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CALORIMETRIC STUDY OF NH_3 AND CO_2 ADSORPTION ON ERIONITES AND ZEOLITES L

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ABSTRACT

The heats of adsorption of CO_2 and NH_3 on sodium–potassium, calcium–potassium and hydrogen erionites and on zeolites L containing Na^+, K^+, Ca^{2+}, Mg^{2+} and La^{3+} ions were calorimetrically measured. At low coverages a considerably smaller number of Ca^{2+} ions in erionites is involved in the interaction with CO_2 molecules compared with NH_3 molecules. The substitution of Na^+ ions by Ca^{2+}, Mg^{2+} or La^{3+} in zeolites L leads to a decrease in heats of adsorption of CO_2. The number of Mg^{2+} ions forming adsorption complexes with NH_3 in zeolites L significantly exceeds the corresponding numbers of Ca^{2+} and La^{3+} ions. The ion exchange data suggest that a greater number of Mg^{2+} ions in contrast to Ca^{2+} and La^{3+} ions occupy the main channel sites.

INTRODUCTION

Crystal lattices of erionites and zeolites L are in the form of columns in which hexagonal prisms alternate with cancrinite cages. The columns are interconnected in such a way that in the case of zeolite L there are large canals formed by twelve-membered rings [1]. In erionites there are large cavities between the columns joined via eight-membered oxygen rings [2]. Some of the exchangeable cations (initially K^+ ions) are located inside the columns. In hydrated zeolites such cations contain no H_2O molecules in either the first or the second coordination spheres and as a rule do not participate in ion-exchange reactions at room temperature. Consequently, they should not be involved in the adsorption interactions even with small polar molecules. This also applies to cations located between the neighbouring cancrinite cages in the zeolite L lattice.

Dehydration at elevated temperatures can lead [3–6] to “an intrinsic ion exchange”, i.e. to the shift of some K^+ ions from the columns to large cavities and canals, and to the occupation of some sites in the columns by other cations. On rehydration, the initial distribution of cations between different crystallographic positions is restored only partly.

Ion-exchange reactions at room temperature usually proceed with the participation of cations occupying positions at 8- and 6-membered oxygen

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rings of large canals in zeolite L. Consequently, cations in these positions will also be involved in the process of formation of adsorption complexes. The heats of adsorption of gases and vapours on erionites and zeolites L should be determined to a considerable degree by the contribution of interactions of these cations with adsorbate molecules.

Reports on the heats of adsorption on erionites are rather scarce and refer mainly to inert gases [7] and some hydrocarbons [8]. The energetic characteristics of adsorption on zeolites L containing cations of polyvalent metals have also been little studied. Studies have only been made on the heats of immersion of some ionic forms of zeolite L in water [9] and benzene [10], the isosteric heats of CO_2 and NH_3 adsorption on zeolites L containing ions of some transitions metals [11] and the calorimetric heats of adsorption of CO_2 on zeolite (Ca,K)-L [12,13]. This work reports experiments on the influence of $Na^+ \rightarrow Ca^{2+}$ substitution in synthetic erionites and zeolites L and $Na^+ \rightarrow Mg^{2+}(La^{3+})$ substitution in zeolites L on the heats of adsorption (Q) of CO_2 and NH_3.

EXPERIMENTAL

The ion-exchanged forms of erionites and zeolites L were obtained by ion-exchange from appropriate potassium–sodium samples. The latter were synthesized by M.A. Shubaeva. All samples were degassed at 673 K for 20 h prior to the determination of heats of adsorption. The chemical composition of the dehydrated crystals is given in Table 1.

The heats of adsorption of CO_2 were measured on a microcalorimeter DAK-1-1 (U.S.S.R.) at 303 K and of NH_3 on a microcalorimeter MS-70 (Setaram, France) at 308 K. Adsorption was measured by volumetric adsorption systems connected to the microcalorimeters. The times of establish-

TABLE 1

Chemical composition of dehydrated crystals

Zeolite	Composition
Erionites	
(Na,K)-E	$0.75\ Na_2O \cdot 0.31\ K_2O \cdot 7.6\ SiO_2 \cdot Al_2O_3$
(Ca,K)-E	$0.67\ CaO \cdot 0.34\ K_2O \cdot 7.6\ SiO_2 \cdot Al_2O_3$
(H,K)-E	$0.03\ Na_2O \cdot 0.42\ K_2O \cdot 7.6\ SiO_2 \cdot Al_2O_3$
Zeolites L	
(Na,K)-L	$0.42\ Na_2O \cdot 0.55\ K_2O \cdot 5.5\ SiO_2 \cdot Al_2O_3$
(Ca,K)-L	$0.47\ CaO \cdot 0.55\ K_2O \cdot 5.5\ SiO_2 \cdot Al_2O_3$
(Mg,K)-L	$0.44\ MgO \cdot 0.63\ K_2O \cdot 5.5\ SiO_2 \cdot Al_2O_3$
(La,K)-L	$0.13\ La_2O_3 \cdot 0.67\ K_2O \cdot 5.8\ SiO_2 \cdot Al_2O_3$

ment of thermal equilibria for various zeolites ranged from several minutes to several hours for CO_2 and from several hours to several days for NH_3.

RESULTS AND DISCUSSION

Sodium–potassium zeolites

The calorimetric heats of adsorption of NH_3 and CO_2 by zeolite (Na,K)-L (Fig. 1) are slightly higher than the isosteric heats of adsorption measured earlier by us [14] but correspond exactly to the latter in the shape of changes with the amount sorbed. In the zeolite (Na,K)-L under study the Na^+ cations (3.8 cations per unit cell) can be involved in the interaction with the adsorbate, and the K^+ cations (5 cations per unit cell) located in the columns are fully screened by oxygen atoms in the lattice. The Na^+ cations are preferential adsorption centres in this zeolite, and the step in the NH_3 heat curve in the region of coverages between 3 and 5 molecules per unit cell (molec. u.c.$^{-1}$) corresponds to the completion of the formation of $Na^+ \ldots NH_3$ adsorption complexes. At higher coverages the adsorbed molecules interact mainly with oxygen atoms.

Unlike zeolite L, there are no steps on the isotherm of NH_3 heats of adsorption in the case of erionite (Fig. 2). The latter contains 5.2 Na^+ ions and 2.3 K^+ ions per unit cell; however, up to a coverage of about 13 molec. u.c.$^{-1}$ Q decreases monotonically. At coverages of from 3 to 4 molec. u.c.$^{-1}$ an acceleration in heat evolution is observed. The amount of the heat

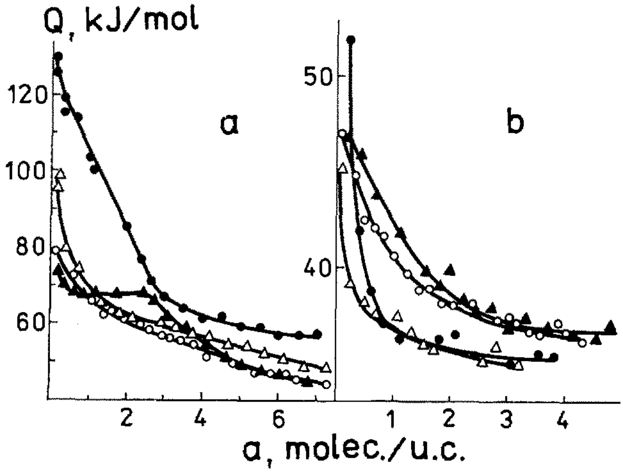

Fig. 1. Heats of adsorption of NH_3 (a) and CO_2 (b) on zeolites L: ▲, (Na,K)-L; ○, (Ca,K)-L; ●, (Mg,K)-L; △, (La,K)-L.

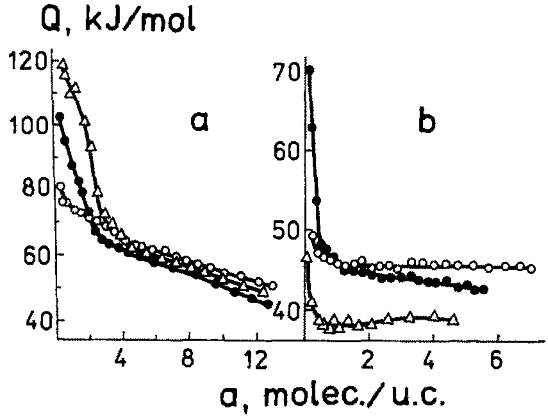

Fig. 2. Heats of adsorption of NH_3 (a) and CO_2 (b) on erionites: ○, (Na,K)-E; ●, (Ca,K)-E, △, (H,K)-E.

evolved after the first two hours decreases here from 3–5% to less than 1% of the adsorption heat.

For zeolite (Na,K)-L evolution of heat accelerates strongly at coverages corresponding to the step on the heat curve. Both these features of the adsorption process can be regarded as the result of a change in the mechanism of adsorption. Prior to this relatively narrow region of coverages the adsorbed molecules interact preferentially with cations, and after it with framework oxygen atoms. In this case the appropriate change for erionite can take place in the region of coverages of from 3 to 4 molec. u.c.$^{-1}$ From 2 to 4 cations per unit cell of erionite should occupy the sites in the hexagonal prisms and cancrinite cages [3,4]. The majority of K^+ ions and some Na^+ ions which moved to these sites during dehydration in the process of "intrinsic ion exchange" can be located there.

The quantity of such Na^+ ions can be estimated from the results of treating zeolite (Na,K)-E with KNO_3 solution after preliminary dehydration. Such a treatment at room temperature with a 100-fold excess of K^+ ions in the solution leads to a decrease in the Na_2O/Al_2O_3 ratio of from 0.75 to 0.11. Thus only about 0.8 Na^+ ions per unit cell of this zeolite is not substituted by K^+ and can be assumed to be located in the columns. These Na^+ ions should not be available for NH_3 molecules. The remaining cations (from 3.5 to 5.5 per unit cell of zeolite (Na,K)-E) can participate in the adsorption interactions. After the formation of adsorption complexes with these cations has been completed, an acceleration in the heat evolution process can be observed.

The heat of CO_2 adsorption on Na,K-erionite does not change at all at coverage of from 1 to 7 molec. u.c.$^{-1}$ This implies that the energies of interaction of adsorbed molecules with all cations which take part in such an interaction must be virtually the same.

The heat of adsorption of CO_2 on zeolite (H,K)-E containing only 3.2 K^+ cations and less than 0.3 Na^+ cation per unit cell is much lower than on zeolite (Na,K)-E (Fig. 2), This suggests that the presence of cations significantly strengthens the adsorption field. Values of Q for CO_2 comparable with the appropriate values for zeolite (Na,K)-E are observed in the case of zeolite (H,K)-E within a very narrow region of small coverages. Thus only a very small number of cations in this zeolite participate in the formation of adsorption complexes.

Calcium–potassium erionite

The heats of adsorption of CO_2 and NH_3 on zeolite (Ca,K)-E (Fig. 2) decrease sharply in the range of low coverages from rather high values to ones close to the appropriate Q for zeolite (Na,K)-E. At higher coverages the changes become more smooth and the Q values appear to be somewhat lower than on Na,K-erionite. The length of the initial part of the heat curve for NH_3 coincides accurately with the total number of Ca^{2+} ions (2.5) per unit cell of zeolite (Ca,K)-E. For CO_2 a sharp decrease in Q is observed only up to coverages of about 1 molec. u.c.$^{-1}$ This can indicate that at low coverages a considerably smaller number of Ca^{2+} ions is involved in the interaction with CO_2 molecules compared with NH_3 molecules.

A substantial number of the Ca^{2+} cations in erionite will probably be located in screened sites, i.e. in hexagonal prisms and cancrinite cages. In hydrated erionite the cancrinite cages are occupied by K^+ ions, and the Ca^{2+} ions are in the large cavities [3,4]. On dehydration of erionite the cancrinite cages are populated by Ca^{2+} ions and the K^+ ions move to the large cavities. Hence, in dehydrated erionite only a small number of Ca^{2+} cations can be located in large cavities.

On hydration some of the Ca^{2+} ions return to the large cavities and their sites are occupied by K^+ ions. Treatment of dehydrated zeolite (Ca,K)-E with KNO_3 solution at room temperature leads to a decrease in the CaO/Al_2O_3 ratio of from 0.67 to 0.27. Thus, almost one-half of the Ca^{2+} ions were not substituted by K^+ and consequently could not be involved in the adsorption interaction with H_2O molecules. An analogous conclusion can be made in respect of NH_3 as the difference in interaction energies of NH_3 and H_2O with cations is small. Some Ca^{2+} cations, capable of exchange for K^+ in dehydrated zeolites should also be located in the columns. These cations move to large cages during the adsorption of H_2O or NH_3.

The CO_2 molecules should interact with cations much more weakly than the NH_3 molecules. It may be assumed that only the Ca^{2+} cations which are located in the large cavities of the dehydrated zeolite will be the preferential adsorption centres for CO_2 molecules. The displacement of the other Ca^{2+} ions from the screened sites to the large cavities should not proceed in this case. This may be one of the reasons for differences in the length of the parts of the heat curves with higher Q for CO_2 and NH_3. Another possible reason is the involvment of NH_3 molecules in interactions with acid sites of zeolite (Ca,K)-E. The possible contribution of such interactions to the total adsorption energy in the case of (Ca,K)-E can be estimated from a comparison of the heats of adsorption on this zeolite and on the hydrogen erionite where they play the determining role. Figure 2 shows that the heat of adsorption of NH_3 on hydrogen erionite is higher at low coverages than on the calcium–potassium zeolite. The number of NH_3 molecules adsorbed in the range of coverages where the heats sharply decrease for zeolite (H,K)-E (to 3–4 molec. u.c.$^{-1}$) agrees well with the possible number of acid sites determined by the cationic deficiency (4.1 per unit cell). For both samples the adsorption heats decrease with increasing coverage, assuming the same values at different parts of the curves. This suggests that the relatively high heats of adsorption of NH_3 on (Ca,K)-E zeolite at small coverages are evidence of the interaction of adsorbed molecules not only with Ca^{2+} cations, but also with acid sites.

Zeolites L with Ca^{2+}, Mg^{2+} and La^{3+} ions

It may seen from Fig. 1 that substitution of Na^+ ions by Ca^{2+}, Mg^{2+} and La^{3+} leads to a decrease in Q for CO_2 in zeolites L. According to ref. 11 an analogous effect is also observed in the case of Na^+ exchange in zeolites L for Cr^{2+}, Co^{2+}, Y^{3+} and Fe^{3+}. For NH_3 the decrease in Q on $Na^+ \rightarrow Ca^{2+}(La^{3+})$ substitution takes place only in a narrow region of coverages (of from 1 to 4–5 molec. u.c.$^{-1}$). At coverages of up to about 1 molec. u.c.$^{-1}$ parts of isotherms with high Q values are observed in these cases. For zeolite (Mg,K)-L the heats of NH_3 adsorption in a wide region of coverages are considerably higher than for other zeolites. This suggests that the number of Mg^{2+} ions involved in a direct interaction with adsorbed NH_3 molecules exceeds significantly the corresponding numbers of Ca^{2+} and La^{3+} ions.

As shown in ref. 15, the number of cations located in screened sites of zeolites L can be estimated from the back-exchange for Na^+ ions at room temperature, since in this case only cations located in 8-membered rings of the large canals (D sites) will be substituted.

Zeolites (Mg,K)-L, (Ca,K)-L and (La,K)-L were treated at room temperature with $NaNO_3$ solution (at a ratio of Na^+ in solution to the zeolite ions of 100 : 1). Treatment was made prior to and after dehydration under conditions corresponding to those of the calorimetric experiments.

As seen from Table 2, treatment with $NaNO_3$ of zeolites not subjected to dehydration leads to a sharp decrease in the Mg/Al and La/Al ratios in the appropriate samples, whereas the Ca/Al ratio in zeolite (Ca,K)-L decreases to a lesser degree. This indicates that in the course of ion exchange (at 363 K) a greater part of Ca^{2+} ions and some Mg^{2+} and La^{3+} ions already

TABLE 2

Influence of treatment with $NaNO_3$ solution on the ionic ratios in zeolites

Sample type	(Ca,K)-L Ca/Al	(Mg,K)-L Mg/Al	(La,K)-L La/Al
Initial samples	0.23	0.22	0.13
Samples treated with $NaNO_3$ prior to dehydration	0.14	0.04	0.04
Samples treated with $NaNO_3$ after dehydration	0.21	0.06	0.12

occupy screened sites in the lattice. On dehydration the number of such cations increases. The La/Al and Ca/Al ratios in zeolites treated with $NaNO_3$ after dehydration appear to be close to the corresponding values for initial samples (Table 2). Consequently, only a small number of La^{3+} and Ca^{2+} ions can occupy D sites in dehydrated zeolites (not more than 0.1 and 0.2 cations per unit cell, respectively). Thus, the decrease in Q for CO_2 and NH_3 on exchange of Na^+ for Ca^{2+} and La^{3+} is a result of the shift of virtually all these cations on dehydration to screened sites where they do not participate in the adsorption interactions.

The Mg/Al ratio in zeolite (Mg,K)-L treated with $NaNO_3$ solution after dehydration is somewhat higher than in the sample treated prior to dehydration, but is lower than in the initial sample. This indicates that the number of Mg^{2+} ions occupying D sites in dehydrated zeolite (Mg,K)-L (1.3 cations per until cell) appears to be considerably higher than the appropriate numbers of Ca^{2+} and La^{3+} ions in dehydrated zeolites (Ca,K)-L and (La,K)-L. Such a result agrees on the whole with data reported in ref. 15. In this case the dehydration of zeolites L in air at 923 K leads to the displacement to screened sites of 60–70% of Ca^{2+} and La^{3+} ions but only 25–30% of ions of smaller size (Co^{2+}, Cu^{2+}, Zn^{2+}).

Low values of Q for CO_2 on zeolite (Mg,K)-L indicate that the number of Mg^{2+} ions forming adsorption complexes should also be small in this case. It is apparent that Mg^{2+} ions capable of substitution by Na^+ shift on dehydration to the positions between the hexagonal prisms (E sites) where they are also screened by oxygen atoms. Such an assumption was made in ref. 1 as applied to other cations. The energies of interaction between CO_2 molecules and cations are apparently insufficiently high to stimulate back-shifts of Mg^{2+} cations from E sites to D sites. This can take place, however, during the NH_3 adsorption and therefore the Q value for NH_3 on zeolite (Mg,K)-L appears to be very high.

Cations of polyvalent metals occupying screened sites in the zeolite L lattice do exert some influence on the energetics of adsorption although they have not been involved in direct interaction with the adsorbate. At small coverages, Q values for CO_2 on zeolites with Ca^{2+}, Mg^{2+} and La^{3+} ions are higher than on zeolite K-L [14], although the number of K^+ ions that moved on dehydration in the process of "intrinsic exchange" from screened sites to D and E sites should not be greater than the number of K^+ ions located in these sites in zeolite K-L [6,15].

The high initial values of Q for NH_3 on zeolites (Ca,K)-L and especially (La,K)-L can hardly be connected only with the influence of Ca^{2+} and La^{3+} cations remaining in screened sites on adsorption. They also cannot be a result of the presence of a small number of Ca^{2+} or La^{3+} ions in D or E sites. It is more probable that the acid centres of these zeolites can be responsible for high values of Q for NH_3. This may also be true for zeolite (Mg,K)-L in which the acid centres, along with Mg^{2+} cations, can form adsorption complexes of high energies with NH_3 molecules. The heats of adsorption of NH_3 on zeolite (Mg,K)-L at small coverages are rather close to the corresponding values for hydrogen zeolites L [16].

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