Electronic Supplementary Material (ESI)
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Gas permeation properties of hollow glass-crystalline microspheres

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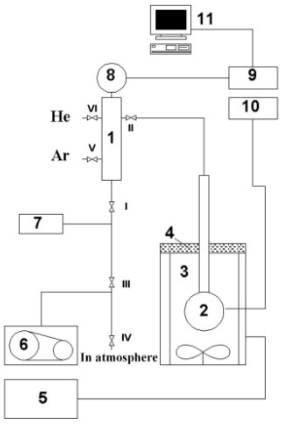
I. Experimental Section

Determination of permeability of hollow glass-crystalline microspheres

The permeability of hollow glass-crystalline microspheres to helium, hydrogen, and neon was measured in a vacuum apparatus (Fig. S1) at a pressure of $3 \cdot 10^4$ Pa in the temperature range from 298 to 623 K for helium and from 553 to 773 K for hydrogen and neon under the conditions of diffusion of the gases from the reactor volume into globules.



1 — manifold;
2 — reactor;
3 — gradientless furnace;
4 — thermal insulator;
5 — temperature controller RIF;
6 — rotary oil vacuum pump DSE-II;
7 — thermocouple vacuum sensor VIT;
8 — pressure sensor AIR-20M;
9, *10* — pressure and temperature converters;
11 — computer;
I-VI — valves.

Fig. S1. Schematic diagram of apparatus for measurements of glass-crystalline microspheres permeability.

A sample (1-2 g) was placed in a reactor (*2*). The reactor was heated in a gradientless furnace (*3*). A thermal insulator (*4*) was used for separating the reactor volume into zones with different temperatures. The temperature control was achieved using a chromel-alumel thermocouple with a temperature converters IRT-2-T (*10*). The reactor (*2*) filled with the sample was evacuated to a residual pressure of approximately 4 Pa. Then, a manifold (*1*) was filled with a gas, the pressure of the gas was determined, and the reactor (*2*) was again filled with the gas. The pressure measurement was carried out using a pressure sensor (*8*) with the simultaneous recording of the results on a computer (*11*). The pressure sensor (*8*) was AIR-20M, from which data were continuously recorded with a frequency of approximately 2 Hz. The reading and recording of the pressure values were implemented using the «Genesis» software environment operating together with «Master OPC». The processing of the results of measurements was performed with the «Matlab» software program.

The diffusion of gases through the microsphere shells occurs as a result of the difference between the gas partial pressures outside and inside the globules. The calculation of the gas permeability Q [mol/(Pa·s·g)] is based on the measurement of the pressure drop time-dependence after the gas injection into the reactor filled with the sample:

$$Q = dP/dt(V_0/T_0+V_p/T_1)/P_{out} \cdot R, \qquad \text{(S1.1)}$$

where V_0 is the volume of the manifold [L], T_0 is the room temperature [K], V_p is the reactor volume [L], T_1 is the temperature of the reactor [K], P_{out} is the gas pressure outside the particles at an instant of time t [Pa], and R = 8.314 (Pa·L)/(mol·K) is the universal gas constant. The relative error in the determination of the permeability of microsphere membranes does not exceed 10%.

The activation energy E_a of gas diffusion through the microsphere shells in the temperature range under investigation was calculated by the least squares method using the dependence of ln$Q$ on $1/T$.

The calculation of the glass phase permeability coefficient K [(mol·m)/(m^2·s·Pa)] for the microsphere shells, which is based on the basic equation for gas diffusion through a membrane, was carried out according to the formula

$$K = (Q \cdot \delta \cdot 100)/(S \cdot C), \qquad \text{(S1.2)}$$

where Q is the gas permeability of microsphere shells [mol/(Pa·s·g)]; δ is the apparent shell thickness [m], S is the geometrical surface of the sample particles, which is calculated as the sum of the surfaces of identical spheres with diameter D_{av} [m^2/g]; and C is the glass phase content according to the quantitative X-ray powder diffraction analysis data [wt %].

II. Characterization of hollow glass-crystalline microspheres

Table S1. Chemical composition of hollow glass-crystalline microspheres (wt %)

Sample	LOI	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	SO_3	P_2O_5	B_2O_3
H-0.08	0.62	60.92	25.92	3.40	1.63	2.31	1.18	3.55	0.21	0.09	0
HM-M-5A	0.82	58.26	32.08	2.80	1.27	1.15	0.72	2.39	0.27	0.08	0
HM-P-5A	0.06	58.12	36.63	0.80	1.54	1.22	0.63	0.56	0.21	0.08	0
3M K37	0	70.62	0.12	0	13.67	0.63	5.40	0.01	0.29	0.08	8.90

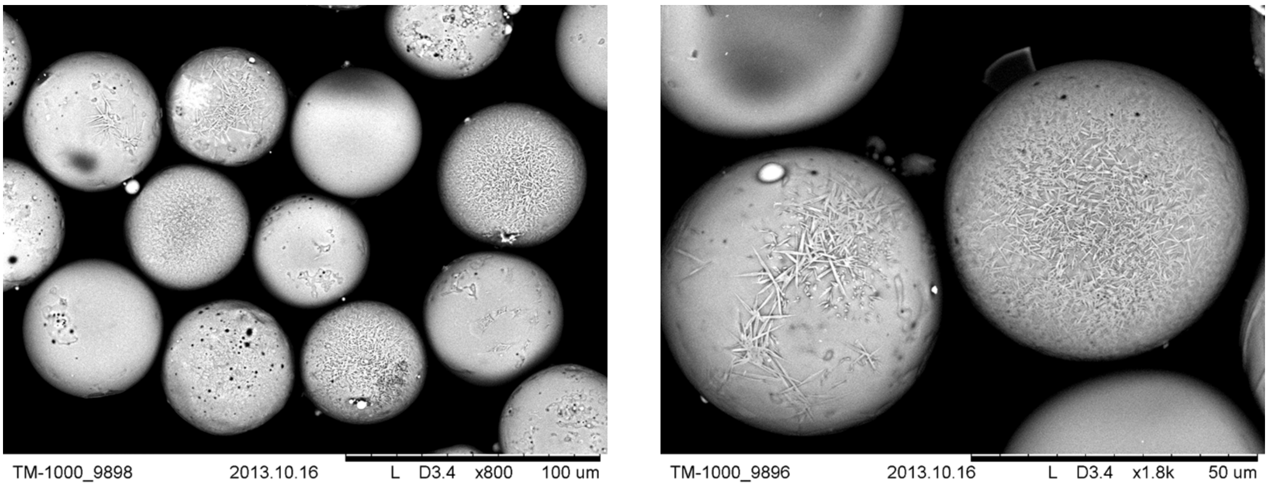


Fig. S2. SEM images of cenospheres HM-P-5A *1273 K,* O_2

Table S2. Lattice parameters (Å) and crystallite size (D_V, nm) of mullite phase in cenospheres

Sample	Mullite(0)	Mullite(I)

	a	*b*	*c*	D_V	*a*	*B*	*c*	D_V
			Initial cenospheres					
HM-M-5A	7.5671(3)	7.6911(3)	2.8873(1)	143	-	-	-	-
HM-P-5A	7.5611(2)	7.6913(2)	2.8885(1)	122	-	-	-	-
			Cenospheres after thermal treatment in different gas atmospheres					
HM-M-5A *1273 K*, O_2	7.5655(3)	7.6894(2)	2.8871(1)	143	7.572(1)	7.7131(9)	2.8929(2)	24
HM-P-5A *1273 K*, O_2	7.5607(2)	7.6908(2)	2.8879(1)	122	7.572(3)	7.715(3)	2.8948(9)	31
HM-P-5A *1373 K*, O_2	7.5619(3)	7.6914(2)	2.8884(1)	122	7.567(2)	7.717(3)	2.8917(8)	27
HM-M-5A *1273 K*, Ar	7.5651(4)	7.6893(3)	2.8862(1)	143	7.5513(7)	7.6993(6)	2.8879(1)	43
HM-M-5A *1273 K*, Ar *1273 K*, O_2	7.5639(4)	7.6886(3)	2.8871(1)	143	7.5531(6)	7.7034(4)	2.8908(1)	44

Table S3. Permeability coefficient of glass phase and activation energy of gas diffusion in hollow glass-crystalline microspheres

Sample	Mullite content (wt %)	Permeability coefficient of glass phase x10[19] (mol·m)/(m[2]·s·Pa)							Activation energy (kJ/mol)		
		298 K	553 K			673 K					
		K_{He}	K_{He}	K_{H2}	K_{Ne}	K_{He}	K_{H2}	K_{Ne}	He	H_2	Ne
3M K37	0	0.44	210	2.8	0.46	763	23	3.3	33	54	51
H-0.08	3.7	0.95	626	ND	5.0	2079	ND	18	31	ND	34
HM-M-5A	8.4	2.4	682	24.7	3.2	2198	118	17	30	40	43
HM-P-5A	30.1	13.7	1759	52.6	5.4	5001	248	36	26	40	49
HM-M-5A *1273 K*, O_2	30.4	16.5	1915	90.7	11.0	5263	285	73	26	30	49
HM-P-5A *1273 K*, O_2	37.2	34.4	3005	104	12.7	7473	ND	75	24	25	46
HM-P-5A *1373 K*, O_2	48.4	62.0	6554	203	29.7	17287	662	149	25	30	42
HM-M-5A *1273 K*, Ar	29.8	6.6	1226	49.3	6.4	3643	207	36	28	37	44
HM-M-5A *1273 K*, Ar *1273 K*, O_2	33.0	8.1	1322	72.2	8.0	3821	202	47	27	27	45

ND: Not detected

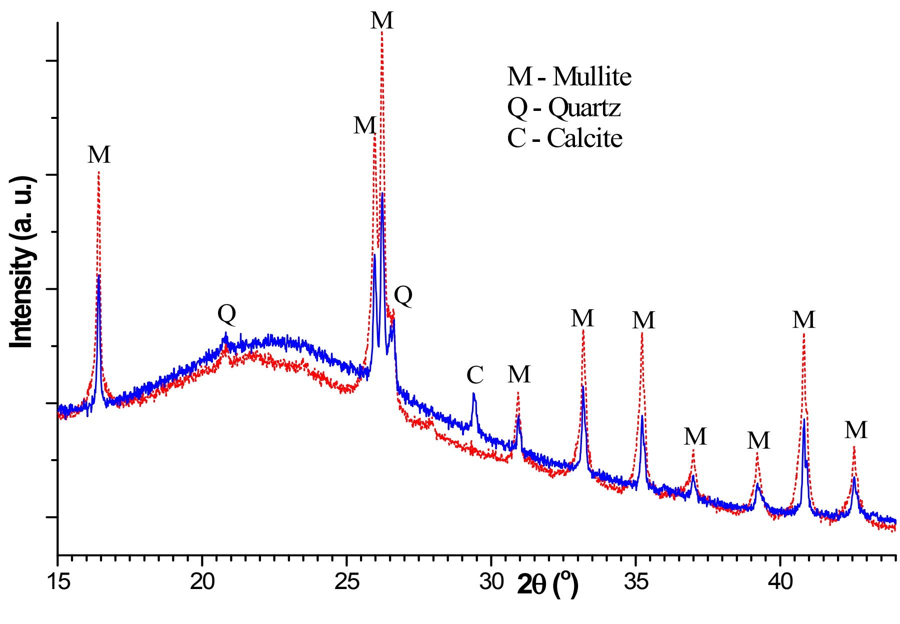


Fig. S3. XRD patterns of sample HM-M-5A before (solid blue) and after (red dashed) thermal treatment in O_2.

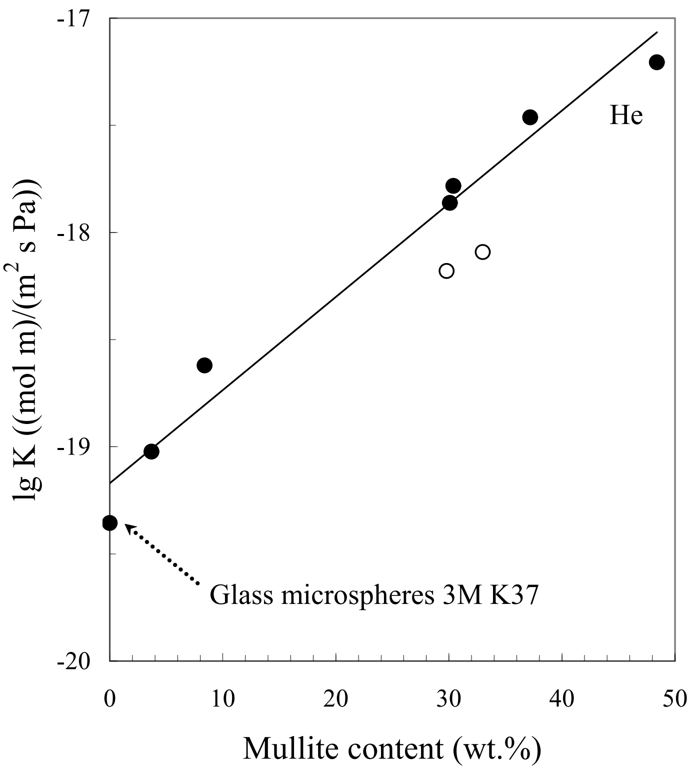


Fig. S4. Dependences of glass phase permeability of hollow glass-crystalline microspheres to He at 298 K on the content of mullite formed during thermal treatment in O_2 (closed symbols) and Ar (open symbols).