ELSEVIER
Thermochimica Acta 379 (2001) 35–44
thermochimica
acta
www.elsevier.com/locate/tca

Analysis of the distribution of adsorbate molecules within zeolite crystals by thermokinetics

T.R. Brueva*, G.I. Kapustin, I.V. Mishin

N.D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
47 Leninsky prosp., 119992 Moscow, Russia

Abstract

A Calvet type microcalorimeter maintained at 30°C was used to measure the differential heats of adsorption of NH_3 over different zeolites. Experiments show that a fast consumption of adsorbate over the early stage of adsorption is followed by a slow redistribution of the guest molecules inside the zeolite pores. The position of the maximum on the kinetic curves depends on the chemical composition of zeolites and degree of filling of zeolite cavities by the molecules adsorbed. The slow liberation of the heat is associated with a redistribution of the adsorbed molecules. It is suggested that once fast adsorption of ammonia is accomplished, slow competition occurs among sorbed species for the strongest adsorption sites. The number of vacated strong sites decreases with coverage to suppress migration of NH_3 molecules to these sites. A kinetic equation is derived which describes this redistribution process. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Thermokinetics; Calorimetry; NH_3; Zeolites; Kinetic equation

1. Introduction

A calorimetric study of ammonia adsorption on zeolites has showed that at 30°C, the process involving a slow redistribution of adsorbed species occurs that retards attainability of thermal equilibrium [1,2]. The rate of heat liberation depends strongly on the amount of ammonia adsorbed. At higher temperature, the process cannot be observed. In this report, an attempt is made to summarize the data related to the thermokinetic behavior of ammonia adsorbed on faujasite, L and mordenite type zeolites, and describe it quantitatively.

2. Experimental

2.1. Investigation technique

Adsorption microcalorimetry was used to investigate the kinetics of adsorption of ammonia. The use of a Calvet type calorimeter made it possible to measure the uptake of ammonia and the heats of adsorption. Moreover, with this method, the kinetics of heat liberation can be followed and the time, needed to establish thermal equilibrium in the zeolite–base system, easily estimated [3]. Differential heats of adsorption of ammonia were measured with a Calvet type microcalorimeter at 30°C. The sensitivity of the microcalorimeter is 7 W, the time constant is 15 min. The experiments were conducted with an accuracy of ±1 kJ/mol. A design of the calorimeter made it possible to observe heat liberation for an indefinitely long period of time.

---

* Corresponding author.

0040-6031/01/$ – see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0040-6031(01)00599-8

Table 1
Chemical composition of Na and K zeolites

Zeolite	Si/Al	Number of cations per unit cell
NaA	1.0	12
NaX-I	1.25	85
NaX-II	1.14	90
NaY-I	2.1	62
NaY-II	2.55	54
NaM	5.1	6.4
KL	2.6	10

The adsorption unit connected to the calorimeter served to conduct controlled admission of ammonia and measurements of the amount adsorbed.

2.2. Adsorbents

Commercial A, X, Y, L and mordenite type zeolites with a definite chemical composition were investigated. Three series of samples were used in this work. The first series included initial Na- and K-forms of zeolites (Table 1). The samples of the second series were prepared by ion-exchange and decationation (Table 2) and zeolites of the third series were produced by dealumination procedures. Dealuminated faujasites and mordenites are designated by DY and DM while the Si/Al ratio in the framework is indicated by the index (for example, DM-24). The results of chemical analysis and the data on the distribution of cations were applied to estimate number of sodium ions available for adsorption [4].

2.3. Adsorption measurements

Adsorption of ammonia was followed until the equilibrium pressure of 100 torr was reached. This value corresponds to the degree of filling around 7–10 mmol/g. Prior to measurements, the samples were evacuated at 480°C for 100 h. About 30–40 individual admissions of ammonia were usually needed to achieve the filling of zeolite cavities and channels by the adsorbed ammonia molecules.

Table 2
Chemical composition of cation exchanged zeolites

Zeolite	Si/Al	Exchange degree (%)
CaX	1.25	93
CaY-54	2.1	54
CaY-60	2.1	60
CaY-85	2.1	85
CaY	2.55	93
NH_4M	5.1	30–94
NH_4KL	2.6	20–82

2.4. Measurements of the heat liberation rate

The time elapsing from the gas intake into the calorimetric cell to the moment at which the intensity of heat liberation had decreased to 20 W was taken as a quantitative measure for the heat liberation rate. This time is arbitrarily called the time taken to establish thermal equilibrium (τ_i). In view of the high sensitivity of the calorimeter (7 W), heat liberation can be observed for a significantly longer period. However, the true time taken to establish equilibrium cannot be determined accurately because the heat liberation curve approaches the zero line asymptotically.

3. Results and discussion

3.1. Na-forms of zeolites

The results on adsorption of bases have shown that the basic distinctions in the behavior of ammonia on different zeolites are exhibited at low pressure, when cation sites are filled, the number and the strength of which are determined by a type of zeolite.

This conclusion is supported by measurements of heats of adsorption. In Fig. 1, the differential heats of adsorption of ammonia as a function of filling are shown for the Na-forms of zeolites. The calorimetric data are supplemented with the dependences of the time taken to establish a thermal equilibrium. From the figure, it is evident that the most significant variations in the heats are observed in the region of small fillings at pressures below 10 torrs.

High heats of adsorption of ammonia indicate a strong specific interaction of ammonia with adsorption sites, i.e. with the sodium cations. Thus, in NaA zeolite the number of molecules of ammonia initially adsorbed with high heats nearly coincides with amount of loosely bound cations. NaX zeolite contains approximately the same amount of weakly bound

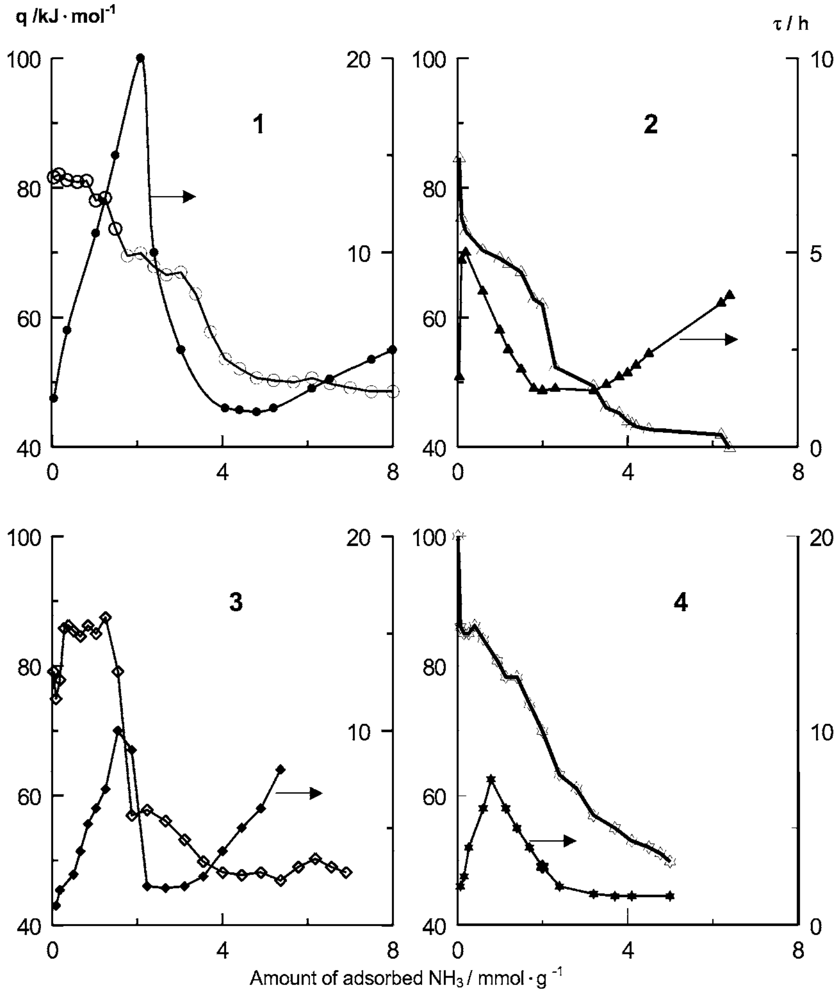

Fig. 1. Heats of ammonia adsorption and time taken to establish thermal equilibrium as a function of amount adsorbed for NaX (1); NaY (2); NaA (3); and NaM (4) zeolites.

cations as NaA. This explains similar initial heats of adsorption (~85 kJ/mol) for NaA and NaX zeolites as well as the same pattern of dependence of heats on filling at low pressures. By contrast, NaY zeolite has an insignificant amount of cations weakly bound to the framework and consequently the high heats of adsorption of ammonia are observed only in the area of very small fillings. Lower initial heats of adsorption on NaA zeolite can involve expansion of the framework at very low fillings followed by lattice contraction at higher coverages [5]. The dependence of the heats of adsorption of ammonia on filling for mordenite suggests that the framework differently binds Na^+ cations in this zeolite. Apparently, stronger interaction of NH_3 molecules with cations can be accounted for by an increased dispersion interaction in narrow channels of mordenite.

By comparing calorimetric and thermokinetic data, a direct relationship between the time taken to establish thermal equilibrium and distribution of cations in zeolites is apparent. As the amount of adsorbed ammonia increases, the time taken to establish thermal equilibrium shows the same behavior for all the zeolites studied. It increases at first, passes through a maximum, then decreases rapidly and after passing through a minimum again increases (Fig. 1). The complexity of behavior indicates that two different slow processes occur.

3.2. The region of small surface coverage

When the surface coverage is low, the admitted ammonia is rapidly adsorbed and the prolonged heat liberation is almost unrelated to the additional adsorption from the gas phase. The position of the maximum in Fig. 1 is characteristic for each type of zeolite. It coincided for two samples of NaX zeolites and two samples of NaY zeolites. In Fig. 1, the curves for NaA and NaM zeolites lie between the curves for NaX and NaY and hence the rate of slow process is independent of the zeolite pore size and cannot be explained by the usual diffusion retardation.

We were able to show earlier that ammonia is primarily adsorbed with a large amount of heat onto Na^+ ions, which are weakly bound to the framework and take the positions in large cavities [1]. The slow process taking place at low surface coverage is observed at the same adsorption values for which enhanced heats of adsorption are recorded. Apparently, the adsorption value that corresponds to the longest time depends on the number of the strongest adsorption sites in each type of zeolite.

In Fig. 2, the adsorption values corresponding to the maxima in Fig. 1 are compared with the number of weakly bound cations (N_0). The N_0 value was calculated as the difference between the total number of cations in a unit cell and the number of cations definitely assigned to specific cation sites. Good agreement confirms that at low fillings, ammonia is adsorbed onto weakly bound cations and the slow liberation of heat is associated with the interaction between ammonia molecules and such cations.

The data for several CaX and CaY zeolites are also presented in Fig. 2. These zeolites follow the same pattern of behavior, as do the Na-forms. In Ca-forms weakly bound cations are unavailable and the strongest adsorption sites are Ca^{2+} ions at S_{II} sites or the proton sites formed by the hydrolysis of cations. The

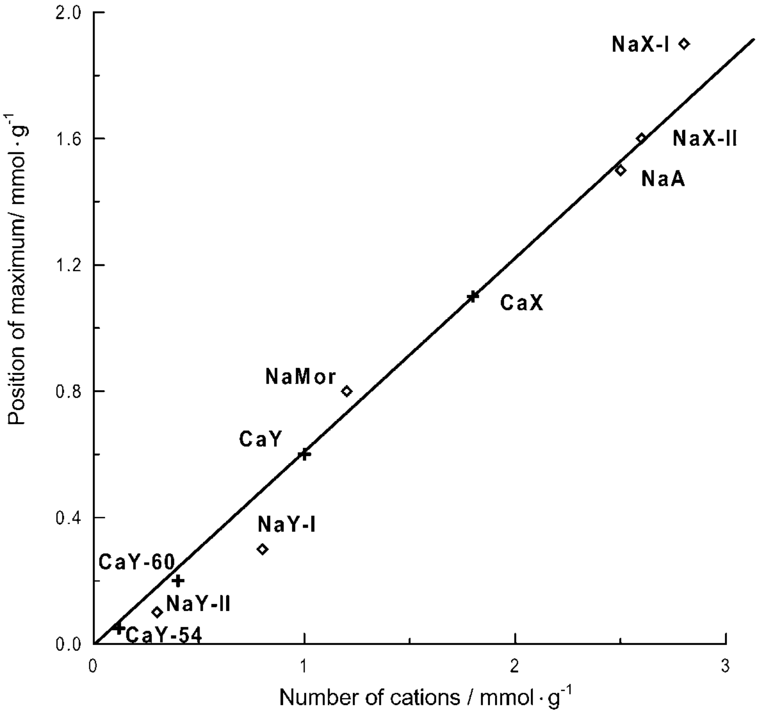

Fig. 2. Dependence of the position of the kinetic-curve maxima on the number of weakly bound Na^+ cations or the number of accessible Ca^{2+} ions.

water molecule interacts with the cation and forms one acid site, and, thus, the total number of strongly adsorbing sites does not change during the hydrolysis. In Fig. 2, the position of the time maximum for the Ca-forms depends on the number of Ca^{2+} ions in the large cavities. The data for the Na- and Ca-forms fit well onto one straight line, thus, the position of the time maximum depends only on the number, and not on the nature of the strongest sites. Apparently, the mechanism of the slow process is also independent of the basic properties of ammonia, since similar maxima on the curves for the dependence of the equilibrium time on the amount of adsorption are observed when water is adsorbed on NaA and NaX zeolites [6,7].

We propose the following mechanism to explain these results. The admitted ammonia is rapidly adsorbed into the zeolite cavities and occupies the various accessible sites. It is then slowly redistributed on the strongest sites. Such a process possibly arises because the initial adsorption occurs in the cavities near the crystal surface and then the adsorbed ammonia redistributes itself onto strong sites throughout the bulk of the crystal. As the amount adsorbed increases, the number of strong sites unoccupied decreases and the rate at which they are occupied slows down. Once all such sites have been filled, equilibrium is rapidly established.

3.3. *The region of large surface coverage*

When all the weakly bound cations are covered, adsorption and thermal equilibrium are rapidly established. However, as the surface coverage increases further, the process again decelerates. In this region, heat is slowly emitted as the gas phase is slowly adsorbed. This process is apparently associated with the penetration of ammonia molecules into the small cavities of zeolites. A similar suggestion was put forward earlier to explain the activated adsorption of ammonia on NaX and NaY zeolites at high temperatures [8]. X-ray diffraction study revealed that

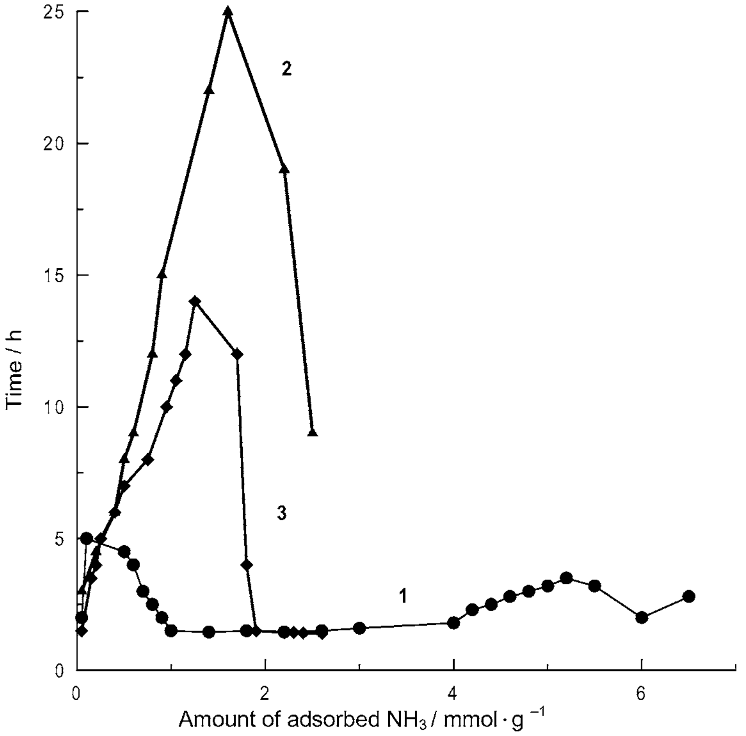

Fig. 3. Time taken to establish thermal equilibrium as a function of ammonium adsorbed on NaY (1); HY (2); and DY-6.3 (3) zeolites.

ammonia molecules can penetrate the small cavities of NaA zeolites [9].

As shown in Fig. 1, the maximum retardation of the process in the region of large surface coverage occurs in the case of NaA zeolite, where all six-membered apertures leading from large to small cavities are occupied by cations. In NaX and NaY zeolites, some of these apertures remain free and, thus, the small cavities are more easily penetrated. The mordenite structure contains no sodalite cages and accordingly the retardation of the heat liberation could not be observed at high fillings of the mordenite channels.

3.4. Hydrogen Y zeolites

A similar trend in the thermal kinetics is observed for decationated and dealuminated faujasites. The corresponding results are depicted in Fig. 3. For all samples the time taken to establish equilibrium sharply increases with growth of filling, passes through a maximum, and then decreases to reach a constant value that is nearly independent of filling.

Thermokinetic curves for hydrogen forms, given in Fig. 3, are similar to the plots derived for sodium Y zeolites. In decationated and dealuminated faujasites, the acid centers represent the strongest adsorption sites. Fig. 4 shows the position of the kinetic-curve maximum against the concentration of the acid sites. The linear dependence indicates that the slow processes are associated with filling of the acid sites. As the number of the free acid sites decreases, more time is required for the adsorbed molecules to reach them. Once all acid sites have been covered with NH_3 the process proceeds rapidly and with smaller heat effect.

When the adsorption temperature is increased to 300°C, equilibrium is established much faster. A time lapse between 3 and 4 h is sufficient to reach equilibrium after admission of ammonia on Y zeolites. Once all acid sites have been covered with ammonia, equilibrium is established in less than 1 h. At high

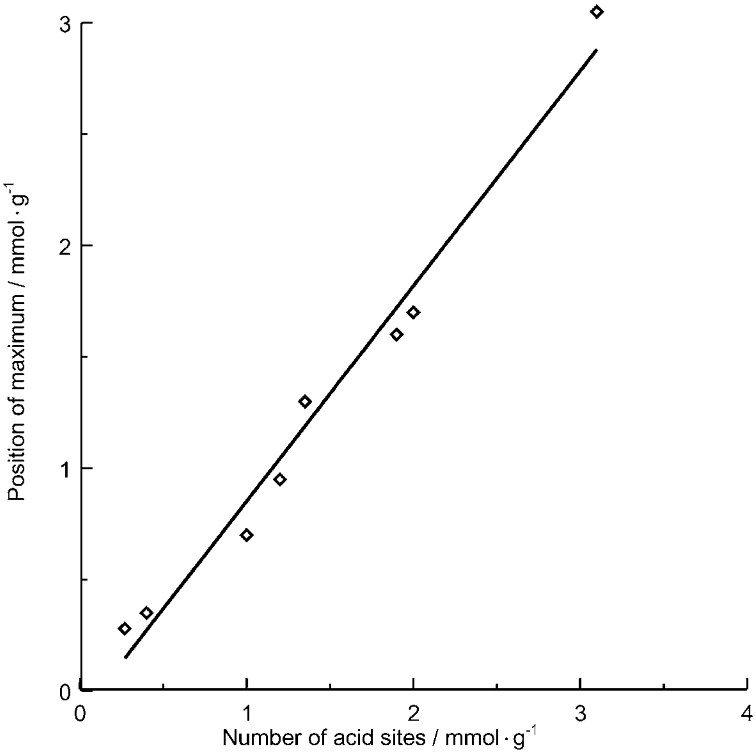

Fig. 4. Dependence of the position of the kinetic-curve maxima on the number of acid sites in hydrogen Y zeolites.

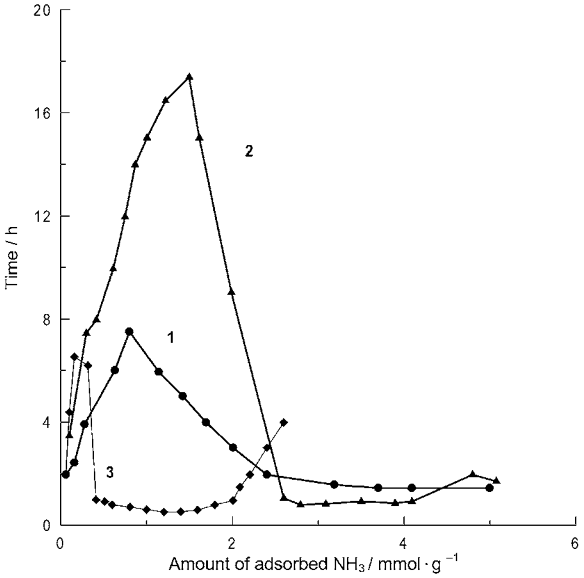

Fig. 5. Time taken to establish thermal equilibrium as a function of ammonium adsorbed on NaM (1); HM-6.3 (2); and DM-24 (3) mordenites.

equilibrium pressure, the secondary retardation of the heat evolution is observed. This process is accompanied by slow absorption of NH_3 from the gas phase that, probably, is related to diffusional phenomena in zeolites.

3.5. Hydrogen mordenites

Decationated and dealuminated mordenites show slower rates of the heat evolution (Fig. 5). For Na-mordenite, the time taken to establish the thermal equilibrium after consumption of 1.5 mmol/g of NH_3 does not exceed 3–5 h, whereas on the hydrogen form with $\mathrm{Si/Al} = 6.3$ the same portion of ammonia is equilibrated only after18 h. With further adsorption, the time taken to establish the thermal equilibrium increases and at fillings above 4 mmol/g adsorption again is slowed down. As the extent of dealumination increases, the profile of curves describing the dependence of the time of heat liberation on filling remains unchanged, but the maximum is moved towards lower uptakes.

Like other zeolites, mordenite shows the slow process of the heat liberation at low coverage when ammonia interacts with the strongest adsorption sites. The reduction of the total number of the strong acid sites on dealumination accelerates an establishment of thermal equlibrium and displaces the kinetic-curve maximum towards smaller fillings.

3.6. L zeolites

Low rates of heat liberation were not observed with KL and NaKL zeolites and the time taken to establish the thermal equilibrium varies ranging from 1 to 1.5 h. The lack of cations weakly bound to the framework seems to be a reason. When ammonia is adsorbed on decationated samples, the time taken to establish thermal equilibrium increases, and the maximum on the curves adsorption–time is displaced towards large fillings. Fig. 6 indicates that the slow liberation of heat is characteristic of such fillings (up to 1 mmol/g), at which interaction of molecules of ammonia with the strongest acid sites can be expected. When these sites are covered with ammonia molecules, equilibrium is established rapidly. However, with further increase of the amount adsorbed, the process is again slowed down. In this region, the slow liberation of heat occurs simultaneously with slow absorption of ammonia from the gas phase.

On the basis of the kinetic results outlined above, it is seen that the time taken to establish thermal equilibrium is dependent on chemical composition of zeolite material and varies with nature of zeolite.

In the region of low fillings, where the interaction with the strongest sites predominate ($q > 90$ kJ/mol), a large liberation of heat is observed which is not connected to adsorption from the gas phase and is caused by redistribution of the sorbed ammonia molecules on energetically most favorable sites. When all such sites have been filled, equilibrium is attained rapidly. As the amount adsorbed increases, the process is again slowed down. In this region, the slow liberation of heat is accompanied by slow absorption of ammonia from the gas phase attributable to diffusion limitations inside zeolite channels.

3.7. The adsorption kinetic equation

According to the proposed mechanism, the adsorption kinetics in the region of small coverages can be described by a second-order equation. The rate of the slow process is a linear function of on the concentration

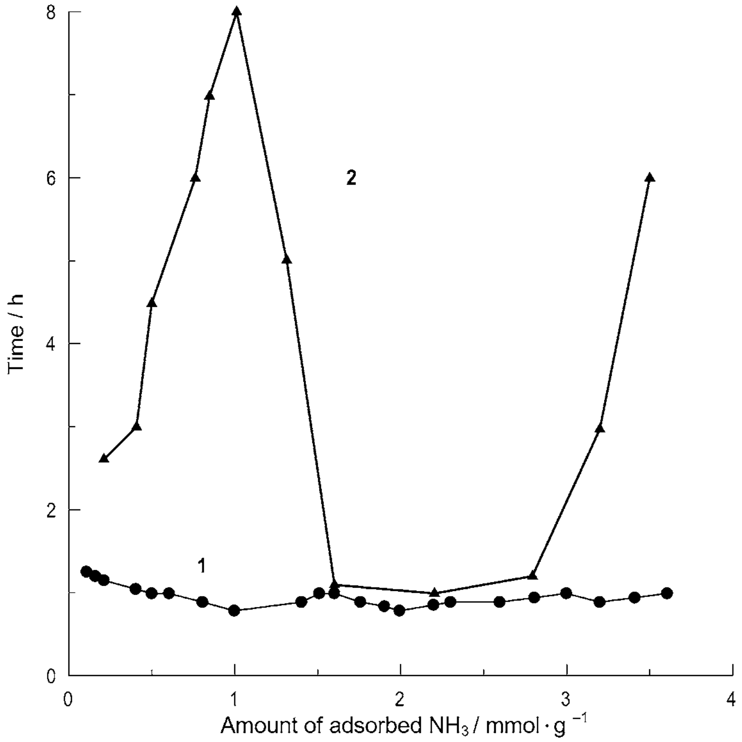

Fig. 6. Time taken to establish thermal equilibrium as a function of ammonium adsorbed on KL (1); and HKL (2) zeolites.

of unoccupied weakly bound cations and of the concentration of ammonia molecules capable for interacting these cations

$$\frac{da}{dt} = k(N_i - a)(A_i - a) \tag{1}$$

where A_i is the size of the i-th dose; N_i the number of unoccupied cations before the i-th dose; $N_i = N_0 - \sum_1^{i-1} A_i$; N_0 the number of weakly bound cations in the initial zeolite; k the rate constant; a is the amount of ammonia interacting with he cation in time t. After each dose, a changes from 0 to A_i. The values a, N and A are expressed in millimoles and related to each weight of sample of zeolite in the calorimetric cell.

For very slow processes, it can be assumed that the deflection of the recording pen is proportional to the thermal output of the process (W) which is equal to

$$W = \frac{da}{dt} q \tag{2}$$

where q is the heat effect of the process.

Integrating Eq. (1) and substituting Eq. (2) into it, we get

$$W_i = \frac{e^{k(N_i - A_i)t}(N_i - A_i)^2 (A_i/N_i)kq}{\left(e^{k(N_i - A_i)t} - (A_i/N_i)\right)^2} \tag{3}$$

This equation describes the heat-liberation kinetic curve, i.e. $W = f(t)$, for the i-th dose of gas. It is difficult to test the applicability of this equation because, in addition to the variables W and t, it contains two unknown constants k and q. To determine these constants, it is necessary to select several t values and their corresponding W values from the experimental curve. For each such pair, by substituting the different k values, it is possible to obtain a curve, which correlates q and k. For several points of the experimental curve, such curve must cross at one point. The coordinates of the point of intersection give the value of q and k for which the experimental curve is described by Eq. (3). However, the test showed that such curves usually do not intersect at one point with sufficient accuracy and hence Eq. (3) does not fully describe the experimental curves. Moreover, we were unable to obtain constant k values for different doses on one sample. It is possible that the equation derived were based on a simplified model. For example, it is assumed that all adsorbed molecules are involved in redistribution, whereas some of them could be adsorbed immediately on strong sites. It may be that the N_0 values selected from literature were insufficiently accurate.

Nevertheless, Eq. (3) can be applied to describe the curves shown in Fig. 1. For this, it is necessary to solve the equation with respect to t, and to determine for each dose the value $\hat{o}_i$ for a constant value of $W_i = 20\mathrm{W}$

$$\tau_i = \frac{2}{k(N_i - A_i)} \ln\left[\frac{1}{2}\sqrt{\frac{A_i qk}{N_i W_i}}\left\{N_i - A_i + \sqrt{(N_i - A_i) + \frac{4W_i}{qk}}\right\}\right] \qquad (4)$$

As the degree of surface coverage increases, N_i decreases, hereby increasing τ_i. In other words, as the number of strong adsorption sites decreases, the process slows down. After all centers have been filled, the slow process ends and $\tau_i = 0$, i.e. the curve passes through a maximum.

The size of the dose, A_i strongly affects the thermal-equilibrium time τ_i. A rapid increase of τ_i with the increase of surface coverage is associated with a decrease in the number of free sites, N_i, but also with the fact that the size of the dose is usually increased gradually from point to point. However, a change in A_i cannot substantially affect the position of the maximum, which depends mainly on the total number of sites N_0. This explains coincidence of the maxima on the curves obtained for two NaX and two NaY samples, although the adsorption was measured with different dose values.

When the applicability of Eq. (4) was tested, we found that for each sample we could select values of the constants k and q for which the equation adequately

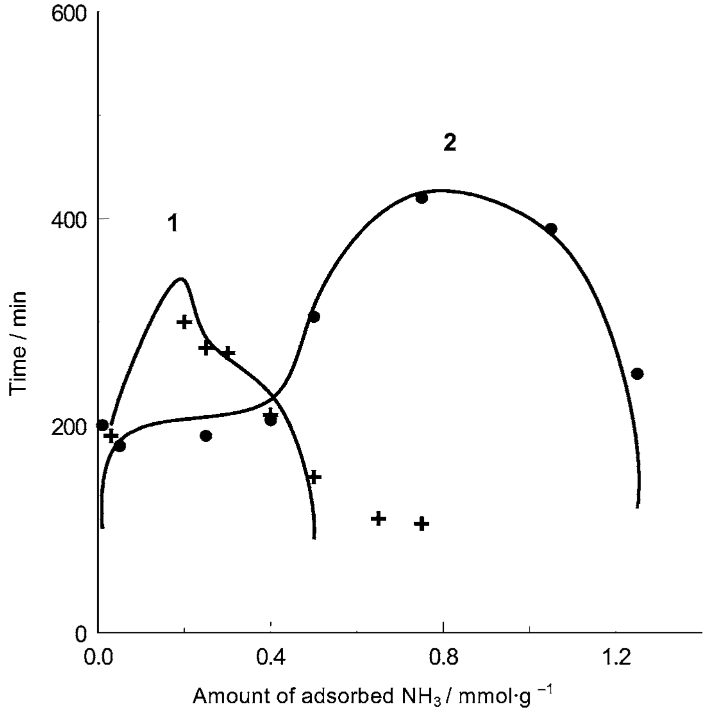

Fig. 7. The kinetic curves for ammonia adsorption on NaY (1); and NaM (2) zeolites; symbols are experimental points and lines are curves calculated from Eq. (4).

fitted the curve shown in Fig. 1. As an example, we present in Fig. 7 the calculated curves and experimental points for the adsorption of ammonia on zeolites NaM and NaY. The coincidence of calculated and experimental results indicates that Eq. (4) approximately describes the kinetics of the process in these two cases.

A study of isotherms, heat liberation, and kinetics of thermal liberation has further clarified the mechanism of ammonia adsorption on zeolites. In the region of small coverage, ammonia molecules interact with the weakly bound cations in the large cavities. This process is associated with a large heat of adsorption and is accompanied by a slow liberation of heat when the adsorbed molecules are redistributed. After the weakly bound cations have been covered, ammonia molecules are adsorbed on cations located on the six-membered rings to yield smaller heat effects. In this case, equilibrium is established rapidly. In the region of large surface coverage, ammonia penetrates into the small cages of A, X and Y zeolites. A slow migration of NH_3-cation adsorption complexes can also be involved in adsorption.

Acknowledgements

The authors are indebted to Professor Ariel Klyachko for valuable assistance in the measurements and fruitful discussions.

References

[1] T.R. Brueva, A.L. Klyachko, I.V. Mishin, A.M. Rubinshtein, Kinet. Catal. 20 (1979) 990.
[2] A.L. Klyachko, T.R. Brueva, A.M. Rubinshtein, Kinet. Catal. 20 (1979) 1521.
[3] G.I. Kapustin, T.R. Brueva, A.L. Klyachko, A.M. Rubinshtein, Kinet. Catal. 22 (1981) 1561.
[4] J.B. Uytterhoeven, R. Schoonheid, B.V. Liengme, W.K. Hall, J. Catal. 13 (1969) 425.
[5] A.A. Fomkin, N.I. Regent, V.A. Sinitsin, Russ. Chem. Bull. (2000) 1018.
[6] M.M. Dubinin, A.A. Isirikyan, G.U. Rakhmatkariev, V.V. Serpinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1972) 1972.
[7] M.M. Dubinin, A.A. Isirikyan, A.I. Sarakhov, V.V. Serpinsky, Bull. Acad. Sci. USSR, Div. Chem. Sci. (1969) 2355.
[8] S.S. Khvoshchev, S.P. Zhdanov, Dokl. Akad. Nauk SSSR 200 (1971) 1156.
[9] R.Y. Yanagida, K. Seff, J. Phys. Chem. 76 (1972) 2597.