Sorption Properties of $Na_xH_{1-x}Y$ Zeolites

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Generation of structural OH groups in a series of zeolites $Na_xH_{1-x}Y$ and their effects on the·adsorption energy of molecules sorbing in a nonspecific way (CH_4, C_2H_6, C_3H_8) and in a specific way (CO, C_2H_4) were studied.

Dependence of the heat of adsorption on the degree of decationization of the zeolite for molecules showing a specific sorption is explained by a decrease of the number of Na^+ ions in large zeolite cavities and on the basis of the properties of the OH groups characterized by an absorption band at 3640 cm^{-1}.

INTRODUCTION

Properties of structurally bound OH groups in zeolite Y are of interest since they are associated with the catalytic action (*1*) in a number of reactions. Similarly to cations of univalent and bivalent metals the location of protons in the zeolite lattice plays an important role (*2–12*). It is known from the literature that different types of structural OH groups are revealed by the infrared spectrum; they are unaffected during the sorption of molecules with various electron structures (*6–12*). It is supposed that the different behavior of the absorption bands at 3640 cm^{-1}(HF) and 3550 cm^{-1}(LF) is caused by the proton location on various oxygen ions of the type O_1–O_4 which is in connection with different accessibility of OH groups for the absorbed molecules. X-ray structural analysis is not yet able to locate protons with respect to certain crystallographic types of oxygen ions (*13,14*).

Since the protons interact with oxygen in the lattice and produce only a weakly polarized covalent bond one can expect that the replacing of Na^+ ions by protons will markedly change the electrostatic field in the cavities of the zeolite. This change can strongly affect the adsorption heat of molecules with electrostatic moments. However, Neddenriep (*15*) who followed chromatographic adsorption heats of a number of compounds on decationized zeolites Na_xH_{1-x}-Y found no remarkable changes. The exchange of Na^+ ions by K^+ ions involved a remarkable change of the adsorption heat (*16*). Similarly it was reported (*17*) that the adsorption heat of CO was significantly higher on CaY, and that on NH_4Y a strong adsorption did not develop unless the NH_4Y was heated to above 500°C.

This work tries to correlate spectral data of structural OH groups with adsorption heats of model adsorbates on a series of zeolites $Na_xH_{1-x}[AlSi_{2.5}O_7]$.

METHODS

Zeolite samples with varying contents of ammonium ions were prepared by ion exchange from NH_4NO_3 solution at 80°C.

The original zeolite was synthesized in our laboratory and its composition was established by a complete chemical analysis. Formulas for an average elementary cell and sorption capacities are presented in Table 1 and Fig. 1, respectively.

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TABLE I
ANALYSIS AND COMPOSITION OF ZEOLITE Y SAMPLES

Sample (abbr. formula)	Analysis	Composition of idealized elementary cell
Na-Y	$0.96Na_2O \cdot 0.041CaO \cdot Al_2O_3 \cdot 5.04SiO_2$	$Na_{52.8}Ca(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.88}H_{0.12}$-Y	$0.88Na_2O \cdot 0.039CaO \cdot 0.079(NH_4)_2O \cdot Al_2O_3 \cdot 5.07SiO_2$	$Na_{48.4}Ca(NH_4)_{4.3}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.81}H_{0.19}$-Y	$0.81Na_2O \cdot 0.035CaO \cdot 0.12(NH_4)_2O \cdot Al_2O_3 \cdot 4.92SiO_2$	$Na_{44.5}Ca(NH_4)_{6.6}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.71}H_{0.29}$-Y	$0.71Na_2O \cdot 0.033CaO \cdot 0.25(NH_4)_2O \cdot Al_2O_3 \cdot 4.95SiO_2$	$Na_{39.0}Ca(NH_4)_{13.7}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.61}H_{0.39}$-Y	$0.61Na_2O \cdot 0.028CaO \cdot 0.36(NH_4)_2O \cdot Al_2O_3 \cdot 4.96SiO_2$	$Na_{33.2}Ca(NH_4)_{19.8}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.54}H_{0.46}$-Y	$0.54Na_2O \cdot 0.039CaO \cdot 0.48(NH_4)_2O \cdot Al_2O_3 \cdot 4.82SiO_2$	$Na_{29.7}Ca(NH_4)_{26.4}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.43}H_{0.57}$-Y	$0.43Na_2O \cdot 0.021CaO \cdot 0.57(NH_4)_2O \cdot Al_2O_3 \cdot 4.97SiO_2$	$Na_{23.6}Ca(NH_4)_{31.3}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.30}H_{0.70}$-Y	$0.29Na_2O \cdot 0.033CaO \cdot 0.72(NH_4)_2O \cdot Al_2O_3 \cdot 4.95SiO_2$	$Na_{16.4}Ca(NH_4)_{39.6}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.13}H_{0.87}$-Y	$0.13Na_2O \cdot 0.36CaO \cdot 0.88(NH_4)_2O \cdot Al_2O_3 \cdot 4.92SiO_2$	$Na_{7.1}Ca(NH_4)_{48.4}(AlO_2)_{55}(SiO_2)_{137}$
$Na_{0.01}H_{0.99}$-Y	$0.012Na_2O \cdot 0.035CaO \cdot 1.01(NH_4)_2O \cdot Al_2O_3 \cdot 4.95SiO_2$	$Na_{0.6}Ca(NH_4)_{55.5}(AlO_2)_{55}(SiO_2)_{137}$

The infrared spectra were scanned on samples which were pressed at a pressure up to 1000 kg/cm² so as to obtain transparent plates of thickness about 8 to 14 mg/cm². The samples were evacuated and thermally decomposed in an apparatus described previously (*18*). The spectra were measured on a Perkin-Elmer 621 spectrometer by a standard program with the double slit. The resolution in the region of 4000 to 3000 cm⁻¹ amounted to ± 3 cm⁻¹.

The chromatographic measurements were carried out on a CHROM 2 instrument with a flame-ionization detector and on a device with a catharometer. Glass columns, 60 cm long and 3.5 mm in internal diameter, were used for all the

FIG. 1. Sorption capacities (argon, −195°C) of $Na_xH_{1-x}Y$ zeolites: (O) powdered zeolites calcined at 350°C overnight; (●) pelleted zeolites calcined at 350°C overnight; (X) rehydrated pellets, then dehydrated at 350°C overnight.

samples. Zeolite pellets were prepared at a pressure of 500 kg/cm² without binder. The zeolite was activated in the column by stepwise increasing of the temperature in a stream of dried He. Completion of the ammonium form decomposition was indicated by use of Nessler reagent. The sample dehydration at 25–150°C took 4 hr, the ammonium ion decomposition was performed for 4–184 hr (according to the zeolite composition) at 150–200°C, and for 4 hr at 350°C.

Helium dried at liquid N₂ temperature was used as the carrier gas. Prior to starting with the experiment itself, optimum working conditions, i.e., temperature interval and linear velocity of the carrier gas, were verified for every adsorbate. The value of the optimum linear velocity was found to be close to those corresponding to the minimum of the van Deemter curve. In the chosen region the measurements were carried out at four to five temperatures, each measurement being repeated four times. The free volume of the column was determined from the retention volume of H₂ at $T = 140°C$. The value of the isosteric heat of adsorption was determined from the slope of the dependence of $\log V_{cor}$ on the reciprocal value of the absolute temperature according to Green and Pust (*19*), by
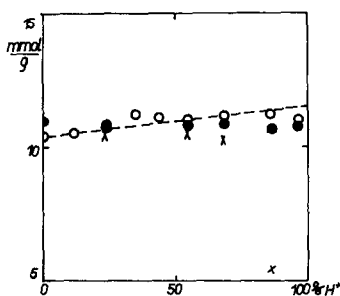
calculation from the linear regression. The isosteric heat value was determined with a standard deviation of about ±5%.

The X-ray diffraction of the powdered zeolites was recorded on a diffractograph (Chirana).

The sorption capacity measurements were performed with argon at −195°C on a quartz spring balance and the saturation of the zeolite was determined from the limiting part of the adsorption isotherm.

RESULTS

The spectrum of structural OH groups of our zeolites $Na_xH_{1-x}Y$ decomposed *in vacuo* at 350°C shows three basic absorption bands which correspond well to data from the literature (6–12). (a) a band at 3740 cm⁻¹, the intensity of which is weak and independent of the composition of the zeolite; (b) a so-called high frequency (HF) band at 3640 cm⁻¹ which is narrow and symmetrical; and (c) a low frequency (LF) band at 3550 cm⁻¹ which is wide and nonsymmetrical. Ammonium forms of zeolites were decomposed *in vacuo* at about 10^{-5} Torr with continuous increasing of the temperature up to 350°C for 4 hr. The final vacuum after the decomposition was about 10^{-6} Torr. The complete decomposition of the ammonium form was achieved under these conditions with production of a maximum number of structural OH groups. Figure 2 shows the dependences of the HF and LF band intensities on the degree of decationization. For a comparison of different samples, intensities of HF and LF bands were expressed as absorbances at the band maximum corrected to the base line, related to 1 mg/cm² thickness of the sample.

It is obvious that the HF band intensity rapidly increases with increasing decationization to almost 70% decationization when it achieves its maximum value. By contrast to the HF band, the LF band is weak at low degrees of exchange but becomes progressively stronger at higher de-
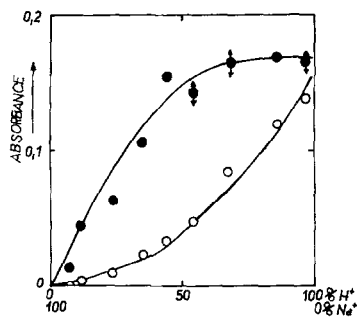

FIG. 2. Intensities of the HF band (3640 cm⁻¹) and LF band (3550 cm⁻¹) of $Na_xH_{1-x}Y$ zeolites (350°C, 4 hr *in vacuo*) in dependence on the degree of decationization. (●) HF band, (○) LF band.

grees of exchange. Individual points in the graph were obtained as average values from about 5 independent measurements for the zeolite of a given composition.

In an independent experiment it was found that pellets of the zeolites prepared without binder at a pressure of 1000 atm show the same spectra of free OH groups after the decomposition as zeolites which were not pelleted. It demonstrates that the process of pelletizing itself exhibits no effect on the character of the spectrum.

The spectra of the series of $Na_xH_{1-x}Y$ pelleted zeolites from the chromatographic columns are plotted in Fig. 3. As follows from a comparison with the spectra of the corresponding samples decomposed *in vacuo* the differences between the spectra increase with increasing degree of decationization. Furthermore, one can see that in the case of samples with a high NH_4^+ cation content in the original material, the intensity of the band at 3740 cm⁻¹ increases. The intensity of the HF band decreases and a new band occurs at 3670 cm⁻¹. The intensity of the LF band is also reduced and its nonsymmetrical shape is changed, probably as a result of forming further absorption bands.

In further experiments the stability of the structure of $Na_xH_{1-x}Y$ zeolites was tested. The sorption capacities are plotted in Fig. 1 for the series of: (a) original powdered zeolites after thermal decomposition
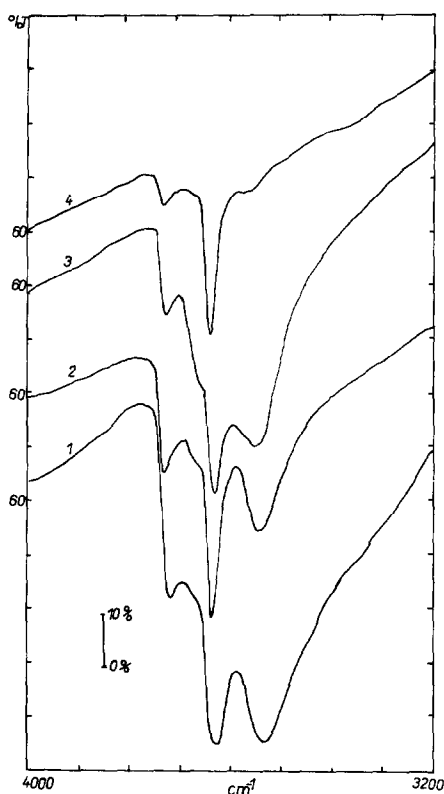
FIG. 3. Hydroxyl stretching region of $Na_xH_{1-x}Y$ zeolite, calcined at 350°C in a stream of He, then hydrated at 25°C and dehydrated at 350°C 4 hr *in vacuo*: (1) $Na_{0.13}H_{0.87}Y$, (2) $Na_{0.03}H_{0.07}Y$, (3) $Na_{0.43}H_{0.57}Y$, (4) $Na_{0.71}H_{0.29}Y$.

at 350°C *in vacuo* (overnight); (b) zeolites pelleted with 500 atm pressure without binder and then decomposed as in (a); (c) zeolites which were again hydrated and dehydrated *in vacuo* at 350°C after the treatment described in (b). The sorption capacites of both the powdered and the pelleted zeolites are preserved and they increase according to the theoretical dependence (broken line) expected from the change of the molecular weight of the zeolite. However, in the case of rehydration and desorption of H_2O at 350°C, the sorption capacities decrease. The samples are becoming amorphous ("amorphization"), as has been proved for these samples by X-ray diffraction. Marked changes are ob-

served in the spectra of OH groups in Fig. 4. The spectrum of the original HY zeolite (curve 1) changes after hydration (25°C) and the dehydration process (350°C), as follows from curve 2. The increase of the 3740 cm^{-1} band and changes in the form of HF and LF bands are remarkable. The repeated hydration dehydration process is followed by further changes in the spectrum (curve 4), as well as by further amorphization.

As mentioned above, the spectra of the zeolites from the chromatographic columns are presented in Fig. 3. It must be pointed out that these spectra correspond
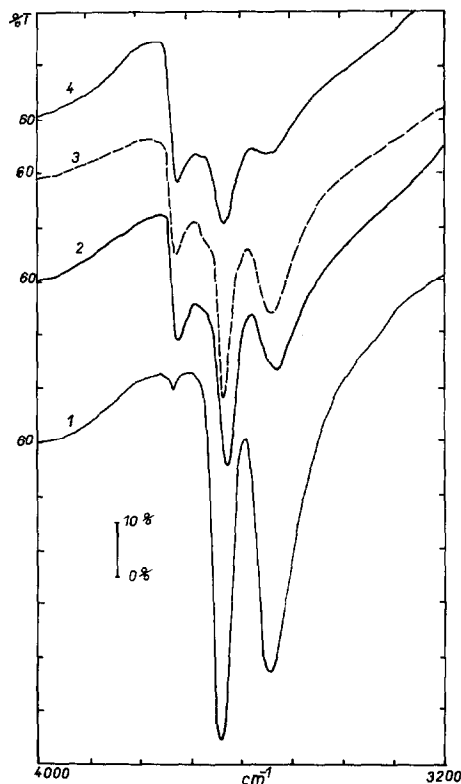
FIG. 4. Hydroxyl stretching region of $Na_{0.03}H_{0.70}Y$ zeolites: (1) calcined at 350°C, 4 hr *in vacuo*; (2) calcined as in (1) then rehydrated at 25°C overnight and dehydrated at 350°C 4 hr *in vacuo*; (3) zeolite of the same composition from the chromatographic column, dehydrated at 350°C, 4 hr *in vacuo*; (4) calcined at 350°C, 4 hr *in vacuo*, then hydrated–dehydrated and the hydration–dehydration cycle repeated.

to the samples which were rehydrated in the HY form during the preparation of transparent plates for ir measurements, and dehydrated *in vacuo* at 350°C. Comparing in Fig. 4 the spectrum of the zeolite treated with hydration–dehydration (curve 2) with the spectrum (curve 3) of the corresponding zeolite from the chromatographic column we find them very similar. This means that the hydration-dehydration process was manifested in the same manner in the two zeolites prepared in different ways. This fact enables us to suppose that the original zeolites used in the chromatographic column for the determination of the heats of adsorption were very similar to those prepared by thermal decomposition *in vacuo*.

One can gain important information about the effect of cations and structural OH groups of zeolites by studying adsorption heats of molecules of gases and vapors with different electron structures. In the present work CH_4, C_2H_6 and C_3H_8 have been studied as molecules which cannot react in a specific way with possible adsorption sites of the zeolite, and CO, C_2H_4 have been studied as molecules capable of specific interaction. Chromatographic heats of adsorption and their standard deviations obtained on a series of samples of a general formula $Na_xH_{1-x}Y$ are plotted in Table 2. The two groups of adsorbates differ qualitatively in their dependences of ΔH on the zeolite composition. Whereas for molecules with nonspecific interaction no significant change of the adsorption heat was observed, in the case of molecules exhibiting specific interaction a significant decrease of the value of the heat of adsorption was found on increasing the decationization.

DISCUSSION

The properties of our synthesized zeolites $Na_xH_{1-x}Y$ are essentially identical with those described in the literature (6–12,20,21,24–27).

The experiments dealing with generation of structural OH groups by thermal decomposition *in vacuo* indicated that on increasing the degree of decationization it is predominantly HF band OH groups which are formed. This band grows in its intensity more rapidly than the nonsymmetrical LF band (Fig. 2). This result agrees qualitatively with observations by Ward (26) and Jacobs and Uytterhoeven (12) who consider this fact to result from the proton location on bridge oxygen O_1. The growth of the intensity of the HF band observed in the present work is moderated with increasing degree of decationization, and approaches a constant limit value from about 70% ion exchange. In the two abovementioned works an almost linear increase of the 3640 cm^{-1} HF band intensity was observed.

This discrepancy seems to be connected with different conditions of the thermal treatment of zeolites [350°C in our work and 450°C by Ward (26)]; the process of partial dehydroxylation was observed by Uytterhoeven, Christner and Hall (6) at temperatures above 385°C. The tendency of the HF band intensity to a constant value at higher degree of decationization was not caused by incomplete decomposition of the NH$_4$Y form. This was proved by Nessler reagent tests and by the fact that no bands of ν_{N-H} vibrations were detectable in the ir spectrum of HY zeolites, even at the highest degree of decationization. Nevertheless it has to be borne in mind that the ir measurements presented in the abovementioned studies as well as in our work have been performed in a region of band intensities unsuitable for exact quantitative analysis.

The wide band at 3550 cm^{-1} grows slowly in its intensity in the region of low degree of ion exchange and more rapidly at higher degrees in agreement with the previous work. Uytterhoeven (12) has shown in a detailed analysis of the LF band structure that this band consists of several

bands which correspond to protons bound in different ways in the zeolite lattice. These authors also consider the possibility of a complex structure for the LF band which is given not only by the proton location on oxygen atoms (O_2–O_4) but also by the coupling of vibrations of OH groups caused by mutual interactions. With respect to the insensitivity of all the components of the LF band to the molecular sorption, many authors tend to assume that protons concerned are situated in the cubo-octahedra and are not accessible to large molecules (8–12). The HF band is very sensitive to the sorption of molecules and Ward (26) demonstrated that it arises from the vibrations of protons formed by decomposition of NH_4^+ cations in large cavities.

As mentioned in the experimental part, all the HY zeolites prepared by thermal decomposition of ammonium form are sensitive to water vapor. For the discussion of the chromatographic heats of model adsorbates it has been necessary to inquire whether it is possible to compare the properties of zeolites prepared *in vacuo* with those prepared in chromatographic columns in a stream of dried helium. It has been established that the properties of HY zeolites are significantly influenced by the conditions prevailing during the thermal decomposition of the ammonium form (22,23). Various products are obtained and designated as "shallow bed," "deep bed" (33–37) or "ultrastable zeolites" (34,35). The method of thermal decomposition of ammonium zeolites used in this work reduced the influence of water vapor and NH_3 at higher temperatures. We conclude on the basis of the determined properties of the zeolites prepared in this way (preserved crystallinity, sorption capacity and identical sensitivity to the first cycle of hydration–dehydration) that the zeolites in the chromatographic columns were similar to "shallow bed" zeolites.

Hydroxyl groups are possible adsorption

sites for specific interactions of molecules with a suitable electron structure. When only those OH groups represented by the HF band are accessible to the adsorbed molecules, then one can assume that the resulting adsorption heat of molecules capable of specific interactions will follow the continuous growth of the OH group concentration in the zeolite cavities. Naturally, in the zeolite there are also adsorption sites in the form of residual Na^+ cations and other sites on the surface of the anionic zeolite structure formed mostly by the large oxygen ions. It is obvious that after the replacing of Na^+ ions by protons, the contribution of the specific interaction will be lower. In the case of an intact zeolite lattice it is possible to show (29) that adsorption sites formed by oxygen anions are less advantageous from the energetical standpoint than cationic sites for molecules with quadrupole and dipole moments.

The adsorption heats of CH_4, C_2H_6 and C_3H_8 do not vary with zeolite composition. The average adsorption heats for these molecules calculated from the data presented in Table 2 are 4.14 kcal/mol for CH_4, 6.00 kcal/mol for C_2H_6, and 7.92 kcal/mol for C_3H_8. This result is easy to understand as the most significant component of the adsorption potential of these molecules is given by dispersion forces which are not essentially changed with the number of Na^+ cations. This phenomenon we can understand by supposing the non-cationic adsorption sites to be more advantageous for these molecules. The electrostatic component which is in these molecules manifested just as a change of their polarization energy adds probably no significant contribution to the adsorption energy and thus, within the range of the measurement precision, the adsorption heat exhibits almost constant values. The adsorption heats on NaY as well as on all the zeolites $Na_xH_{1-x}Y$ can be listed as follows in order of increasing values: CH_4 <

TABLE 2

HEATS OF ADSORPTION (kcal/mole) AS A FUNCTION OF DEGREE OF DECATIONIZATION

Ad-sorbates	Degree of decationization of zeolite (mol%)									
	0	12	19	29	39	46	57	70	87	99
CH$_4$	4.33 ± 0.14	4.10 ± 0.20	4.39 ± 0.11	4.30 ± 0.04	4.12 ± 0.10	4.05 ± 0.05	4.11 ± 0.16	4.17 ± 0.11	3.75 ± 0.08	4.12 ± 0.17
C$_2$H$_6$	6.16 ± 0.35	5.92 ± 0.21	6.17 ± 0.21	6.14 ± 0.25	5.72 ± 0.18	5.78 ± 0.14	5.77 ± 0.16	6.33 ± 0.35	6.20 ± 0.26	5.69 ± 0.15
C$_3$H$_8$	8.12 ± 0.30	8.03 ± 0.30	8.15 ± 0.27	8.11 ± 0.25	7.84 ± 0.29	7.95 ± 0.21	7.44 ± 0.28	8.08 ± 0.20	7.92 ± 0.14	7.60 ± 0.32
CO	5.79 ± 0.13	5.71 ± 0.25	5.47 ± 0.23	5.66 ± 0.12	4.92 ± 0.11	4.84 ± 0.17	5.19 ± 0.20	5.26 ± 0.18	4.85 ± 0.20	4.76 ± 0.10
C$_2$H$_4$	11.26 ± 0.37	10.05 ± 0.24	9.64 ± 0.22	9.33 ± 0.24	9.03 ± 0.18	9.11 ± 0.21	9.29 ± 0.25	9.50 ± 0.21	9.15 ± 0.12	8.87 ± 0.27

$C_2H_6 < C_3H_8$, with a constant increment $\Delta H = 1.9 \pm 0.1$ kcal/mol per one CH_2 group for hydrocarbons in agreement with published data (28,30–32).

The specifically sorbing CO and C_2H_4 molecules exhibit a statistically significant decrease of adsorption heats with increasing degree of decationization. In the case of CO the scatter of experimental heats does not allow us to determine the form of the decreasing function (linear or parabolic). The plotted differences of adsorption heats of molecules with similar nonspecific parts for the adsorption energy on zeolites Na_xH_{1-x}-Y in Fig. 5 indicate the existence of a contribution from a specific part of the interaction. This specific interaction may
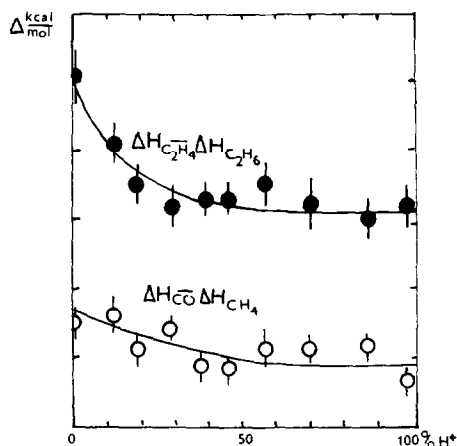

FIG. 5. Differences between the adsorption heats of molecules with a similar nonspecific part of the adsorption energy as a function of the composition of the adsorbent $Na_xH_{1-x}Y$ zeolite.

be understood in the electrostatic approximation as a contribution of the electrostatic interaction of the quadrupole moments of CO and C_2H_4 as well as of the dipole moment of the CO molecule. This specific part of the interaction is in general attenuated with the change of the composition of the zeolite. This trend, presented in Fig. 5, may be explained if Na^+ cations disappear from their positions in large cavities and are replaced by protons. At higher decationization degrees OH groups of the LF band are already formed which are probably oriented to the inside of the faujasite structure replacing cations at the sites I,I' and II' in the nomenclature of Smith (38). These cations do not affect the sorption of molecules in large cavities and thus also the OH groups formed at their sites do not affect the sorption of molecules. That is why constant values of the specific part of the adsorption heats were found in samples with a higher decationization degree. This effect is also in good agreement with the limiting intensity of the HF band at higher degrees of decationization.

CONCLUSIONS

1. The substitution of Na^+ cations located in the large cavities by protons was indirectly proved by the predominant increase of the 3640 cm^{-1} absorption band in the series of $Na_xH_{1-x}Y$ zeolites.

2. The decrease of the heats of adsorption of carbon monoxide and ethylene is

determined by the decrease of specific interaction of these molecules with Na$^+$ cations disappearing from the large cavities.

3. Nonspecifically adsorbed molecules of methane, ethane and propane do not exhibit any significant changes in adsorption heats across the Na$_x$H$_{1-x}$Y series.

4. The sensitivity of all "shallow bed" HY zeolites to the hydration–dehydration cycle has been proved.

ACKNOWLEDGMENTS

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