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The Adsorption of NH_3, N_2O and CO_2 Gases on the 5A Molecular Sieve

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The Adsorption of NH_3, N_2O and CO_2 Gases on the 5A Molecular Sieve

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ABSTRACT

The adsorption of NH_3, N_20 and $C0_2$ gases at various temperatures on activated 5A molecular sieve has been investigated using the volumetric method and their isotherms have been determined. Using the adsorption isotherm at the normal condensation temperature of ammonia, the surface area of the adsorbent has been calculated with Langmuir equation. Whether the adsorbate phase was solidated or not has been investigated with thermal analyis.

INTRODUCTION

In the recent years synthetic zeolites having a high and selective adsorption capacity have been prepared by the help of analogy of natural zeolites[1,2]. They are called molecular sieves, since they were separated the adsorbates according to their molecular dimentions by the adsorption method. The unit cell edge length of 5A molecular sieve is 12.3 A° and ist formula is

$$4Na\ 8Ca\ (A10_2)_{12}\ (Si0_2)_{12}.\ 27\ H_20$$

The crystallized water in the adsorbent can be separeted reversibly by heating. The structures and specifications of molecular sieves have been determined by Breck and coworkers[3,4], Barrer and coworkers[5,6,7,8], Broussard and Shoemaker[9] and Dubinin[10]. 5A, which is udes in this work obtained commercially (BDH) and used as it is.

EXPERIMENTAL

As seen in Fig. 1, a volumetric adsorption apparatus, based on the volume determination of the adsorbed gas, has been deve-

loped and used in experimental studies. This apparatus consists of mainly three parts. The mechanic and mercury diffusion pumps and liquid nitrogen trap in the first part is used to produce a high vacuum. In the second part, small bulbs like A_1 and A_2 where gases are distilled and large bulbs like B_1, B_2, B_3, B_4, are used as gases storage. The third part consist of B burette which is used to measure the volume of adsorbed gas, M manometer shows the presure of adsorbed gas and an electronic thermostate keeping the adsorption systhem under constant temperature, and M_2 manometer which shows the equilibrium pressure on the system.

The 5A molecular sieve is activated by heating at 350° C, and under about 10^{-3} mm Hg presure for 8–10 hours. It is Weighed and placed into a thermostat as seen in Fig. 1. After the thermostat is adjusted to the desired temperature, the gas which is its volume and presure is measured at constant temperature brought in contact with adsorbent for adsorption. When the system reaches to an equilibrium, the equilibrium presure is measured by M_2 manometer. We continued to take above measurment periodically until adsoption stops. At the end of the experiment, the total volume of the gas adsorbed under normal conditions by one gram of adsorbent under each equilibrium presure, was found. For each temperature of the system, adsorption isotherms are found by drawing $p = f(v)$ graphs.

Fig. 2 shows the adsorption isotherms of NH_3 at -20 °C and -33 °C, of N_20 at -20 °C and -80 °C; of $C0_2$ at -50 °C and -70 °C.

On the other hand, the saturated system with ammonia at -33 °C is cooled down to -179 °C with liquid nitrogen and then thermally analysed by gradually heating to see if there was a physical change in the state of adsorbed ammonia, for example whether there was a melting or not. We have not observed any kind of change at the working temperatures.

CONCLUSION

The adsorption isotherms show that polar molecules like ammonia adsorbed more and adsorption has increased to a great extent as temperature decreased. It has been understood that adsorption is monomolecular by the Langmuir equation.

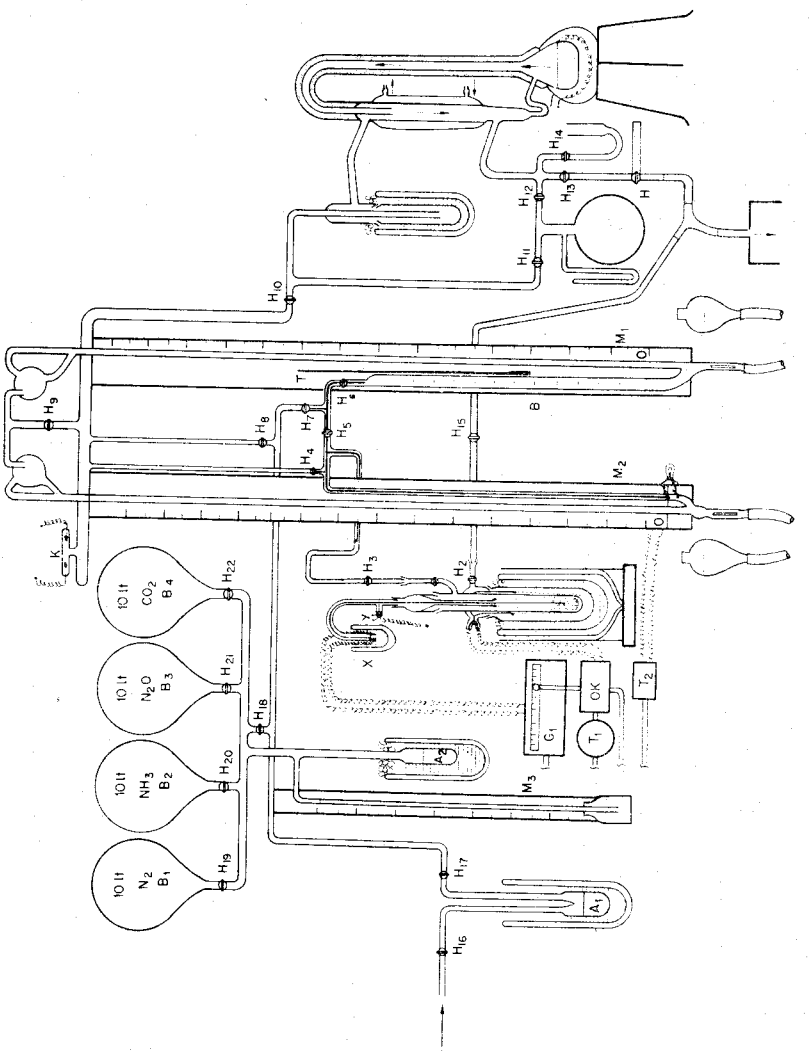

Fig. 1. Adsorption apparatus

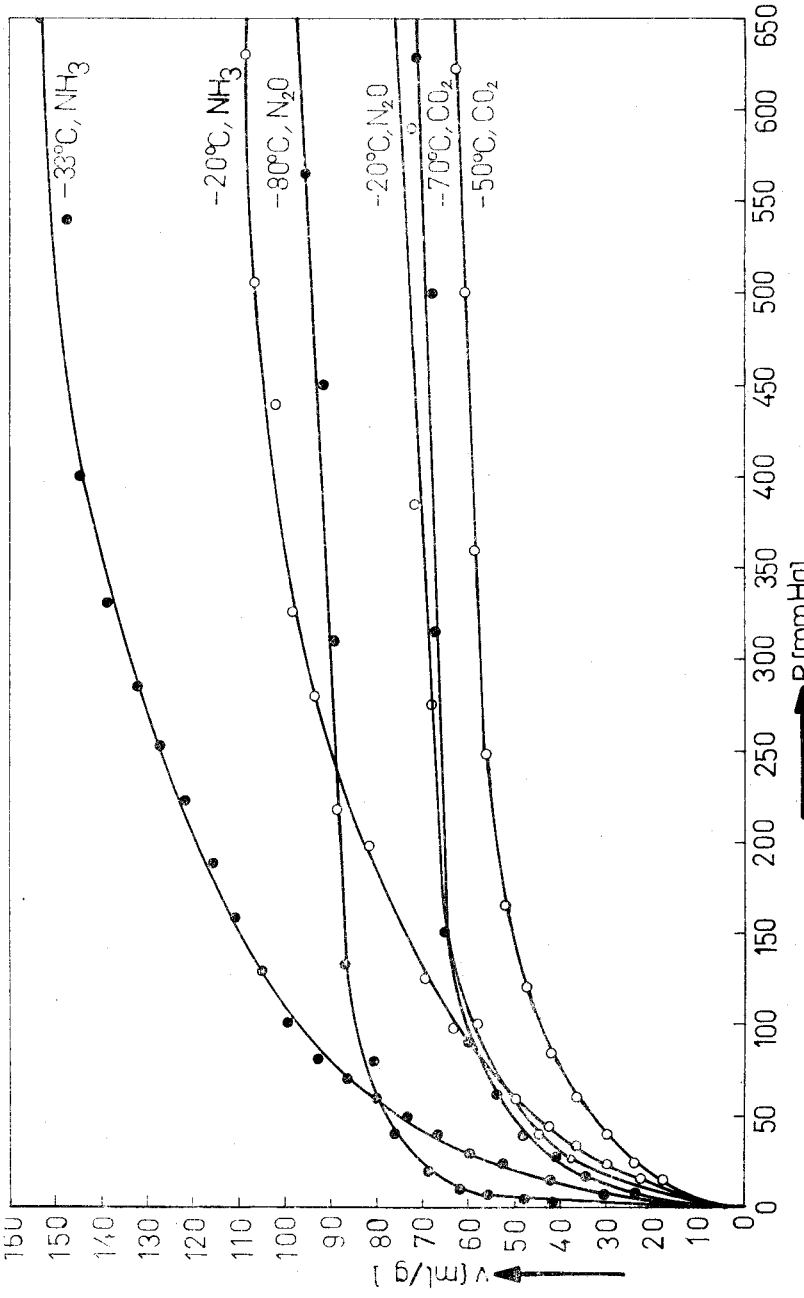

Fig. 2. Adsorption isotherms

$$\frac{p}{v} = \frac{1}{v_m b} - \frac{1}{v_m} p$$

derived by Langmuir[11,12,13] kinetically, Volmer[14] thermodynamically and Fowler[15] statistically. Where b and v_m show two constants. The value of v_m is equal to the volume of the necessary gas under normal conditions for one gram of adsorbent surface to be covered monomolecularly.

It is observed that the test results do not suit to the B.E.T[16,17,18] equation derived for multimolecular adsorption.

If the values measured for the adsorption of a ammonia gas, which has a condensation temperature of –33 °C, are recorded to the graph according to the Langmuir equation, the straight line seen in Fig. 3 is obtained.

From the slope of this straight line $v_m = 164$ ml/g is reached. Now let us suppose that the adsorbent surface is covered mono-

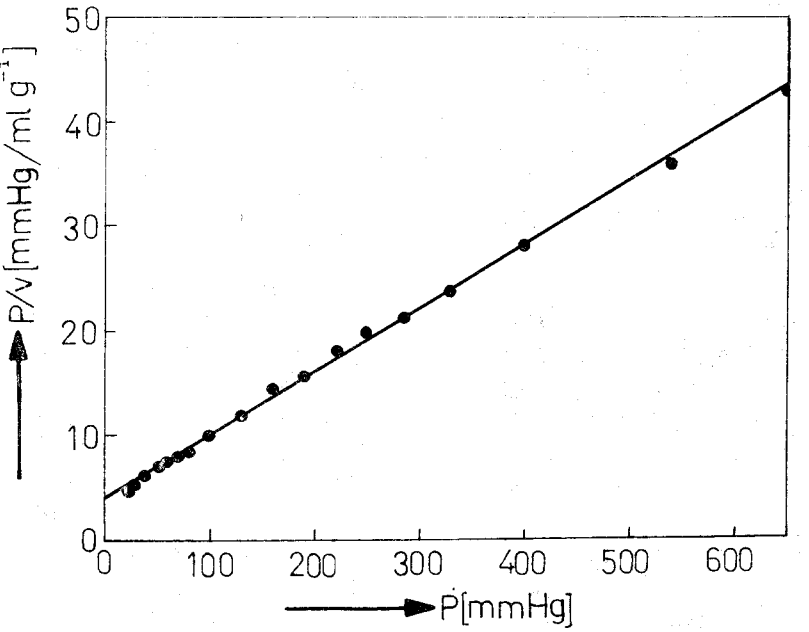

Fig. 3. Langmuir adsorption isotherm

molecularly by two dimentional close-packed. In the two dimentional closely packed layer the average area[19] covered by single molecule is calsculated by the following equation.

$$S = 1{,}096 \left(\frac{M}{N_A \cdot \rho}\right)^{2/3}$$

Where N_A is the Avogadro number; M is the molecular weight and ρ the density of liquid state of adsorbed material. Since the density of the bulk liquid ammonia at the boiling temperature 0.668 g /ml, the average area of per single molecule is calciulated as

$$S = 12,9 . 10^{-25} \text{ m}^2.$$

According to this, the surface area of the 5A molecular sieve is calculated as 568 m^2/g, from the

$$A = \frac{V_m}{V} \cdot N_A \cdot S$$

relationship. Where V is the volume of one mole gas at the normal conditions. This value is the surface area of 5A which is mixed with inactive mud. The surface area of 5A which is composed of pure crystals must be higher.

DISCUSSION

5A molecular sieve is an ideal porous solid in which cavities with 11.4A° and 6.6A° dimentions are regularly dispersed and connected with canals having a diameter of 5A°. The cavities are about 45 % of the sieve volume. As soon as the surface area of 5A occupied by the molecules in the closely packed monolayer the cavities could be filled. In this case, there is no possibility for the multimolecular adsorption and capillary condensations in the cavities. Because the molecules adsorbed monomolecularly in the cavities touch eachother, they are in a nearly liquid state at the below boiling temperature. When such a system is cooled below the freezing point, perhaps the molecules adsorbed at the inner faces of cavities cannot make two dimentional translational movement however this cannot be considered as freezing conditions. During the freezing time crystallization takes place. It is impos-

sible for the molecules, attached to the surface monomolecularly with a force stronger than the force attached to each other, to be separated from there, and reordered among themselves. Even we assume that the molecules are separated from the surface to from crystal, the molecules in the small cavities are not as many as to form a crystal large enough. Even a crystal nucleus is formed, there is no possibility to grow. Then, a freezing case connot be expected at lower temperatures than we can reach.

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ÖZET

Aktiflendirilmiş 5 A moleküler eleği üzerinde NH_3, N_20 ve $C0_2$ gazlarının çeşitli sıcaklıklardaki adsorpsiyonu volumetrik yoldan ölçülerek adsorpsiyon izotermleri belirlenmiştir. Amonyağın normal yoğunlaşma sıcaklığındaki adsorpsiyon izoterminden Langmuir denklemi kullanılarak adsorplayıcının yüzey alanı ölçülmüştür. Adsorplanmış fazın katılaşıp katılaşmadığı termik analiz ile araştırılmıştır.

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