INFLUENCE OF BASICITY OF NITROGEN BASES ON THE HEAT OF THEIR PROTONATION ON THE SURFACE OF HNaY ZEOLITE

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ABSTRACT

The heats of protonation of ammonia, butylamines, triethylamine, pyridine and a series of its derivatives on HNaY zeolite have been measured by calorimetric method. The heat of protonation has been shown to depend primarily on proton affinity of the base and on the number and strength of hydrogen bonds between ions and oxygen atoms on the zeolite surface.

INTRODUCTION

One of the key problems of heterogeneous acid catalysis is elucidation of the principles that determine the capability of acid centers to protonate probe and reagent molecules. Accumulated numerous experimental data indicate that the interaction of nitrogen bases with protic catalytic centers leads to the formation of ions. In this work the heats of protonation of ammonia and a series of amines that differ in their basicity (primary, secondary and tertiary butylamines, triethylamine, pyridine, 2-chloropyridine, 2,3- 2,5- and 3,5-dimethylpyridines and 2,4,6-trimethylpyridine) on HNaY zeolite were measured by calorimetric method. The molecule of ammonia as the simplest one of the above molecules was used for the analysis of the specificity of the interaction between ions and the surface. The use of other bases was necessitated by the elucidation of all factors determining the protonation heat.

EXPERIMENTAL

The 2.2 wt.% Na zeolite with $SiO_2/Al_2O_3=4.8$ was used. Prior to IR spectroscopic experiments, the zeolite was pressed into tablets (8-12 mg/cm^2) and calcined in vacuum at 723 K for 2 hr. Adsorbates were dried with the NaA zeolite and outgassed by repeated freezing out. Adsorption was performed at room temperature at a pressure of saturated vapors (10 mm Hg for ammonia) for 15-30 min. Spectra were taken at room temperature (at 77 K for ammonia) using a UR-20 spectrometer immediately after adsorption, as well as after evacuation at 298, 423, 523, 623 and 723 K for 1 hr.

Prior to adsorption-calorimetric measurements, the zeolite samples were treated either in vacuum or in pure helium at 723 K for 3 h. The adsorption of ammonia was examined at 423 K in a volumetric system.

The adsorption of organic bases was studied at 373-473 K in a flow system containing a gas chromatograph furnished with an integrator (see Fig. 1). Such simple construction provides measurements of the quantity of the adsorbate at the inlet and outlet of the calorimetric cell filled with a catalyst. The difference between these quantities allows of the determination of the adsorption value, provided that no blowing out of the adsorbed substance by the carrier-gas occurs. With adsorption heats of 40-80 kJ/mol the blowing out is observed at low surface coverages of the catalyst by the substance under study.

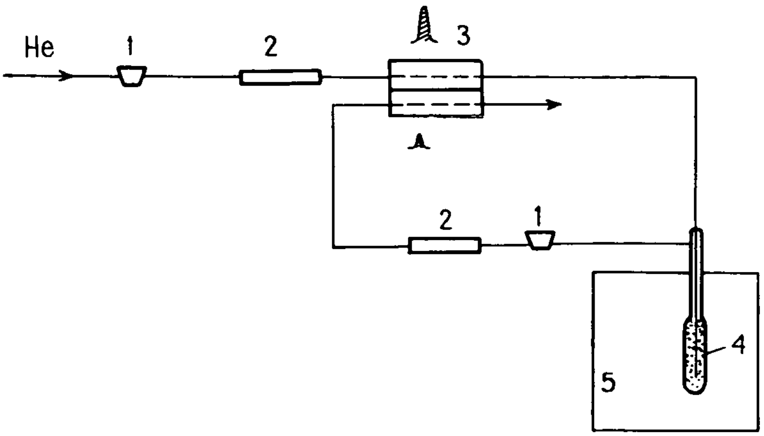

Fig. 1. Flow-adsorption system:
1 - vaporizer,
2 - chromatographic column,
3 - heat-conducting detector,
4 - calorimetric cell filled with the catalyst,
5 - Tian-Calvet-type calorimeter

Dozing of the adsorbates was made by microsyringe. All parts of the system were heated up to 400-423 K to prevent vapor adsorption on its walls. Purified helium (content of impurities was no more than 1 ppm) was used as carrier-gas, its flow velocity being 30 cm^3/min. Adsorption heat measurements were stopped with the first signs of blowing out of the adsorbed substance from the catalyst surface.

RESULTS AND DISCUSSION

1. As shown by IR data, during the adsorption of all bases used in the work the intensity of the ν_{OH} 3640 cm^{-1} absorption band ascribed to OH-groups localized in large cavities of the zeolite framework decreases. This decrease is proportional to the quantity of the adsorbed base. In the case of ammonia, the intensity of the ν_{OH} 3550 cm^{-1} absorption band, corresponding to OH-groups in small zeolite cavities, also decreases. The variations in both line intensities were nearly the same. One may suppose that the difference in the behavior of OH-groups with respect to ammonia and organic amines is due to their different accessibilities. During the course of desorption over the temperature range from 423 to 723 K the line intensities of the adsorbed bases decrease and the line intensities of hydroxyl groups are reduced in a similar way. Spectra of amines themselves on the HNaY zeolite considerably differ from spectra of liquid bases and those physically adsorbed on NaY and silica, as well as from spectra of amines on alumina. They are similar to the corresponding spectra of hydrochlorides. To our opinion, these facts provide a sufficient evidence for the protonation of amines during their interaction with the HNaY zeolite surface producing BH^+ ions.

2. Adsorption heats of ammonia, pyridine and its derivatives, butylamines and triethylamine on HNaY zeolite at 373, 423 and 473 K are shown in Figs. 2-4. For ammonia, the adsorption heat almost linearly falls with a coverage increase at the initial period of time, then reaches a minimum (25 kJ/mol) at adsorption about 2500 μmol/g and further remains constant. In the region of the adsorption heat constancy the equilibrium pressure of ammonia over the sample increases almost linearly with coverage. It is reasonable to suppose [1] that this linear region is the part of the Henry isotherm of ammonia adsorption, which is characterized by an adsorption heat of 25 kJ/mol. Unfortunately we failed to strictly identify the nature of these adsorption sites.

By subtracting the linear component from the total adsorption isotherm we have obtained curve 2, which seems to describe the interaction of ammonia with the most acidic hydroxyl groups of the zeolite

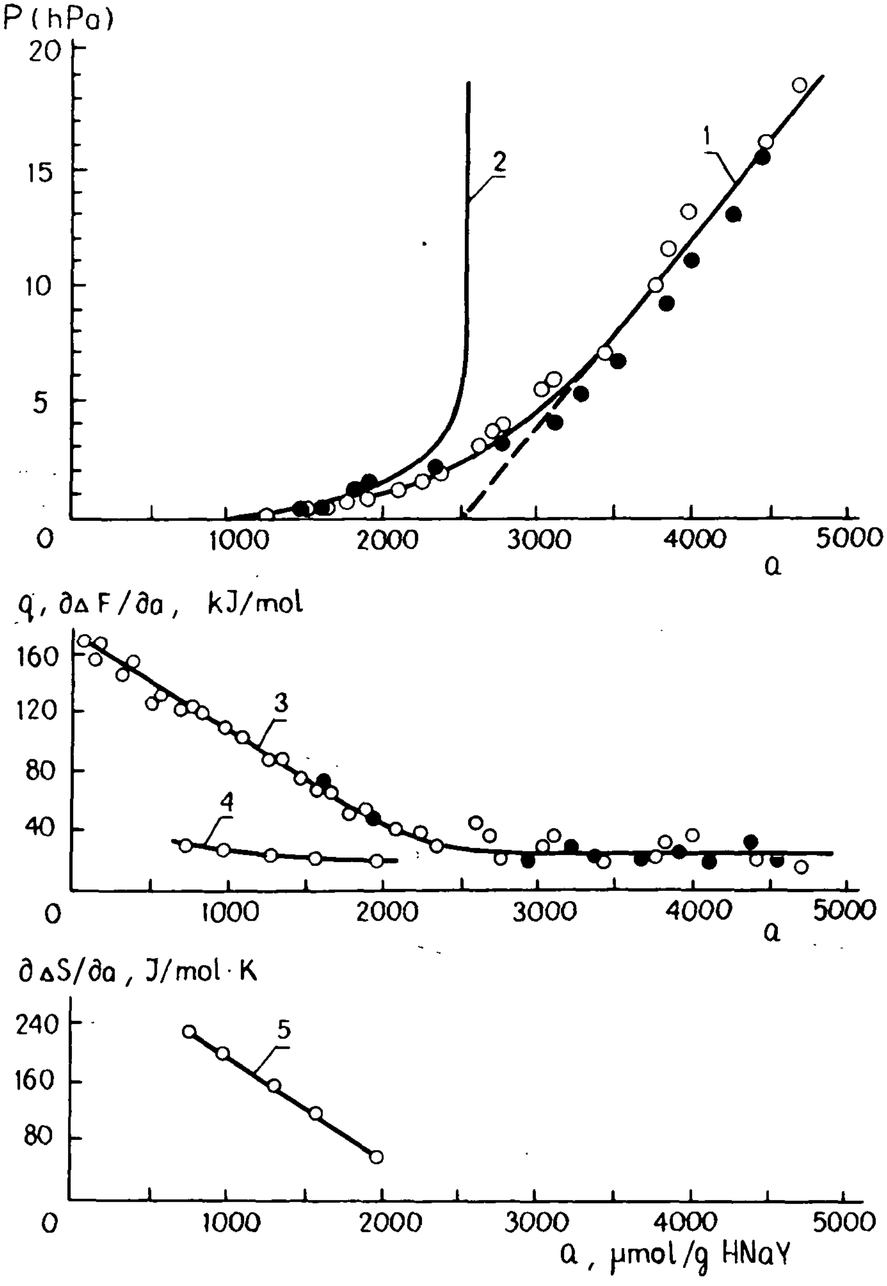

Fig. 2. Equilibrium pressure (1), differential values of heat (3), free energy (4) and entropy (5) of ammonia adsorption on HNaY zeolite at 423 K versus adsorption (light points - adsorption, filled points - desorption)

surface. For the range of surface coverages from 750 to 2000 μmol NH_3/g HNaY, within which the equilibrium pressure of ammonia increases from 0.017 up to 1.6 hPa, from curve 2 we have calculated the dependence of the integral free energy of NH_3 protonation ($\Delta F(a) = -RT \ln K(a)$, where $K(a) = a/p(a^{max} - a)$) and the differential free energy (curve 4). As is seen, in contrast to the adsorption heat, the free energy of ammonia protonation changes slightly with coverage variations, i.e. nearly complete compensation effect occurs. The adsorption entropy (curve 5) is close to the total entropy of gaseous ammonia at the temperature of experiment when the surface coverage does not exceed 1000 μmol NH_3/g HNaY. This indicates a very rigid binding of NH_3 molecules to the zeolite surface at these coverages. The molecules thus lose all translational and rotational degrees of freedom.

Fig. 3 shows the adsorption heats of pyridine and its derivatives on HNaY measured by successive delivery of the substances on the same zeolite sample. It is seen that the chemical nature and the number of substituents reveal a strong effect on the base adsorption heat. The adsorption heats of butylamines, triethylamine and pyridine measured on different zeolite samples over a wide range of surface coverages are presented in Fig. 4. Noticeable dependence of the adsorption heats on coverage is observed only for pyridine and triethylamine.

3. The protonation heat of bases on the catalyst surface can be defined as a sum of three terms [2]: $q_{H^+} = PA^B - PA^a + q_B$, where PA^B and PA^a are affinities to proton of the base and acid residue, respectively; q_B is the energy of BH^+ binding to the surface. In turn, q_B can be described as a sum: $q_B = q_x + nq'$, where q_x in the first approximation is the electrostatic component of the bond and q' is the energy of the hydrogen bond formation. For HNaY q_x was found to be constant for all bases. Thus, we obtain $(q_{H^+} - nq') = PA^B - (PA^a - q_x)$, i.e. the protonation heat of bases on HNaY (after subtraction of the energy of formation of hydrogen bonds) is linearly dependent on their proton affinities. In order to find q', it is possible to use a known formula: $q' = 1.3(\nu_{NH}^{0} - \nu_{NH}^{c.g.} - 40)^{0.5}$, which relates the heat of formation of H-complexes with the shift of the NH-bond stretching band [3].

For all studied bases, except for ammonia and butylamines, a single hydrogen bond is formed during the adsorption. In the case of ammonia and butylamines, the formation of two or even three hydrogen bonds seems to be possible. This supposition is supported by

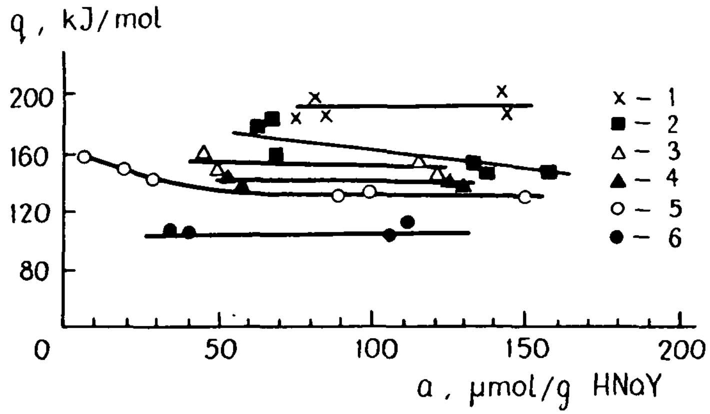

Fig. 3. Adsorption heats of pyridine and its derivatives on HNaY zeolite at 473 K: (1) 2,4,6-trimethylpyridine, (2) 3,5-dimethylpyridine, (3) 2,3-dimethylpyridine, (4) 2,5-dimethylpyridine, (5) pyridine, (6) 2-chloropyridine

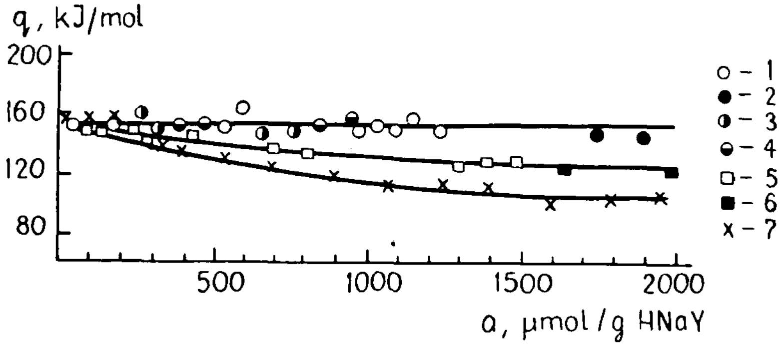

Fig. 4. Adsorption heats of primary butylamine at 423 (1) and 373 K (2); secondary (3) and tertiary (4) butylamines at 423 K, triethylamine at 423 K (5) and 373 K (6), pyridine (7) at 423 K on HNaY zeolite

the above data on entropy variations during ammonia adsorption on the HNaY zeolite, as well as by the analysis of IR spectra in the region of deformation vibrations. At 90-100 K in the range 1300-2000 cm^{-1} the bands at 1370, 1433 and 1490 cm^{-1}, and also at 1690 and 1850 cm^{-1} were observed. The former bands are attributed to the splitted components of antisymmetric deformation vibration of the free ion, while the latter bands correspond to the splitted components of symmetric deformation vibration of the same ion. According to the calculations made by E.B. Burgina, for the ion bound to the zeolite surface only via one hydrogen bond one can expect

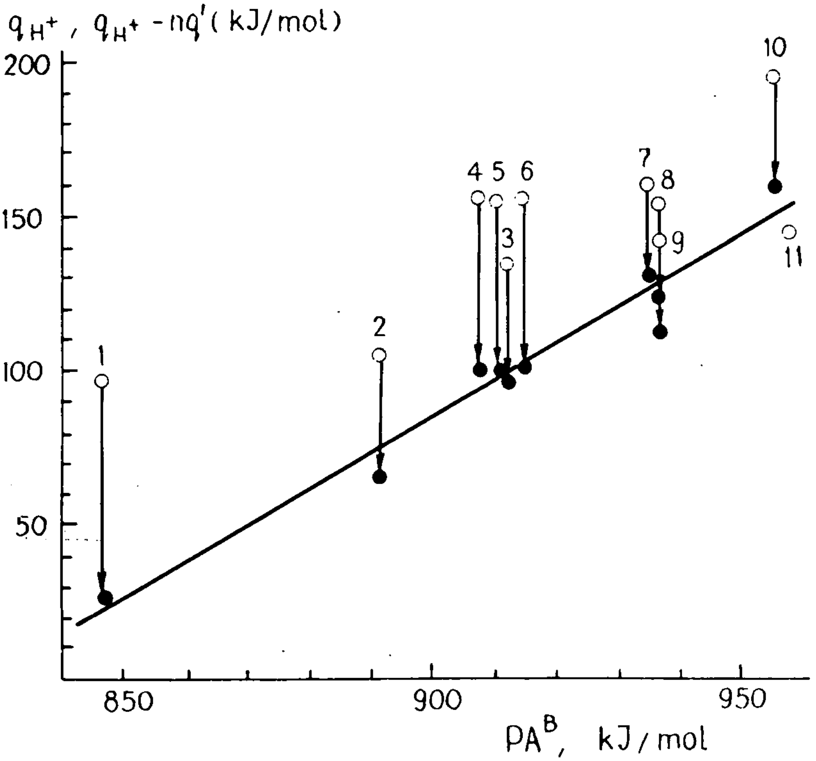

Fig. 5. Comparison of integral heats of protonation of bases on the surface of HNaY zeolite (light points) and theirfrom calculated values of $(q_{H^+} - nq')$ (filled points) with proton affinity of adsorbed molecules (PA^B): (1) ammonia, (2) 2-chloropyridine, (3) pyridine, (4) primary butylamine, (5) secondary butylamine, (6) tertiary butylamine, (7) 3,5-dimethylpyridine, (8) 2,3-dimethylpyridine, (9) 2,5-dimethylpyridine, (10) 2,4,6-trimethylpyridine, (11) triethylamine

the same number of components in the range from 1300 to 2000 cm^{-1}. However, the splitting values between them seem to be much smaller.

A comparison of measured integral heats of protonation of the bases on the HNaY zeolite surface and theirfrom calculated values of $(q_{H^+} - nq')$ with proton affinities PA^B is shown in Fig. 5. If one assumes that in the case of ammonia and butylamines n=2, i.e. during the adsorption of each molecule two hydrogen bonds are formed, there is a good correlation between $(q_{H^+} - nq')$ and PA^B. Low value of the heat of triethylamine protonation may be accounted for by steric hindrances during its adsorption on the zeolite [4].

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