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SURFACE AREA AND PORE SIZE DETERMINATION BY SORPTION MEASUREMENT

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ABSTRACT

A survey of the instruments available at the Battelle-Institut in Frankfurt for surface area and pore size determination is presented.

For automatic sorption measurements, surface area and pore size determinations an apparatus equipped with electronic microbalances has been developed. Routine surface area determinations are carried out with a volumetric instrument after Haul and Dümbgen[1]. Porosimeters, an electron microscope, a microprobe and an X-ray diffraction analyser are available for additional investigations of the surface structure. Optical methods using light and laser radiation have been developed for particle size analysis of fine powders.

OBJECTIVES OF SURFACE AREA AND PORE SIZE DETERMINATION

Until some years ago it was assumed that determination of the specific surface area and the pore structure of porous or finely divided solids is only necessary in particular fields of technological research and production control, e.g. in the manufacture of catalysts. Today, it is realized that this way of characterising raw materials and products is advantageous whenever quantitative data are required for reactions at the surface of a solid. This applies to physical reactions, such as adsorption or absorption, dissolution and crystallisation, to electrochemical reactions at electrodes and to chemical reactions in which the solid is converted, e.g. corrosion.

Battelle–Frankfurt (G.F.R.) has been engaged for many years in investigating the specific surface area and the pore structure of a large variety of industrial products. The methods used have been developed to such an advanced stage that they deserve to be discussed in a wider circle.

METHODS OF ANALYSIS

The specific surface area is normally calculated from a nitrogen or krypton adsorption isotherm according to the Brunauer–Emmett–Teller (BET) method. BET surface area determinations, which cover the entire (internal and external) surface, have been discussed in various publications[2,3]. BET methods have been standardised in several countries[7,8].

In many cases it is important to know the pore structure of a material in addition to its specific surface area because small pores though increasing the specific surface area, may be inaccessible to large molecules. Furthermore, the rate of mass transfer into and out of the pores is critically dependent on the pore radius. The structure of pores of a width between about 0.4 and 50 nm (4 and 500 Å) can be determined from complete adsorption and desorption isotherms[2,3]. Pores of a larger width which play an important part, for instance in flow processes can be investigated by porosimetry[3].

Automatic sorption measurement

Some years ago, Battelle developed an automatic apparatus* (see Figs. 1 and 2) for gravimetric gas sorption measurements on solids[4–6].

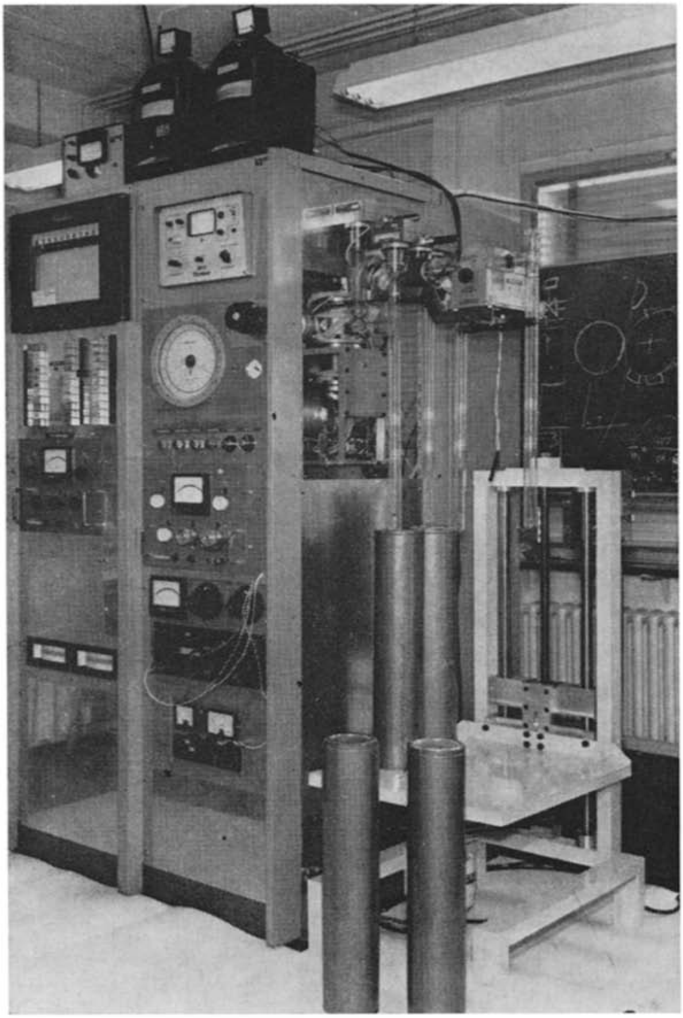

Fig. 1. Automatic apparatus for gravimetric sorption measurements.

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*The instrument called "Gravimat" is manufactured by Sartorius-Werke, Göttingen, G.F.R.

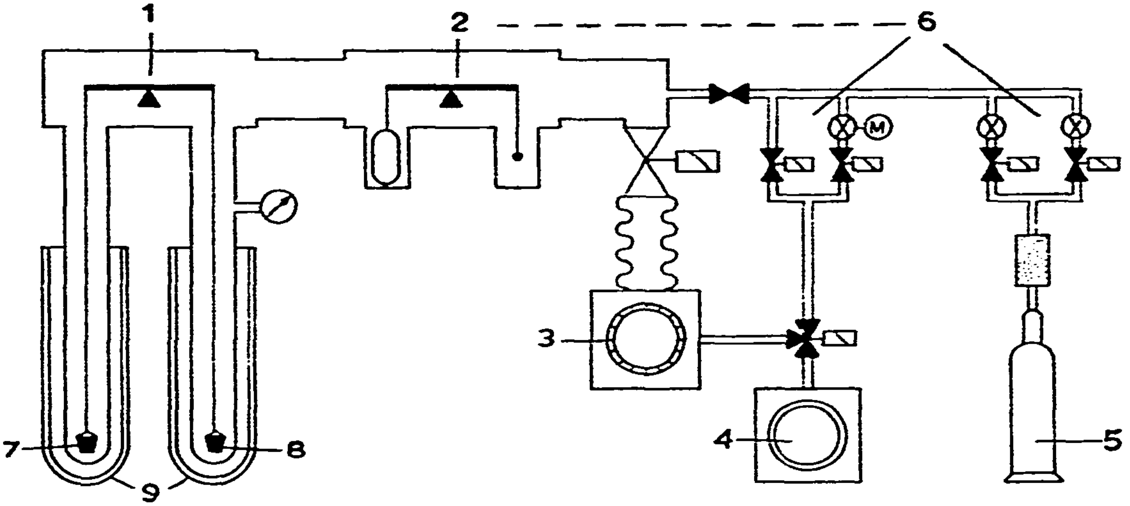

Fig. 2. Schematic view of apparatus. 1 = Balance; 2 = buoyancy gauge; 3 = turbomolecular pump; 4 = rotary vane pump; 5 = gas tank; 6 = pressure control system; 7 = sample; 8 = counterweight; 9 = Dewar vessels.

The instrument consists of an electromagnetic microbalance after Gast (1) used for weighing, a second balance (2) serving as a buoyancy gauge, a vacuum unit (3, 4), a gas tank (5) and a programmed pressure control system (6). The sample (7) and the counterweight (8) are suspended in tubes over which heaters or Dewar vessels (9) may be slipped. The Dewar vessels are filled with a thermostating liquid, e.g. liquid nitrogen. The temperature of the nitrogen is measured with a Numec® thermistor thermometer or a vapour pressure thermometer. The vacuum is measured by means of Pirani, Penning and ionisation gauges.

Measurement of nitrogen adsorption isotherms

An important application of the gravimetric apparatus is the measurement of nitrogen adsorption isotherms at the temperature of liquid nitrogen for surface area and pore size determinations. The gravimetric method, unlike the volumetric method, permits the degassing of the surface to be observed. It is possible to recognise the termination of the degassing process, and to examine whether the surface of the sample has been changed irreversibly by decomposition during heating. In addition, each parameter can be determined directly so that systematic errors are avoided.

Before analysing the sample, its specific surface area and its gas load (e.g. moisture content) are estimated. On the basis of this estimate the sample mass most suitable for the analysis is determined to ensure on the one hand that errors are minimised and on the other that the weighing range of the balance is large enough to measure the entire isotherm without retarding. The maximum load for one balance is 2.5 g (including about 0.5 g for the balance pan) and the weighing range is 40 mg. For the other balance the maximum load is 25 g and the weighing range is about 3 g. To minimise the buoyancy error, the weight of the sample is balanced by a counterweight (which consists of a mixture of quartz and gold) of approximately the same density. The residual buoyancy is determined by measurement with nitrogen at room temperature and considered in the calculation. The buoyancy permits the density of the dry sample to be calculated. The sample is degassed in vacuum at a gradually increased temperature. The temperature has to be such that the substance neither decomposes nor sinters. After degassing, the sample is cooled with liquid nitrogen and the sorption isotherm is measured automatically.

According to the standards specified in Refs. 7 and 8, three points in the lower range of the isotherm are sufficient to determine the surface area; determination of the pore size requires measurement of the entire adsorption and desorption isotherm.

Measurement of krypton adsorption isotherms

If the specific surface area is very small ($<0.02\ \mathrm{m^2\ g^{-1}}$), it is advisable to analyse the sample on the basis of a krypton isotherm measured at the temperature of liquid oxygen.

The weight of a monomolecular krypton layer is about twice that of a nitrogen layer, and the pressures, at which a krypton isotherm is measured, are so low that buoyancy errors are insignificant. Since the exact space required by a krypton molecule is not known, the method yields a less accurate value for the specific surface area than measurements with nitrogen, but it allows the determination of differences in surface area as small as 10 $\mathrm{cm^2}$. Pore size analysis, however, is not possible because at 90 K krypton is adsorbed in solid form.

EVALUATION

The measurements are evaluated by an electronic data processing system and represented in the form of tables and diagrams[9]. Pore size determinations require an additional discussion of the results.

The specific surface area is calculated in the usual way. First, the mass of a monolayer of the substance adsorbed is determined with the aid of the BET diagram, and from this the surface area of the sample is calculated. When the complete isotherm has been measured, the mass adsorbed at saturation pressure is used to calculate the pore volume, the porosity and—with the aid of the BET surface area—the mean pore radius.

The distribution of the surface area of pores with a width between 2 and 50 nm is calculated on the basis of the Kelvin equation* using a method described by Cranston and Inkley[3,10]. The method considers the effect of multilayer adsorption. Depending on the type of pores prevailing in the sample, the calculation is based on a slit model or a cylinder model of the pores. Information on the prevailing type of pores is obtained from the shape of the isotherm. The result is plotted as a function

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*The Kelvin equation relates the vapour pressure of a liquid to the radius of curvature of its surface, which in turn depends on the radius of the pore in which the liquid is contained.

$a_{\mathrm{cum}}(d)$, which indicates the surface area of pores with widths between zero and d. The final value of cumulative surface area again gives the specific surface area, independent of the BET theory.

In a t-diagram the isotherm is compared with an ideal isotherm averaged from a large number of isotherms obtained for non-porous oxide and hydroxide surfaces[2,3]. The mass of adsorbate of the measured isotherm is plotted in this diagram as abscissa, while the layer thickness t of the ideal isotherm obtained at the same relative pressure is plotted as ordinate. The shape of the curve shows whether the sample contains micropores with a width of less than 2 nm. From the slope of the curve an additional value for the specific surface area can be calculated.

The specific surface areas obtained by these three methods normally differ. The differences yield information on the pore structure and on the proportions of the surface area of mesopores and macropores.

OTHER MEASUREMENTS

In some cases it may be useful to perform additional sorption measurements with the microgravimetric apparatus using different gases and different temperatures. If, for example, the adsorbent has very narrow pores, the rate of nitrogen adsorption at 77 K may be so low that too small a value is obtained for the specific surface area. This applies, for instance, to some types of activated carbon. On the other hand, the sorption capacity of the adsorbent may be smaller than that calculated from the specific surface area because part of the pores is inaccessible to large molecules. Another example is the determination of the active surface area of a carrier catalyst by adsorption measurements with the gas to be converted. Adsorption measurements with nitrogen yield the total active and inactive surface area.

For the investigation of the adsorption of a gas mixture or the adsorption of a gas on a surface already covered with an adsorbate, it is not sufficient to measure the gross adsorbate mass. In these cases it is also necessary to determine the composition of the adsorbate, e.g. by mass spectrometric analysis of the desorbate[11]. For this purpose a small mass spectrometer (MS 10 of AEI) attached to the balance casing is used.

The gravimetric apparatus may further be employed for typical desorption measurements, e.g. drying, evaporation and thermogravimetric analysis, and for investigating chemical reactions and their kinetics, e.g. corrosion or decomposition processes.

ADDITIONAL METHODS OF ANALYSIS[12, 13]

Series of surface area determinations can be carried out with the "Areameter" developed by Haul and Dümbgen[1]. With this instrument a single point of a nitrogen adsorption isotherm is determined volumetrically. The sample (maximum weight 100 g) is degassed in a nitrogen current at elevated temperature. For reference, one sample of each series is analysed gravimetrically.

The range of pore size analysis can be extended by the additional use of a porosimeter to include macropores with a width of more than 50 nm. For this purpose a mercury porosimeter (Carlo Erba) and an air–water porosimeter after Žagar are available.

Frequently, it is appropriate to supplement surface area and pore size determinations by measurements of other characteristics. The equipment available for such measurements includes a Blaine analyser, various optical particle size spectrometers, an electron microscope (Siemens "Elmiskop"), a microprobe analyser (Cambridge Instruments) and an X-ray fluorescence spectrometer (Siemens "Kristalloflex IV").

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