Reversible Adsorption of Hydrogen on Near-Faujasites

In a recent paper King and Benson (*1*) point out that the high heat of physical adsorption of hydrogen on alumina of about 1.5 kcal/mole cannot be satisfactorily explained by dispersion forces. By considering only electrostatic polarization forces they are able to account in principle for the chromatographic separation of the spin isomers and the mass isotopes of hydrogen. Pickert *et al.* (*2*) have studied the isomerization activity of near-faujasites containing various monovalent and divalent cations, and they ascribe the greatly enhanced activity of Ca-13Y over Na-13Y to the much stronger electrostatic field around the calcium ion at site II. In an earlier paper Bachmann, Bechtold, and Cremer (*3*), using a gas chromatographic technique, reported the heat of adsorption of a 3:1 ortho–para mixture of hydrogen on Na-13X to be substantial, 2.02 kcal/mole, even greater than that on alumina.

These results suggested to us that the adsorption of hydrogen in the molecular form should be a sensitive probe for the high electrostatic fields around cations in molecular sieves and that the heat of adsorption of hydrogen on Ca-13Y should be abnormally high. We have therefore determined the isosteric heats of adsorption on Na-13Y (for comparison with Cremer's data on Na-13X) and on Ca-13Y. We believe that the heat of adsorption on Ca-13Y reported here is the highest ever measured for adsorption of hydrogen without dissociation.

EXPERIMENTAL

The adsorption apparatus, gas purification, and experimental procedures have been described previously (*4*). The Na-13Y near-faujasite sample was prepared by washing Linde Na-13Y (type SK-40) overnight at room temperature with a 2.0 *M* solution of NaCl to remove soluble impurities, then washing it free of chloride and drying overnight in a vacuum oven at 60°C preparatory to the final outgassing. Two samples of Ca-13Y were used and were prepared by ion exchange of Linde Na-13Y at room temperature for 3 days with a 1.7 *M* $CaCl_2$ solution, then washing them free of chloride and drying overnight in a vacuum oven at room temperature preparatory to the final outgas. The three samples, weighing initially from 8 to 13 g, were outgassed *in situ* at 120°C for 1 hr, then heated *in vacuo* to 430–440°C in 3–5 hr and evacuated at that temperature for 12 hr. The final pressure in the system was about 10^{-5} torr, and the outgassed samples were white. Adsorbent temperature was maintained by appropriate melting baths in Dewars. The dead space was determined with helium at the conclusion of the adsorption experiments, and the sample was reweighed to get the dry weight, on which the results in the next section are based.

RESULTS

Adsorption on the two samples of the Ca-13Y sample was measured at four temperatures from 222° to 296°K and was rapid, reversible, and linear with pressure except at the higher coverages (greater than about 40 μmoles/g) at the lowest temperature, where a slight deviation from linearity was observed. The two samples gave identical results. Three adsorption isotherms on the Na-13Y sample were determined; the adsorption was similarly rapid and reversible in the temperature range from 195° to 245°K and linear with pressure except at coverages above 30 μmoles/g at the lowest temperature. Pressures from 100 to 700 torr were used, and check points on each isotherm indicated excellent reproducibility.

From the linear isotherms Henry's Law constants, k in μmoles/g torr, were calculated, and plots of log k vs. $1/T$ are given in Fig. 1. Isosteric heats calculated from the data in Fig. 1 are 2.06 kcal/mole from Na-13Y and 2.49 kcal/mole for Ca-13Y.

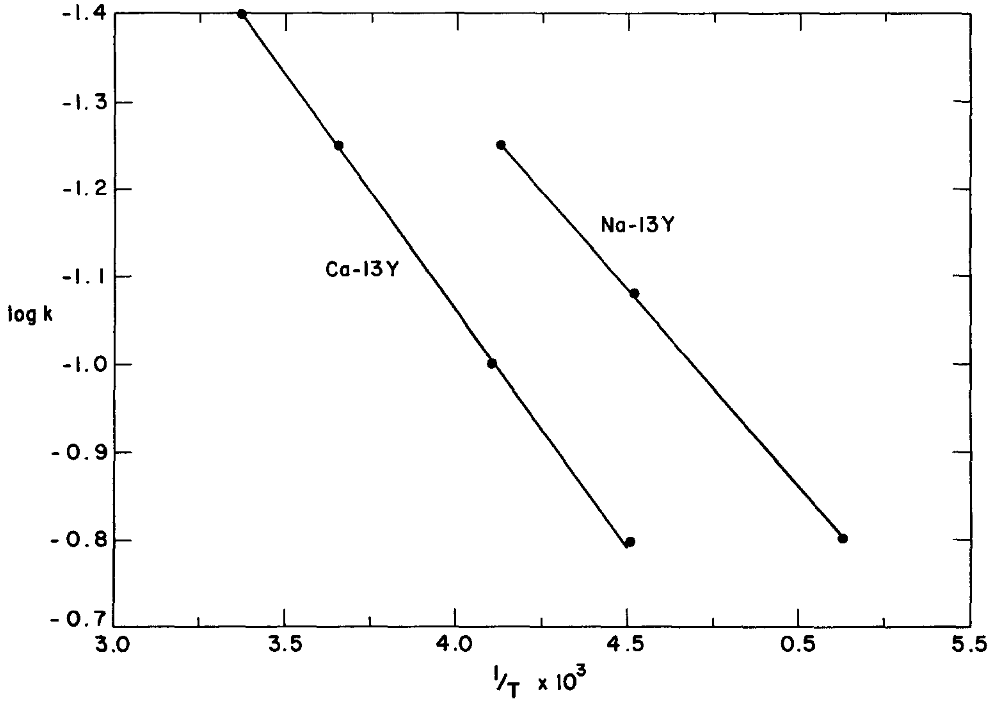

FIG. 1. Adsorption data. A Clapeyron-Clausius plot of decimal logarithms of Henry's law constants k (μmole/g torr) versus inverse of absolute temperature T in °K.

DISCUSSION

The isosteric heat of adsorption on Na-13Y, 2.06 kcal/mole, is in excellent agreement with the value of Cremer *et al.* on Na-13X of 2.02 kcal/mole, calculated for a 3:1 ortho-para mixture from their values for the pure spin isomers at their lowest coverage of 1.5 μmoles/g.

As already pointed out, the isosteric heat of adsorption on Ca-13Y is much larger and is abnormally high for adsorption of molecular hydrogen. Even if we assume that the substantial increase in the heat of adsorption for Ca-13Y is due entirely to the increased field around the calcium ion, we are unable to justify the change quantitatively by using the data of Rabo *et al.* (*5*) for the fields calculated for an ideally ionic structure of the X and Y faujasites. Table 1 is a summary of these calculations. Column 1 gives the measured difference in the isosteric heats of adsorption; in column 2 are given the corresponding differences in the squares of the fields in volts^2/Å^2, calculated from the data in column 1, the average polarizability of hydrogen of 0.79 Å^3/molecule and the conversion factor 1 volt^2 cm/molecule = 1.60×10^8 kcal/mole. The third column gives the difference in the square of the fields as reported by Rabo *et al.* (*5*) at three distances from S II sites in the near-faujasite structure.

TABLE 1
EXPERIMENTAL AND CALCULATED DIFFERENCES IN THE SQUARE OF ELECTROSTATIC FIELDS

	Δq_{st} (kcal/mole)	Exptl. ΔF^2 (V^2/Å^2)	Calcd. ΔF^2 (V^2/Å^2) at		
			2 Å	3 Å	4 Å
NaY-NaX	0.04	0.063	2.98	0.54	0.144
CaY-NaY	0.43	0.34	34.4	5.71	1.44

The isosteric heat difference suggests that the fields around the cations are not as strong as calculated on the basis of an ideally ionic structure. Indeed, the difference in the square of the fields calculated from the isosteric heats is probably high to start with since the entire difference has been assumed to be due to polarization with no dispersion contribution at all.

It appears therefore that the adsorption of simple molecules in Henry's Law region may give a measure of the electrostatic fields in near-faujasite. Further work along these lines is now in progress in our laboratory.

ACKNOWLEDGMENT

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Temperature Profiles in a Rapidly Fouling Catalyst Bed

If the product of a catalytic reaction covers the catalyst surface, the activity of the catalyst will decrease rapidly. In a fixed-bed reactor for an exothermic reaction this will lead to a nonstationary state as follows: Consider an intermediate layer A (Fig. 1) in the catalyst bed. In the beginning the catalyst layers above A are getting fouled. The concentrations of the reactants reaching A will be small and the heat of the reaction liberated in A will also be small. As the layers above A are progressively fouled, the concentration of reactants arriving, and hence the reaction rate and heat liberation, in A will increase steadily. Soon the catalyst in this zone is fouled and the rate and heat liberation fall. Similarly, the lower layers of catalyst also experience in turn increasing rate and higher temperature followed by a fall in both. Thus a zone of highest activity and highest temperature moves through the catalyst bed as a function of time. Froment and Bischoff (*1*) have analyzed such a nonstationary system in the formation of carbonaceous deposits on catalysts in a reaction parallel or consecutive to the main reaction; for the latter case they have predicted that both the rate and temperature profiles should exhibit peak values the loci of which travel through the reactor as time increases.

Such nonstationary situations can also

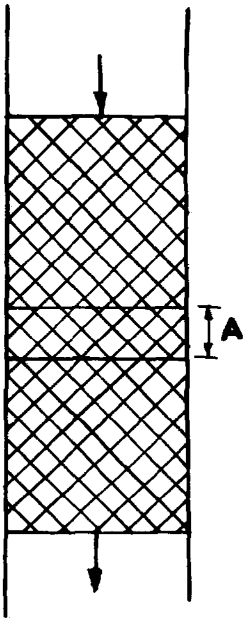

Fig. 1. Diagram of catalyst bed.