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Features of Profound Processing of Natural Gas of Eastern Siberia

S. N. VERESHCHAGIN[1], A. G. ANSHITS[1,3], E. V. FOMENKO[1] and V. M. FOMIN[2]

[1]Institute of Chemistry and Chemical Technology, Siberian Branch of the Russian Academy of Sciences,
Ul. K. Marksa 42, Krasnoyarsk 660049 (Russia)

E-mail: snv@icct.ru

[2]Khristianovich Institute of Theoretical and Applied Mechanics, Siberian Branch of the Russian Academy of Sciences,
Ul. Institutskaya 4/1, Novosibirsk 630090 (Russia)

[3]Siberian Federal University,
Prospekt Svobodny 79, Krasnoyarsk 664041 (Russia)

Abstract

Features of physicochemical processing of the natural gas of Eastern Siberia for the purpose of obtaining valuable products are considered. Special attention is paid to the processes based on the microspherical components of energy ash: non-cryogenic process of helium isolation using cenospheres, and the process of oxidative dimerization of methane (ODM) into ethane and ethylene in the presence of ferrospheres. A scheme of natural gas processing taking into account the features of composition and involving the stages of ODM is proposed.

Key words: natural gas, oxidative dimerization of methane, helium

INTRODUCTION

Krasnoyarsk Territory occupies the second place in Russia after the Tyumen Region in the forecast reserves of hydrocarbon raw material – oil, natural gas and condensate. At the same time, poorly developed gas transportation infrastructure and the absence of gas processing facilities require substantial investment and time for the industrial development of hydrocarbon resources. The reserves of natural gas are concentrated in three major oil and gas regions: Bolshekhetskiy (Vankorskiy, 118.1 milliard m^3), Yurubchen-Tokhom (Yurubchenskiy, 383.9 milliard m^3), and Sobinsk-Teterinskiy (Sobinsk, 158.3 milliard m^3). According to the departmental goal programme “Development of crude oil and natural gas production at the territory of the Krasnoyarsk Territory for the years 2009–2011”, by 2011 the amount of natural gas production mush increase by a factor of 4.2 with respect to 2007, while in the long-term outlook it is to increase more than by a factor of 20, to be brought to 28.5 milliard m^3 by 2020 (Fig. 1).

“The energy strategy of Russia for the period till 2020” puts forward the goals to form and develop new large centres of gas production in Eastern Siberia and in the Far East, and to make Russia enter the market of countries in the Asian-Pacific region considering natural gas mainly as the raw material for power engi-

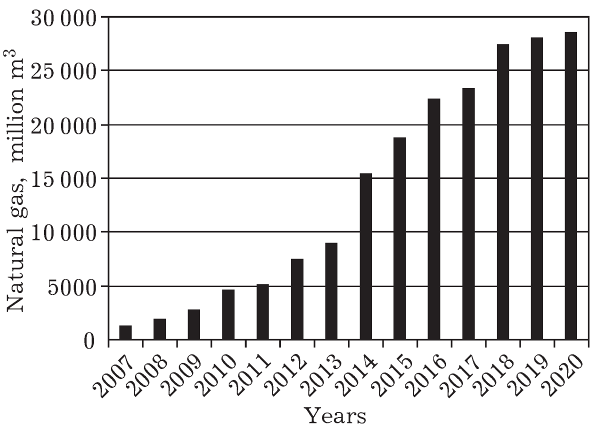


Fig. 1. Planned indices of the development of natural gas production in the Krasnoyarsk Territory for up to 2020 year [1].

neering. However, due to the complicated multicomponent composition of natural gas from the deposits of Eastern Siberia [2, 3, 5] the programme aimed at the development of these gas-bearing deposits should differ from the corresponding programmes developed previously for West Siberia. The major difference must be aiming at the integrated use of all the components present in produced gas. The composition of natural gas depending on the deposit varies within rather broad range: in addition to the major component, methane (55–92 %), natural gas also contains ethane (1–10 %) and higher hydrocarbons (propane + butane up to 10 %, hydrocarbons C_5 and higher 1–5 %), as well as nitrogen, carbon dioxide, sulphurous compounds, and helium [4]. In this connection, large-scale production of natural gas at the deposits of Eastern Siberia should rely on compulsory isolation of ethane and other hydrocarbon components of natural gas. Special attention should be paid to the isolation of helium, which is present in gas from the Sobinskoye deposit of the Krasnoyarsk Territory in the concentration up to 0.6 %, while gas from unique Chayandinskoye and Kovyktinskoye deposits contains up to 70 % of helium reserves of Russia. It is admissible to launch full-scale development of these deposits only under the condition of complete isolation of helium.

At present, deviation from exclusively energy-supplying role of natural gas is observed in the world. Light hydrocarbons (including methane) are considered as promising raw material for petrochemical synthesis. First of all, this is expressed as increased attention to the so-called gas-to-liquid technologies (GTL) allowing one to obtain liquid hydrocarbons and motor fuel from C_1–C_4 alkanes [6, 7].

Attention to this problem is expressed by large world oil and gas producing companies who give publicity to the plans of designing and building new enterprises. More than fifty projects under consideration are aimed at the construction of enterprises using the GTL technology, with the total capacity of 166 milliard m^3 of natural gas per year and the productivity with respect to synthetic hydrocarbons about 2 million barrels per day. The activity of patenting in this area is high [8].

Taking into account the outlined trends, two major tasks may be distinguished in chemical-technological processing of natural gas from Eastern Siberia: compulsory isolation of helium and development of the methods providing chemical processing of light alkanes for the purpose of obtaining valuable products, including high-quality motor fuel.

BASIC DIRECTIONS OF NATURAL GAS PROCESSING TO OBTAIN VALUABLE PRODUCTS

The problems of chemical transformation of the components of natural gas into a product or intermediate product of are urgent only for the lightest hydrocarbon – methane, and (to a definite extent) for ethane, while the transformation of propane and heavier alkanes has been well investigated and implemented on the industrial scale.

Two major directions in the development of gas chemical transformations can be outlined:

1. Two-stage technologies based on preliminary conversion of C_1–C_2 hydrocarbons into synthesis gas, followed by processing into synthetic hydrocarbons (Fischer–Tropsch synthesis) and synthetic motor fuel on their basis, methanol, dimethyl ether (though the concentration of oxygenates in fuel is strictly standardized now), and ethylene.

2. One-stage technologies based on the direct oxidation of hydrocarbon gases into alcohols (methanol) or oxidative dimerization of methane into ethylene. This process is under development by a number of scientific institutions (ICP of RAS, ICCT of SB RAS *etc.*).

It should be noted that the classical processes involved in the transformations of hydrocarbon gases, including methane, into synthesis gas by means of steam or steam-oxygen conversion followed by the synthesis of methanol or motor fuel have been brought to the high level of industrial perfection. However, technical and economic assessment shows that the production is economically reasonable only in the case of substantial amounts. With the existing price for raw material, equipment, energy carriers and the trend of continuously growing demand for the production output, the scale of economically reasonable production will be 250–300 thousand t/y [9].

One-stage technology based on the direct oxidation of hydrocarbon gases into methanol has been well developed, too [10], though efforts aimed at the improvement of process characteristics and its introduction are still continuing [11]. Similar research is being carried out also in Russia (for example, see [12]).

The reaction of heterogeneous-homogeneous oxidative dimerization of methane (ODM) discovered in early 1980s had been studied in detail during the last decades of the past century. A thorough review of studies dealing with ODM was presented in [11, 13–15, 54]. Some decrease in the number of publications dealing with ODM is due to the current market conditions for hydrocarbons and the absence of economical advantages of the production of ethylene from ethane by means of ODM in comparison with alternative processes – cracking of oil raw material, Fischer–Tropsch synthesis *etc*. Estimations made in 1990s showed that the minimal economically reasonable efficiency of ODM process depending on the cost of ethylene will be 16–30 % with respect to the yield of C_2H_4, with methane transformation selectivity exceeding 80 % [16–18].

Kinetic modelling carried out during different years [19, 20] showed that the maximal yield of ethylene from the ODM process cannot exceed 25–30 % due to the contribution from homogeneous reactions of profound oxidation and competitive interaction of the surface active oxygen with methane, on the one hand, and with ethylene on the other hand. Newer theoretical investigation [21], in which the search for optimal macrokinetic and thermochemical characteristics of catalyst was carried out, confirmed the conclusion that the upper limit of C_2 yield from ODM with optimal characteristics and under the conditions of flow reactor with immobile catalyst layer is 28 %.

In this connection, during the recent years the activity of the majority of studies moved from the area of catalyst improvements to the area of process modifying and optimizing. At present, the most actively developing technological approaches include:

1. A usual scheme implying the joint supply of methane and oxidizer (oxygen) to the catalyst layer. With the evident simplicity of this solution, its implementation gets complicated due to the necessity to perform expensive isolation of oxygen from the air. In addition, due to the high concentration of O_2 in the gas phase, the joint supply will certainly involve undesirable side gas-phase reactions of complete oxidation, which decreases the yield of C_2 hydrocarbons.

2. Alternate separate introduction of CH_4 and O_2 into the reactor, in the form of separate pulses. Re-oxidation of the catalyst may be performed with the air, which excludes the necessity of expensive stage of oxygen isolation. Methane dimerization proceeds in the absence of gas-phase oxygen, due to the oxidative potential of oxygen present in the catalyst, which has a positive effect on the process selectivity, which can reach 96–100 % [25]. The shortcomings of this approach include complications in the scheme and a decrease in the productivity.

3. Membrane arrangement of the process. With this arrangement, methane and O_2 are separated with a membrane through which dosed amounts of oxygen are introduced to the hydrocarbon part of the reactor due to usual diffusion or ionic (oxygen) conductivity. ODM catalysts may be deposited on the membrane, or the membrane material itself may act as a catalyst. Though the most impressing results were obtained with this process arrangement (catalyst: $Na-W-Mn/Ba_{0.5}Ce_{0.4}Gd_{0.1}Co_{0.8}Fe_{0.2}O_3$, yield of C_2: 34.7 %. conversion degree: 51.6 %, selectivity: 67.4 % [28]), the major problem remains the stability of the membrane under reducing conditions and the value of maximal oxygen flux through the membrane, which defines the productivity of the apparatus in whole.

It should be stressed that in spite of a noticeable increase in the yield within the framework of a definite catalytic system, achieved using the proposed approaches, it still seems impossible to overcome principal limitations. The maximal increase in the yield of C_2 products was achieved by arranging the circulation of reaction mixture with the intermediate isolation of ethylene. These conditions help full realization of the high selectivity of catalytic systems under low conversion of CH_4 per pass. The resulting yield of C_2 products reached 70 % [22] and even 88 % (85 % for C_2H_4) with methane conversion degree 97 % and selectivity with respect to ethylene 88 % [23]. However, the scheme of the process became much more complicated. It is stressed that for practical purposes it is necessary to provide not less than 15–20 % degree of methane conversion per pass, so that the circulating factor should not exceed 5–8 [24].

In spite of the existing principal limitations, there is published opinion that the ODM process can be implemented even now in the countries with cheap natural gas (Russia, Iran) [14, 27]. In this connection, the development of novel, more efficient approaches to the implementation of the ODM process and search for general regularities providing the synthesis of a catalyst possessing the highest efficiency within the framework of a definite catalytic system are surely urgent.

A catalyst is a compulsory element of the ODM process, so its cost affects the general economic indexes of ODM technologies. Other parameters being kept the same, the processes involving cheap and technologically simple catalysts would have unquestionable economic advantages. One of the possibilities to make a simple efficient catalytic system of hydrocarbon transformation was demonstrated in the research cycle performed at the ICCT, SB RAS [28–30].

On the basis of the criteria of catalyst selection proposed by the authors [31], it was assumed that the microspheric iron-containing components of fuel ash (ferrospheres) are an efficient system for making the catalysts for ODM processes. The physicochemical investigation of ferrospheres isolated from different kinds of ash showed that they favourably combine high thermal stability, low specific surface (necessary for ODM processes) and the presence of iron-containing oxide phases of different structures (structural types of spinel, corundum) with varying distribution of iron cations over non-equivalent lattice positions and the presence of structural defects [55].

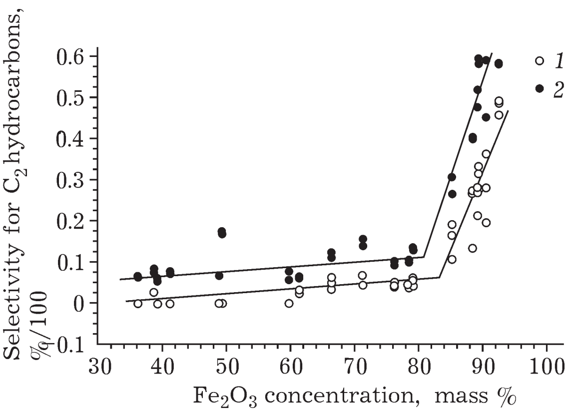


Fig. 2. Dependence of the selectivity of formation of C_2 hydrocarbons on the concentration of Fe_2O_3 in ferrospheres at a temperature of 700 (*1*) and 750 °C (*2*). Reaction mixture: $CH_4 : O_2 : N_2 = 82 : 9 : 9$.

To test this assumption, we studied the catalytic properties of a number of narrow size fractions of ferrospheres from the microspheres of fuel ash with the mass concentration of Fe_2O_3 36.2–92.5 % (Fig. 2). As a result, three regions of the compositions of ferrospheres differing substantially from each other in catalytic properties were distinguished. They differ from each other in the general activity and in the selectivity of the formation of C_2 products. The first group includes ferrospheres with the mass concentration of Fe_2O_3 below 60 %; they possess low activity and selectivity (15–18 %) for the formation of C_2H_6 and C_2H_4. Low selectivity of the catalysts of this group is connected with blockage of the ferrospinel phase by the glass phase and its unavailability for reagents, which is confirmed by the high content of the glass phase (22–56 mass %) in ferrospheres and the high specific surface of the samples. The second region includes the particles with the mass concentration of Fe_2O_3 60–80 %, characterized by high activity but low selectivity for the formation of C_2 hydrocarbons. The third group includes the samples with the mass concentration of Fe_2O_3 more than 80 %, possessing both high activity and substantial selectivity with respect to C_2H_6, which increases in proportion to the concentration of Fe. The highest selectivity for C_2 products (up to 60 %) is observed for ferrospheres containing the maximal amount of Fe, which are the Ca system ferrite with the lowest silicon and aluminium content. The activity of these samples is determined by an increase in the concentration of defects of iron-containing phases present in the system – ferrospinel, hematite and solid solutions based on them. They stabilize oxygen in the form of active atomic species. At present, investigation of these systems goes on, and the results will be published separately.

The most interesting fact is that the treatment of one of the most selective microspheric systems with hydrofluoric acid causes an increase in methane transformation degree to 24 % with the selectivity up to 70 %, which corresponds to the yield of C_2 hydrocarbons up to 17 % [30].

The data on the catalytic characteristics of some most efficient ODM systems and the point corresponding to modified ferrospheres are shown in Fig. 3. One can see that neither system at present fits the region of industrially significant transformation parameters and only some of the systems exhibit the excess over the theoretical limit (28–30 %) of the yield of C_2 hydrocarbons. The systems based on ferrospheres somewhat lag behind the listed catalysts, but due to exceptional cheapness and the possibility of further modification of catalytic properties they are attractive as the subject to study the fundamentals of the ODM process with the outlook for coming up to the industrial application.

As far as ethane present in natural gas is concerned, several approaches to processing can be indicated. One of the simplest versions implies the introduction of not pure methane but natural gas containing a definite amount of C_2–C_5 alkanes to the ODM catalyst. In this case, the degree of methane transformation decreases, but the selectivity towards olefins exceeds 80 % while the conversion degree (calculated for carbon) is 18–20 % [32], which is close to the parameters of economically reasonable industrial implementation.

The second way involves dehydrogenation of ethane to form ethylene, followed by the transformation of the latter into the components of liquid fuel, polymers, ethanol and other substances, using the developed processes. In this case, additional gain can be achieved if we bind the heats for the highly exothermic ODM reaction and endothermic non-oxidative dehydrogenation. Our calculations show [38] that the reaction can be successfully run in the thermally neutral mode with the help of this approach. This means that the reaction can be carried out without heat input, which allows one to save energy. A possible route of ethane transformation is also its direct transformation into liquid (mainly aromatic) hydrocarbons on Mo-containing zeolite catalysts with the formation of the components of liquid motor fuel [39–41]. Though attention to aromatic hydrocarbons as the components of motor fuel has decreased substantially during the recent years, works dealing with dehydroaromatization of lower alkanes (mainly methane) on Mo zeolite catalysts go on also at present [42, 43].

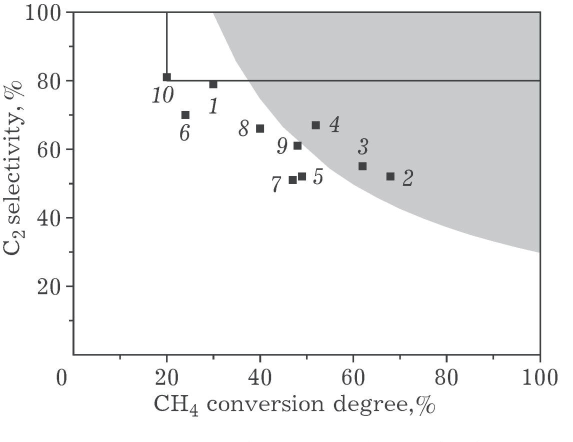


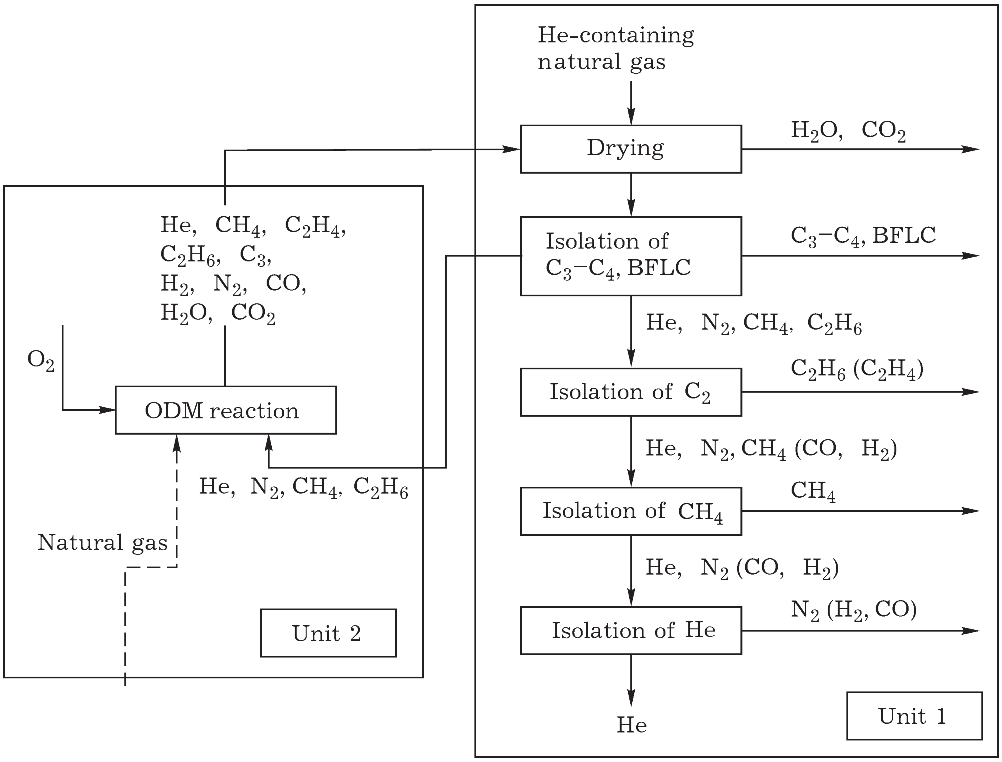
Fig. 3. Transformation degree for CH_4 and selectivity of the formation of C_2 hydrocarbons for some catalysts. Shadowed area corresponds to the yields of C_2 above 30 %, rectange is the area of interest for industry at present: *1* – Rb_2WO_4/SiO_2 [35], *2* – $Ba_{(1-0.5x)}TiO_3SnCl_{2(0.05x)}$ [36], 3 – $Bi_{1.5}Y_{0.3}Sm_{0.2}O_{3-d}$ [37], *4* – Na–W–Mn/$Ba_{0.5}Ce_{0.4}Gd_{0.1}Co_{0.8}Fe_{0.2}O_3$ [26], *5* – Na–Mn–W/SiO_2 [34], *6* – ferrospheres [30], 7 – $NaBaSrTiO_3$ [33], *8* – K–Mn–W/SiO_2 [34], *9* – Rb–Mn–W/SiO_2 [34], *10* – SrO/La_2O_3, natural gas [32].

Taking into account the features of the natural gas of Eastern Siberia, namely its high helium content, we may propose a version of processing it by means of ODM, with the requirements to the efficiency of the catalytic system below those shown in Fig. 2.

At present, it is planned to construct the new Boguchany Gas Processing Plant with the productivity of 20 milliard m^3 of gas per year. It is assumed to form a system of works on gas separation using the technologies based on cryogenic separation of natural gas into fractions with consecutive isolation of the condensate, broad fraction of light hydrocarbons (BFLH), propane-butane mixture, separation of the methane-ethane fraction with the isolation of ethane and helium [5] (Scheme 1, unit 1). Additional stages of ODM reaction normally get built into the proposed basic scheme (see Scheme 1, unit 2), so that the region of selectivity/ODM conversion relations of interest for practical realization (see Fig. 3) may be broadened due to the following factors:

1. Within the framework of the proposed cryogenic technology, the production of pure oxygen necessary for the reaction becomes cheaper.

2. The necessity to construct installations for the separation of ODM products is eliminated because the major reaction products (C_2–C_3



Scheme 1.

hydrocarbons) are the components of natural gas and their separation is implied by the basic technology. The behaviour of additional substances formed during ODM in the cycle of major separation is shown in parentheses in Scheme 1.

3. Depending on the fraction of gas introduced into the ODM reactor, the concentration of C_2–C_4 hydrocarbons which are more valuable than methane increases in the mixture; at the same time, the amount of low-temperature cold decreases due to a decrease in the amount of processed CH_4.

4. The possibility to perform ODM using non-purified natural gas arises (see Scheme 1, unit 2), including high pressure process, which allows one to plan the non-cryogenic diffusion sorption stage of helium isolation from the products of ODM.

5. Selective transformation of methane into ethylene and ethane after the removal of H_2O and CO_2 is accompanied by a decrease in volume, so the concentration of helium in ODM products will be higher than that in the initial gas, which also enhances the economic efficiency of its isolation.

So, the above considerations provide evidence of the urgency of special economic calculations for estimating the reasonableness of including ODM process into the scheme of processing the natural gas of Eastern Siberia and the relevant necessary level of efficiency of the catalytic system taking into account the features of gas composition.

NON-CRYOGENIC SEPARATION OF HELIUM

At present, helium is manufactured on commercial scale only with the help of cryogenic separation of natural gas with the volume concentration of helium 0.1–2 %. The physical basis of the cryogenic technology is condensation of hydrocarbon fractions which are the major components of natural gas. Low-temperature technologies are capital- and energy-intensive [44] and thus they are economically reasonable only if large amounts of natural gas are processed.

A distinguishing feature of helium is its exclusively high permeability, which provides the possibility to use membrane technologies for separation of He-containing gases. However, efficient use of membranes in helium-treating industrial operations requires the solution of a number of applied and fundamental tasks connected with the selectivity of diffusion process, manufacture of defect-free large-sized membranes possessing the necessary mechanical strength and thermal stability. The problem of making the objects selectively permeable for light gases is urgent also at present taking into account the outlooks for developing the technology of helium isolation alternative against the cryogenic method.

Institute of Chemistry and Chemical Technology, SB RAS (Krasnoyarsk) together with Institute of Theoretical and Applied Mechanics, SB RAS (Novosibirsk) are engaged for several years in developing a new sorption diffusion non-cryogenic method of the selective isolation of helium from natural gas using selectively helium-permeable microspherical membranes from volatile ash from the combustion of coal [48].

Cenospheres are hollow tightly closed spheres 5–500 μm in size; their walls are composed of aluminosilicate glass (up to 90 %) containing mullite, quartz and spinel crystals, as well as gaseous and some other inclusions. It is known that aluminosilicate glass combines high helium permeability with very low diffusion permeability for heavier gases (oxygen, nitrogen, methane); the selectivity of separation may reach 10^6 [45]. Permeability changes substantially with changes in glass composition; the permeability of quartz glass is maximal. Investigation showed that helium diffusion inside cenospheres occurs with high selectivity indeed [47].

The proposed new approach to the problem of helium isolation from natural gas is based on the use of spherical membranes. This allows one to combine the membrane principle and sorption; manufacture of membrane materials from cenospheres of combustion ash decreases the expenses for their production [46]. The physical basis of the process is selective penetration of helium inside cenospheres (diffusive sorption). In this connection, in order to arrange a steady process, unlike for flat membranes, either a moving layer of cenospheres is necessary [50, which is rather complicated from the technological viewpoint and causes enhanced requirements to the strength and wear stability of particles, or separation in the simulated moving bed (SMB) with changing flows is needed [56]. The most promising version seems the isolation of helium from natural gas in the sorption mode with pressure drop (pressure swing adsorption – PSA).

To test the efficiency of this realization, numerical calculation of the complete cycle for non-steady modes for a column with hollow microspheres was carried out. The results showed that the steady-periodical mode of column operation is established rather quickly (after 4–10 cycles). During definite intervals of time, it is possible to obtain the flow of mixture with increased helium concentration near the inlet or outlet ends of the column. By choosing the temperature parameters of non-steady and cyclic processes, it is possible to obtain theoretical limiting values of concentrating coefficient for helium in a cycle, which is equal to 3–4 [49].

Experimental tests of the results of theoretical calculation of concentrating degree was carried out using the cenosphere fraction (+0.07–0.1) mm with bulk density of 0.18 g/cm^3, isolated from the concentrate of cenospheres from Heat and Electric Power Plant (HEPP) No. 22 in Moscow; the calculated wall thickness was 1.6 μm. Separation was performed for the mixture of helium with argon; the volume concentration of helium was 1.18 %. The following parameters were varied: adsorber temperature (25–520 °C), limiting pressure (3–10 atm), method of removal of adsorbed He (pumping out, blowing with a gas mixture). It was shown that the cyclic process with pressure drop on cenospheres isolated from energy ash involves the separation of helium-containing mixture into two flows: depleted and enriched with helium with respect to the initial mixture. With the parameters close to the optimal ones within the studied range: T = 352 °C, $P_{\max}$ = 10 atm, the mean value of concentrating coefficient per cycle was equal to 2.2. The efficiency of separation did not change after multiple repetitions of sorption-desorption cycles, which points to the absence of noticeable destruction of particles or their perforation (the formation of additional porosity) during the operation. The mentioned process characteristics are evidently not limiting because optimization was not carried out.

A substantial disadvantage of cenospheres as diffusion sorbents is insufficient permeability of their walls for helium at low temperatures. Helium gets into the globules at a noticeable rate only at a temperature above 350 °C [47].

Several methods were proposed to increase the permeability of globule walls with the conservation of the high selectivity of separation:

1. To decrease the thickness of particle walls by isolating narrow size fractions from the concentrate of cenospheres during separation over size, apparent density (in aero- and hydrodynamic separation processes) and magnetic properties. This results in additional stabilization over chemical composition, which provides more uniform distribution of diffusion characteristics for different particles inside the fractions. Studies involving separation of narrow cenosphere fractions showed that the mechanical strength of the particles decreases substantially when wall thickness becomes less than 1–1.5 μm; in addition, cenospheres with thin walls are concentrated in the fractions −0.05 mm. The strength of separate globules can be somewhat in-creased due to the isolation of cenospheres containing a layer of planar mullite crystals on the surface (Fig. 4); inconvenience of manipulations with fine fractions can be overcome due to the formation of larger granules from small particles (molding with binders, agglomeration *etc.*), with the conservation of wall integrity and the formation of a system of large pores inside a granule.

2. Changes of the chemical composition of the wall and introduction of artificial heterogeneity (directed decrystallization). The possibilities to control permeability by changing the gross chemical composition of walls are rather limited because the composition is determined by the mineral component of coal under combustion and dispersion of the composition inside the fraction, while the variation of major components in cenospheres with thin walls is insignificant, mass %: SiO_2 58–65, Al_2O_3 21–36, ferric oxide Fe_2O_3 <2.5, alkaline metals and alkaline earths <7.

However, definite kinds of treatment may result in local heterogeneities of chemical and phase composition in particle walls; permeability of the formed composite material will exceed the additive value of permeability of the components, as this was observed in particular for hollow fibres (membranes) of YSZ-SiO_2 [51]. In the case of aluminosilicate glass, an increase in permeability with the formation of a polyphase system can be due to a number of factors.

It is known that helium permeability is connected with the glass composition through an empirical equation [52]

$$K_{\mathrm{He}} = 1.54 \cdot 10^{-13} e^{-(15040 - 126G)/T} \qquad (1)$$

where K_{He} is helium permeability, mol/(m · s · Pa); T is temperature, K; G is the molar fraction of glass-forming oxides ($SiO_2 + B_2O_3 + P_2O_5$), %.

The experimental value of permeability of the samples of quartz glass at 25 °C for helium is $5.7 \cdot 10^{-17}$ [53], while the value calculated using equation (1) is $4.3 \cdot 10^{-17}$ mol/(m · s · Pa), which is quite satisfactory coincidence. It is evident from equation (1) that with a change in glass composition, namely with an increase in the fraction of SiO_2, the diffusion flow of helium should increase.

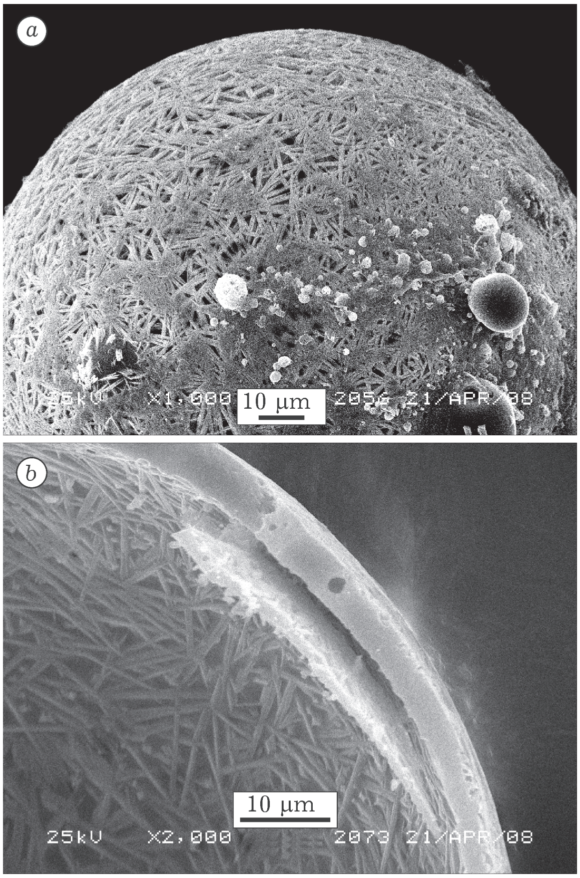


Fig. 4. XEM micrographs of initial cenospheres isolated from the concentrate of Moscow HEPP-22. Fraction (−0.16+0.125) mm with planar mullite crystallites at the external (*a*) and internal (*b*, purposefully destroyed particle) surfaces.

We demonstrated experimentally that thermal treatment of cenospheres leads to a decrease in the fraction of glass phase in the sample due to its partial transformation into mullite phase (M1) which differs from the initial mullite (M0, see Fig. 4) by lattice parameters and Si/Al ratio. The formed M1 crystallites 10–15 nm in size are localized inside the particle wall, that is, glass decrystallization occurs with the formation of glass-mullite composite material. If the transformation of aluminosilicate material of walls into mullite occurs *via* the gross reaction

$$\underset{\text{glass phase 1}}{n\mathrm{SiO_2}\cdot m\mathrm{Al_2O_3}\cdot k\mathrm{MeO}} \rightarrow \underset{\text{mullite (M1)}}{x(2\mathrm{SiO_2}\cdot 3\mathrm{Al_2O_3})} + \underset{\text{glass phase 2}}{(n-2x)\mathrm{SiO_2}\cdot(m-3x)\mathrm{Al_2O_3}\cdot k\mathrm{MeO}} \tag{2}$$

it becomes evident that the formed glass phase 2 is enriched with $\mathrm{SiO_2}$ in comparison with glass phase 1, so it must have higher K_{He}.

Equation (1) allows us to estimate the change of permeability while reaction (2) proceeds. For example, for the initial composition of glass phase 1 $\mathrm{SiO_2} : \mathrm{Al_2O_3} : \mathrm{MeO} = 60 : 31 : 9$ (mass %) and the composition of glass phase 2 $\mathrm{SiO_2} : \mathrm{Al_2O_3} : \mathrm{MeO} = 70 : 21 : 9$ (mass %), which corresponds to the transformation of 34 % of $\mathrm{Al_2O_3}$ from glass into mullite phase M1, the calculated permeability of glass itself at 25 °C will increase by a factor of 27. Actual increase in the permeability of the formed two-phase system mullite-glass will be lower than the calculated value because He diffusion in mullite is substantially hindered in comparison with diffusion in the glass phase. Nevertheless, the mentioned calculation data provide evidence that the transformation of a part of the glass crystal aluminosilicate material into mullite causes a substantial change of the helium permeability of the material. In agreement with equation (1), the effect grown with temperature decrease.

An additional factor increasing the rate of gas permeation through the composite material can be the presence of boundaries between phases; diffusion along these boundaries is simplified substantially.

The experimental verification performed using the cenosphere fraction (−0.063+0.05) mm (mass fraction of $\mathrm{SiO_2}$ and $\mathrm{Al_2O_3}$ 60 and 31 %, respectively), isolated from the concentrate of HEPP-22 in Moscow by means of consecutive application of granulometric and magnetic separation, showed that thermal treatment at 1000 °C causes an increase in the mass fraction of mullite in the sample from 9 % in the initial cenospheres to 32 % in thermally treated ones. The permeability of particles with respect to helium increases by a factor of 14 at 23 °C. So, the experimental increase in permeability corresponds in the order of magnitude to the theoretically predicted value, and decrystallization of wall material can be considered as a promising way to increase permeability. This opens novel possibilities for the development of diffusion-sorption material based on cenospheres of energy ash for non-cryogenic concentrating of helium-containing mixtures.

CONCLUSION

New materials based on modified microspherical products – ferrospheres and cenospheres isolated from volatile ash – can be successfully used in the processes of profound chemical processing of natural gas of Eastern Siberia for the purpose of obtaining valuable products (components of motor fuel and helium). The oxidative dimerization of methane using efficient catalysts synthesized on the basis of cenospheres naturally fits the planned cryogenic technology of separation of natural gas; microspherical sorbents for helium prepared from cenospheres can become the basis for the development of non-cryogenic stages if the processes involved in concentrating helium-containing mixtures.

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REFERENCES

1 Vedomstvennaya Tselevaya Programma “Razvitiye Dobychi Syroy Nefti i Prirodnogo Gaza na Territorii Krasnoyarskogo Kraya na Period 2009–2011 Gody”. URL: http://www.krskstate.ru/econom/vcp/prir/0/id/727

2 Serdyuk S. S. (Ed.), Mineralnye Resursy Krasnoyarskogo Kraya, Krasnoyarsk, 2002.

3 Orlov V. P., *Mineralnye Resursy Rossii. Ekonomika i Upravleniye*, 2 (1999) 2.

4 Kuznetsov L. L., Kontorovich A. A., Sibgatulin V. G. Third Workshop C_1–C_3 Hydrocarbon Conversion (Book

of Abstracts), July 14–17, 1997, Krasnoyarsk, Russia, 1997, A0.

5 Korzhubaev A. G., Filimonova I. V., Eder L. V., Strategiya Kompleksnogo Osvoyeniya Resursov i Zapasov Gaza Vostochnoy Sibiri i Dalnego Vostoka, URL: http://www.vipstd.ru/journal/content/view/25/39/.

6 Krylov O. V., *Kinet. Catal.*, 46, 1 (2005) 159.

7 Arutyunov V. S., Lapidus A. L., *Ros. Khim. Zh.*, XLVII, 2 (2003) 23.

8 Kuznetsov P. N., Kuznetsova L. I., Tverdokhlebov V. P., *Zh. Sib. Feder. Un-ta. Ser. Tekhn. i Tekhnol.*, 2 (2008) 168.

9 Arutyunov V. S., Chaika S. E., Shkoda A. M., Gazokhimicheskiye Tekhnologii v Sistemakh Utilizatsii Prirodnykh Gazov (Treatises of Gubkin Russian State University of Oil and Gas), Moscow, 2007.
URL: http://www.ameng.ru/publ.php

10 Bukhgalter E. B., Metanol i Yego Ispolzovaniye v Gazovoy Promyshlennosti, Nedra, Moscow, 1986.

11 Kondratenko E. V., Future Feedstocks for Fuel and Chemicals DGMK Conf. (Proceedings), Berlin, 2008, pp. 45–58.

12 Chaika S. E., Shkoda A. M., Malotonnazhnoye Proizvodstvo Metanola dlya razmeshcheniya na Promyslakh (Treatises of Gubkin Russian State University of Oil and Gas), Moscow, 2007.
URL: http ://www.ameng.ru/publ_prom.php

13 Arutyunov V. S., Krylov O. V., Okislitelnye Prevrashcheniya Metana, Nauka, Moscow, 1998.

14 Arutyunov V. S., Krylov O. V., *Usp. Khim.*, 74, 12 (2005) 1216.

15 Choudhary V. R., Uphade B. S., *Catal. Surv. Asia*, 8, 1 (2004) 15.

16 Tomlinson G. D., Contractor Rep. SAND-88-7110, 1988.

17 Field S., Niruta S. C., McCarthy J. G., A SRI International Project, Report No. 6: 9129-01-SQ, 1989.

18 Gradassi M. J., Green N. W., *Fuel Proc. Technol.,* 42 (1995) 65.

19 Labinder J., *Catal. Lett.*, 1, 11 (1988) 371.

20 Arutyunov V. S., Basevich V. Ya., Vedeneev V. I., Natural Gas Conversion IV. Studies in Surface Science and Catalysis, Elsevier, Amsterdam *etc.* 1997. vol. 107. p. 351.

21 Su Y. S., Ying J. Y., Green W. H., *J. Catal.*, 218 (2003) 321.

22 Lansford J. H., Cordy E. M., Qin P., Rosinek M. P., 5th Int. Natural Gas Conversion Symp. (Proceedings), Giardini-Naxos, Sicily, vol. 119, 1998, p. 5.

23 Jiang Y., Yentekakis I. V., Vayenas C. G., *Science*, 264, 5165 (1994) 1563.

24 Makri M., Jiang Y., Yentekakis I. V., Vayenas C. G., XI Int. Congr. on Catalysis (Proceedings), Elsevier, Amsterdam, 1996, p. 387.

25 Il′chenko N. I., Pavlenko N. V., Raevskaya L. N., Bostan A. I., *Theor. Exp. Chem.*, 36, 1 (2000) 48.

26 Bhatia S., Thien C. Y., Mohamed A. R., *Chem. Eng. J.*, 148, 2–3 (2009) 525.

27 Menshchikov A. V., Sinev M. Yu., *Kataliz v Prom-sti*, 1 (2005) 25.

28 Vereshchagin S. N., Anshits N. N., Salanov A. N., Sharonova O. M., Vereshchagina T. A., Anshits A. G., *Chem. Sust. Dev.*, 11 (2003) 303.
URL: http://www.sibran.ru/English/csde.htm

29 Fomenko E. V., Kondratenko E. V., Salanov A. N., Bajukov O. A., Talyshev A. A., Maksimov N. G., Nizov V. A, Anshits A. G., *Catal. Today*, 42 (1998) 267.

30 Fomenko E. V., Kondratenko E. V., Sharonova O. M., Plekhanov V. P., Koshcheev S. V., Boronin A. I., Salanov A. N., Bajukov O. A., Anshits A. G., *Catal. Today*, 42 (1998) 273.

31 Voskresenskaya E. N., Roguleva V. G., Anshits A. G., *Catal. Rev.- Sci. Eng.*, 37, 1 (1995) 101.

32 Choudhury V. R., Mulla S. A. R., *Ind. Eng. Chem. Res.*, 36 (1997) 3520.

33 Fakhroueian Z., Farzane F., Afrookhteh N., *Fuel*, 87, 12 (2008) 2512.

34 Nipan G. D., Dedov A. G., Loktev A. S., Ketsko V. A., Koltsova T. N., Tyunyaev A. A., Moissev I. I., *Dokl. RAN*, 419, 5 (2008) 646.

35 Palermo A., Vazquez J. P. H., Lambert R. M., *Catal. Lett.*, 68 (2000) 191.

36 WO Pat. No. 2005005042, 2005.

37 Akin F. T., Lin Y. S., *Catal. Lett.*, 78 (2002) 239.

38 Anshits A. G., Gupalov V. K., Vereshchagin S. N., Pervaya Nauch.-Prakt. Konf. "FTsP Razvitiya Nizhnego Priangarya" (Treatises), Krasnoyarsk, 1997, p. 269.

39 Vereshchagin S. N., Shishkina N. N., Anshits A. G., I Sov.-Ind. Sem. po Katalizu (Thesises), Novosibirsk, 1984, p. 230.

40 Inventor’s Certificate No. 1004335 USSR, 1983.

41 Vereshchagin S. N., Shishkina N. N., Anshits A. G., *Catal. Today*, 42 (1998) 303.

42 Vosmerikov A. V., Echevskii G. V., Korobitsyna L. L., Barabashin Ya. E., Arbuzova N. V., Kodenev E. G., Zhuravkov S. P., *Kinet. Catal.*, 46, 5 (2005) 724.

43 Yide Xu, Liwu Lin, *Appl. Catal. A: Gen.*, 188, 1–2 (1999), 53.

44 Andreev I. L., *Khim. Neft. Mashinostr.*, 2 (1995) 16.

45 Berrer R., Diffusiya v Tverdykh Telakh, Khimiya, Moscow, 1948.

46 Fomin V. M., Dolgushev S. V., Vereshchagin A. S. *et al.*, *Tekhnol. TEK*, 6 (2004) 89.

47 Vereshchagin S. N., Kurteeva L. I., Rabchevskaya A. A., Vereshchagin A. S., Fomin V. M., Anshits A. G., Vseros. Konf. “Protsessy Goreniya i Vzryva v Fiziko-Khimii i Tekhnologii Neorganicheskikh Materialov” (Treatises), Moscow, 2002, p. 70

48 RU Pat. No. 2291740, 2005.

49 Fomin V. M., Dolgushev S. V., *Vych. Mekhanika Sploshnykh Sred*, 1, 3 (2008) 66.

50 Vereshchagin S. N., Anshits A. G., Vereshchagin A. S., Fomin V. M., 19 Vseros. Konf. po Chislennym Metodam Resheniya Zadach Teorii Uprugosti i Plastichnosti (Proceedings), August 29–31, 2005, Biysk, Parallel, Novosibirsk, 2005, p. 274.

51 Wang Bo, Wu Zhentao, Livingston A. G., Li K, *J. Membr. Sci.*, 339 (2009) 5.

52 Tsugawa P. T., Moem J., Roberts P. E., Souers P. G., *J. Appl. Phys.*, 47, 5 (1976) 1987.

53 Altemose V. O., *J. Appl. Phys.*, 32, 7 (1961) 1309.

54 Kondratenko E. V., Baerns M., in: Handbook of Heterogeneous Catalysis, in G. Ertl, F. Shuth and J. Wietkamp (Eds.), 2nd ed., Wiley-VCH Verlag Gmbh&Co. KGaA, Weinheim, 2008, vol. 6, pp. 3010–3023.

55 Bayukov O. A., Anshits N. N., Petrov M. I., Balaev A. D., Anshits A. G., *Mater. Chem. Phys.*, 114, 1 (2009) 495.

56 Balannec B., Hotier G., Preparative and Production Scale Chromatography, in G. Ganetsos, P. E. Barker (Eds.), Marcel Decker, New York, 1993.