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HEATS OF ADSORPTION OF CO_2 and NH_3 ON NATURAL MORDENITES

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The heats of adsorption of CO_2 and NH_3 were studied for sodium, lithium, calcium and decationized forms of natural mordenites. The exchange of Na^+ for Ca^{2+} leads to increasing adsorption heats at low coverages. For CO_2 the region of elevated heats corresponds to the formation of $Ca^{2+} \ldots CO_2$ adsorption complexes. Two molecules of NH_3 probably interact with each Ca^{2+} ion (or with the Li^+ ions in Li-mordenite). The heats of adsorption of NH_3 on decationized mordenite are much higher than those on calcium mordenite.

The heats of adsorption of various substances on synthetic mordenites have been widely studied [1]. At the same time the most reliable structural data about the peculiarities of the crystal lattice geometry and the distribution of ion-exchange cations in it have been obtained from single-crystal studies of natural mordenites [2]. The use of these data for the interpretation of changes in heats of adsorption on synthetic mordenites seems not completely correct.

This paper reports the results of measurements of the heats of adsorption of CO_2 and NH_3 on a natural mordenite from Siberia (zeolite (Ca, Na)—M) and on its sodium and lithium ion-exchanged forms. The adsorption heats were also measured on the hydrogen mordenite obtained by acid treatment of the parent sample.

Experimental

All samples were outgassed at 673 K for 20 h prior to the determination of adsorption heats. The heats of adsorption of CO_2 were measured on a DAK–I–I microcalorimeter (USSR) at 303 K and those of NH_3 on an MS–70 microcalorimeter (France) at 308 K.

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Table 1

Zeolite	Chemical composition of dehydrated crystals
Na—M	0.95 Na_2O, 0.08 CaO, 9.6 $SiO_2 \cdot Al_2O_3$
(Ca, Na)—M	0.47 CaO, 0.56 Na_2O, 9.6 $SiO_2 \cdot Al_2O_3$
(Li, Na)—M	0.88 Li_2O, 0.10 Na_2O, 9.6 $SiO_2 \cdot Al_2O_3$
H—M	0.02 Na_2O, 9.9 $SiO_2 \cdot Al_2O_3$

Results and discussion

It is usually assumed that cations occupying some or other crystallographic positions in the zeolite framework should be the preferential adsorption centres. There are 7.9 Na^+ cations and 0.2–0.3 Ca^{2+} cations per unit cell of zeolite Na—M. The initial decrease in the heats of adsorption (from 90 to 85 kJ/mole for NH_3 and from 85 to 70 kJ/mole for CO_2) probably corresponds to the interaction of adsorbed molecules with the Ca^{2+} cations.

Out of the 7.2 Na^+ ions per unit cell of the sodium form of the natural mordenite described in [2], 1.5 Na^+ ions are located on the walls of the main channels (site VI), while the remaining ions are in the adjoining side-pockets. About 3.1 Na^+ cations occupy strongly distorted eight-membered oxygen rings in the depths of the side-pockets (site I), and 2.6 Na^+ cations occupy eight-membered oxygen rings giving access from the main channels to the side-pockets (site IV).

Studies of the ^{13}C NMR spectra showed [3] that CO_2 molecules adsorbed on Na-mordenite should interact first of all with cations in side-pockets. The NH_3 molecules at small coverages can also do this. Since not all the possible positions in the side-pockets are occupied by cations, the side-pockets themselves appear to be not fully equivalent. Some of them contain two cations, others one cation (in site I or IV), and finally some side-pockets are empty. Thus, the energy states of the molecules in side-pockets (as well as in the main channels if the molecules there interact with cations in sites IV) should differ. This results in a smooth decrease of the heats of adsorption of CO_2 and NH_3 in a wide region of coverages.

There are four side-pockets per unit cell in mordenite. Only one CO_2 molecule can be in each of them. For smaller molecules, such as NH_3, there is a possibility of the population of the side-pockets existing in pairs. This is apparently more probable for side-pockets containing Na^+ cations in sites I and IV simultaneously. The number of such side-pockets per unit cell for zeolite Na—M should be close to two. In this case about six NH_3 molecules can be accommodated in side-pockets and a sharp decrease in the adsorption heat of NH_3, which begins after the adsorption of 5.5–6.0 mol/u.c., corresponds to the completion of formation of adsorption complexes "$NH_3 \ldots Na^+$" in side-pockets.

As seen from Figs 1 and 2, at a coverage of less than 5.5–6.0 mol/u.c. the heat of adsorption of CO_2 decreases more sharply than that of NH_3. This is in contrast to the results obtained for other zeolites [1]. Such a peculiarity of mordenite is probably due to the more pronounced cooperative nature of the influence of cations and framework oxygen ions on the molecules in the narrow side-pockets. The differences in the energy states of the larger CO_2 molecules occupying different side-pockets are greater compared to those for NH_3 molecules.

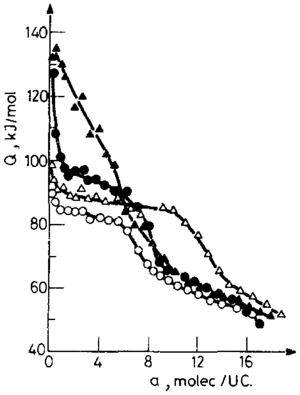

Fig. 1 The differential heats of adsorption of NH_3 on mordenites: 1 ○ – Na—M; 2 ● – (Ca, Na)—M; 3 △ – (Li, Na)—M; 4 ▲ – H—M

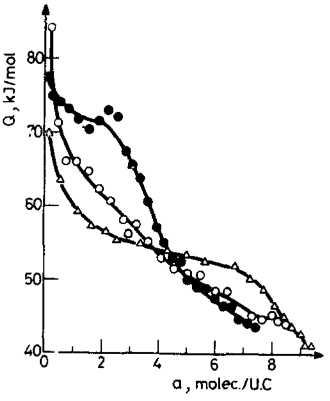

Fig. 2 The differential heats of adsorption of CO_2 on mordenites: 1 ○ – Na—M; 2 ● – (Ca, Na)—M; 3 △ – (Li, Na)—M

In mordenite, like other zeolites, the charges on cations at different sites are compensated to different degrees by the electron density of the oxygen atoms. As the conditions of cation coordination at sites IV and VI are less favourable than at sites I [2], the charge densities on the cations located in the depths of the side-pockets will apparently be lower compared to other cations. The cations with high charge densities have been regarded as preferential adsorption centres [4]. In mordernite, however, the first adsorbed molecules are located in the side-pockets and consequently interact with cations at sites I, although the charge densities on these cations may be relatively low.

If Na^+ and Li^+ ions occupy the same framework sites, the charge densities on the cations decrease the more sharply from Na^+ to Li^+, the more favourable the conditions of their coordination [4]. The decrease in charge density from Na^+ to Li^+ can result in a decrease of adsorption heats at coverages corresponding to the interaction of adsorbed molecules with cations. However, the decrease in cation size leads to an increase in adsorption heat. The tendency to a decrease in adsorption heat will be the predominant factor if the charge densities decrease sufficiently sharply.

If it is assumed that Li^+ and Na^+ ions occupy similar sites in the mordenite framework, the charge densities will decrease from Na^+ to Li^+ most sharply for cations at sites I. As seen from Fig. 2, at low coverages when the CO_2 molecules are adsorbed in the side-pockets and therefore interact with cations in sites I, the adsorption heats on zeolite (Li, Na)—M are lower than those on Na—M.

After one CO_2 molecule has been adsorbed on each of these cations (at a coverage of above 3.5 mol/u.c.), those at sites IV and VI start to be involved in the adsorption interaction. The differences in charge density on the Na^+ and Li^+ ions at these sites are not as large as for those at sites I. As a result, the tendency to an increase in the heat of adsorption at the expense of a decrease in cation size starts to be the predominant factor.

Whereas the exchange of Na^+ for Li^+ in zeolites leads to a decrease in the adsorption heat of CO_2 [5, 6], that of NH_3 usually increases. This is apparently a general rule for zeolites: as seen from Fig. 1, even at low coverages the heat of NH_3 adsorption on zeolite (Li, Na)—M is higher compared to that on Na—M. The adsorption of NH_3 may change the cation location [8]. This provides more favourable conditions for the adsorption complexes to form. A step is observed in the adsorption heat isotherm for NH_3 on zeolite (Li, Na)—M at coverages from 11 to 14 mol/u.c. There are 7.3 Li^+ and 0.8 Na^+ ions per unit cell of this zeolite. It is obvious that the majority of the Li^+ ions are involved in the formation of adsorption complexes "$NH_3 \ldots Li^+ \ldots NH_3$".

There are about 2.0 Ca^{2+} ions per unit cell of zeolite (Ca, Na)—M. The heat of CO_2 adsorption on this zeolite is higher in a wide region of coverages than on zeolite Na—M. According to [2], about 70% of the Ca^{2+} ions in Ca, Na-mordenites are located in side-pockets and the remaining ions are at sites IV and VI. As only one CO_2 molecule can be accommodated in each side-pocket, the possibility of the formation of "$CO_2 \ldots Ca^{2+} \ldots CO_2$" adsorption complexes is excluded for the majority of the cations. This implies that at coverages above 2 mol/u.c. the preferential adsorption centres should be Na^+ cations (4.6 per unit cell). The relatively high heats in the range 2.0–4.5 mol/u.c. indicate the presence of Ca^{2+} cations screened by adsorbed molecules. At higher coverages the heats of CO_2 adsorption on zeolites (Ca, Na)—M and Na—M are practically the same.

Figure 1 shows that the step in the isotherm for NH_3 adsorption on zeolite (Ca, Na)—M is completed at practically the same coverages as for zeolite Na—M. The total amount of cations in zeolite (Ca, Na)—M is much less than that in Na—M. This may indicate that each Ca^{2+} ion (like the Li^+ ion) forms an adsorption complex with two NH_3 molecules.

Zeolites with polyvalent cations usually possess some acidity and the bases can chemisorb at Brönsted or Lewis acid sites. The addition of NH_3 to Ca, Na-mordenite causes the appearance of the absorption spectrum of NH_4^+ ions [9]. The possible contribution of the interaction of NH_3 molecules with acid sites of zeolite (Ca, Na)—M to the total adsorption energy can be estimated from a comparison of the heats of adsorption on this zeolite and on the hydrogen mordenite where such interactions play the determining role.

Our experimental results for zeolite H—M (Fig. 1) are close to the data for the synthetic hydrogen mordenite reported in [10]. The part of the adsorption heat curve up to about 8 mol/u.c. corresponds to the interaction of NH_3 molecules with acid sites (their possible number, as determined from the cation deficiency in zeolite H—M, is 8.1 per unit cell).

Calcium mordenites dehydrated at 673 K mainly contain Brönsted acid sites [11]. In terms of the usual model of the formation of acid sites in zeolites with two-charged cations, the maximum number of protonic sites should be equal to the number of appropriate cations. The TGA study showed that the amount of residual water in the crystals after dehydration ($\sim$1.3 mol/u.c.) is somewhat greater than necessary for two Brönsted sites per unit cell to form.

The heat of NH_3 adsorption on zeolite H—M is significantly higher in a wide range of coverages than on (Ca, Na)—M. However, for both samples the adsorption heat decreases with increasing coverage, assuming the same values at different parts of the isotherms. This suggests that the relatively high heats for NH_3 on (Ca, Na)—M zeolites at small coverages are evidence of the interaction of the adsorbed molecules not only with Ca^{2+} cations, but also with acid sites. Definite conclusions about the correlations of the various forms of adsorbed NH_3 molecules can be drawn only on the basis of additional (and primarily spectroscopic) investigations.

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Zusammenfassung — Adsorptionswärmen von CO_2 und NH_3 an der Na-, Li-, Ca- und dekationisierten Form von natürlichem Mordenit wurden bestimmt. Der Austausch von Na^+ gegen Ca^{2+} führt zu einer Erhöhung der Adsorptionswärmen bei geringen Bedeckungen. Bei CO_2 erfolgt im Bereich hoher Adsorptionswärmen die Bildung des Adsorptionskomplexes $Ca^{2+}\dots CO_2$. Mit jedem Ca^{2+}-Ion (bzw. Li^+-Ion im Li-Mordenit) treten wahrscheinlich zwei NH_3-Moleküle in Wechselwirkung. An dekationisiertem Mordenit sind die Adsorptionswärmen von NH_3 höher als an Ca-Mordenit.

Резюме — Изучены теплоты адсорбции двуокиси углерода и аммиака натриевой, литиевой, кальциевой и декатионизированной формами природных морденитов. Обмен натрия на кальций приводит к увеличению теплот адсорбции при низких степенях заполнения. Область повышенных значений теплот адсорбции двуокиси углерода соответствует образованию адсорбционных комплексов типа $Ca^{2+}\dots CO_2$. В случае аммиака, вероятно, две его молекулы взаимодействуют с каждым ионом кальция (или с ионами лития в литий-мордените). Теплоты адсорбции аммиака на декатионизированном мордените намного выше, чем на кальций-мордените.