ISBN 963 481 628 2
Acta Phys. et Chem. Szeged 33 99-107 (1987)

ADSORPTION OF PROPENE IN NaA ZEOLITE IN HENRY'S - LAW REGION

By

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(Received 1 October 1987)

Adsorption equipment designed for the performance of adsorption measurements in the pressure range 10^{-3}-10^{3} Torr is described. Its applicability is demonstrated on the example of the adsorption of propene in NaA zeolite at low coverages. Henry's constant was determined at different temperatures.

Introduction

The theoretical adsorption isotherms derived from different gas-solid adsorption models include the Henry's law constant as parameter [1, 2]. In certain cases it is very important to estimate this constant, irrespective of any a priori adsorption model. Examples of the theoretical calculation of Henry's constant can be found in the literature only for simple molecules (such as CH_4) and for the noble gases [3]. Isotherms are the most promising means for its experi-

mental determination, provided the isotherms are measured at low coverages. For this purpose, a well-calibrated adsorption equipment is needed and the measurements should be performed very accurately.

This preliminary paper reports on a precise adsorption equipment designed for adsorption measurements in a wide pressure range, and its applicability is demonstrated by results obtained in an investigation of the adsorption of propene in NaA zeolite at low coverages.

Experimental

An outline of the volumetric adsorption equipment can be seen in Fig. 1.
With this set-up, adsorption measurements could be performed in the pressure range 10^{-3}-10^{3} Torr[+]. Two types of heaters were applied. During activation, the sample holder was heated by an electrical oven and the temperature could be stabilized within $\pm$ 1 K at 673 K. A thermostat filled with silicone oil was used to adjust the temperature of the sorbent within $\pm$ 0.1 K between 293 K and 523 K. The McLeod manometer and the mercury gas burette were tempered at 313 $\pm$ 0.1 K. During the measurements, the temperature of the sorbent was continuously checked with a Ni-CrNi thermocouple.

[+] 1 Torr = 101325/760 Pa

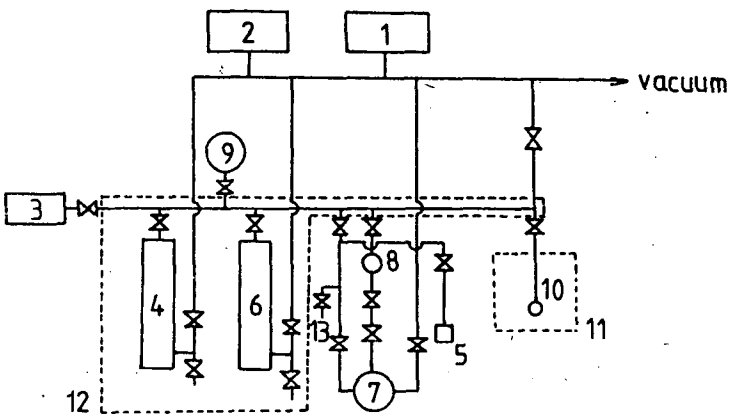

Figure 1.: Outline sketch of the volumetric adsorption apparatus.
1. Penning gauge; 2. Pirani gauge;
3. Barocel electronic manometer; 4. McLeod gauge;
5. Mercury manometer; 6. Mercury gas burette;
7. Propene storage; 8. Dosing part;
9. Helium storage; 10. Adsorber;
11. Silicone oil thermostat; 12. Water thermostat;
13. Gas inlet

Helium was used to determine the dead volume of the sample container.

The commercial NaA (Linde 4A) was exchanged in

0.1 mol/dm^3 NaCl solution in order to obtain a homoionic sample. Zeolite powder was stored in an exsiccator over saturated NH_4Cl solution.

Fresh samples of adsorbent (0.2-0.5 g) were used in each experiment.

The adsorbent placed into the sample container was dehydrated at 673 K for 12 h under high vacuum (the final vacuum was better than $1x10^{-6}$ Torr).

After pretreatment, the adsorbent was cooled to the desired temperature under continuous evacuation. In order to stabilize the temperature, the sorbent was equilibrated for 2 h prior to the measurements.

No change in crystallinity during activation could be observed by means of XRD, TG and IR.

For adsorption measurements, commercial propene (Merck, 99 %) was purified further with Linde 3A molecular sieve.

In the calculation of the adsorbed amounts, propene was regarded as a slightly imperfect gas [4]. The thermal transpiration effect for propene can be considered via the Takaishi-Sensui equation at low pressures [7,8].

Results and discussion

Figures 2 and 3 show the isotherms of propene over NaA at low coverages in the temperature range 343-493 K. Inspection of the Figures permits the following conclusions:

(i) Independently of the temperature, the accuracy and reproducibility of the measurements are good.

(ii) The adsorption of propene is reversible and non-dissociative, in accordance with the IR and GC investiga-

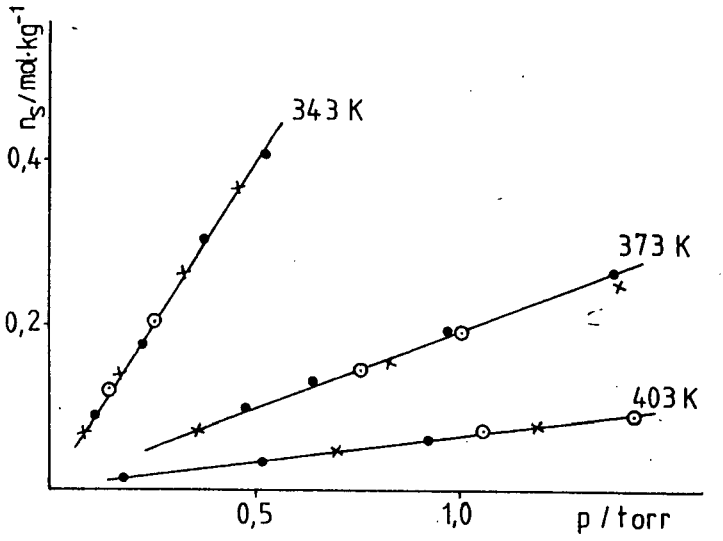

Figure 2.: Propene adsorption isotherms on NaA at low coverages. ●, x: adsorption points; ⊙: desorption points

tions [5, 6].

At low coverages, under conditions of no adsorbate-adsorbate interactions, a linear relationship exists between the specific adsorbed amount (n_s) and the equilibrium pressure (p): $n_s = K_H p$, where K_H is Henry's constant [9]. For the estimation of K_H, several independent ad- and desorption data sets were used at each temperature. The estimated values of K_H obtained with the ordinary least squares method are listed in Table I. In all cases the linear correlation

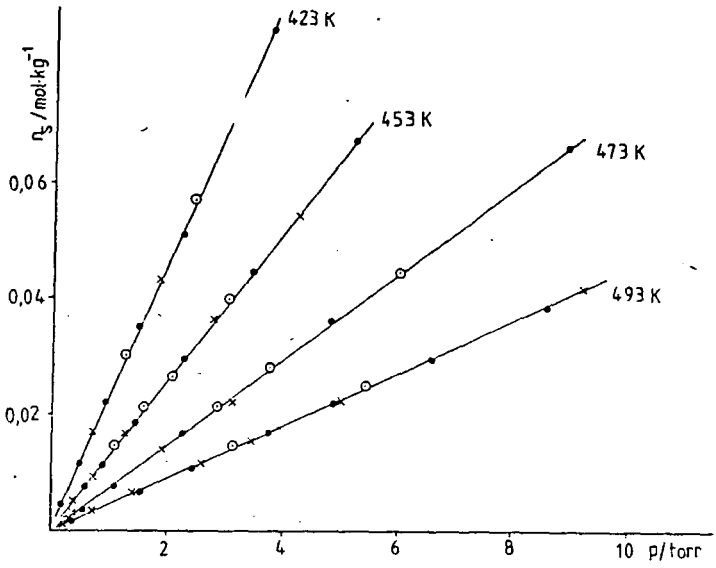

Figure 3.: Propene adsorption isotherms on NaA at low coverages. ●, x: adsorption points; ⊙: desorption points

coefficient was found to be > 0.995.

The temperature-dependence of K_H can be given by the van't Hoff equation:

$$K_H = K_o \exp [q_o/RT]$$

where q_o is the isosteric heat of adsorption at low coverages. The log K_H vs. 1/T plot is depicted in Fig. 4. Curve-fitting by the weighted least squares method resulted in the following values:

$$q_o = 47.83 \pm 0.13 \text{ kJ/mol}$$

$$K_o = 2.979 \times 10^{-10} \pm 6.6 \times 10^{-12} \text{ mol.kg}^{-1}.\text{Pa}^{-1}.$$

Table I

Henry's constants determined at different temperatures

Temperatures/K	K_H/mol.kg^{-1}.Pa^{-1}	S.E*[K_H]/mol.kg^{-1}Pa^{-1}
343	5.72×10^{-3}	3.5×10^{-5}
373	1.48×10^{-3}	2.0×10^{-5}
403	4.79×10^{-4}	1.0×10^{-5}
432	1.69×10^{-4}	1.7×10^{-6}
453	9.55×10^{-5}	6.0×10^{-7}
473	5.60×10^{-5}	4.0×10^{-7}
493	3.45×10^{-5}	2.0×10^{-7}

* Standard error of K_H [10]

The linear correlation coefficient was found to be 0.9997.

The adsorption of propene in A-type zeolites of different cationic forms (such as Li^+, Ca^{2+}, Mg^{2+}, Co^{2+}, Ni^{2+} and Mn^{2+}) was also investigated by means of IR spectroscopy and volumetry.

The results and their detailed discussion will be described in later papers.

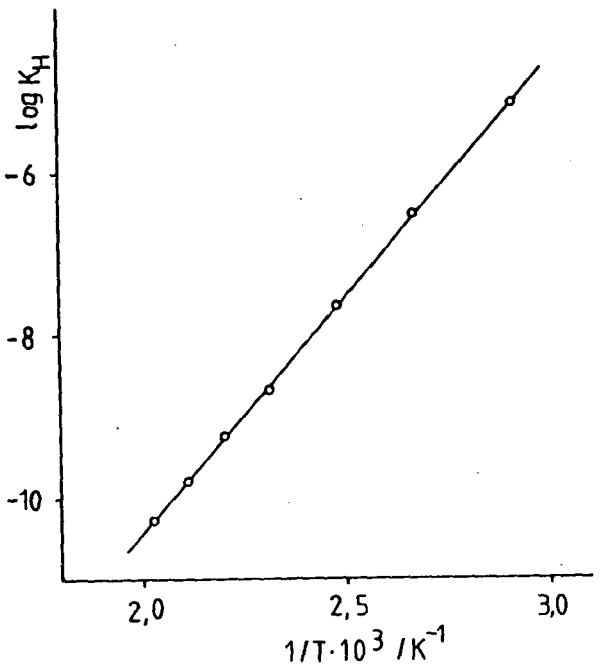

Figure 4.: Plots of log K_H against reciprocal absolute temperature.

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АДСОРБЦИЯ ПРОПЕНА НА ЦЕОЛИТЕ ТИПА NaA В ОБЛАСТИ ДЕЙСТВИЯ ЗАКОНА ГЕНРИ.

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Ф. Бергер и П. Феешл

Описан прибор для проведения адсорбционных измерений в интервале давлений 10^{-3} – 10^{3} торр. Пригодность прибора показана на примере адсорбции пропена на цеолите типа NaA при низких степенях покрытия. Определены константы Генри при различных температурах.