Nanoporous Ceramic Membranes Modified by Carbon Nanotubes Used to Separate Gaseous Mixtures

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Abstract—Studies devoted to the development of ceramic membranes, which are capable of separating gaseous mixtures, first and foremost of H_2-CH_4, are presented in this paper. The membranes from alumina prepared on the basis of thermochemical activation (TCA) products of gibbsite contain a considerable amount of macropores and possess low selectivity in gas separation. In order to reduce the contribution of macropores to the porous structure of membranes, we have introduced glass additives, which sinter more easily than alumina. Tests of the samples, in which a part of TCA product is replaced by glass, have shown that the factor of separation for gaseous mixtures of H_2-CH_4 increases to 2.2. In the next part of this work, we synthesize the ceramic membranes, which were modified by carbon nanotubes (CNTs) with an external diameter of 3–5 nm. It is shown that when CNTs are introduced into the composition of a ceramic membrane, the selectivity in the separation of gaseous mixtures of H_2-CH_4 increases to 2.4.

INTRODUCTION

In the last few years, due to a decrease in oil energy sources, the attention of researchers has been shifted towards alternative sources such as natural gas and biomass [1]. Hydrogen fuel elements convert chemical energy of the fuel (hydrogen) into electricity without using low-efficient combustion processes, which are accompanied by large losses. This electrochemical device directly produces electrical energy as a result of high-efficient "cold" fuel combustion. Hydrogen can be obtained by various methods, but the most efficient ones are the reforming of hydrocarbons, alcohols, and biomass [2–6]. There is a significant number of dehydration reactions of light hydrocarbons, in which hydrogen removal can enhance the yield of reaction olefins. Therefore, the replacement of conventional reactors with a stationary catalyst layer by membrane-catalytic ones is at present a promising scientific direction [7–10].

The advantage of the membrane catalytic reactors over conventional ones consists of the possibility of carrying out both a reaction and separation of the reaction mixture in a joint reactor volume [11–13]. Special attention in pioneering works [14–19] was paid to the processes of selective transfer of the reagents and reaction products through the membrane in the membrane-catalytic reactors.

At present, significant progress in the development of polymer membranes is being achieved [20–25]. Hybrid membranes, including polymer ones modified by CNTs, making it possible to achieve a considerable increase in the selectivity compared to polymer ones, are also described in the literature [26, 27]. However, one peculiarity of most catalytic processes is the necessity of keeping the temperature at a level of 400–800°C, when the polymer and hybrid membranes cannot operate.

Metal membranes do not possess this disadvantage. The high selectivity of the close-coupled metal membranes in the separation of hydrogen-containing mixtures is well known. Various types of solid membranes used to extract hydrogen from a gaseous mixture are considered in [28]. The author of [28] proposes using thin palladium films (of about 10 μm and smaller) in order to enhance the selective penetrability of Pd membranes. Ultrathin palladium films are proposed for use in [29, 30].

The disadvantages of the Pd membranes are their fragility, high cost, and low filtration rate. Furthermore, the application of the palladium films is limited by the adsorption of CO and other molecules, as well as the irreversible corrosion under the action of sulfur compounds, which inhibit the membrane penetrability.

Ceramic porous membranes are most promising for the development of the membrane-catalytic processes [31−33]. The advantages of the porous ceramic membranes include, in particular, high thermal stability (they can be applied up to a temperature of 800°C), chemical passivity, and high mechanical strength. Porous ceramic membranes, as a rule, are fabricated on the basis of oxides of aluminum, zirconium, or titanium using sintering or sol-gel technology [34, 35].

When choosing membranes for the membrane-catalytic process, it is necessary that the rates of the catalytic reaction and diffusion through the membrane be synchronized, i.e., not differ significantly. One important characteristic in this case is the penetrability of a membrane measured in the volume of gas (in m^3), which passed in 1 h through 1 m^2 of membrane area at a pressure difference of 1 atm ($m^3/(m^2$ atm h)). The comparatively low mobility of the structural elements and the high density of their packing in inorganic solid compounds (metals, alloys, glass, etc.,) predetermine their very low penetrability even on the simplest gases. In the case of the mechanisms based on the dissolution of gases in a solid phase and their subsequent diffusion, even in the case of an activated diffusion, the penetrability of the close-coupled membranes appears to be 1−2 orders of magnitude lower than in the Knudsen diffusion case.

Carbon nanotubes (CNTs) are promising materials for the development of composite membranes, which is associated with the peculiarities in the CNT structure, their chemical passivity, and outstanding mechanical characteristics. Significant progress has been achieved both in studying the mechanism of the formation of CNTs and control over their geometric dimensions [36−41]. CNTs have hollow internal channels of nanometer sizes and, therefore, are convenient components by the development of the hybride nanoporous membranes. The diameters of CNTs are known to vary in a range of 1−50 nm and their length can reach 10−20 μm and higher. Thus, by introducing CNTs into a ceramic membrane, we can vary the number and diameter of the pores in the manufactured membranes.

In our work we study the possibility of using CNTs to modify the ceramics on purpose to obtain nanoporous ceramic membranes for the separation of gaseous mixtures of the CH_4/H_2 type.

EXPERIMENTAL

Product of Thermochemical Activation (TCA) of Gibbsite

We used gibbsite, $Al(OH)_3$, as the basic material and a binder for manufacturing ceramic membranes after its thermochemical activation and subsequent hydration. The thermal treatment of gibbsite at temperatures on the order of 300°C under conditions far from thermodynamic equilibrium leads to the removal of chemically bound water molecules and makes it possible to implement the "incomplete" decomposition "stopping" of it by quenching at a stage of hydroxide crystalline structure destruction, when the structure of a stable "low-temperature" oxide is still not formed. The thermal decomposition occurs for several seconds. When the temperature sharply increases and the heating is carried out at a rate of several hundreds of degrees per second, the initial aluminum trihydroxide can convert into a metastable state with a strongly disordered structure, the so-called TCA product [42−44].

The TCA product used by us after hydration contained a mixture of aluminum hydroxides: amorphous aluminum hydroxide 65%, pseudoboehmite 23%, and bayerite 12%.

The CNTs are promising for controlling the porous structure of the composite ceramic membranes. It is possible to expect that, along with controlling the porous structure, the use of CNTs can enhance the strength of the materials and exclude cracking of the ceramic membranes. CNTs with an external diameter of 3−5 nm, which were used in this work, were obtained by a catalytic methane decomposition on a catalyst of 0.5 wt % $CoO−1$ wt % $MoO_3−MgO$ at a temperature of 800°C. The CNTs possessed mainly a three-layered structure, and the specific surface according to BET was 400 m^2/g.

The studies of the state of oxide phases and their transformations upon thermal treatments were carried out using X-ray phase analysis. The X-ray diffraction study of the samples was carried out on a D-500 diffractometer (Siemens). A Cu K_α-monochromatized radiation was used (a graphite monochromator on a reflected beam).

Powder samples were studied by the transmission electron microscopy of high resolution (HRTEM) on a JEM-2010 device with an accelerating voltage of 200 kV and resolution of 0.14 nm on the lines.

The microstructure and morphology of the membranes were studied using scanning electron microscopy on a JSM 6460 LV (JEOL) device.

The isotherms of nitrogen adsorption on BET were measured on a Micromeritics ASAP-2400 automated device (United States). The pore size distribution was calculated from the isotherms of nitrogen adsorption at 77 K.

The specific surface of the samples was measured using argon thermal desorption.

Methane used in this work has a purity of 99 vol %. The purity of ethane was 99 vol %, nitrogen was 99 vol %, hydrogen was 99.9 vol %, helium was 99.99 vol %, and argon was 99.99 vol %.

The tests of the membranes on gas penetrability were carried out on an installation which was divided
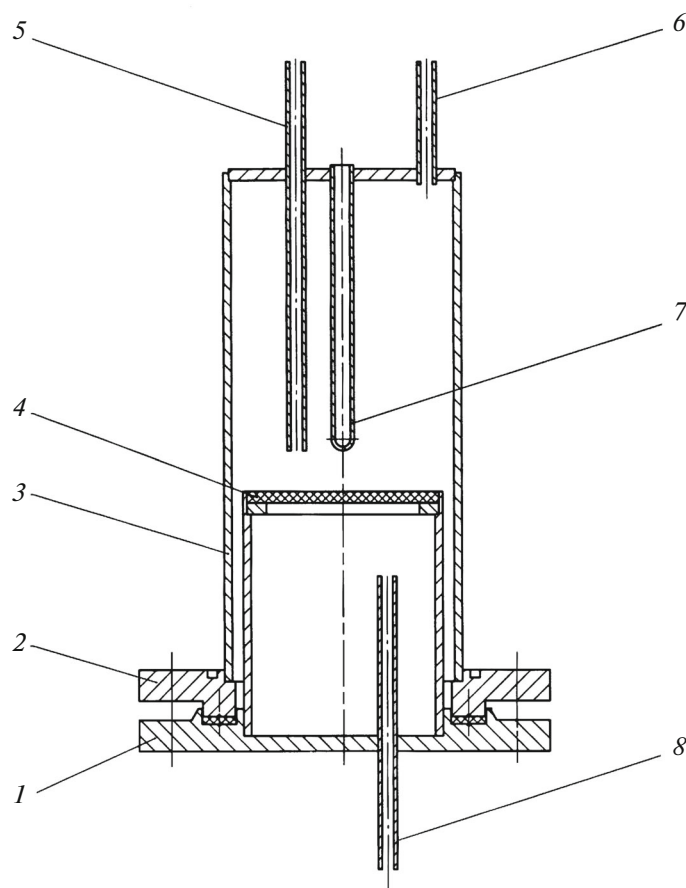
Fig. 1. Scheme of the installation used for membranes: (*1, 2*) flange, (*3*) cabinet of reactor, (*4*) membrane, (*5*) input for gases into the first contour, (*6*) output to manometer, (*7*) thermocouple tube, and (*8*) output for gases after passing the membrane.

by the membrane into two parts: the first and second contours. The scheme of the installation is presented in Fig. 1.

The selectivity of the membranes, i.e., the ability of a membrane to separate the components of a mixture, is measured quantitatively by the membrane separation factor. Numerically the selectivity is determined by the value, which is characterized by the penetrability ratio of pure substances. The penetrabilities of individual gases were measured using the device presented in Fig. 1. A gas was constantly introduced into the first contour of the reactor using an inlet tube (5). With the gas pressure increasing, its flow through the membrane increased. A stationary state became established at a definite pressure. The pressure in the first reactor contour (before the membrane) and the amount of the gas passed through it were measured. According to the measured parameters, the membrane penetrability with respect to individual gases was determined by the formula $Pen = V/(PS\tau)$, where V is the volume of the gas reduced to a standard temperature and pressure, S is the membrane area, and τ is the measurement duration.

RESULTS AND DISCUSSION

Manufacturing of Membranes

The initial TCA (2.9 g) was plastified by 7 mL of an aqueous solution of 6% nitric acid. The mass was intensively stirred; then the water excesses were evaporated and compacted in a press-form under a pressure of 100 MPa. The compacted sample was exposed under the conditions of an intense removal of a physically bound water at a temperature of 150°C for an hour and then under the conditions of phase conversion of aluminum hydroxides into aluminum oxide at 350°C for an hour. Then the sample was heat-treated without air access at a temperature of 1100°C. Figure 2 shows a sample of the ceramic membrane heat-treated at 1100°C.

Figure 3 presents the results of the measurement of pore volume size distribution for a membrane based on aluminum oxide without adding CNTs. It can be seen that the main fraction of mesopores accessible for nitrogen has sizes of 5−35 nm.
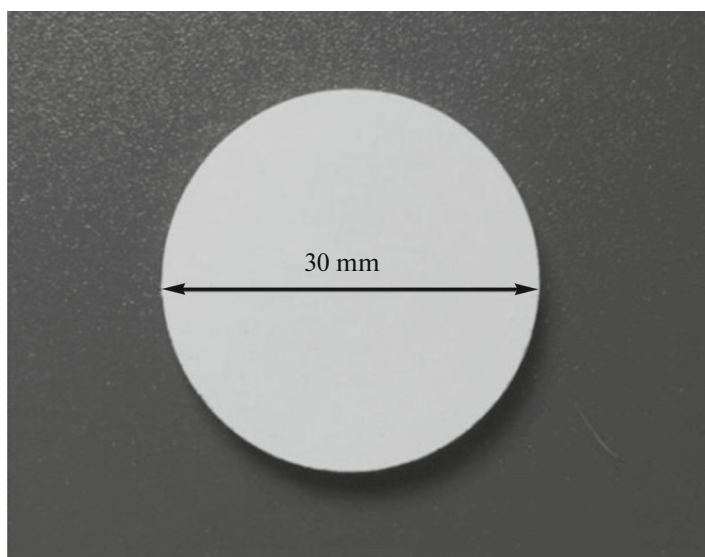
Fig. 2. Photograph of a typical sample of ceramic membrane used in this work. Diameter of the membrane is 30 mm and thickness is 2 mm.

The porous structure of a ceramic membrane based on aluminum oxide is studied by adsorption measurements. The results are presented in Table 1.

Figure 4 shows the results of the studies on gas penetrabilities of the synthesized membrane for individual (argon, nitrogen, methane, ethane, helium, and hydrogen) gases.

The synthesized membranes based on aluminum oxide not modified by CNTs possess a rather high penetrability. It can be seen from Fig. 4 that the penetrability of gases increases with a reduction of the molecule mass. Figure 4 shows the dependence of the pen-

etrability on the value $\left(\dfrac{1}{\sqrt{m_{mol}}}\right)$, where m_{mol} is the mass of a gas molecule. When the membranes are used in the membrane-catalytic reactors for the reactions of conversions of hydrocarbons, e.g., dehydration of light alkanes, the most interesting is a comparison of the penetrabilities for hydrogen and methane. In our case, for the membranes based on aluminum oxide, the calculated factor of the separation for a methane–hydrogen mixture appears to be equal to 1.8.

A membrane prepared from aluminum oxide was broken into two parts, and the structure of the break-
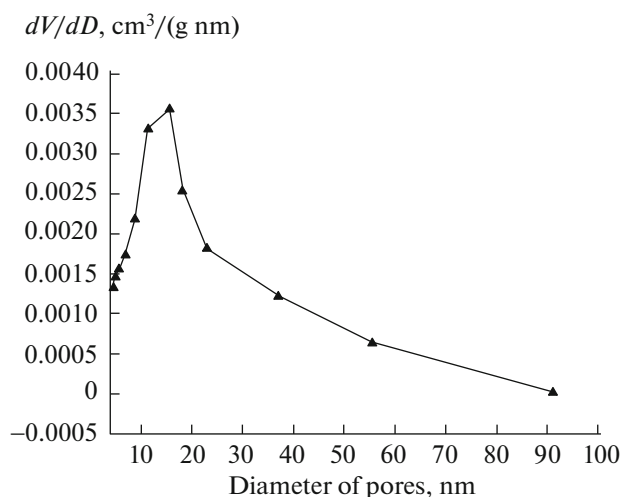

Fig. 3. Size distribution of pore volume for a ceramic membrane based on aluminum oxide without the addition of CNTs.
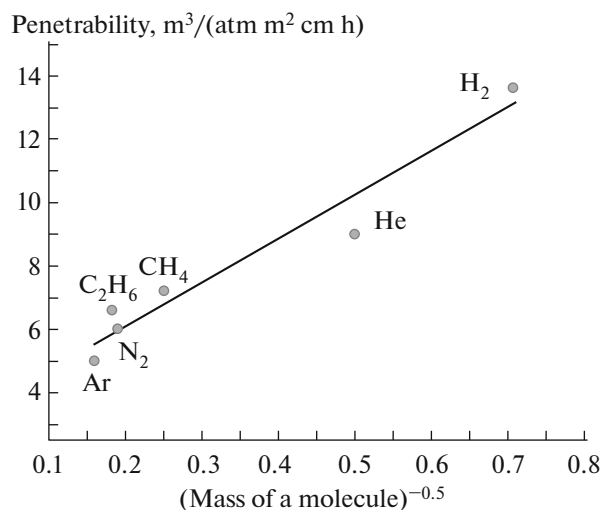

Fig. 4. Penetrability of individual gases through the membrane based on aluminum oxide. The thetmal treatment of the sample at 1100°C; time is 1 h.

ing was studied by a scanning electron microscope. Figure 5 shows an electron-microscopic image of the sample breaking structure. It can be seen that the sample has macropores (Fig. 5a) and, with greater magnification, mesopores are also seen (Fig. 5b).

It is considered that the penetrability selective on the gas nature of the membranes in the case of the Knudsen diffusion is achieved by pore radiuses from 2 to 50 nm, i.e., in the case of the presence of micro- (with a diameter to 2 nm) and mesopores (pores with a size from 2 to 50 nm). The presence of macropores reduces the factor of separation of gaseous mixtures. In a gaseous mixture at a preset temperature, molecules of different masses possess the same kinetic energy $mu^2/2$, and their average velocities are inversely proportional to the square root of the mass. If the free path of the molecules was larger than the sizes of pores, then the gas molecules practically do not collide with each other in a pore and the value of gas flow through the membrane will be proportional to the average gas velocity; i.e., the Knudsen diffusion is achieved in the pores. By the Knudsen flow, the flux is inversely proportional to the square root of the mass of molecules. This dependence determines the coefficient of diffusion D_k:

$$D_k = f(r, T^{0.5}, M^{0.5}),$$

where r is the radius of molecules, T is the temperature in Kelvins, and M is the molecular mass.

The fact that the experimentally measured gas flux through the membrane appeared to be inversely proportional to the square root of the mass of molecules proves the Knudsen character of diffusion of gases through the ceramic membrane synthesized by us (Fig. 4). It should be noted that the maximal factor of division by the Knudsen flow of the flux for H_2/CH_4 mixture is equal to $(m_{CH_4}/m_{H_2})^{0.5} = 2.8$.

Table 1. Porous structure of a ceramic membrane based on aluminum oxide. The thermal treatment at 1100°C, time is 1 h

Sample	S_{sp}, m²/g	Volume of mesopores, cm³/g	Summary volume of pores, cm³/g
Al_2O_3	23	0.11	0.22

Table 2. Composition of glass used for the preparation of ceramic membranes

Composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O, Na_2O	BaO
Mass content, %	71	0.8	0.1	5.5	3.5	17.1	2

Therefore, in order to increase the selectivity of separating the gaseous mixtures, it was necessary to decrease the size of the pores. To reduce the contribution of macropores to the porous structure of the membranes from TCA, additives of glass were introduced, which are sintered more easily than aluminum oxide. The composition of the glass mass used by us is presented in Table 2.

In order to obtain the samples of ceramic membranes, we used a fraction of glass of 0.08 mm. The initial TCA was mixed with the glass fraction and then plastified using an aqueous solution of nitric acid. This mass was intensively stirred and then water excesses were evaporated and compacted in a press form under a pressure of 100 MPa. The compacted samples were exposed at a temperature of 150°C for an hour, and then heat-treated without air access in a range of 900–1000°C.

The membranes prepared from the initial mixture (70 wt % product TCA–30% glass and 60 wt % product TCA–40% glass) were heat-treated at tempera-
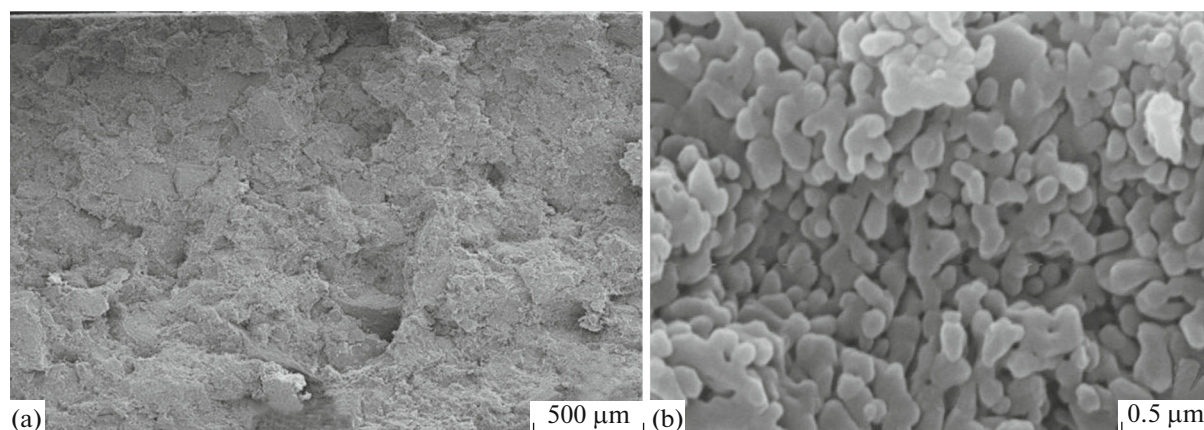

Fig. 5. Electron-microscopic image of the membrane breaking structure based on aluminum oxide. The membrane was heat-treated at 1100°C; time is 1 h.

Table 3. Influence of the thermal treatment on the properties of the sample 70 wt % product TCA−30% glass and 60 wt % product TCA−40% glass

Sample composition, mass %	Temperature of treatment, °C	S_{sp}, m²/g	Volume of mesopores, cm³/g	Summary volume of pores, cm³/g
70 wt % product TCA−30% glass	900	70	0.23	0.27
	1100	37	0.16	0.23
60 wt % product TCA−40% glass	900	50	0.16	0.2
	1100	16	0.08	0.1

tures of 900 and 1100°C. The effect of the thermal treatment temperature on the sample properties is presented in Table 3.

The main advantage of the TCA−glass system appeared to be that at high-temperature quenchings a mesoporous structure is maintained by a rather insignificant volume of macropores (see Table 3). By varying the temperature of treatment and the sample composition, it is possible to control the porous structure of membranes.

When the glass concentration is increased, a decrease in the specific surface and summary volume of sample pores takes place (see Table 3).

Figure 6 presents a size distribution of the pores for the samples 70 wt % product TCA−30 wt % glass (Fig. 6a) and 60 wt % product TCA−40 wt % glass (Fig. 6b) quenched at different temperatures.

It can be seen from Fig. 6 that an increase in the temperature of treatment leads to a decrease in the volume of mesopores and to an insignificant growth in the average value of their sizes.

As was shown above, an increase in the glass composition in a sample and in the temperature of treatment results in a decrease in the specific surface and the volume of pores. It is especially important that the

volume of mesopores is approximately equal to the summary volume of pores of the sample. Thus, the penetrability of the TCA−glass samples is determined by thin mesopores.

Figure 7 presents the data on the penetrability of various gases through a membrane of 60 wt % product TCA−40 wt % glass.

A comparison of Figs. 4 and 7 allows us to conclude that, by adding glass into the composition of a ceramic membrane, the selectivity of separation of gases increases; however, the penetrability of individual gases sharply falls. The calculated factor of separation for a methane−hydrogen mixture appears to be equal to 2.1.

To develop nanoporous ceramics, the membranes were modified by CNTs. The CNTs were mixed with the TCA product and this mixture was plastified by the introduction of an aqueous solution of nitric acid. By thermal treatment in an inert medium, the decomposition of TCA products occurred with the formation of aluminum oxides.

The composition of the ceramic membranes modified by CNTs is presented in Table 4.

Figure 8 presents the dependence of the penetrability of gas molecules in Knudsen coordinates.
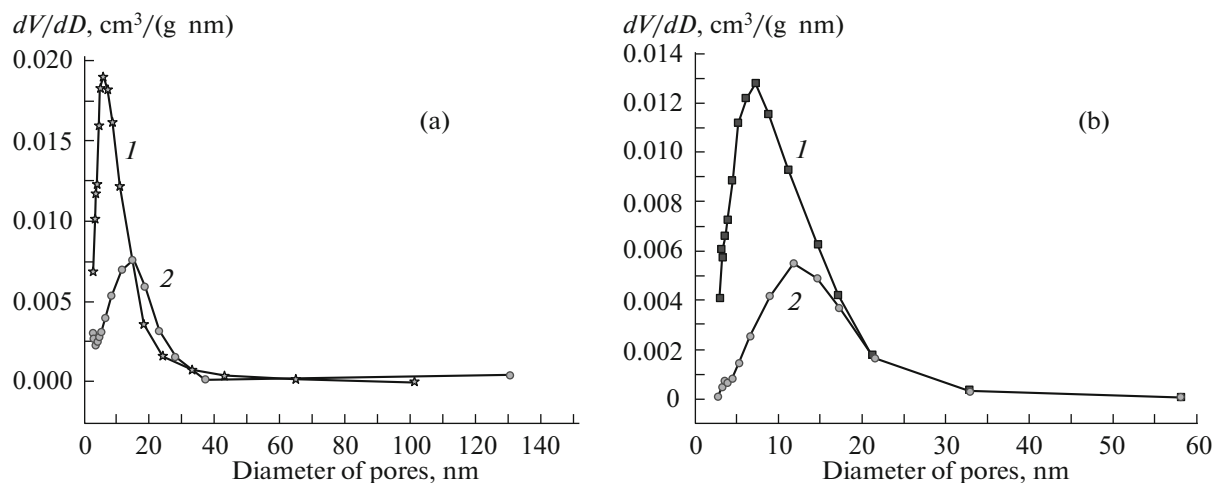
Fig. 6. Size distribution of pore volume for ceramic samples: (a) 70 wt % product TCA, 30% glass and (b) 60 wt % product TCA, 40% glass heat-treated at temperatures of 900 (*1*) and 1100°C (*2*).
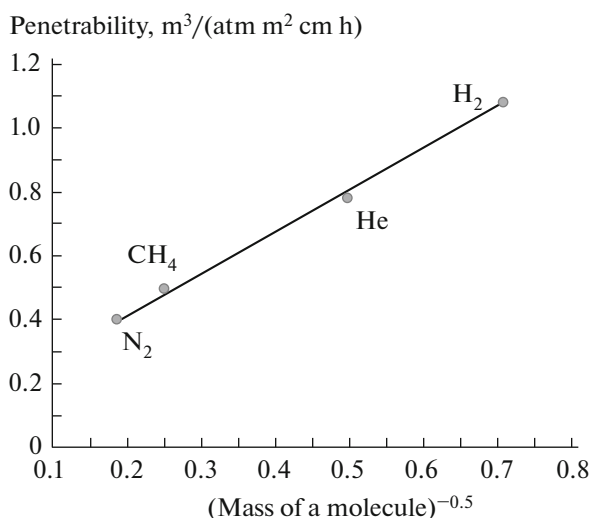
Penetrability, m^3/(atm m^2 cm h)

Fig. 7. Penetrability of individual gases through the membrane 60 wt % product TCA, 40 wt % glass. The thermal treatment of the membrane at 1000°C; time is 3 h.
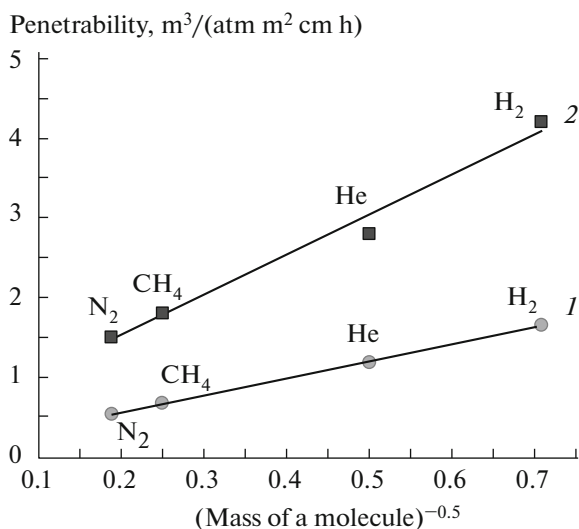
Penetrability, m^3/(atm m^2 cm h)

Fig. 8. Penetrability of individual gases through the membranes: (*1*) 59% product TCA, 38% glass, 3% CNT; (*2*) 56% product TCA, 36% glass, 8% CNT. The thermal treatment of the membranes at 1100°C.

A calculation has shown that the selectivity in the separation of H$_2$–CH$_4$ mixture for a sample of 59% product TCA–38% glass–3% CNT amounts to 2.4.

Table 4. Composition of ceramic membranes modified by CNTs

Sample	Composition, wt %		
	product TCA	glass	CNT
1	59	38	3
2	56	36	8

Thus, the introduction of CNTs into the composition of a ceramic membrane can really substantially increase the calculated selectivity of gas separation.

By a further increase in the CNT content in the membrane composition, the penetrability significantly increases; however, the selectivity of the separation of gaseous mixtures somewhat decreases to 2.2.

CONCLUSIONS

The possibility of developing ceramic membranes modified by CNTs is studied. A hydrated TCA product was used as the basic component, which was plastified by an aqueous solution of nitric acid. The compacted samples were exposed under the conditions of the intense removal of physically bound water at a temperature of 150°C for an hour, then in the region of phase conversion of aluminum hydroxides into aluminum oxide at 350°C for an hour. Then, the samples, depending on their composition, were heat-treated without air access at a temperature range from 900 to 1100°C in order to strengthen the material.

The membranes prepared on basis of TCA products without CNTs contain a considerable amount of macropores and therefore possess low selectivity (1.8) in the separation of gases. In order to decrease the contribution of macropores to the porous structure of membranes, additives of glass were introduced, which is sintered easier than aluminum oxide. The tests of the samples, in which a fraction of the product TCA was replaced by glass, have shown that the factor of separation for gaseous mixtures of H$_2$–CH$_4$ distinctly increases.

In order to increase the fraction of nanopores and decrease their sizes, ceramic membranes were synthesized, which were modified by CNTs with an external diameter of 3–5 nm. The specific surface of CNTs was 400 m^2/g. It is shown that, by the introduction of 3 wt % of CNTs into the composition of a ceramic membrane, an increase in the penetrability of gases through the membrane is observed by the separation of CH$_4$/H$_2$ mixture, while the selectivity of separation achieves a value of 2.4.

Thus, by varying the composition, amount of CNTs, and temperature of treatment, it is possible to control the size of pores; level of porosity; and, respectively, gas-separation properties of the ceramic membrane modified by carbon nanotubes.

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