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communication

## Gas permeation properties of hollow glass-crystalline microspheres

Elena V. Fomenko,<sup>\*a</sup> Elena S. Rogovenko<sup>a</sup>, Leonid A. Solovyov<sup>a</sup> and Alexander G. Anshits<sup>a,b</sup>

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5 Permeation of He, H<sub>2</sub> and Ne was studied for hollow glass-crystalline microspheres. Microspheres demonstrated high permeability to helium with high selectivity for He/H<sub>2</sub> and He/Ne owing to the composition and structure of their shells.

Helium is a key component in many high-tech industries. The modern industrial technology for the production of high-purity helium (99.9950 vol %) is based on its release from the natural gas using the energy-intensive cryogenic process. This process includes the low-temperature condensation stage with the formation of a helium concentrate containing approximately 80 vol % He, followed by several stages of its purification from methane, hydrogen, oxygen, nitrogen, argon, and neon.<sup>1</sup>

An alternative helium production direction is the energy-efficient diffusion-sorption technology<sup>2</sup> combining pressure swing adsorption (PSA) and membrane separation. An implementation of the membrane separation in practice requires the use of membrane materials with high helium permeability and selectivity, high chemical and thermal stability, high strength, and low cost.

It is known that polymeric materials exhibit a high permeability to helium (Table 1). However, the selectivity for He/CH<sub>4</sub> of different polymers varies in the range from 6 to 184 and, in rare cases, reaches a value of the order of 10<sup>3</sup>.<sup>3</sup> In addition to the poor selectivity, the disadvantages of polymeric membranes are the low strength, low thermal stability, and, in some cases, high cost and synthesis complexity. For these reasons, among several hundreds of known polymeric materials, only few have been used by industry for the isolation of H<sub>2</sub>, production of O<sub>2</sub> and N<sub>2</sub>, and CO<sub>2</sub> extraction.<sup>5</sup>

Carbon molecular sieve membranes,<sup>6</sup> which can be produced by pyrolysis of polymeric precursor, are characterized by a high temperature operations but a low selectivity for He/CH<sub>4</sub>.<sup>7</sup>

By their permeability to helium, polymeric materials correspond to nanoporous and microporous materials (Table 1), in particular, zeolite T membranes prepared by the hydrothermal synthesis on porous mullite tubes<sup>8</sup> and metal-organic frameworks (MOFs) membranes.<sup>9,10</sup> These materials, as well as polymers, are characterized by a low selectivity for He/CH<sub>4</sub>. Moreover, it is problematic for them to obtain defect-free layers of large surface area.

**Table 1** Permeability and selectivity of membrane materials

Sample	Temperature (K)	Permeability coefficient for He (mol·m)/(m <sup>2</sup> ·s·Pa)	Selectivity		Ref.
			He/CH <sub>4</sub>	He/Ne	
Polymeric membranes					
Polypyrrolone	298	8·10 <sup>-15</sup>	3041		3
Polyimide	308	7·10 <sup>-15</sup>	92		4
Teflon AF-2400	298	1·10 <sup>-12</sup>	6		3
Carbon molecular sieve membranes					
C-HBPI-1	308	2·10 <sup>-13</sup>	33		7
Nano- and microporous membranes					
Zeolite T	378	2·10 <sup>-13</sup>	25-51		8
Cu-MOF	298	3·10 <sup>-11</sup> - 6·10 <sup>-14</sup>	2-7		9, 10
Ultra microporous glass hollow-fiber	473	2·10 <sup>-14</sup>	10 <sup>4</sup>		12
Microporous glass	300	3·10 <sup>-13</sup>	10 <sup>4</sup>		13
Silicate glasses					
Silica glass	298	3·10 <sup>-17</sup>		10 <sup>3</sup>	15,
	553	1·10 <sup>-15</sup>			16
	673	3·10 <sup>-15</sup>	10 <sup>6</sup>		
CGW-7740	298	5·10 <sup>-18</sup>			17
	553	5·10 <sup>-16</sup>		10 <sup>2</sup>	

Permeability coefficients are given in the SI units: 1 (mol·m)/(m<sup>2</sup>·s·Pa) = 2.9·10<sup>15</sup> Barrer

A specific direction is the preparation of porous membrane materials by chemical etching of silicate glasses.<sup>11-13</sup> The ultra-microporous and microporous membranes thus produced are characterized by a high permeability to helium and the selectivity for He/CH<sub>4</sub> at a level of 10<sup>4</sup>, which significantly exceeds the corresponding value for polymers (Table 1).

Taking into account the technical requirements to helium quality,<sup>14</sup> in which the concentration of impurities should not exceed 0.005%, including neon (no more than 0.004%), the most suitable for selective extraction of helium are silicate glasses characterized by high values of selectivity for He/CH<sub>4</sub> and He/Ne (Table 1).<sup>15-17</sup> The diffusion properties of silicate glasses are determined by their composition and structure. With a decrease in the content of network modifier oxides (Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, Na<sub>2</sub>O, MgO, CaO, Fe<sub>2</sub>O<sub>3</sub>), their permeability to helium increases<sup>15</sup> due to its diffusion primarily through the silica-rich phase.<sup>17</sup> The silica glass structure, presenting a three-dimensional network of multi-membered rings formed by the SiO<sub>4</sub> tetrahedra, was described for the first time by the theoretical model proposed by Zachariassen<sup>18</sup> and confirmed experimentally by transmission electron microscopy of silica glass supported on graphene.<sup>19</sup>

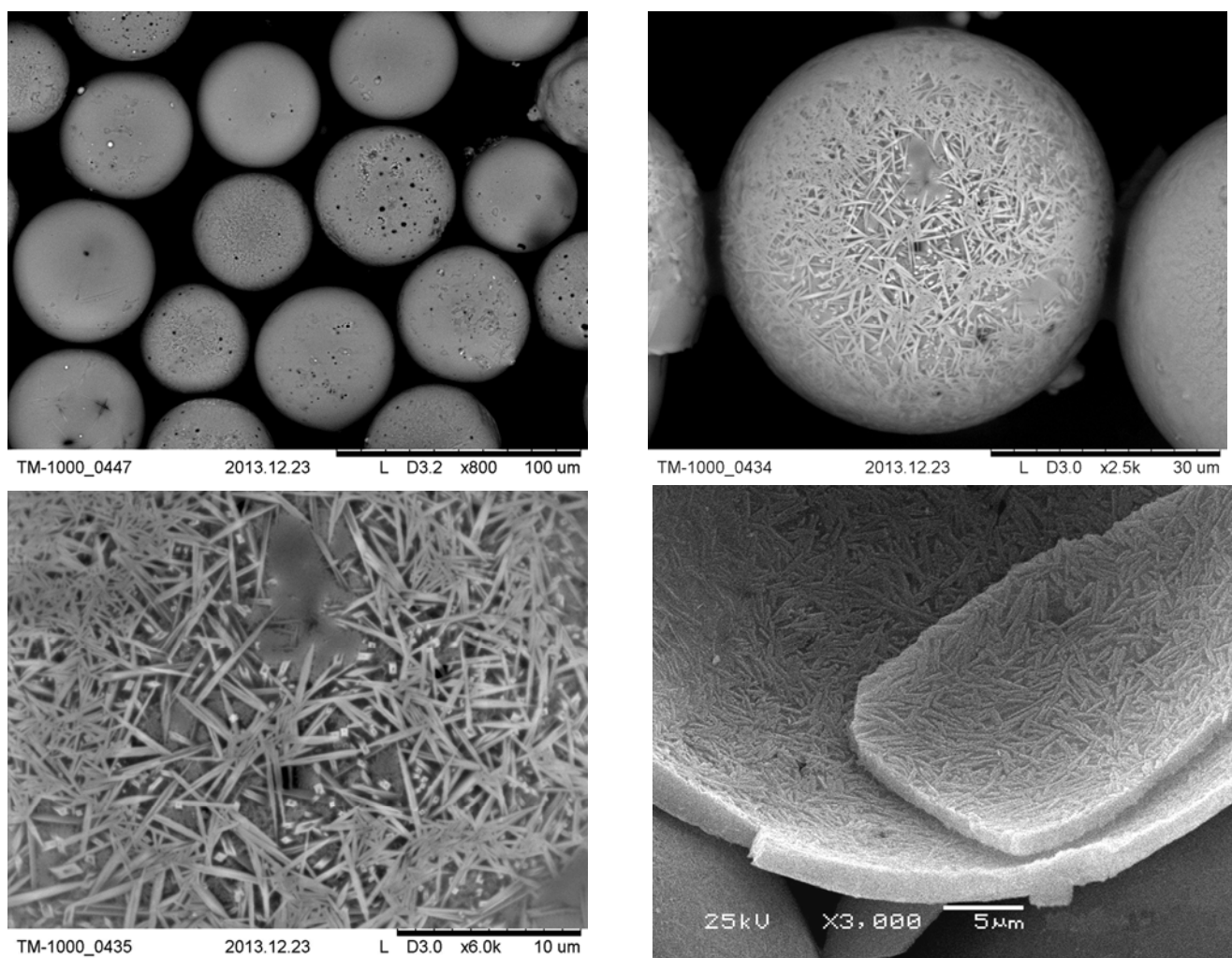


Fig. 1. SEM images of cenospheres HM-P-5A 1273 K, O<sub>2</sub>

In this communication, we present results of investigation into the permeability of hollow glass-crystalline microspheres to helium, hydrogen, and neon as a function of the composition and structure of their shells. We used the fractions of nonmagnetic nonperforated aluminosilicate cenospheres (Fig. 1) with narrow size distributions of globules with a certain composition, morphology, and thickness of glass-crystalline shell.<sup>20-22</sup> The extraction of cenosphere narrow fractions was carried out from cenosphere concentrates of fly ash with the use of a technological setup,<sup>20</sup> which included the stages of hydrodynamic separation, sizing, magnetic separation, and aerodynamic classification with the subsequent hydrostatic isolation of the destroyed globules. The average diameter of cenospheres in the fraction - 0.063+0.05 mm is equal to 58-61 μm, with the shell thickness being 2.5-3.1 μm.<sup>21</sup> According to the chemical composition, the cenospheres are considered as a multi-component system with the contents of the major components SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> in the ranges of 58-61 and 26-37 wt %, respectively. The cenosphere shell consists of the glass phase and crystalline phases, such as mullite, quartz, and calcite. The outer and

inner surfaces of the globules are covered with a nanometer-sized (30-50 nm) film.<sup>23, 24</sup>

In order to increase the content of crystalline phases and to decrease the content of network modifier oxides in the glass phase, the cenospheres were subjected to thermal treatment at temperatures of 1273 and 1373 K in an oxygen or argon atmosphere (Table 2). This resulted in the formation of an additional mullite (I) phase, which differed from the original mullite (0) by smaller crystallite sizes and different lattice parameters. In some cases, the cristobalite phase also appeared (Table 2).

The composition of the mullite (I) phase depends on the thermal treatment atmosphere, as evidenced by variations in its lattice parameters. The formation of this phase in an oxygen atmosphere is accompanied by the oxidation of Fe<sup>2+</sup> ions to Fe<sup>3+</sup>, their extraction from the glass phase, and incorporation into the Al<sup>3+</sup> ion positions of the crystallized mullite lattice. This results in the formation of a defective iron-containing phase of mullite (I), whose lattice parameters exceed the data available in the literature over the entire range of possible Al/Si ratios in mullite.<sup>25, 26</sup> The lattice parameters

**Table 2** Phase composition of cenospheres (wt %)

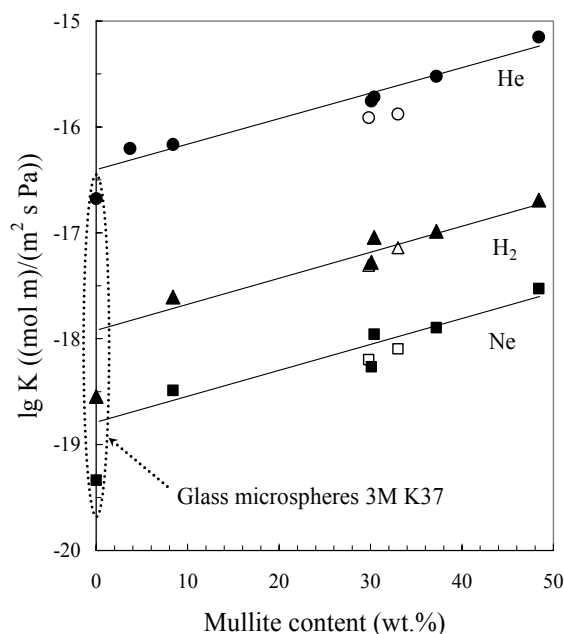
Sample	Mullite (0)	Mullite (I)	Quartz	Cristobalite	Calcite	Glass phase
Initial cenospheres						
H-0.08	3.7	0	3.0	0	0.6	92.7
HM-M-5A	8.4	0	1.5	0	0.7	89.4
HM-P-5A	30.1	0	1.4	0	0.3	68.2
Cenospheres after thermal treatment in different gas atmospheres						
HM-M-5A 1273 K, O <sub>2</sub>	9.5	20.9	1.7	0	0	67.9
HM-P-5A 1273 K, O <sub>2</sub>	31.3	5.9	2.4	0.5	0	59.9
HM-P-5A 1373 K, O <sub>2</sub>	37.0	11.4	2.1	14.1	0	35.4
HM-M-5A 1273 K, Ar	8.6	21.2	2.9	0	0	67.3
HM-M-5A 1273 K, Ar	9.4	23.6	2.6	0.4	0	64.0
HM-M-5A 1273 K, O <sub>2</sub>						

of mullite (I) formed in an inert atmosphere of argon are characterized by systematically lower values corresponding to 5 defect-free phases.

The permeability of cenosphere shells was investigated in comparison with synthetic hollow glass microspheres 3M™ (Glass Bubbles K37, fraction -0.063+0.05 mm) with the average globule diameter of 57 μm and the shell thickness of 10 1.4 μm, in which the content of the major components was as follows: 70.62 wt % SiO<sub>2</sub>, 13.67 wt % CaO, and 8.90 wt %. The glass microspheres contained 1 wt % of cristobalite.

The permeability of the cenospheres and microspheres to single gas He, H<sub>2</sub>, and Ne was investigated in a vacuum 15 apparatus under the conditions of gas diffusion from the reactor volume into globules at a pressure of 3·10<sup>4</sup> Pa in the temperature range from 298 to 623 K for helium and from 553 to 773 K for hydrogen and neon.<sup>21</sup> The diffusion of gases through the globule shells occurred as a result of the 20 difference between the gas partial pressures outside and inside the globules. The permeability determination of the microsphere and cenosphere shells was based on measuring the time-dependence of the gas pressure drop after the re- 25 passage into the reactor filled with the sample. The relative error in the determination of the permeability does not exceed 10%. The permeability coefficient values K of the glass phase were calculated taking into account its content and keeping in mind that the permeability of the crystalline phases is several orders of magnitude lower than that of the glass phase.<sup>27</sup> The 30 selectivity was defined as ratio of K for single gases.

The increase in the mullite phase content led to respective increase in the cenosphere shell permeability for the studied gases over the entire temperature range. Figure 2 shows the dependences of the permeability coefficients  $K_{\text{He}}$ ,  $K_{\text{H}_2}$ , and 35  $K_{\text{Ne}}$  at 553 K on the mullite phase content in the cenospheres. Exceptions were cenospheres in which the crystallization of mullite (I) occurred in an inert atmosphere. In this case, there was no oxidation of Fe<sup>2+</sup> ions to the Fe<sup>3+</sup> state in which iron could be embedded into the lattice of the mullite formed, 40 which was confirmed by the decreased values of its lattice parameters. The iron ions remaining in the glass phase hindered the diffusion of helium. A subsequent oxidation Fe<sup>2+</sup>



**Fig. 2** Dependences of glass phase permeability of cenospheres to He, H<sub>2</sub>, and Ne at 553 K on the content of mullite formed during thermal 45 treatment in O<sub>2</sub> (closed symbols) and Ar (open symbols).

→ Fe<sup>3+</sup> (sample HM-M-5A 1273 K, Ar 1273 K, O<sub>2</sub>) did not lead to any significant changes in the diffusion properties of the cenospheres, since the iron ions were kept in the 50 phase.

The crystallization of mullite in an oxidizing atmosphere led to a decrease in the content of network modifier cations in the glass phase and to an increase in the permeability of the cenosphere shell with high values of selectivity for He/H<sub>2</sub> and 55 He/Ne. The cenospheres with the maximum mullite phase content (48.4 wt %) are characterized by the permeability coefficient  $K_{\text{He}}$  corresponding to the level of silica glass (Table 1), which is several orders of magnitude higher than the permeability coefficient  $K_{\text{He}}$  for synthetic glass- 60 microspheres 3M K37. The values of the selectivity for He/H<sub>2</sub> and He/Ne at a temperature of 553 K are equal to 32 and 221, respectively. The activation energies for He, H<sub>2</sub>, and Ne diffusion are equal to 25, 30, and 42 kJ/mol, respectively.

In conclusion, microsphere materials with a high 65 permeability to helium and a high selectivity for He/H<sub>2</sub> and He/Ne have been prepared by thermal treatment of narrow fractions of fly ash cenospheres in an oxygen atmosphere. The mullite phase formed during the high-temperature 70 crystallization favors both purification of the silicate glass phase from network modifier cations and additional strengthening of the cenosphere shell. The use of these materials underlies the energy-efficient diffusion technology for the separation of gas mixtures.<sup>2,28</sup> The modules on the base 75 of cenosphere are characterized by a large surface area per unit volume 60000 m<sup>2</sup>/m<sup>3</sup>, which higher than the value for membrane cells fabricated from hollow fibers (20000 m<sup>2</sup>/m<sup>3</sup>) and exceeds that of rolling (1000 m<sup>2</sup>/m<sup>3</sup>) and flat membranes (100 m<sup>2</sup>/m<sup>3</sup>) by several orders of magnitude.<sup>29</sup> Moreover, such modules possess reliable gas-separation properties for a long

time, because the efficiency of the process does not depend on the damage of individual globules. These advantages, in combination with high values of permeability to helium and the selectivity for He/H<sub>2</sub> and He/Ne, can provide high efficiency of the diffusion process for helium isolation and purification. The present results are promising for actual applications of glass-crystalline microspheres for helium capture.

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## Notes and references

<sup>a</sup> Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences, Akademgorodok 50/24, Krasnoyarsk, 660036 Russia. Fax: +7 391 249 41 08.; Tel: +7 391 243 93 17; E-mail: fom@icct.ru

<sup>b</sup> Siberian Federal University, Svobodny pr. 79, Krasnoyarsk, 660041 Russia. Fax: 7 391 243 31 94; Tel: +7 391 243 94 31; E-mail: anshits@icct.ru

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## Table of contents

Microsphere materials for helium capture have been prepared on the base of narrow fractions of fly ash cenospheres.

