DETERMINATION OF THE DEGREE OF ADSORPTION AND THE HEAT OF ADSORPTION FOR 1-BUTYLAMINE AND AMMONIA ON NaHY ZEOLITES

Miloslav KŘIVÁNEK and Pavel JÍRŮ

J. Heyrovský Institute of Physical Chemistry and Electrochemistry, Czechoslovak Academy of Sciences, 121 38 Prague 2

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The degree and heat of adsorption of 1-butylamine and ammonia were measured on samples of NaHY zeolites activated at 400—600°C. The adsorption isotherms and calorimetric curves were compared for the two bases, and the amount of Brønsted and Lewis acid centres was determined from the calorimetric curves.

A number of papers concerned with zeolites have dealt with catalytic reaction and the relation between the acid and catalytic properties. The catalytically active sites are Brønsted and Lewis acid centres. Their number and strength can be studied by various methods[1], of which most frequently used is the adsorption of gaseous bases investigated by infrared spectroscopy, temperature-programmed desorption, or, recently, by the calorimetric techniques. Ammonia or, to a lesser extent, 1-butylamine are usually employed for the calorimetric determination of acidity of zeolites. Attempts to relate the adsorption of 1-butylamine, as evaluated calorimetrically, with the quality and quantity of Brønsted and Lewis acid centres have been made previously[2].

The aim of the present work was to compare the adsorption on NaY and NaHY zeolites for ammonia and 1-butylamine, two bases which have close pK_a values (9·2 and 10·6, respectively) but different values of the kinetic diameter (difference about 100%).

EXPERIMENTAL

The adsoption of 1-butylamine and ammonia vapours was measured in a volumetric apparatus fitted with Teflon taps. The adsorption vessel was accomodated in a Calvet type DAK 1-1 differential calorimeter (USSR). 1-Butylamine and ammonia were purified by multiple distillation in vacuum. Two zeolite samples were used, *viz.* NaY (Linde), with the unit cell composition $Na_{56}Al_{56}Si_{136}O_{384}$ ($4{\cdot}7 \cdot 10^{19}$ unit cells per g zeolite), and NaHY (95), composition $Na_{2{\cdot}5} \cdot H_{46{\cdot}5}Al_{49}Si_{143}O_{384}$ ($5{\cdot}2 \cdot 10^{19}$ unit cells per g zeolite), prepared by ion exchange from the sodium form NaY (VÚRUP Bratislava). Prior to the measurements, the zeolites were activated in a vacuum of 10^{-3} Pa at 400—600°C for 15 h.

The measurements were performed at 130°C. The activated zeolite (~0·15 g) in a layer 0·6 mm thick was accomodated in the thin-walled adsorption vessel, which was then sealed up, transferred to the calorimeter and attached, *via* a glass valve, to the adsorption apparatus. 1-Butylamine or ammonia was admitted portionwise in amounts of 150—200 μmol g^{-1}.

RESULTS AND DISCUSSION

Fig. 1 shows the adsorption isotherms and calorimetric curves for NaY zeolite activated at 400°C. The two adsorbates behave in a different manner. While for 1-butylamine the calorimetric curve decreases sharply after about 2·3 mmol g^{-1} is sorbed, for ammonia the curve continues, with a slow decrease in the heat of adsorption, to higher degrees of coverage. The adsorption isotherms are also different. 1-Butylamine appears in the gas phase with a measurable vapour pressure only after occupying the zeolite in amounts in excess of 2 mmol g^{-1}, whereas the equilibrium pressure of ammonia in the gas phase increases virtually from the beginning of the adsorption. The heat of adsorption of 1-butylamine on Na^+ ions increases slightly over the 100–110 kJ mol^{-1} range, that of ammonia decreases over the 70–60 kJ mol^{-1} range for the same degree of coverage.

The Na^+ ions are located in the NaY zeolite structure in differently accessible sites. For the various sites in a unit cell of dehydrate NaY zeolite, Eulenberger and coworkers[3] report the following values: SI 7·5, SI′ 19·5, SII 30 Na^+, which are 0·59, 1·52, and 2·35 mmol per g zeolite, respectively. The cations in the SII sites

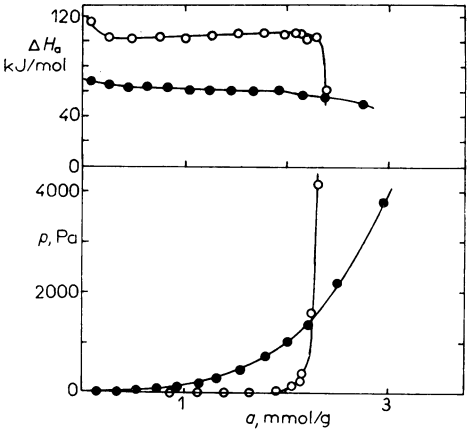

FIG. 1

Heat of adsorption ΔH_a in dependence on the adsorbed amount and pressure p corresponding to the adsorbed amount a (adsorption isotherm), for 1-butylamine (○) and ammonia (●) on NaY zeolite activated at 400°C

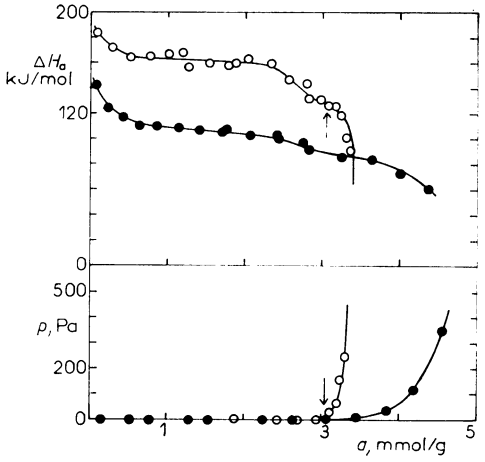

FIG. 2

Heat of adsorption ΔH_a in dependence on the adsorbed amount and pressure p corresponding to the adsorbed amount a (adsorption isotherm), for 1-butylamine (○) and ammonia (●) on NaHY zeolite activated at 400°C

are in large cavities and so they are most readily accessible. The facts that for 1-butylamine the adsorption isotherm attains its limiting value at the occupation of 2·3 to 2·4 mmol g^{-1} and at this value the heat of adsorption drops rapidly indicate that 1-butylamine is able to penetrate into large cavities and react with cations in SII sites only. At this degree of occupation, large cavities are approximately 85% filled with 1-butylamine. (The volume of large cavities of 6·7 nm^3 per unit cell and the density of liquid 1-butylamine[4] of 0·635 g cm^{-3} were taken for the calculation.)

Ammonia can penetrate also into small cavities in NaY zeolite, where they can interact with Na^+ ions also in other sites, and so the calorimetric curve continues at higher degrees of occupation. At the degree where the calorimetric curve of 1-butylamine bends down, the curve of ammonia only exhibits a slight decrease in the heat of adsorption.

Figs 2–4 show the dependences for NaHY (95) zeolite activated at 400, 500, and 600°C, respectively. The calorimetric curves for 1-butylamine adsorbed on NaHY zeolite have been discussed previously[2]. The horizontal part of the calorimetric curve grows narrower and ultimately vanishes as the temperature of zeolite activation is increased. This curve segment has been identified with the adsorption on Brønsted centres. The following, descending branch extends with increasing temperature

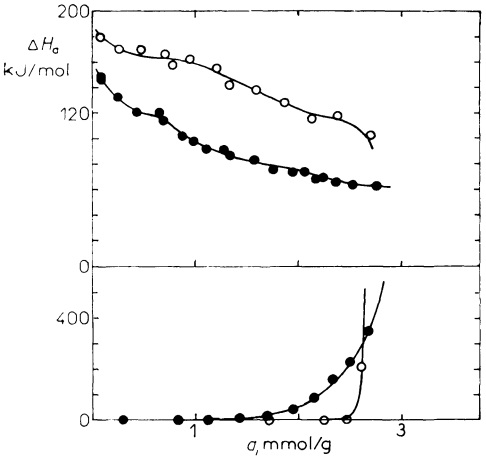

FIG. 3

Heat of adsorption ΔH_a in dependence on the adsorbed amount and pressure p corresponding to the adsorbed amount a (adsorption isotherm), for 1-butylamine (○) and ammonia (●) on NaHY zeolite activated at 500°C

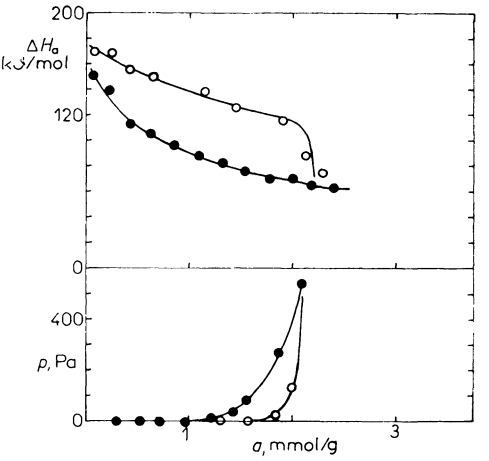

FIG. 4

Heat of adsorption ΔH_a in dependence on the adsorbed amount and pressure p corresponding to the adsorbed amount a a (adsorption isotherm), for 1-butylamine (○) and ammonia (●) on NaHY zeolite activated at 600°C

of activation; it has been attributed to the adsorption on Lewis centres. Over this region, the heat of adsorption decreases by 40–50 kJ mol^{-1}. This curve segment turns into the adsorption on Na^+ ions. For 1-butylamine, the heat of adsorption drops now rapidly. In contrast to NaY, here the decrease is due to the cavities in NaHY being now fully occupied by 1-butylamine (the amount of 1-butylamine adsorbed, 3·05 mmol g^{-1}, corresponds, by a simple calculation, to 100% occupation of large cavities; see the arrow in Fig. 2). This implies that in the large cavities a fraction of Na^+ ions remains unoccupied by the amine. This has been found by us also for NaHY exchanged to 50 and 70%. As the degree of exchange of Na^+ by H^+ is increased, the curve segment corresponding to the adsorption on Na^+ ions becomes narrower and indicates a smaller number of Na^+ ions than as are available in the SII sites. The three curves, for NaHY exchanged to 50, 70, and 95%, exhibit a sharp decrease in the heat of adsorption within a narrow region of degrees of occupation, near 3 mmol g^{-1}.

For ammonia sorbed on NaHY (95) heated at 400°C (Fig. 2), a slight decrease in the heat of adsorption (about 11 kJ mol^{-1}) is observed in the region corresponding to the adsorption on Lewis centres, and the curve continued due to adsorption on the remaining Na^+ ions or to physical adsorption on the surface.

For ammonia on samples of NaHY (95) activated at 500 and 600°C, the shape of the calorimetric curves is the same as for 1-butylamine. The part of the curve corresponding to adsorption on Lewis centres decreases by 40–50 kJ mol^{-1}, similarly as for 1-butylamine. The adsorption of ammonia on acid centres passes into adsorption on Na^+ ions. This transition, however, is even less marked than with 1-butylamine.

While for samples activated at 500 and 600°C the heat of adsorption in the region of adsorption on Na^+ ions decreases to a value near to that for NaY, the heat of adsorption of the two adsorbates on sample activated at 400°C is 25–35 kJ mol^{-1}

TABLE I

The obtained number of Brønsted (B) and Lewis (L) acid centres and the maximum value $(OH)_{max}$, in mmol g^{-1}

Temperature of activation, °C	1-Butylamine			Ammonia			$(OH)_{max}$
	B	L	B + 2 L	B	L	B + 2 L	
400	2·25	0·9	4·05	2·6	0·6	3·8	4·04
500	0·9	1·55	4·0	0·6	1·7	4·0	
600	—	2·0	4·0	—	2·2	4·4	

higher than on NaY. For 1-butylamine, this can be explained so that the large cavities are filled with the adsorbate before adsorption on all Na^+ ions could occur. As the temperature of activation is increased, the total number of acid centres (B + L) decreases and so adsorption on Na^+ ions can take place before the large cavities are completely filled up. For ammonia, however, this explanation fails because at this degree of occupation the large cavities are approximately one third filled.

Table I gives the number of Brønsted and *Lewis centres* (in mmol g^{-1}) for the two adsorbates read from the calorimetric curves by the method described previously[2]. The sum B + 2 L is the total number of acid centres in terms of Brønsted centres (assuming that two B centres provide an L centre hy dehydroxylation[5]). The number of protons given in the unit cell formula multiplied by the number of unit cells per gram zeolite is regarded as the maximum number of Brønsted centres $(OH)_{max}$.

The adsorption isotherms of 1-butylamine indicate that all the amine is strongly adsorbed over the whole region of the calorimetric curve (the pressure in the gas phase is units of Pa). With ammonia, the situation is different: all ammonia is sorbed only as long as the heat of adsorption is higher than 90 kJ mol^{-1}. For samples activated at 500 and 600°C, the equilibrium pressure of ammonia in the gas phase increases even in the range of adsorption on acid centres. whereas for sample activated at 400°C, ammonia appears in the gas phase only in the region of adsorption on Na^+ ions, at higher degrees fo occupation than for 1-butylamine. The strong adsorption bonding of ammonia to Na^+ ions may be due to the change in the electrostatic field induced by the high concentration of OH groups inside the cavities. The number of Brønsted centres decreases with increasing temperature of activation, whereupon the electrostatic field inside the zeolite becomes weaker, as does the adsorption bonding.

The region of adsorption of ammonia on Lewis acid centres ends with a heat of adsorption of approximately 70 kJ mol^{-1}, the region of adsorption characterized by the heat of adsorption of 90–70 kJ mol^{-1} is reversible.

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