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STABILIZED Y-TYPE ZEOLITES FOR GAS CHROMATOGRAPHIC SEPARATION

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SUMMARY

A partially decationized Y zeolite was pretreated under specific conditions. It was found that this calcinated zeolite retains its separation properties for mixtures of the gases H_2, O_2, N_2, CH_4 and CO but has much lower affinity for water molecules than untreated, *e.g.*, A- or X-type zeolites. The observed effect is discussed on the basis of the results of adsorption measurements (adsorption isotherms, capacities, heats of adsorption).

INTRODUCTION

The different types of synthetic zeolites are at present the best available adsorbents for gas chromatographic (GC) separation of some mixtures of gases. One of the first applications of zeolites was described by Kuryacos and Boord in 1957[1]. Martin *et al.*[2] published the separation of H_2, O_2, N_2, CH_4 and CO on zeolites at room temperature. When CO_2 is present in the mixtures of gases the dual column system described by Murakami[3] must be employed because of the very strong interaction of CO_2 with zeolites.

The strong interactions of zeolites with small polar molecules, *e.g.*, CO_2, H_2O, H_2S, SO_2, is due to the presence of cations in the zeolite lattice. The loss of the separation properties of a zeolite in a chromatographic column is caused by blocking of the adsorption centres with H_2O and CO_2 molecules, which can be desorbed only at temperatures above 600° K.

The number of cations present in a zeolite can be decreased by exchange of part of original sodium cations for ammonia ions and followed by thermal dissociation of ammonia. The partially decationized zeolite thus obtained is characterized by its decreased participation in specific interactions[4], but its thermal stability is not satisfactory. Loss of crystalline structure occurs during dehydration at 640°K and increases with increase in the number of hydration–dehydration cycles. The sensitivity to thermal lattic collapse is also proportional to the number of cations in the original forms, *i.e.*, NaA > NaX > NaY. Y-type zeolites are relatively more resistant and suitable thermal treatment can yield complete stability even for the decationized forms. Ultrastable Y-type zeolites, their synthesis and properties, were first described

by McDaniel and Maher[5]. Other methods for the preparation of stabilized Y-type zeolites have since been published[6-8], and the crystal structures, sorption and catalytic properties of these substances have been described. All these zeolites are characterized by high thermal stability, but their Na^+ content is so low that their GC separation properties are unsatisfactory.

The aim of this work was to prepare a stable form of the partially decationized Y zeolite (NaHY) having suitable separation properties, *i.e.*, with a higher content of Na^+ and with decreased sorption affinity for water molecules. Account has been taken of results obtained in our earlier work[8,9].

EXPERIMENTAL

The initial material comprised the sodium–ammonium forms of $NaNH_4Y$ zeolites with the following compositions:

$$Na_{33}(NH_4)_{16}(AlO_2)_{49}(SiO_2)_{143}; \quad Na_{43}(NH_4)_6(AlO_2)_{49}(SiO_2)_{143}$$
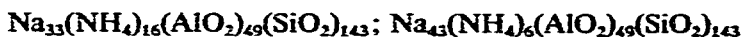
These compositions correspond to Na^+ contents of 67% and 87% of the original NaY form. Stabilization was carried out in a quartz reactor at 825°K under "self steaming" conditions[12]. The instrumental arrangement is depicted in Fig. 1. The quartz reactor was two-thirds filled with $NaNH_4Y$ zeolite and gradually heated in a tube oven to 823.5°K at a rate of 2.5°/min. The pressure of the system was maintained at *ca*. 7800 Pa by use of a manostat connected to the outlet from the reactor. The stabilized powder product was pressed into pellets without a binder, ground and sieved. The fraction of 0.2–0.5 mm was employed in subsequent measurements. The samples were designated USC-87 and USC-67, where the numbers indicate the percent Na^+ content relative to the original NaY form.
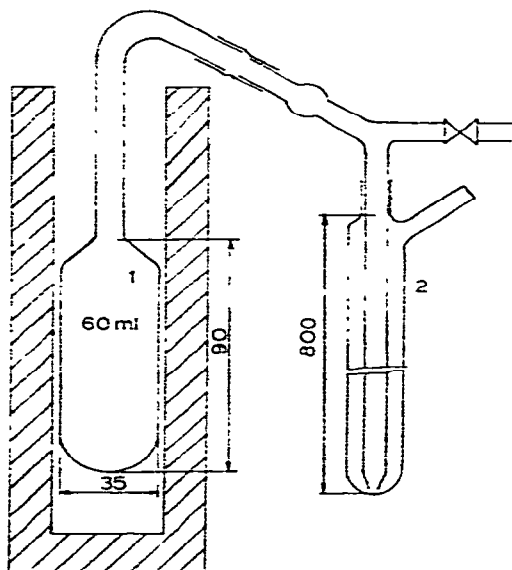

Fig. 1. The apparatus for zeolite stabilization: 1 = quartz reactor; 2 = manostat.

The adsorption capacities, kinetic curves and isotherms were measured on a quartz spring balance.

Chromatographic measurements were carried out on a Chrom-4 laboratory chromatograph (Laboratorní Přístroje, Prague, Czechoslovakia) equipped with a thermal conductivity detector. A 650 × 3.5 mm glass column was employed. The H_2, O_2, N_2, CH_4, CO mixture was separated at laboratory temperature. Heats of adsorption were calculated from the dependence of the retention volumes on temperature using the usual relationship[10].

RESULTS AND DISCUSSION

As has already been mentioned, the lattice of unstable partially decationized zeolites collapses during dehydration. The degree of loss of crystalline structure is proportional to the number of hydration–dehydration cycles. As was found earlier, this decrease in crystallinity is reflected most markedly in the sorption values, measured using argon. For comparison, Table I lists the capacity values for stabilized forms and nonstabilized forms having corresponding numbers of cations, before and after four cycles of hydration at 295°K with dehydration at 633°K *in vacuo*.

TABLE I

SORPTION CAPACITIES, a_s, OF ARGON AT 78° K: INFLUENCE OF REPEATED HYDRA-TION-DEHYDRATION (RH-D)

Adsorbent	Adsorption capacity (mmole/g)	
	Before RH-D	After RH-D
NaHY-67	12.02	6.11
USC-67	10.35	10.26
NaHY-87	12.17	5.34
USC-87	10.21	10.34

The results confirm the positive effect of stabilization. This effect is also important from the point of view of chromatographic separation, since loss of crystallinity of the adsorbent leads to a decrease in its separation effectiveness.

Chromatograms of mixtures of H_2, O_2, N_2, CH_4 and CO on USC-87 and USC-67 zeolites are shown in Fig. 2a and b.

It is interesting that a decrease in the number of cations changes the retention times of all adsorbates by *ca.* 20%, regardless of their ability to interact with the cation. This suppression of specific interactions was also confirmed for stabilized zeolites by the values of the heats of adsorption, given in Table II. It was found that the hydration process for stabilized zeolites exposed to the air at laboratory temperature proceeds more slowly than for the original sodium form. The results of the study of the effect of kinetic factors on the rate of hydration of US zeolites are given in Fig. 3. The time required for attainment of equilibrium both for NaY and for USC-67 zeolites is not greater than 25 min even for the greatest active site occupation. For comparison, the values for the fully cationized form and for USC-67 are also listed. It follows that equilibrium is established equally rapidly for
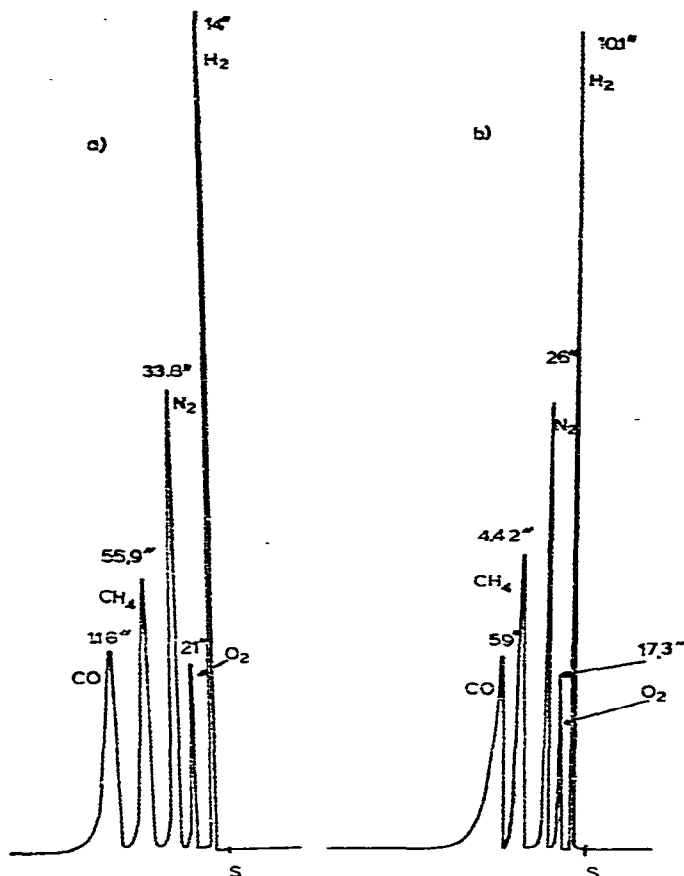
Fig. 2. GC separation of H₂, O₂, N₂, CH₄ and CO on USC-87 (a) and USC-67 (b). Flow-rate, 100 cm/min⁻¹; temperature, 293° K. Column, 600 × 3 mm I.D. Retention times in sec.

TABLE II

CHROMATOGRAPHIC HEATS OF ADSORPTION (kJ/mole) FOR N_2, CH_4, CO ADSORBA TES ON STABILIZED AND NONSTABILIZED NaHY ZEOLITES

Adsorbent	N_2	CH_4	CO
NaHY-87		17.9 ± 0.3	23.9 ± 1.0
USC-87	16.4 ± 0.5	18.1 ± 0.3	21.1 ± 0.8
NaHY-67		18.0 ± 0.2	20.7 ± 0.5
USC-67	16.6 ± 0.7	17.7 ± 0.5	20.9 ± 0.9

both samples, indicating that kinetic factors have no effect on the observed differences in behaviour of the zeolites during hydration.

Fig. 4 depicts the different shapes of the adsorption isotherms of H_2O for NaY and USC-67 zeolites. The practically rectangular isotherm on NaY, which is typical for zeolites, indicates that marked adsorption occurs at very low partial
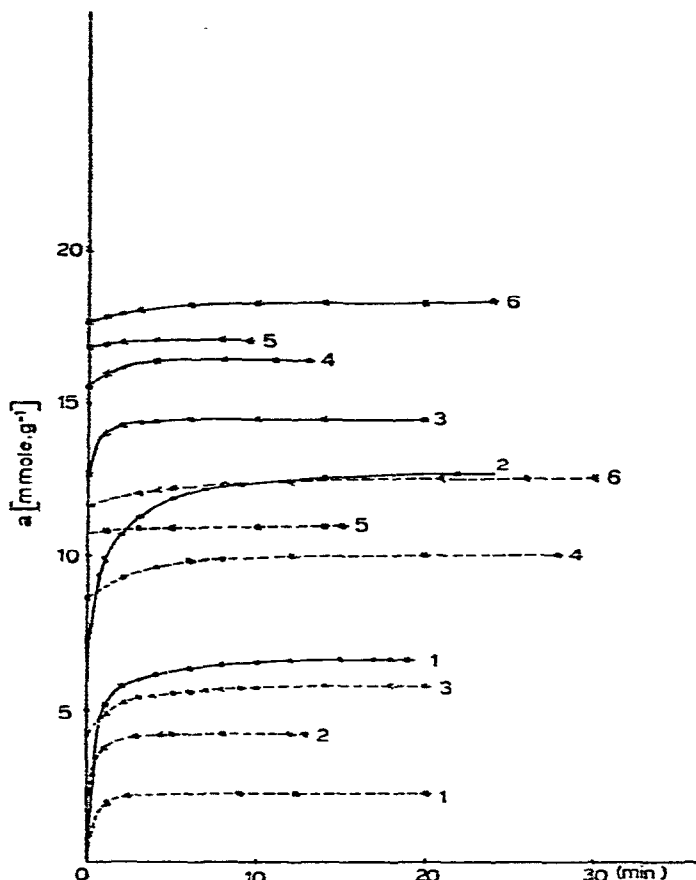
Fig. 3. Kinetic curves for H_2O adsorption on NaY (——) and USC-67 (– – –) zeolites at 294.1° K. p_{H_2O} = 48 Pa (1), 116 Pa (2), 162.6 Pa (3), 695.8 Pa (4), 1250.4 Pa (5) and 2252.8 Pa (6).

pressures. For example, at a relative humidity of 5.9% (294.1°K), the NaY zeolite is saturated, corresponding to 75% of the adsorption capacity; at the same relative humidity, zeolite USC-67 exhibits only 29% of its overall adsorption capacity at this temperature. With NaY, 90% adsorption saturation is attained at a relative humidity of 27.8%, and for USC-67 at a relative humidity of 57.4%. It follows that the stabilization process suppresses the cation sorption activity, i.e., decreases the participation of specific interactions. X-ray structural data and kinetic measurements, however, exclude the occlusion of cations by amorphous components and thus a decrease in their accessibility for adsorbate molecules.

It should be noted, however, that the stabilization process has a marked effect on the crystal lattice. It has been shown[6] that part of the lattice aluminium passes into the cation vacancies, that the values of the lattice constants decrease and that the cations are redistributed. It was found by X-ray photoelectron spectroscopy[11] that the Si/Al ratio and thus the number of cations in the surface layers is substantially different from the values found by elemental analysis of the crystal. This indicates the marked effect on the charge distribution in the crystal and thus on the
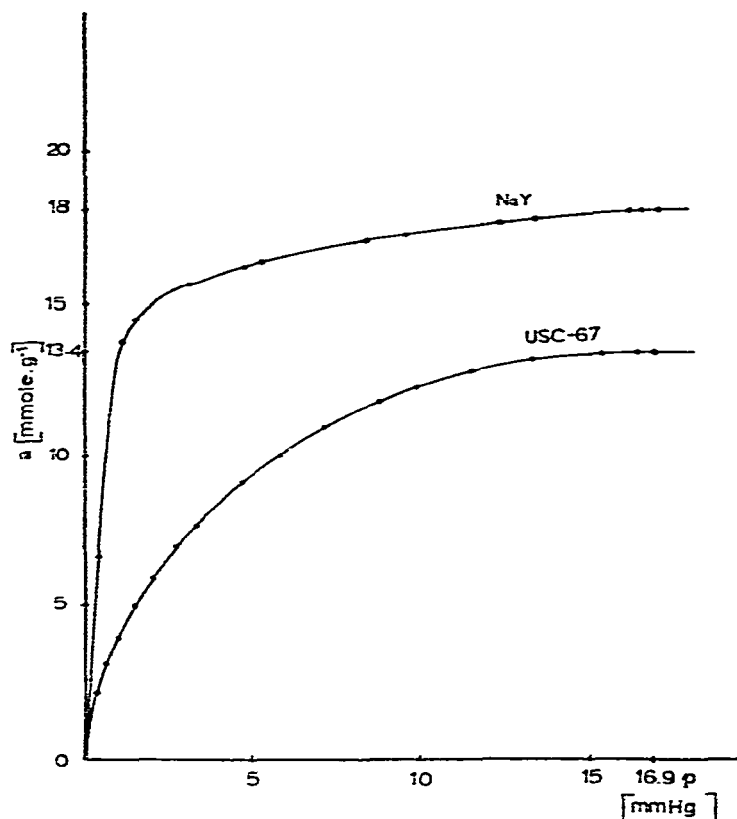
Fig. 4. Adsorption isotherms of H_2O on NaY and USC-67 zeolites at 294.1° K.

character of the interaction of the zeolite with molecules that are preferentially adsorbed on cations.

We feel that these facts are the reason for the marked difference in behaviour of stabilized and non-stabilized forms of NaHY zeolites and could be important for the application of zeolites in gas chromatography.

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