment by converting the peak intensity into OH concentration, and by comparing this concentration to the value expected on the basis of the chemical composition of the ammonium sample.

On adsorption of amines both OH bands decrease linearly with the amount of amine molecules adsorbed. The maximum amount of amines adsorbed in the infrared experiments is listed in Table 2a. This amount was such that no residual pressure of amine molecules build up in the infrared cell except for piperidine at room temperature as has been verified by adsorption isotherms.

The intensity of the ∂NH^+ bands has been compared to the intensity of the OH bands, after conversion into absolute concentrations using the appropriate absorption coefficients.

It is shown (Table 2b) that adsorption of amines provokes a dehydroxylation.

The partly saturated samples in the infrared experiment were then outgassed again at 450°C and the reversibility of the amine adsorption was controlled. The intensity of the OH bands (% of the original intensity) is given in Table 2c.

Columns b and c reveal that the subsequent deamination has not an important dehydroxylating effect if compared to the effect of the amine adsorption itself. These

TABLE 2
Adsorption of Amines on Y70

Adsorbate	(a) OH protonated (%) after the last adsorption step	(b) Dehydroxylation after amine adsorption[a]	(c) % Reversibility of deamination (450°C)		(d) k_2: apparent integr. intensities for LF band (cm μmole^{-1})
			Total OH	Ratio C_{HF}/C_{LF}	
NH_3-11	—	—	—	—	9.5
E1-11	41	11.0	84.3	1.02	1.31
E2-11	45	12.0	89.5	0.90	0.80
E2-75	67	17.0	83.5	1.17	1.09
E2-150	52	33.5	65.0	1.17	1.45
E3-11	49	9.0	89.5	0.99	$N_2 = 0$
IP-11	42	8.0	90.3	1.03	1.03
B1-11	32	14.0	85.0	0.93	1.10
B1-75	60	15.0	75.4	1.15	0.74
B1-150	25	23.0	71.5	1.14	0.56
PY-11	51	18.0	85.0	0.89	1.67
PY-150	45	—	50.0	0.82	0.83
PI-150	33	—	65.0	0.86	3.5

[a] After adsorption of the amount indicated in column a.

data also reveal that the dehydroxylating action of the amines increases with the adsorption temperature. The dehydroxylation was most pronounced for pyridine at 150°C (PY-150). The dehydroxylating effect of the pyridine can also be deduced from the spectra in Fig. 2 curves a, b, c, d. The intensity of the band at 1455 cm^{-1} typical for Lewis bonded pyridine on dehydroxylated sites, is indeed more important after adsorption at 150°C (curves a and b) than at 11°C (curves c and d). Some pyridine is hydrogen bonded to the LF band and gives a band at 1442 cm^{-1}: this component also is more intense at room temperature than at 150°C.

Computation of the reactivity of both kind of hydroxyls towards the amines must take into account that the hydroxyls do not have the same absorption coefficient, and that there may be a selective reactivity of the amines for one type of hydroxyl. Such selectivity can be deduced from Fig. 3 where the intensity of the LF band is plotted as a function of the total amount of adsorbed amines. The slope of this line depends on the affinity of the amines for the LF hydroxyls.

The relation between the decrease in intensity of the bands and the amount of amine adsorbed leads to the following set of equations in the case of samples with two OH bands like in Y70:

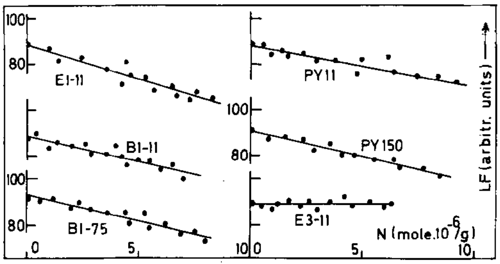

Fig. 3. Decrease of the LF band intensity against the total amount amine adsorbed (arbitrary units).

$$\Delta A_1 = k_1 N_1$$

$$\Delta A_2 = k_2 N_2$$

$$N_1 + N_2 = N$$

ΔA_1 and ΔA_2 are the decrease of HF and LF bands, respectively, while k_1 and k_2 are the corresponding apparent integrated intensity values. N_1 and N_2 are the amounts of amine adsorbed on the OH groups of the HF and of the LF bands per unit area of the sample. At each adsorption step N, ΔA_1 and ΔA_2 are measured. To solve the three equations with 4 unknowns a supplementary assumption must be made.

If it is assumed that the OH groups of the HF band react 1:1 with the adsorbed amines, both in X40 and in Y70, and that the hydroxyl concentration can be calculated with the AI coefficient determined with NH_3, k_2 can be calculated. The values are listed in Table 2d. The fact that for (E3-11), N_2 was found equal to zero is a support for the validity of the assumptions since E3 does not adsorb on the LF hydroxyls. For reasons explained in earlier paragraphs the AI values of Table 1a, obtained by adsorption of amines on X40, cannot be used in this calculation.

The values obtained in this way are indicated as k_2: they are not real adsorption coefficients since the amines adsorbed on dehydroxylated sites were not taken into account separately. In any case k_2 is a measure of the reactivity of the LF hydroxyls with amines.

The ratio of the band areas of the LF and HF bands was followed as a function of the amount of amine adsorbed. Some examples are given in Fig. 4. For IP-11, B1-11, E2-150, E2-75, PY-11 straight-line relations were observed. For E2-11, PY-150 and P1-150 the relations are of a higher degree. When the hydroxyls of the HF band react selectively with the amines adsorbed the ratio LF/HF increases. This ratio decreases when the hydroxyls of the LF band react faster than the hydroxyls of the HF band. In order to give a quantitative relationship to this selectivity we calculated for each amine the coefficient of the experimental relation:

$$\frac{C_2}{C_1} = k'N + b$$

In this relation C_2 and C_1 are the concentrations of the OH groups of LF and HF bands. The k' values are listed in Table 3. For the nonlinear curves two tangent lines were drawn at the curves. The slope of these two lines is also given in Table 3.

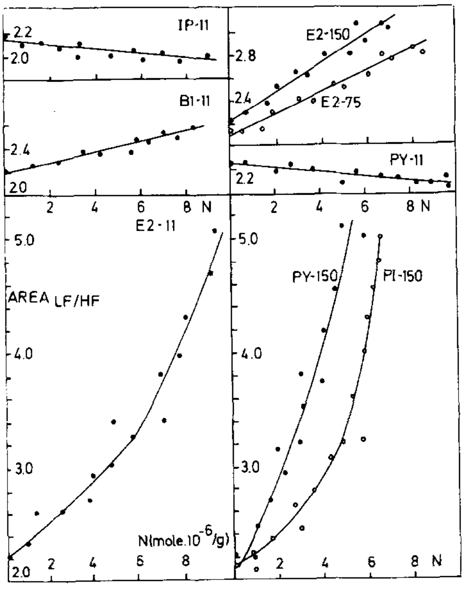

FIG. 4. Ratio of the areas of LF and HF bands against the amount of amine adsorbed.

TABLE 3

ESTIMATE OF THE SELECTIVITY OF ADSORPTION ON HF OR LF HYDROXYLS

Adsorbate	k'	Interpretation
NH_3-11	−0.12	More or less selective adsorption on LF
E1-11	−0.06	
IP-11	−0.03	
PY-11	−0.03	
B1-11	0.06	More or less selective adsorption on HF
B1-150	0.03	
E2-75	0.14	
E2-150	0.20	
E2-11	2.39–7.09	Selective adsorption on HF
E3-11	4.24–13.76	
Pip-150	3.03–20.00	
PY-150	5.71–10.18	

OH Frequency Shift

The OH bands of the residual hydroxyls shifted to higher wavenumbers when amines were adsorbed. The shifts could be expressed by an empirical equation $\nu = fN + b$ for the bands of X40 and of Y70. The shift is generally more pronounced for the LF than for the HF band. The slopes (f) and intercepts (b) are tabulated in Table 4.

DISCUSSION

Adsorption Mechanism

Amines can be adsorbed on the hydrogen zeolites X and Y by interaction with the hydroxyl groups, by adsorption on dehy-

TABLE 4

PARAMETERS OF THE EQUATION $\nu = fN + b$, EXPRESSING THE SHIFT OF THE HYDROXYL BANDS INDUCED BY THE ADSORPTION OF AMINES

	Y70				X40	
	HF hydroxyls		LF hydroxyls		HF hydroxyls	
Adsorbate	f	$b_{\mathrm{cm}^{-1}}$	f	$b_{\mathrm{cm}^{-1}}$	f	$b_{\mathrm{cm}^{-1}}$
E1-11	0.86	3650	0.87	3545	1.36	3665
E2-11	1.24	3650	1.34	3542	1.88	3665
E2-75	1.14	3650	1.18	3544	1.74	3663
E2-150	0.82	3650	1.09	3543	1.60	3664
E3-11	1.90	3650	1.75	3543	2.40	3665
IP-11	0.70	3650	0.74	3545	1.44	3665
B1-11	0.40	3650	0.88	3543	1.42	3664
B1-75	0.16	3650	0.77	3544	1.25	3663
B1-150	0.10	3649	0.50	3545	1.03	3664

droxylated sites, and by coordination to the residual Na^+ ions.

The decrease of the integrated absorbance of the hydroxyl bands upon the adsorption of amines cannot be used to determine the apparent integrated intensity (AI) of the OH bands. The deviation of the apparent integrated intensity (Table 1a) from the standard value 5.28 cm μmole^{-1} obtained with ammonia, is a measure of the contribution of the other reaction paths.

Coordination of the amines to the Na^+ ions is most important for the X40 sample which is discussed first. Following the newest XR data (*14*) about the distribution of the exchangeable ions, we estimated that 27 Na^+ ions/unit cell are located in the large cages at sites II. In the X40 sample the amine adsorption on Na^+ ions is more important than the dehydroxylation (Table 1d, f). In several cases the amount of amine coordinately bonded to sodium ions tends to the value of 1 amine molecule/Na^+ ion on site II. This was especially true for the adsorptions at room temperature.

In the adsorptions at higher temperature the apparent integrated intensities tend to increase. This effect can be due partly to dehydroxylation, but it is also influenced by a decrease of the amount of amine coordinately bonded to Na ions. The AI is still lower than the value obtained with NH_3. Only for pyridine at 150°C is the AI value (10.36) much higher than the standard value (5.28). This value is comparable with that of 12.23 published by Hughes and White (*7*). The very high value can only be explained by a considerable dehydroxylation. The comparison with the other amines brings us to the conclusion that pyridine molecules must play an active role in the dehydroxylation.

In the Y70 sample the coordination of amines to Na^+ ions must not be considered since no considerable amount of Na^+ ions is left in the large cavities. Physical adsorption, adsorption on hydroxylated sites, and a 1:1 reaction with hydroxyls of HF and LF band are the only reactions to be considered. As explained in the Results section, the contribution of the HF hydroxyls is calculated by making use of the AI of 5.28 cm μmole^{-1}. Then the absorption coefficients of the LF band can be calculated. These k_2 values are only apparent values and not real and absolute absorption coefficients since all the side-effects are incorporated in this value. Only with PI at 150°C is the value obtained equal to the one derived by NH_3 adsorption (3.5 cm μmole^{-1}). This proves that the very strong base piperidine reacts with the hydroxyls much more quantitatively than the other amines. Nevertheless, the value 3.5 cm μmole^{-1} results not only from the reaction between PI and hydroxyls, but also from a dehydroxylation, and cannot be immediately compared to the values obtained with NH_3.

The low k_2 values obtained with the other amines indicate that amine molecules are adsorbed which are not protonated, although there is no direct evidence for high amounts of this species in the NH deformation zone of the spectra. Adsorption on the dehydroxylated sites only is not sufficient to explain the low k_2 values and we must postulate the presence of physically adsorbed amines not reacting with the LF hydroxyls.

An important part of the LF type of hydroxyls is at sites inside the small cavities not immediately accessible to the amine molecules (*7, 8, 10, 11, 15, 16*). In agreement with Hughes and White (*7*), we believe that the protons are mobile and can in this way react with amines. It results from our data that the reactivity of the LF hydroxyls is not sufficient to ensure a complete reaction. In this way the k_2 values are a measure of the extent to which the protonation reaction of the following equation is shifted to the right:

$$\text{R-NH}_2 + \text{zeol.-OH} \rightleftharpoons \text{RNH}_3^+\ \bar{\text{O}}\text{-zeol.}$$

Therefore we tested on k_2 the relation used by Clotman and Zeegers-Huyskens (*17*) for the association between amines and alcohols:

$$k'_2 = a\Sigma\sigma^* + b\Sigma E_S + c.$$

$\Sigma\sigma^*$ and ΣE_S represent the polar and steric effects of the substituting organic groups. For our set of primary amines adsorbed at 11°C the constants could be evaluated and the relation becomes:

$$k_2 = 1.018\Sigma\sigma^* + 0.446\Sigma E_S - 0.675.$$

The electron donor properties of the alkyl-groups seem to be more important than the steric effects. This is not unexpected since we can assume the aliphatic chain to be orientated more or less perpendicular to the walls of the cages.

In Figure 5 some k_2 values are plotted as a function of $\Sigma\sigma^*$ and of ΣE_S. We have only a limited number of points for which identical experimental conditions make a valid comparison possible. Nevertheless we see that for the primary amines the polar effect is more important than for E2. The steric effect would dominate for secondary and tertiary amines: E3 shows indeed no reaction with the LF hydroxyls.

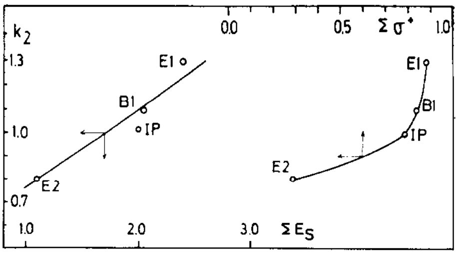

FIG. 5. Reactivity of the LF band (k_2) against the polar and steric effects of the substituting groups on the amine molecules.

The change of the LF/HF ratio as a function of the amount of amines adsorbed shown in Fig. 4 and also expressed in Table 3, indicates that at room temperature, for many of the amines adsorbed, there is not a strongly pronounced selectivity for the HF or LF hydroxyls. At higher temperatures the selectivity generally increases in favor of the more accessible HF groups.

For PY (Fig. 2) an important band at 1442 cm^{-1} develops as the HF band has disappeared and the LF starts to decrease. This band has always been assigned to hydrogen-bonded pyridine (*6, 8, 9, 17*). At 150°C this species is not stable, since outgassing at this temperature restores a great deal of the intensity of the LF band (*7*)

Frequency Shifts

Adsorption of inert gases is known to shift the HF band to lower frequencies (*16, 18*). This was explained in terms of an increase of the electrostatic field operating on the vibrating hydroxyls by the reaction field of the polarizable hydroxyls. This treatment is valid for an unlocalized adsorption, but cannot be applied to explain the frequency shift upwards observed in this work.

When amines are adsorbed, they are localized at specific spots as RNH_3^+ ions, or coordinated to cations, and they are not immediately influencing the unreacted hydroxyls. It can be expected that they screen the influence of the residual Na^+ ions, or of that part of the hydroxyls with which they reacted. This screening could reduce the resultant field which influences the frequency of the remaining hydroxyls. Such a reduction of the field could explain the small frequency shift upwards, which was found to be proportional to the amount of amines adsorbed.

A similar conclusion was put forward by Venuto and Landis (*19*), Hansford and Ward (*20*) and Ward (*21*) in a discussion of the possible influence of Brønsted acidity, Lewis acidity and electric fields upon the catalytic activity of the synthetic zeolites. They stated that it is doubtful that, under reaction conditions, strong electrostatic fields exist in the zeolites, since adsorption of water preferentially on the cations would decrease the field by dielectric screening.

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