A RAPID AND ACCURATE GRAVIMETRIC TECHNIQUE FOR MEASURING THE SPECIFIC SURFACE AREAS OF POROUS SOLIDS

E.E. GONZO

INIQUI - UNSa., Buenos Aires 177, 4400 Salta, Argentina.

INTRODUCTION

In this contribution a new gravimetric technique based on n-hexane adsorption near room temperature is presented. It avoids most of the disadvantages of the classical BET method [1], using nitrogen at its normal boiling temperature as adsorbate. Therefore, an accurate, rapid method is achieved. The experimental technique is described and the results obtained are thoroughly discussed to illustrate the advantages of the technique.

EXPERIMENTAL

With a Cahn R.G. electrobalance, the amount of adsorbed species was measured as a function of the total pressure of the system at a given temperature. n-Hexane, Merck (LAB), was used as the adsorbing species and the following porous solids of known specific areas were investigated: Alcoa F110 alumina, Davison G 62 silica gel, Regal 660 carbon, Cr/Al Houdry catalyst and Davison 980 silica-alumina.

The experimental procedure was as follows: about 300 mg of solid was placed on the balance plate, the entire system was evacuated to a pressure of 10^{-4} Torr and the zone occupied by the sample heated until the temperature reached 523 K. The system was held for at least 3 h under these conditions. The heat was then removed and the system left to cool. When the temperature was about 323 K the balance adsorption sample tube was immersed in an electronically controlled thermostatic bath at this temperature, where all n-hexane adsorption isotherms were determined. The temperature (± 0.2 K) was measured with a thermocouple inserted in a tube near the solid sample. The relative vapor pressure (p/ps) range covered in the experiments was $0.1 < p/ps < 0.3$. Equilibrium conditions were reached very quickly (in about 5 min), except for the first point, for which about 15 min was necessary.

RESULTS

It should be pointed out that the specific areas of most solids, used as references in this study, were first determined by the conventional BET method with nitrogen at its normal boiling point, using the value of 16.2 $\mathring{A}^2$ for the transverse area per molecule of adsorbed species.

Specific area measurements with n-hexane adsorption isotherms were obtained using the same procedure as in the BET method. A summary of results for the number of molecules to form a n-hexane monolayer (X_m) and the values of its cross-sectional molecular area (A_t) are given in Table 1

TABLE 1

Sample	X_m /mmol g^{-1}	S /m^2 g^{-1} (BET, N_2)	A_t / $\mathring{A}^2$ molec.$^{-1}$
Davison G62 silica	1.1547	340	50.4
Alcoa F110 alumina	0.4935	156	51.8
Regal 660 carbon	0.3299	103	51.3
Houdry catalyst	0.1965	60.5	51.1
Davison 980 silica-alumina	1.2631	388	51.0

In Table 2 specific area values of other solids, prepared in our laboratory or of the same solid reported in Table 1 but with different heat pretreatments, are presented using n-hexane adsorption isotherms.

TABLE 2

Sample	X_m /mmol g^{-1}	S /m^2 g^{-1}(At=51 $\mathring{A}^2$)	S /m^2 g^{-1}(BET, N_2)
Alcoa F110 alumina (outgassed at 973 K)	0.2914	89.5	87
Davison G 62 silica (outgassed at 723 K)	0.4915	151	150
Spheralites	0.6965	214	210
Mo-Bi-Co catalyst	0.009613	3	3

As can be seen from Table 1, the results are fairly consistent. The mean value of the n-hexane cross-sectional area is 51.0 $\mathring{A}^2$. This does not agree either with that calculated through the Davis et al [2] equation or the Van der Waalls constants whose resultant values are 40.5 $\mathring{A}^2$ and 42 $\mathring{A}^2$,respectively. If one considers the thickness (t) of an extended n-hexane molecule on the surface (t $\cong$ 4.4 $\mathring{A}$), the cross-sectional area can be calculated with $A_t = (V_m/N)/t$, where V_m is the molar volume of the liquid adsorbate at the temperature of the experiment and N is

Avogadro's constant, to be 51.4 $Å^2$, which is in agreement with the value in Table 1 and also with that reported by Isirikian and Kiselev [3,4] at 293 K.

It must be stressed that the values of specific areas determined through n-hexane isotherms, with A_t = 51.0 $Å^2$, are very close to those obtained with the classical BET method. Maximum deviations are below 4 %.

However, there are other advantages. Firstly, the time required (less than 1 h for eight points) is well below that needed with the classical BET method. Secondly, it is easy to maintain a constant temperature (±0.2 K) throughout the experiment because the actual value is near room temperature.

Moreover, at 323 K the n-hexane pressure in the equipment must be varied from 20 to 120 Torr, which is easily measured with considerable precision (within 1 % of its actual value) with an ordinary laboratory manometer. If it is taken into account that (dp_s/dt) is about 14 Torr K^{-1} for n-hexane, compared to 70 or 80 Torr K^{-1} for nitrogen, constant pressure conditions are more easily maintained in our system, thus minimizing experimental errors. In the classical BET method the lack of isothermal conditions is a serious source of error, especially when liquid air is used in the thermostatic bath. Also, as the top portion of the balance is at room temperature, it is difficult for the sample to achieve liquid-nitrogen temperature due to thermal exchange. Cutting [5] suggests the use of baffles between the sample and the balance arm to alleviate this problem.

The effects of thermomolecular flow [6] are minimal under the experimental conditions employed in this work.

Finally, n-hexane can be used with porous solids, with pore diameters as low as ~20 Å, since Alcoa F110 alumina posesses a pore-diameter distribution with values as small as 20 Å and with a mean value of 54 Å [7].

CONCLUSIONS

It has been shown that n-hexane adsorption isotherms can be safely used for measuring specific surface areas of porous solids. The method presented here is easy to carry out since there is no need for cryogenic equipment.

Results obtained are shown to be very accurate in comparison with those obtained with the BET method. The maximum deviation, using A_t = 51.0 $Å^2$ for n-hexane, is below 4 %.

The method can be used for almost all kinds of porous solids since the range of investigated surface areas varied from 1 to 500 m^2 g^{-1}.

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