CALORIMETRIC STUDY OF ZEOLITE ACIDITY

By

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The microcalorimetric technique has been applied to investigate the adsorption of ammonia, pyridine and n-butylamine on A, X, Y and mordenite zeolites modified by the ion exchange and aluminium extraction. The results show that the sodium ions weakly bound with the framework are the strongest adsorption sites. The heats of adsorption measured on hydrogen zeolites are higher than in the case of cationic forms. Aluminium extraction of H-zeolites reduces the number of protonic acid sites.

The results imply that the heats of the adsorption of bases are quite sensitive to the variations of zeolite acidity induced by chemical treatment. A new approach to represent the acidity spectra from calorimetric values is described.

The search for a way to determine the number and the strength of acidic sites remains one of the most important problems of zeolite catalysis. Nearly all investigations along this line were concerned with the measurements of the adsorption of certain bases on zeolites. In our laboratory an extensive calorimetric research has been undertaken to study the behaviour of bases sorbed by the zeolites with different structure and chemistry. Ammonia, pyridine and n-butylamine, which are currently among the most widely used bases for the acidity measurements, were selected as sorbates.

The isotherms and the heats of adsorption were measured by a Calvet type microcalorimeter connected with a volumetric system. Before the measurements all samples were evacuated for 100 hours at 480 °C.

Adsorption of ammonia on NaA, NaX and NaY zeolites

By comparing the isotherms it is seen that sodium A, X and Y sieves adsorb different amounts of ammonia. At high coverage the forms of isotherms are exactly similar and they fit the same curve when properly displaced along the ordinate. The variations in the adsorption can be thus ascribed to the different amounts of NH_3 consumed by zeolites at low pressures. Under these conditions a greater influence of the specific zeolite type is to be expected since the ammonia molecules interact with the strongest sites, the strength and the number of which depend on the frame-

work structure and chemical environment. The differences in the adsorption heats are also the most pronounced at low coverage, whereas at the increased loadings the variations in the heats for single zeolites are rather small (Fig. 1).

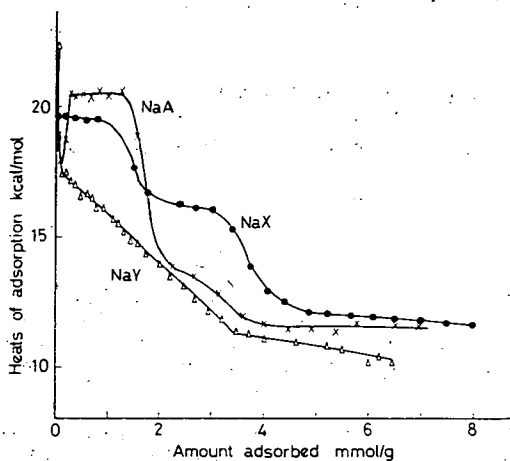The data for the adsorption of NH_3 on Na-zeolites indicate that the sodium cations function as adsorption sites. They further suggest that the cations less tightly bound in the lattice interact with ammonia molecules more strongly than the cations which are more completely screened by the framework oxygen. Ammonia molecules seem to prefer unlocated cations as adsorption sites at low coverage.

One unit cell of NaA zeolite contains 4 slightly bound cations. A sharp decrease in the adsorption heats from 20 to 14 kcal/mole corresponds to the NH_3 uptake equal to 4 molecules per unit cell. The same cations apparently occupy the large cavities in NaX zeolite and that leads to the similar initial heats obtained for both zeolites. On the contrary a very limited number of unlocated cations in NaY zeolite accounts for the drastic decrease of the adsorption heats at low coverage. As the adsorption of NH_3 molecules by the cations loosely bound with the lattice is completed, the cations located in 6-rings become involved in the interaction with ammonia.

Fig. 1. Adsorption heats of ammonia on NaA, NaX and NaY zeolites

With the decrease in aluminium content in zeolites the heterogenity of the rings increases in the series: NaA→NaX→NaY and the heats of adsorption for NaY show a monotonic decline, while the curves for NaX and especially for NaA zeolites reveal a step-shape decrease.

Kinetic measurements supported the suggestion about the preferential adsorption of NH_3 on loosely bound cations. In addition a slow penetration of ammonia molecules into sodalite cages was observed.

Adsorption of ammonia on mordenite

The heats of NH_3 adsorption have been measured on Na-mordenite and on acid-treated samples with SiO_2/Al_2O_3 ratios of 12.6, 20 and 47 (Fig. 2). Compared to other Na-forms, sodium mordenite adsorbs ammonia with the highest heats at low coverage, apparently due to the poor Al content in the lattice and relatively weak interaction of cations with the zeolite framework. Step-shape curve for Na-mordenite indicates the location of cations in several different crystallographic positions.

Ion exchange of Na^+ by protons doesn't alter the total number of the adsorption centers but modifies the nature of the sites as evidenced by the enhancement of ad-
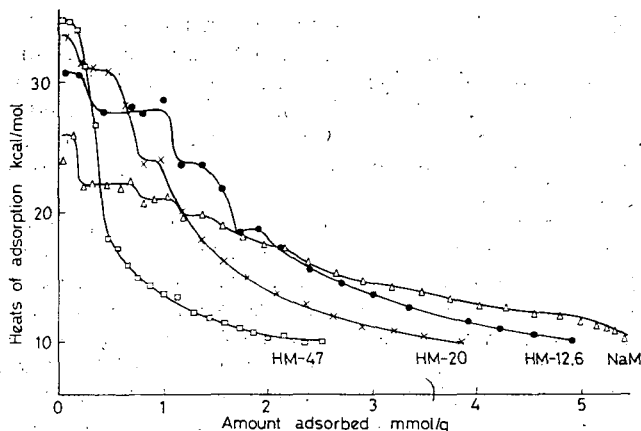
Fig. 2. Adsorption heats of ammonia on mordenites

sorption heats. By progressively increasing the Si/Al ratio the initial heats increased, however, they decreased more rapidly with the filling. Such behaviour may be explained by two opposing effects resulting from Al extraction: the increase of acid strength of protonic sites and the decrease of the number of the sites.

Adsorption of n-butylamine on decationized and dealuminized zeolites

NaY zeolite adsorbs n-butylamine with heats of ~ 25 kcal/mol over a wide range of coverage [1]. After removing the cations the heats increase to reach the ~ 37 kcal/mol level. The sample exchanged to 20% shows behaviour similar to NaY zeolite [2]. The highest increase in the adsorption heats (from 26 to 35 kcal/mol) was observed when the extent of decationization was raised from 20 to 45%. This suggests that removal of exchangeable cations from 6-rings creates strong protonic sites capable of converting butylamine molecules into butylammonium ions. The further NH_4^+ ions contribute little to the adsorption heats, probably because of poor accessibility or/and weak acidity of protons associated with high exchange levels.

The enhancement of the initial adsorption heat from 30 to 47.5 kcal/mol caused by decationization of mordenite is greater than in the case of Y zeolite [1]. Another feature of hydrogen mordenite is a significant decrease of the adsorption heat with coverage, that indicates a heterogeneity of the acidic sites.

To evaluate the effect of Si/Al ratio on the acidity of Al deficient samples, the
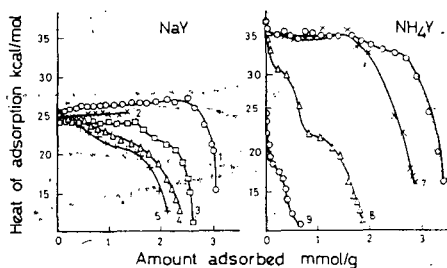

Fig. 3. Adsorption heats of n-butylamine on aluminium deficient NaY and NH_4Y zeolites with SiO_2/Al_2O_3 ratios of 4.7 (curves 1 and 6), 7.1 (curves 2 and 7), 10.1 (curve 3), 22.6 (curves 4 and 8), 104 (curve 5), curve 9 — silica gel

adsorption of n-butylamine has been investigated on two series of NaY and NH_4Y zeolites (Fig. 3). Al removal was accomplished by treating Na- and NH_4-zeolites with different amounts of EDTA. The initial heats were not changed by the extraction of aluminium but the fraction of butylamine sorbed with elevated heats decreased progressively as Si/Al was increased. Since no enhancement of the adsorption heats was observed for either series, the generation of more strong sites by extraction was not detectable with n-butylamine.

The curves, obtained for the samples from which more than 30% of Al has been removed, showed a distinct step near 20—22 kcal/mol at the high loadings. This suggests the formation of new adsorption centers resulted from dealumination which interact with the sorbed molecules more weakly than either the cations or the protonic sites do. A parallel IR study has established the appearance of additional OH-bands at 3745 cm^{-1} in aluminium deficient samples. Intensities of this band increased as Si/Al ratio was increased. This band may be thus ascribed to silanol Si—OH groups which, in contrast to cations or protonic sites, interact only weakly with n-butylamine through H-bonding.

Acid treated mordenite with $SiO_2/Al_2O_3 = 20$ adsorb n-butylamine with ~ 5—7 kcal/mole lower heat than parent hydrogen sample. Again it seems that Si—OH groups are responsible for the adsorption at high coverage. The strongest acidic centers appear to associate with readily removable Al atoms.

Comparison of the adsorption heats of the bases

The data concerning the adsorption of different bases indicate that the sorbed bases interact with zeolites more strongly than hydrocarbons of similar structure and molecular weight. Increased adsorption heats on NaY may be related to coordinative bonding between sodium ions and nitrogen atoms. In this case the highest value was found for pyridine (Fig. 4) apparently because the coordinate bonding is superimposed by the interaction with π-ring. Replacement of Na^+ by protons results in the ~ 8—9 kcal/mol higher adsorption heats of ammonia and butylamine. Pyridine is a somewhat weaker base and Py-ion formation is accompanied by lower heat effect. The
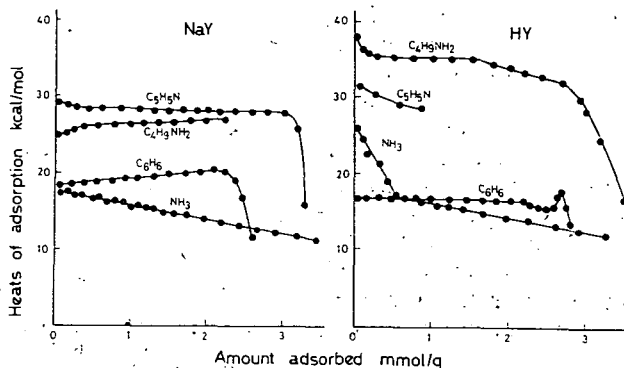

Fig. 4. Comparison of adsorption heats
of bases on NaY and HY zeolites

heats of pyridine adsorption are virtually the same both on sodium and hydrogen zeolites. Thus pyridine seems to be insensitive probe molecule for counting the number of protonic sites by calorimetric technique [3].

Thermochemical study of adsorption on zeolites is fraught with considerable difficulties. The main problem comes from a very slow attainment of the heat equilibrium. Moreover in many cases this technique fails to distinguish between cations and protonic sites due to the insufficient selectivity of the adsorption. Finally, the sorbed amounts of large molecules such as pyridine and butylamine are very limited by the definite void volumes of zeolites. In the case of ammonia complications arise because of penetration of NH_3 molecules into the small cages.

In spite of the difficulties outlined above, adsorption heats provide a valuable information about zeolite acidity. A quantitative approach may be undertaken with the help of acidity spectra calculated from the adsorption heats.

Acidity spectra of zeolites

In some cases the variation of the adsorption heats with progressive filling is represented by step-shape curves. Adsorption heats of NH_3 on NaA and NaY zeolites are typical (Fig. 1). Such behaviour may be associated with the discrete surface heterogeneity due to the existence of several energetic levels. In analyzing the adsorption equilibrium on these surfaces an equation has been derived to describe the change in the adsorption heats with filling.

If the homogeneity of the sites within the single energy level is assumed, the applicability of Langmuir equation can be postulated. Under condition of equilibrium the sorbed amount a is distributed through all levels and the pressure over all parts of the surface would be equal. By using this assumption and taking the adsorption on the first level as independent variable, the adsorption on other levels a_i and the total uptake a can be then determined:

$$a = \sum_{i=1}^{n} a_i = \sum_{i=1}^{n} \frac{a_i a_{mi}}{\gamma_i a_{m1} - (\gamma_c - 1) a_1} \tag{1}$$

where a_{mi} — limiting value for the adsorption on the level i, γ — selectivity coefficient.

Once the adsorption and the heat of adsorption for the sites of either type is known, the differential heat of adsorption may be given by:

$$q_a = \frac{\displaystyle\sum_{i=1}^{n} \frac{q_i a_{mi} \gamma_i}{[\gamma_i a_{m1} - (\gamma_i - 1) \cdot a_1]^2}}{\displaystyle\sum_{i=1}^{n} \frac{a_{mi} \gamma_i}{[\gamma_i a_{mi} - (\gamma_i - 1) \cdot a_1]^2}} \tag{2}$$

In order to describe the experimental plot of adsorption heats against filling, by the equations (1) and (2), the values of a_{mi}, q_i and γ_i should be found by trial-and-error method. The constants thus evaluated can be represented as energetic spectrum which for the adsorption of bases is spectrum of zeolite acidity. Such spectra are depicted in Fig. 5.

There is still another approach to find acidity spectra. Assuming that the variations in the adsorption heats coincide with energy distributions, a graphical differentiation of the experimental curve and the construction of the plot of $\dfrac{da}{dq}$ vs. q should produce the spectrum. For step-shape curves the agreement between the spectra
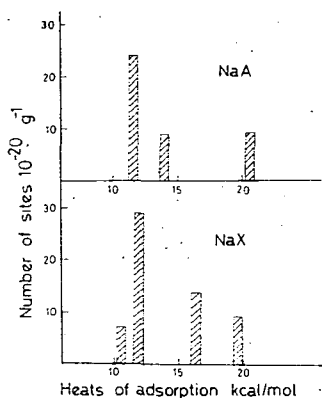

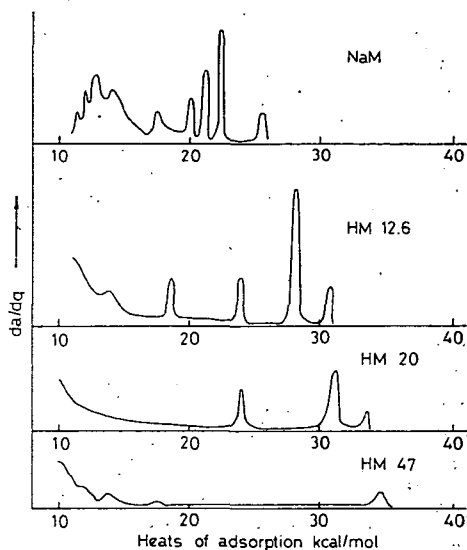Fig. 5. Acidity spectra for NaA and NaX zeolites

Fig. 6. Acidity spectra for mordenites. Spectra have been obtained by graphical differentiation of the curves in Fig. 2.

obtained by this method and the results of the calculations according to (1) and (2) is very satisfactory.

Fig. 6 represents the acidity spectra calculated for mordenites by using the graphical treatment of the curves in Fig. 2. The variations in the strength and in the number of adsorption sites following aluminium removal are evident.

References

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