Diffusion diagnostics of microporosity in nanoporous amorphous silicas and porous glasses

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Polymodal nanoporosity of silica materials has been studied by two new methods. The first method of diffusion diagnostics is based on the high-sensitive mass spectral registration of kinetics of gas desorption from pores into high vacuum. The second method resides in the analysis of equilibrium desorption and adsorption isotherms at low partial pressures. The computer fitting of equilibrium isotherms and diffusion kinetics of nitrogen, oxygen and argon desorption at 77.5 K has revealed the availability of microporous substructure in mesoporous amorphous silicas and porous glasses. Trimodal nanoporous structure of silicas and porous glasses consists essentially of transporting mesopores with mean diameter from 3 to 15 nm and two kinds of adsorbing micropores with diameter 0.3-0.4 and 0.6-0.7 nm what corresponds 1 and 2 diameters of gas molecules. The morphology of pores in porous glasses depends on method of glass producing by leaching of alkali borosilicate glasses. Gas adsorption in micropores has a character of volume filling. Micropore volume in porous glasses is equal to 3-6% from total pore volume. For amorphous silicas the volume of micropores depends on method of synthesis and on the size of globules. Gas diffusion in mesopores is mainly Knudsen diffusion although the effective diffusion coefficient is the complicated function of Knudsen diffusion coefficient, surface diffusion coefficient and Henry's adsorption constant. The mechanism of diffusion in micropores is surface-diffusion one. The perspective direction of using the diffusion method for pore morphology diagnostics is its application for researching the systems with small pore volume: nanoporous coatings, films and surface defective layers on optical materials.

Introduction

According to the IUPAC classification [1] the pores in solids are subdivided into macro- (with mean diameter larger than 50 nm), meso- (2–50 nm) and micropores (less than 2 nm). Nanoporosity is understood by us as the pores of nano-size and includes micro- and mesopores. Macro- and mesopores in solid bulk are successfully diagnosed by mercury penetration and common adsorption method from capillary condensation region with the hysteresis loop on the adsorption-desorption isotherms. Micropores remain *terra incognita.* At the present time the quantitative methods for the simultaneous diagnosing the micro- and mesopores in nanoporous systems and for diagnostics of nanopores of small volume are absent. The availability of micropores affects many adsorptive, adhesive, mechanical and capillary properties of solids because of high adsorptive potential of micropores. Producing micropores on surface and in the bulk of glass is possible under mechanical, chemical and heat treatments and under the action of high energies.

New method for microporosity research

Diffusion diagnostics (DD-method)

The new method of diffusion diagnostics (DD-method) has been developed for study of polymodal nanoporosity of silica materials. It is based on the high-sensitive mass spectral registration of kinetics of gas desorption from pores into high vacuum [2]. After preliminary gas adsorption at low partial pressure and at temperature of liquid nitrogen, the pumping out and mass spectral recording of gas flow desorbed at the same temperature from porous sample into high vacuum are carried out. Distinguishing in the diffusion drag of the gas transport in the pores of various morphology results in the essential difference in the type of isothermal kinetic curves of desorption of which the corresponding diffusion coefficients can be calculated. For polydispertional materials with volume porosity, the diffusion is radially symmetric as for a sphere and diffusion coefficients can be calculated from an equation

$$C / C_0 = \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\exp\left(-\frac{n^2\pi^2 s^2\rho^2 D}{9}t\right)$$

where ρ - density, s – outer specific surface, m - mass of sample, t - time, C_0 and C - initial and actual concentrations of gas in solid. The algorithm of the diffusion coefficients calculation includes a dispersion function of particle size and the coefficient taken into account the deviation of particle shape from spherical one.

Equilibrium adsorption or desorption at low pressure (LPEA- or LPED-method)

This method is based on computer analysis of equilibrium desorption and adsorption isotherms at low partial pressures. It has been earlier detected that adsorption and desorption isotherms on model monomodal porous systems – zeolites A and X with window diameter equal to 0.36 and 0.78 nm - have s-like shape and are fitted by Bolzmann equation. With decreasing the window diameter, the pressure in inflection point decreases and adsorption constant equal to the reciprocal of the pressure in inflection point, analogous to Henry’s adsorption constant, increases. Consequently, the increase of adsorption pressure in the low-pressure range for polymodal porous systems brings to the sequential volume filling of larger micropores.

Experimental

Polydispersional silica samples containing meso- and micropores have been the subject of investigation. The structural characteristics of the samples are given in Table 1. Three samples of amorphous silica have had globular structure. The size of globules has been measured by electron microscope. Three samples of porous glasses with fraction 0.1–0.135 mm have been produced by liquation and leaching of alkali borosilicate glasses. The glasses contain an almost pure phase of silica (up to 99% SiO_2), a main impurity of boron oxide and traces of sodium oxide. The structure of porous glasses is normally considered as mixed globular–sponge structure where secondary silica globules are formed at leaching. The values of specific surface s_{BET} have been measured from nitrogen adsorption isotherms by BET method; the mesoporous specific surface s_{meso} - from s_{BET} in terms of adsorption in micropores; the outer specific surface s_{out} - from the particle

Table 1. Structural and diffusion characteristics of porous samples

Sample	s_{BET} m^2/g	s_{meso} m^2/g	s_{out} cm^2/g	v_p cm^3/g	d_{gl} nm	ρ_a g/cm^3	d_{meso} nm	$D'_1\cdot 10^{14}$ cm^2/s	$D'_2\cdot 10^{14}$ cm^2/s	$D'_3\cdot 10^{7}$ cm^2/s	$v_1\cdot 10^3$ cm^3/g	$V_2\cdot 10^3$ cm^3/g
Amorphous silicas (AS)												
AS-A	469	417	31300	0.625	4.9	0.926	4.32	1.5	5.6	1.32	11.0	13.8
AS-B	366	338	5000	1.167	6.8	0.617	10.3	1.8	5.2	3.29	3.5	10.3
AS-C	101	95.6	152	0.300	25.5	1.325	9.32	1.2	6.1	2.98	0.6	2.4
Porous glasses (PG)												
PG-A	137	105	535	0.152	17.3*	1.649	3.91	0.6	7.7	1.18	6.2	9.3
PG-B	123	104	555	0.174	19.9*	1.591	4.76	0.4	7.5	1.46	3.7	5.6
PG-C	111	82.7	694	0.332	23.3*	1.271	11.6	1.5	7.3	3.73	5.5	7.5

* calculated with the assumption of globular structure of porous glasses

size and shape coefficient; the pore volume v_p - by water condensation; the mean diameter of globules d_{gl} - from s_{BET}; the apparent density - from true density of silica (2.2 g/cm^3) and pore volume; the mean diameter of mesopore entrances in silica particles - from volume and surface of mesopores with the formula $d_{meso} = 3\ v_{meso}\ /\ s_{meso}$. The mean diameters are close to the values of maximum of mesopore-size distribution determined from the isotherms of nitrogen adsorption and desorption in the range polymolecular condensation.

Results and discution

The computer analysis of kinetic curves of nitrogen, oxygen and argon diffusion from silicas and porous glasses at 77.5 K by DD-method has allowed to detect three main diffusion processes with various characteristic degassing times, to calculate the coefficients of gas diffusion in the three types of pores, to correlate the diffusion coefficients with the trimodal structure of nanopores and to obtain the curves of pore-size distribution (Fig. 1). Nanoporous structure of the silicas and porous glasses consists essentially of transporting mesopores with mean diameter from 3 to 15 nm and two kinds of adsorbing micropores diameter of which was estimated to be equal to about 0.3-0.4 and 0.6-0.7 nm what corresponds one and two diameters of gas molecules. Gas diffusion from mesopores is the fastest process and is mainly Knudsen diffusion. The effective diffusion coefficient is the complicated function of Knudsen diffusion coefficient D_g (proportional to diameter of mesopores), surface diffusion coefficient D_s, Henry's adsorption constant K_H, porosity ε and tortuosity τ:

$$D_{eff} = \frac{\varepsilon}{\tau^2}\left(\frac{D_g + K_H D_s}{1 + K_H}\right)$$

Henry's adsorption constant K_H used in DD-method has agreed with one obtained by LPED-method for mesopores. The gas diffusion from two types of micropores is the slowest processes and can be considered as sequential passage through microporous regions and transporting mesopores. Therefore the total diffusion resistance for gas evolution from micropores is added from diffusion resistances in micro- and mesopores. The relationship between the diffusion resistances in micro- and mesopores can be changed by the variation of particle size and hence diffusion way in mesopores. The mechanism of diffusion in micropores is surface-diffusion one. The mean values of nitrogen diffusion coefficients at 77.5 K for micropores of I type (D'_1), II type (D'_2) and mesopores (D'_3) are tabulated in Table 1 ($D' = D_{eff}\ /\ \varepsilon$). Diffusion coefficients decrease in the row from nitrogen to argon, i.e. in the row of decreasing the value of quadrupole moment of the molecules. Micropore diffusion coefficients depend also on pore diameter and can be related for micropores with coefficients of gas diffusion in zeolite channels of similar size. Diffusion coefficients for micropores of I and II types in silica materials with globular structure are some lower than in zeolite A and X with windows 0.36 and 0.78 nm correspondingly. But the micropores in globular structure can be modeled as wedge-shaped pores in gaps between globules around contact points. Micropores in the zeolites can be presented as cylindrical pores with variable cross section and mean effective diameter of zeolite channels are determined by not only diameter of windows but also diameter of large cavities (1.1–1.2 nm).

By the LPED-method, two types of micropores, apart from mesopores, have been identified in studied silica materials as well (Fig. 2). The micropores in silica materials have adsorption constants at Bolzmann fitting close (but some larger) to ones for zeolites A and

X. Maxima on the curves of pore-size distribution are appropriate to 1 and 2 diameter of gas molecules as well as by DD-method. Gas adsorption in micropores, in distinction to mesopores, has not depended (or depended slightly) on adsorption pressure for pressure larger than the reciprocal of adsorption constant and has a character of volume filling. The volume of micropores of I and II types determined from nitrogen desorption by equilibrium LPED- (v_1 and v_2 in Table 1) and kinetic DD–methods have been the same within 10%. Package of oxygen and argon in adsorbed layer, in contrast to nitrogen, has been less close than in liquid phase. Micropore volume measured by DD- and LPED-methods is correlated with estimations from the isotherms of nitrogen adsorption at 77.5 K by Sing's α_s–method. For porous glasses the micropore volume is equal to 3 - 6% from total pore volume. For amorphous silicas the volume of micropores depends on method of synthesis and on the size of globules: with decreasing size of globules micropore volume rises (Table 1). Micropores surface can be also estimated easily for different geometrical model of pores knowing volume and size of pore. Volume of different types of pores and other morphological properties of porous structure (mean pore diameter, width of peak on pore size distribution curve) depend on method of producing porous glasses. The porous glass PG-A with the largest volume of micropores and the lowest diameter of mesopores has been obtained at the highest temperature of liquation. From the comparison of results obtained by DD- and LPED-methods it has been established that the microporous globular regions in porous glasses form only part of solid matrix (upto 15%).

Conclusion

Polymodal nanoporosity of silica materials has been studied by two new methods. The computer fitting of equilibrium isotherms and diffusion of nitrogen, oxygen and argon desorption at 77.5 K revealed the availability microporous substructure in mesoporous amorphous silicas and porous glasses. Trimodal nanoporous structure of the silicas and porous glasses consists essentially of transporting mesopores with mean diameter from 3 to 15 nm and two kinds of adsorbing micropores with diameter 0.3 - 0.4 and 0.6 - 0.7 nm what corresponds 1 and 2 diameters of gas molecules. The new DD- and LPED-methods have enabled not only to determine mean sizes of pores but also to characterize the width of peaks on pore-size distribution curve and to determine the volume of all kinds of nanopores. The perspective direction for using the diffusion method for diagnostics of pore morphology is its application for researching the systems with small pore volume: nanoporous coatings, films and surface defective layers on optical materials what is possible owing to the high sensitivity of mass spectral analysis and is not possible by common adsorption methods. In this case the algorithm of calculation will include diffusion equations for one-sided plate symmetry.

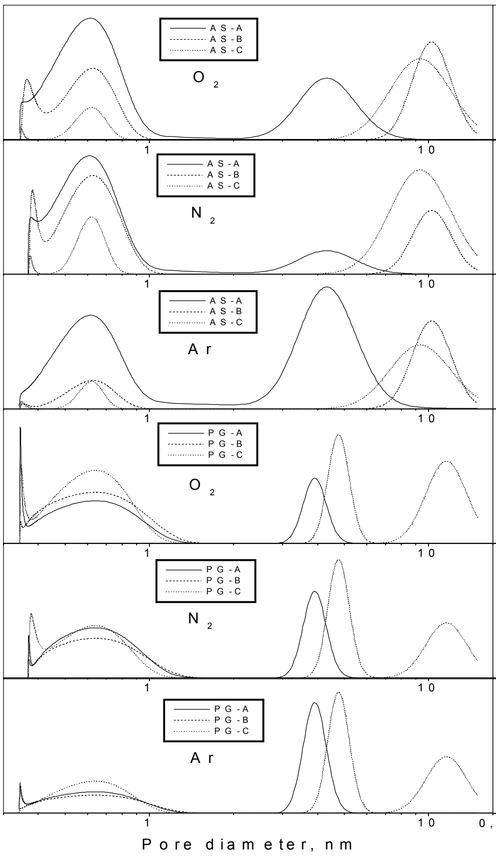

Figure 1. Trimodal nanopore-size distribution of amorthous silicas and porous glasses detected by DD-method after gas adsorption at 0.001 – 0.01 Torr.

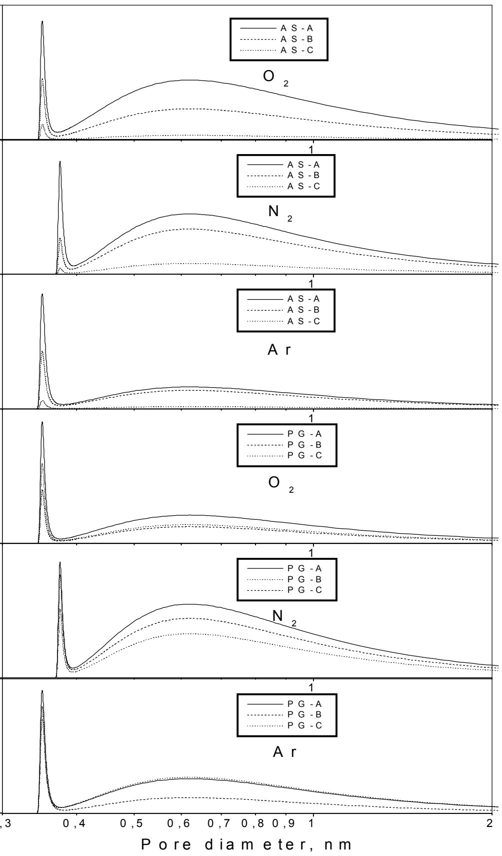

Figure 2. Microporous substructure in amorthous silicas and porous glasses detected by LPED-method after gas adsorption at 0.1 – 0.5 Torr.

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