

ACIDITY OF DEALUMINATED Y-TYPE ZEOLITES DETERMINED BY ADSORPTION MICROCALORIMETRY

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ABSTRACT

(Na,H)-Y zeolites, prepared by dealumination of Na-Y by means of SiCl_4 and transformed to an acidic form, have been used for the determination of acidic properties. The acidity was measured by the calorimetric adsorption method. Agreement has been found between the amount of the Bronsted and Lewis acid centres determined by the calorimetric method (adsorption of n-butylamine) and the IR spectroscopic method (adsorption of pyridine).

INTRODUCTION

Some catalytic reactions, such as cracking, isomerization or polymerization, are performed on zeolites with acid centres. For this reason, the determination of acid sites, their quality (Bronsted or Lewis sites and their acid strength) and their quantity (number of sites) is important for evaluating the activity and selectivity of a given catalyst.

The acidic properties of solids may be determined by various methods [1,2]. Recently, several papers have been published [3–7] which used the calorimetric method to study the adsorption of gaseous bases on zeolites. In some of these papers [6,7], it was shown that the amount of the individual types of acid sites in (Na,H)-Y zeolite could be obtained from one calorimetric curve (ΔH_a vs. α).

The present work aims to determine for the H-Y zeolite and its dealuminated forms (with Si/Al ratio in the range 2.5–20) the amount of Bronsted and Lewis acid sites by the adsorption of n-butylamine and to compare them with the values [8] determined by IR spectroscopy by means of the spectrum of adsorbed pyridine. The results are then correlated with the amount of aluminium in the zeolite.

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EXPERIMENTAL

The heat of adsorption was measured at 405 K in a volumetric apparatus connected to a Calvet type differential microcalorimeter (DAK 1-1, U.S.S.R.). Prior to the measurement of adsorption, the zeolites were activated in a vacuum of 10^{-3} Pa at 670 K for about 15 h. After the activation was finished, the adsorption vessel with 0.15 g of zeolite was sealed off, transferred to the calorimeter and attached, by means of a glass valve, to the adsorption apparatus. Calibrated doses of n-butylamine were admitted to the sample in 150–200 $\mu\text{mol g}^{-1}$ amounts. n-Butylamine was purified by a freeze–pump–thaw technique before it was transferred into the reservoir.

The measurement was performed on the H-Y (70) samples (decahydration to 70%) and on the dealuminated forms of primary Na-Y. The dealumination with SiCl_4 , the designation of the samples and the analysis results have been described in ref. 8.

RESULTS AND DISCUSSION

The heat of adsorption, ΔH_a (kJ mol^{-1}), of n-butylamine was determined by its dependence on the amount adsorbed α (mmol g^{-1}) for the individual samples at 405 K. This dependence and the corresponding adsorption isotherms are given in Fig. 1. The highest heat of adsorption was found with sample H-Y (170 kJ mol^{-1}). With increasing dealumination, the heat of adsorption decreases slowly and simultaneously the total amount of adsorbed n-butylamine goes down. The calorimetric curves of samples E, D and C with Si/Al_t ratios 3.4, 5.1 and 5.75 lie close together. Al_t denotes the total amount of aluminium in the zeolite.

When the calorimetric curves are evaluated by the method described earlier [6], it is evident that the number of acid sites on the H-Y sample is about twice that on samples E, D and C and about ten times higher than that on sample B. This decrease in acid sites follows the decrease of aluminium in the individual samples of zeolite. The corresponding values of Al_t , Al_s (lattice aluminium) and the difference $\text{Al}_s - \text{Na}$ determined for 1 g of dry zeolite are given in Table 1. The amount of Bronsted (B) and Lewis (L) acid sites evaluated from the calorimetric curves is also shown in Table 1.

From the chemical composition of a unit cell of H-Y zeolite, we have obtained the number of unit cells in 1 g of zeolite (5.08×10^{19}) and the total amount of hydrogen in 1 g of zeolite (equal to $\text{Al}_s - \text{Na}$), 3.23 mmol g^{-1} . This amount of hydrogen can be regarded as the maximum number of Bronsted centres in 1 g of zeolite $(\text{OH})_{\text{th}}$. If we assume that two B centres provides one L centre after dehydroxylation, the sum $\text{B} + 2\text{L}$ for the H-Y zeolite (3.45 mmol g^{-1}) should be comparable with $(\text{OH})_{\text{th}}$. The difference in

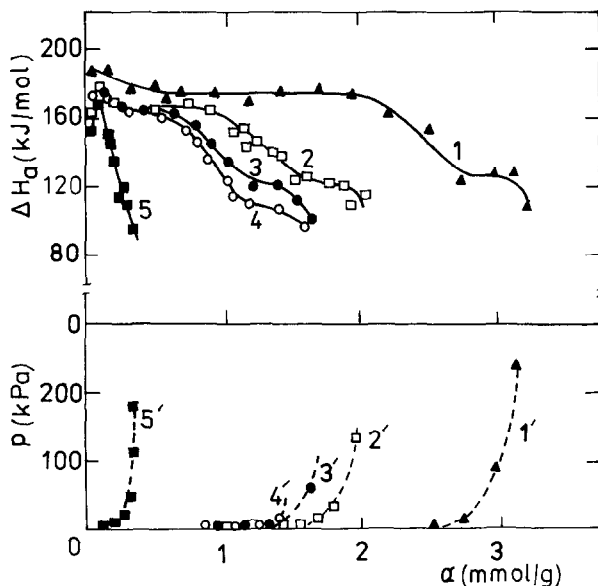


Fig. 1. Heat of adsorption ΔH_a and equilibrium pressure p of *n*-butylamine in dependence on the adsorbed amount α , determined for samples H-Y (1, 1'), E (2, 2'), D (3, 3'), C (4, 4') and B (5, 5').

both values (3.45 and 3.25 mmol g⁻¹) is 6%. The same kind of comparison cannot be made for other samples of zeolite because we do not know how much of the extra-lattice aluminium, which may be a source of electron-acceptor sites, takes part in the compensation of the lattice charge and in which form [8].

On the other hand we may suppose that the extra-lattice aluminium is chargeless. If we now plot $B + 2L$ values against the hydrogen concentration ($Al_s - Na$) we should get a straight line. If large deviations from this straight line occur we may suppose that on this zeolite sample the extra-lattice

TABLE 1

Concentrations of sodium, aluminium in lattice (Al_s), total (Al_t), $Al_s - Na$ and the measured concentrations of the Bronsted and Lewis acid centres

Sample	Si/Al molar ratio	Na (mmol g ⁻¹)	Al_s (mmol g ⁻¹)	Al_t (mmol g ⁻¹)	$Al_s - Na$ (mmol g ⁻¹)	B (mmol g ⁻¹)	L (mmol g ⁻¹)	$B + 2L$ (mmol g ⁻¹)
H-Y	2.5	1.16	4.39	4.28	3.23	2.05	0.7	3.45
E	3.4	0.29	2.49	3.81	2.20	0.95	0.7	2.35
D	5.1	0.09	1.90	2.67	1.81	0.75	0.45	1.65
C	5.7	0.04	1.37	2.37	1.33	0.65	0.6	1.85
B	19.5	0.05	0.65	0.70	0.60	0.05	0.2	0.45

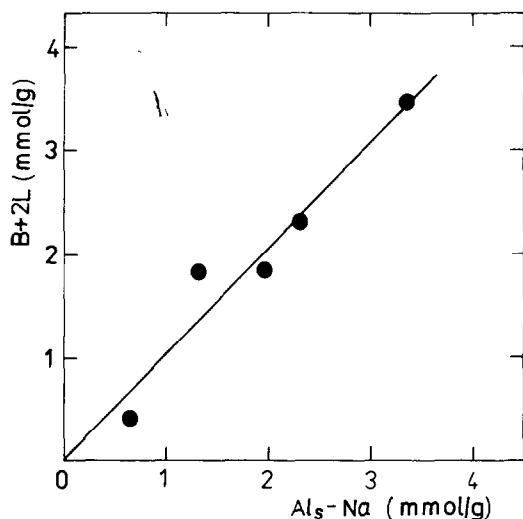


Fig. 2. Relation between the amount of $Al_s - Na$ and amount of acid centres $B + 2L$ in zeolite samples.

aluminium has the properties of electron-acceptor sites. This case is quite evident only for sample C (Fig. 2).

All calorimetric curves, except that of sample B, form a short plateau of the heat of adsorption (ca. 120 kJ mol^{-1}). As it has been shown [6], this part of the curve corresponds to the adsorption of n-butylamine on Na^+ ions. In this region, the adsorbed n-butylamine is bound reversibly.

The lower part of Fig. 1 shows the corresponding adsorption isotherms (curves 1'–5'). It is interesting to note that the pressure of n-butylamine in the gas phase goes up only after the adsorption heat has dropped below 120 kJ mol^{-1} . This means that the pressure in the gas phase starts to increase only after the acid centres in the zeolite have been occupied with adsorbed n-butylamine. A similar behaviour of n-butylamine was observed previously [7].

Figure 3 illustrates the dependence of the concentration of Bronsted and Lewis acid centres, determined calorimetrically, on the amount of aluminium in the lattice Al_s and on the total Al_t . The concentration of both types of acid centres decreases with the decreasing aluminium. For comparison we give the concentrations of both types of acid centres, determined for the above samples of zeolite after adsorption of pyridine by IR spectroscopy, as previously published [8]. It has been shown that the concentrations of Bronsted and Lewis acid centres obtained by both methods are practically the same. Only for sample H-Y do we find a large difference. The concentration of the Lewis acid centres, determined calorimetrically, is about 20 times higher than the corresponding value found spectroscopically. The reason for this difference may be sought in both the spectroscopic and calorimetric

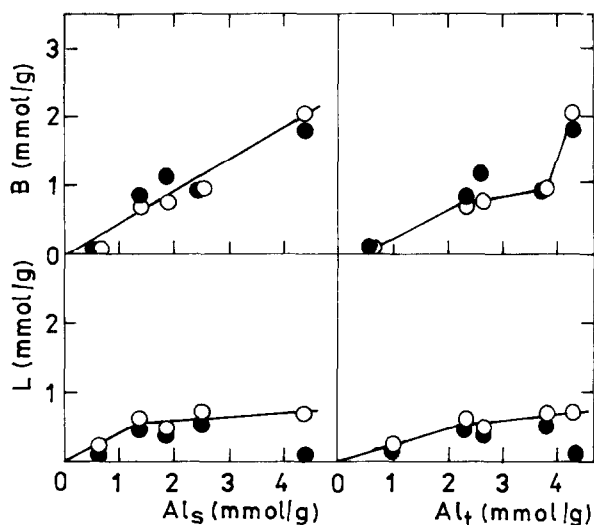


Fig. 3. Dependence of the amount of Bronsted (B) and Lewis (L) acid sites on the amount of aluminium in the lattice (Al_s) and total (Al_t). The values are determined by the calorimetric (○) and IR spectroscopic (●) methods.

measurements. As given in ref. 8 in the H-Y zeolite, pyridine reacts only in the large cavities. So we may suppose that the spectroscopically determined value will not be quantitative when a small number of Lewis acid centres are inaccessible to the pyridine molecules. This possibility indicates the value of the sum $B + 2L$, equal to 1.87 mmol g^{-1} , which is much lower than $(OH)_{th}$. Dealuminated zeolites contain a smaller number of acid centres and part of the aluminium is in extra-lattice positions, all this enhances the contact with pyridine molecules. Therefore we may suppose that the determined values of both types of acid centres on dealuminated samples will be nearer to the real state. On the other hand it may be supposed that the calorimetrically determined value of Lewis acid centres on the H-Y zeolite will be higher than the real one, since the number of weak acid Bronsted centres is also included which is characterized by a low heat of adsorption. The dealuminated zeolites do not contain these weak acid centres and therefore the numbers of Lewis acid centres determined by both methods are the same.

As given by Ward [9], the H-Y zeolite (activated at 670 K) contains about 8% of Lewis acid centres. Using this information, our H-Y zeolite contains 0.25 mmol g^{-1} of Lewis acid centres, 0.45 mmol g^{-1} of weak and 2.05 mmol g^{-1} of strong acid Bronsted centres. The sum $B + 2L$ (3.0 mmol g^{-1}) is about 7% lower than $(OH)_{th}$. Figure 4 shows the dependences of the extra-lattice aluminium (Al_{ex}) and of the concentration of Lewis acid centres, on the amount of aluminium (Al_t). In this figure both values of

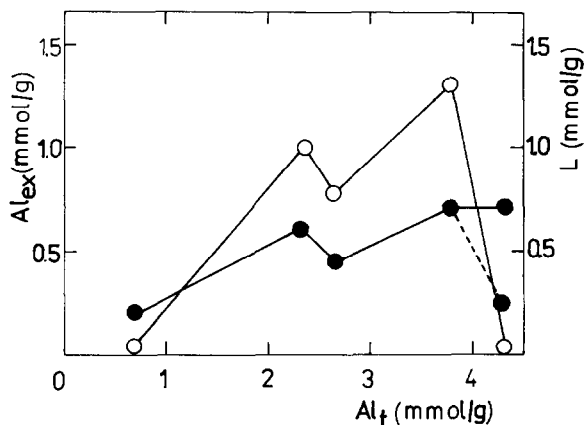


Fig. 4. The dependence of the amount of extra-lattice aluminium (○) and of the Lewis acid centres (●) on amount of aluminium (Al_t).

Lewis acid centres (determined and corrected) are given for the H-Y sample. Both curves have similar shapes.

From the results obtained it is evident that using the method of analysis of the calorimetric curve described, one can determine the amount of both types of acid centres. From the value of the heat of adsorption, conclusions can be drawn on the acid strength of these centres. The acid strength of the Bronsted sites is mostly homogeneous while that of the Lewis centres is heterogeneous. The different results found by both methods on the H-Y zeolite in the concentration of the Lewis acid centres indicates that it is necessary to analyse the calorimetric curve in more detail.

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