POSSIBILITIES OF DETERMINING THE POLYMODAL PORE-SIZE DISTRIBUTION FROM PHYSICAL ADSORPTION OF NITROGEN

Dagmar Tomanová and Petr Schneider

Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchdol

It is shown, on the basis of experimentally determined adsorption isotherms of physical adsorption of nitrogen on two- and three-component mixtures of fine grained porous glasses with narrow pore-size distributions, that the polymodal mesopore-size distribution curves can be evaluated in case that the porous sample contains groups of mesopores differing rather significantly in size. The differentiation of groups of pores gets worse with wider pores where the demands on the accuracy of the relative pressure measurement grow stronger.

One of the methods for obtaining the mesopore-size distributions of porous substances (catalysts, adsorbents, *etc.*) is the evaluation of adsorption isotherms of nitrogen physical adsorption at boiling point of nitrogen (for survey see refs[1-3]). The method stems from the validity of the Kelvin equation which expresses the dependence of nitrogen saturated vapour pressure over the surface of liquid nitrogen of various radii of curvature. Simultaneously, it takes into account the change of thickness of nitrogen layer adsorbed on the inner surface of porous substance due to pressure changes in the system adsorbate (nitrogen)–adsorbent.

In most cases, the porous substances containing mesopores of only one prevailing size are characterized in this way so that the differential pore-size distribution curves have only one maximum (monomodal distributions). However, it is to be expected that, *e.g.*, in catalysts prepared by pelleting porous powders under higher pressure, the mesopores of two or even more prevailing sizes may appear (bimodal and polymodal pore-size distributions). The narrower pores are characteristic of microcrystalline powders, the wider pores are voids between particles or agglomerates of particles and depend, therefore, considerably on pelleting conditions (compare refs[4,5]).

For this reason it was of interest to determine what is the resolution of this method, *i.e.*, to what extent it is possible to apprehend the presence of mesopores with several prevailing sizes.

As model substances, fine grained mesoporous glasses with differing mean pore radii and very narrow monomodal pore-size distributions were used. By mechanical mixing of glass samples with different pore sizes, the samples were obtained containing two or three prevailing mesopore sizes.

EXPERIMENTAL

Measurement of nitrogen adsorption and desorption isotherms was made with an automatic apparatus Sorptomatic 1826 (Erba Science, Italy) which is considered to be a standard for nitrogen physical adsorption yielding reliable results of good accuracy. The evaluation of meso-pore-size distribution curves was carried out numerically from desorption branches of isotherms by the Roberts method[6] which represents the algorithmization of the generally used procedure of Barret, Joyner, and Halenda[7]. It is assumed in this method that the real porous medium can be replaced by a bundle of parallel, straight, and non-intersecting cylindrical capillaries. To describe the dependence of the adsorbed nitrogen layer thickness, t, on the nitrogen pressure, p, the Halsey equation[8]

$$t = k(-5/\log{(p/p_0)})^{1/3}$$

was used, where $k = 0.354$ nm and p_0 is the nitrogen saturated vapour pressure at the temperature of measurement.

Porous glasses. Porous glasses for permeation liquid chromatography (Controlled Pore-Glass CPG-10) supplied by BDH Ltd. (Poole, England) were used with particle size 100—200 mesh (U.S.) (*i.e.*, 100 μm), marked by producer as CPG-10—75 Å (sample A), CPG-10—170 Å (sample B), and CPG-10—240 Å (sample C). These samples have very narrow pore-size distributions; their textural properties are summarized in Table I.

Mixtures of porous glasses. The mixtures A : B, A : C, and B : C in mass ratios 1 : 1 were prepared from the samples A, B, and C. These mixtures are denoted hereafter as A/B, A/C, B/C samples. The three-component mixture A : B : C with mass ratio 1 : 1 : 1 (A/B/C sample) was prepared as well.

TABLE I

Textural properties of porous glasses

Property		CPG-10—75 Å A	CPG-10—170 Å B	CPG-10—240 Å C
Apparent density ϱ_p, g cm^{-3}	*a*	0·993	0·710	0·520
Specific volume	*b*	0·550	0·952	1·468
of pores V_p, cm^3 g^{-1}	*c*	0·49 (0·37)	0·90 (0·73)	1·40 (1·13)
Specific surface S, m^2 g^{-1}	*d*	186 (185)	123 (119)	132

Values in parentheses are given by producer. [a] Pycnometrically with mercury (using porosimeter AutoPore 9200, Micromeritics, U.S.A.); [b] $V_p = \varrho_p^{-1} - \varrho^{-1}$, skeletal density $\varrho = 2.189$ g cm^{-3} (pycnometrically with helium, using AutoPycnometer 1320, Micromeritics, U.S.A.); [c] from nitrogen volume adsorbed at relative pressure $p/p_0 \rightarrow 1$; [d] BET method.

* $1 \text{ Å} = 10^{-10}$ m

RESULTS

The nitrogen adsorption isotherms of samples A, B, and C are illustrated in Fig. 1. All the isotherms are of type IV of the Brunauer classification[1-3] and exhibit distinct hysteresis loops. The isotherms for the A/B, A/C, and B/C two-component mixtures (Fig. 2) are always cumulative curves of isotherms of mixture components. Whereas the hysteresis loops corresponding to the components A, B, or C are clearly separated on the isotherms of A/B and A/C mixtures, this separation is less clear with the B/C mixture. The isotherm of the three-component A/B/C mixture (Fig. 3) is of the same character: only the part of hysteresis loop pertaining to component A is clearly separated.

It follows from the repeated isotherm measurements that the vertical parts of adsorption and desorption branches of hysteresis loops may be shifted by as many as 0.01 units of adsorbate relative pressure p/p_0. This uncertainty in the region of higher p/p_0 values is characteristic of the used automatic apparatus Sorptomatic and is a consequence of accumulation of a number of small errors (in measuring the adsorbate pressure and its saturated vapour pressure with electronic pressure transducers, determination of establishing the adsorption–desorption equilibrium, *etc.*).

The specific surfaces of mixed samples determined from the BET isotherm[1-3] (with the data within the range of $p/p_0 = 0.05-0.3$) agree well with the values calculated from specific surfaces of components A, B, and C (Table I). The found mean deviation (5%) does not exceed the usually accepted tolerance of determining the specific surfaces by the BET method, *i.e.*, 10%. Similarly the mesopore volumes
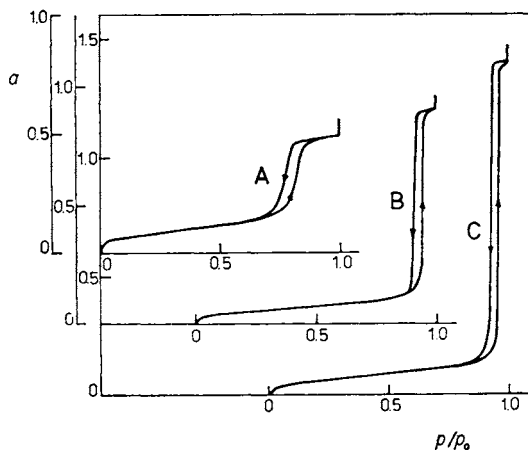

Fig. 1

Nitrogen adsorption isotherms on porous glasses A, B, and C

given by the volume of liquid adsorbate at the relative pressure $p/p_0 \rightarrow 1$, agree well with the values obtained from the pore volumes of mixture components (mean deviation 4%).

The cumulative pore-size distribution curves (the dependences of volume of over-sized pores, $V(r)$ on pore radii r) of the two-component porous glass mixtures, calculated from the desorption branches of adsorption isotherms, are summarized in Fig. 4 in which the pore-size distributions of samples A, B, and C are given as well
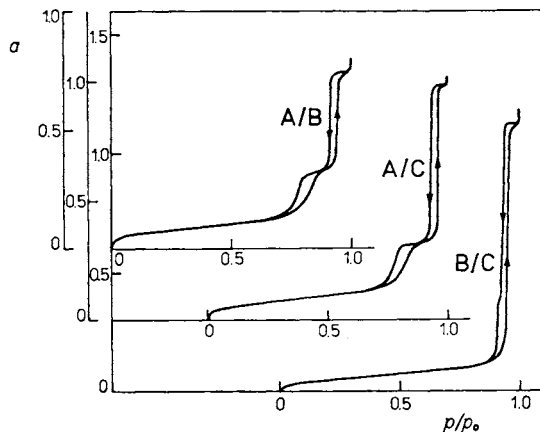

FIG. 2

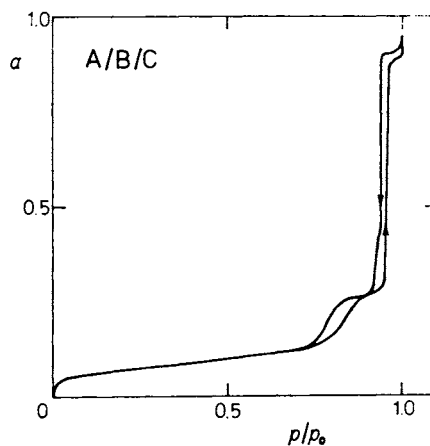Nitrogen adsorption isotherms on glass mixtures A/B, A/C, and B/C

FIG. 3

Nitrogen adsorption isotherm for the three-component glass mixture A/B/C

(in half scale). Inflexion points (as found from numerically smoothed curves), which correspond to the radii of the most frequent pores, are shown on the curves. The requirement, for the cumulative pore-size distribution of mixed sample to be the summation curve of components, is qualitatively fulfilled in all the cases. However, for some parts of distribution curves pertaining to the component with wider pores (component B in the A/B mixture, component C in the A/C and B/C mixtures), the shifts along the pore radii axes are evident. Similar situation is encountered with the A/B/C three-component mixture whose cumulative distribution is depicted in Fig. 5.

Radii of the most frequent pores found are summarized in Table II. The largest difference between the most frequent pore radius for a pure component and the same component in mixture (1·2 nm) was found for the porous glass C in the A/C mixture. Somewhat lower difference (0·8 nm) exhibits this component in the B/C mixture.

These differences result from small shifts of the isotherm desorption branches discussed above. Owing to the logarithmic form of the Kelvin equation ($r \sim [-\ln (p/p_0)]^{-1}$), the error in the radius determination, due to the error in p/p_0, is considerably strengthened. This strengthening is especially intense for the adsorbate pressures approaching its saturated vapour pressure (i.e., for $p/p_0 \to 1$). It can be shown easily that for relative errors in determining the pore radius $(\delta(r))$ and the relative pressure $(\delta(p/p_0))$ the following relationship holds approximately

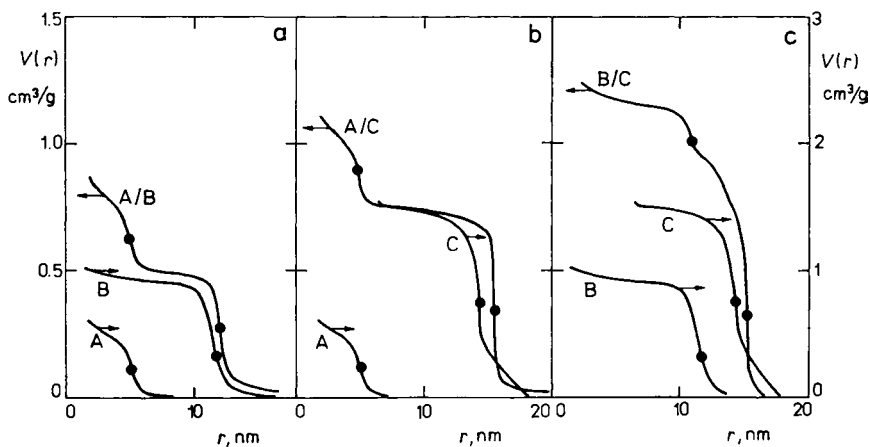$$\delta(r) = \delta(p/p_0)/[-\ln (p/p_0)]$$

FIG. 4

Cumulative mesopore-size distribution. a Sample A/B, b sample A/C, c sample B/C. Distribution curves for samples A, B, and C are shown, too

so that, *e.g.*, for $p/p_0 = 0.93$ (position of the desorption branch for sample **C**; Fig. 1), the error in p/p_0 is strengthened about 14 times $(\delta(r) = 14 \cdot \delta(p/p_0))$. Therefore, the error in the determination of p/p_0 equal to 0.6% causes an error of 8% in affixing the radius, that means a shift in the most frequent pore radius from 14·4 nm to 15·6 nm, which is in agreement with the value for the **A/C** mixture in Table II.

DISCUSSION

It follows from the results obtained that for mechanical mixtures prepared from porous glasses with narrow monomodal pore-size distributions, the forms of the nitrogen physical adsorption isotherms and of the respective hysteresis loops reflect

TABLE II
Radii of the most frequent pores

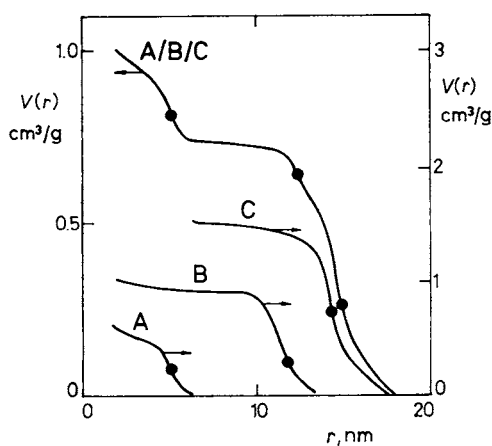| Sample	Radius, nm		
A	5	—	—
B	—	11·8	—
C	—	—	14·4
A/B	4·9	12·0	—
A/C	4·8	—	15·6
B/C	—	11·0	15·2
A/B/C	5·1	12·5	14·8

FIG. 5

Cumulative mesopore-size distribution for sample A/B/C

the characters of individual components of mixture. The more differing are the mean mesopore radii of components the better perceptible are the contributions of mixture components. The position of desorption branches in the region close to $p/p_0 = 1$ which corresponds to wide pores is rather insensitive to pore sizes. It makes the differentiation of contributions of individual components more difficult; if some of the wide-pore-size components are in excess, the contributions may merge completely.

Specific surfaces follow from the low pressure parts of isotherms which are not influenced by pore-size distribution. Therefore, specific surfaces are obtained with standard accuracy regardless whether the sample is mono- or polymodal. The total mesopore volume does not depend on the particularities of pore-size distribution as well.

Polymodal mesopore-size distributions can be determined if several mesopore groups differing sufficiently in pore sizes are present. Furthermore, the differentiation of these groups is the more difficult the wider the pores are. This is due to the relative pressure error propagation into the error in pore-size determination which is especially unfavourable close to saturation where the wide mesopores have their desorption branches. A role plays also the ratio of volumes of mesopore groups: The possibility of separating their contributions seems improbable in case that some pore group is predominating.

REFERENCES

1. Gregg S. J., Sing K. S. W.: *Adsorption, Surface Area and Porosity* (2nd edition). Academic Press, London 1982.
2. Broekhoff J. C. F.: Stud. Surf. Sci. Catal. *3*, 663 (1979).
3. Lecloux A. J. in the book: *Texture of Catalysts. Catalysis, Science and Technology* (J. R. Anderson and M. Boudart, Eds). Springer Verlag, West Berlin 1981.
4. Valuš J., Schneider P.: Appl. Catal. *16*, 329 (1985).
5. Ernekrová Z., Jirátová K., Círová A., Grosser V., Schneider P.: Chem. Prum. *35*, 583 (1985).
6. Roberts B. F.: J. Colloid Interface Sci. *23*, 266 (1967).
7. Barret E. P., Joyner L. G., Halenda P. P.: J. Am. Chem. Soc. *73*, 373 (1951).
8. Halsey G.: J. Chem. Phys. *16*, 931 (1948).