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A RAPID CHROMATOGRAPHIC METHOD FOR MEASURING ADSORPTION ISOTHERMS OF GASES AND VAPORS

The development of rapid and reliable methods for measuring the specific surface area of solids is a problem of considerable practical and scientific importance. In heterogeneous catalysis the magnitude of the specific surface area is highly significant for the productivity of many technical processes.

At present, vacuum methods for determining specific surface area—gravimetric, volumetric, and manometric—have become most widespread. The need to carry out experiments in complex vacuum apparatus and the prolonged evacuation of samples before measurements (conditioning) are substantial obstacles to the use of these methods in broad surveys of large numbers of samples of adsorbents and catalysts.

A chromatographic procedure for measuring adsorption isotherms is very promising; it follows from the work of Wilson ([1]), who as early as 1940 theoretically analyzed the dependence of the form of the chromatographic curve on the form of the isotherm under conditions in which complications associated with adsorption kinetics and longitudinal diffusion are absent. These conditions are realized most fully in gas-adsorption chromatography ([2]-[4]).

In the present work, two variants of chromatographic measurement of adsorption isotherms are compared with the usual vacuum procedure.

Experimental Part

The scheme of the chromatographic apparatus is shown in Fig. 1. The main part of the instrument consisted of a dynamic tube 3, filled with adsorbent or catalyst, a thermostated bubbler 2 with adsorbate, a sensitive gas analyzer 4, the readings of which were automatically recorded by potentiometer 5. As the gas analyzer we used an ionization detector based on Pm^{147}, the design of which

Fig. 1. Diagram of the apparatus.

Figure 1: Fig. 1. Diagram of the apparatus.

has recently been described (⁵). As carrier gas we usually used nitrogen. In those cases where higher sensitivity was required (in determining small surface areas), argon was used, which made it possible to increase the sensitivity of the detector by approximately two orders of magnitude. With the aid of

Fig. 1. Diagram of the apparatus. 1 —cylinder with carrier gas; 2 —bubbler with adsorbate; 3 —chromatographic column; 4 —gas analyzer; 5 —self-recording potentiometer; 6, 7, 8, 9, 10 —precision-control valves; 11 —four-way valve; 12, 13, 14, 15 —flowmeters

determination of small surface areas), argon was used, making it possible to increase the sensitivity of the detector by approximately 2 orders of magnitude. With the aid of

of fine-control valves 7 and 8 the required ratio of gas flows was established, providing the necessary concentration of the adsorbed substance, as determined by the ionization detector 4. During the time required for preparing the mixture of the required concentration, the column and all communications are purged with inert gas through valve 10 and rheometer 14. After a steady state has been established, by turning the four-way valve 11 the flow of carrier gas containing the vapors of the sorbed substance is directed into the column. This moment was marked on the recorder chart as the beginning of the experiment. The curve recorded on the chart of the dependence of the gas-analyzer readings on time is called the frontal diagram (the right-hand branch of the curve in Fig. 2b). The height h of the step of the frontal diagram corresponds to the initial concentration C_0 of adsorbate in the stream.

After completion of the frontal experiment, valve 11 is again turned to its initial position, and a pure carrier is passed through the column. In order to exclude the possibility that a change in velocity during instantaneous switching of the flow by valve 11 may have an effect, while the frontal diagram is being recorded a parallel purge of pure carrier gas is carried out through fine-control valve 10, whose resistance is set equal to the resistance of the dynamic tube. Only in this case are no kinks observed on the chromatogram when the flows are switched. The moment at which purging of the dynamic tube with a stream of pure carrier gas begins is marked on the chromatogram as the beginning of the desorption curve (the left-hand branch of the curve in Fig. 2b), the appropriate treatment of which (see below) makes it possible to determine the adsorption isotherm.

Another variant of the chromatographic determination of the isotherm is still simpler. In this case no preliminary saturation of the bed is carried out, and the sample is periodically injected into the column, continuously purged with carrier gas, through a rubber cap by means of a microsyringe. The chromatographic curve is shown in Fig. 2a. The duration of one experiment is 10–15 min.

Fig. 2. Exit curve. a—development variant, b—frontal variant

Figure 2: Fig. 2. Exit curve. a—development variant, b—frontal variant

Fig. 3. Adsorption isotherms of heptane measured by chromatographic (a) and gravimetric (b) methods. 1 —MgO from $Mg(NO_3)_2$; 2 —silica gel E; 3 —sample 862; 4 —brick

Figure 3: Fig. 3. Adsorption isotherms of heptane measured by chromatographic (a) and gravimetric (b) methods. 1 —MgO from $Mg(NO_3)_2$; 2 —silica gel E; 3 —sample 862; 4 —brick

Fig. 2. Exit curve. **a**—development variant, **b**—frontal variant

Treatment of Experimental Data

As is known, from the material balance of the chromatographic process one can obtain the equation $(^{2-4})$

$$\varkappa q\left(\frac{\partial C}{\partial t}\right)_x + (1-\varkappa)\left(\frac{\partial a}{\partial t}\right)_x = \omega\left(\frac{\partial C}{\partial x}\right)_t . \tag{1}$$

Here C is the concentration of the substance in the gas stream (mg/cm^3); a is the amount of adsorbed substance (mg per 1 cm^3 of adsorbent); q is the cross section of the chromatographic column (cm^2); $\varkappa$ is the fraction of the cross section not occupied by adsorbent; w is the volumetric flow rate of gas (cm^3/min); t is the time measured from the beginning of the experiment (min.); x is the distance measured from the column inlet in the direction of flow (cm).

Suppose that adsorption equilibrium is established instantaneously and longitudinal diffusion is absent; then, after integration of (1), the following simple calculation equation can be obtained for determining the adsorption isotherm

$$f(C) = \frac{\omega k}{ug} S_i ; \tag{2}$$

here $f(C)$ is the amount of substance (mmol/g) adsorbed by 1 g of adsorbent at the equilibrium concentration C; k is the detector constant (mmol/cm^3·cm); u is the chart speed of the recorder (cm/min); g is the weight of adsorbent (g); S_i is the area under the desorption curve (Fig. 2 *a* and *b*).

Fig. 3. Adsorption isotherms of heptane measured by chromatographic (*a*) and gravimetric (*b*) methods. 1 —MgO from $Mg(NO_3)_2$; 2 —silica gel E; 3 —sample 862; 4 —brick.

In Fig. 3 *a* and *b* are presented the isotherms of heptane on various catalysts and adsorbents, measured at 23° by the chromatographic method and with the

Fig. 4. Isotherm of adsorption of heptane on refractory diatomaceous brick, obtained in 4 parallel chromatographic experiments

Figure 4: Fig. 4. Isotherm of adsorption of heptane on refractory diatomaceous brick, obtained in 4 parallel chromatographic experiments

aid of quartz balances in a vacuum apparatus. The specific surface area was calculated by BET. Table 1 gives a summary of the results obtained.

Table 1

Adsorbent or catalyst	Specific surface area, m^2/g, measured chromatographically	Specific surface area, m^2/g, measured under static conditions	Adsorbent or catalyst	Specific surface area, m^2/g, measured chromatographically	Specific surface area, m^2/g, measured under static conditions
Refractory diatomaceous brick	34.2	41.4	Nickel catalyst	16	20
Silica gel E	103	97.4	Magnesium oxide from $Mg(NO_3)_2$	220	217
Sample 862 (nickel hydroxide gel)	47.5	61.4	ZnO + 14.5 $ZnSO_4$	6.0	5.3
			Carbon black	116	95

Figure 4 shows the satisfactory reproducibility of the data obtained in four parallel experiments on brick. Special experiments showed that, in the case of smooth and wide-pore adsorbents, the results obtained depend comparatively little on the flow rates of the inert gas, and also on the amount of adsorbent and catalyst.

Measurement by the chromatographic method of the surfaces of some adsorbents with a large number of narrow pores (for example, activated carbon) did not give satisfactory results. Further investigations will be required for a final conclusion about the limits of applicability of the method.

Fig. 4. Isotherm of adsorption of heptane on refractory diatomaceous brick, obtained in 4 parallel chromatographic experiments

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Note: Figure translations are in progress. See original paper for figures.