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Oxidative Transformations of Methane: From the Fixed Bed to Nanoreactors

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Abstract—Oxidative transformations of methane on a catalyst (0.9 wt % of La_2O_3 + 0.1 wt % of CeO_2)/MgO located inside the pores of a ceramic membrane occur at temperatures as low as 550°C with a high selectivity that was not previously observed, and terminate mainly with the formation of synthesis gas (carbon monoxide and hydrogen). The observed result is composed of the thermolysis reaction of methane yielding hydrogen and carbon, and comprises the subsequent reverse Buduar reaction. The reforming of carbon dioxide runs intensively when a methane–carbon dioxide mixture is fed into a membrane reactor at 650°C.

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INTRODUCTION

Methane, the main component in natural gas, should not only be utilized as fuel, but also involved in the processes of manufacturing petrochemical products and semi-products. Analogous processes can also be used for the utilization of light alkanes, the components of oil-associated gas and by-products of destructive oil processing.

The aim of the present work is the comparison of catalytic transformations of a mixture containing CH_4 and O_2 on the conventional contact with the layer of a fixed catalyst and under the conditions of nanosized transport pores of the catalytic membrane. The mixture of lanthanum and cerium oxides supported on magnesium oxide (periclase), which has proven to be effective as a catalyst for oxidative dimerization of methane (ODM), was employed in both cases as an active phase [1, 2].

The process of oxidative dimerization of methane, a promising single-stage method of ethylene production from methane, is composed of reactions (1)–(3):

$$4CH_4 + O_2 \longrightarrow 2CH_3\text{–}CH_3 + 2H_2O, \qquad (1)$$

$$CH_3\text{–}CH_3 \longrightarrow CH_2{=}CH_2 + H_2, \qquad (2)$$

$$2CH_4 + O_2 \longrightarrow CH_2{=}CH_2 + 2H_2O. \qquad (3)$$

The presence of an oxidant allows avoiding carbon formation on the catalyst. The process execution is complicated by a nonselective methane conversion resulting in the formation of carbon oxides. Kinetic investigations in a labratory [3] indicate the existence of the ultimate yield of the dimerization products, which is from 20 to 30%.

While developing the catalysts for the oxidative dimerization of methane, the authors revealed a nonadditivity effect for catalytic activity of lanthanum and cerium oxides [4]. An admixture of cerium oxide to the comparatively active lanthanum oxide did not reduce but instead increased the efficiency of the resultant oxide mixture as a catalyst for ODM.

The mixture of these oxides allowed obtaining C_{2+}–products (mainly ethylene and ethane, and traces of propylene and propane) in a yield of more than 22%. The investigation of the revealed effect demonstrated that lanthanum and cerium oxides form defective solid solutions having oxygen vacancies and catalytic centers that stabilize active forms of oxygen. Moreover, cerium oxide is capable of acting as a supplier of active forms of oxygen due to the ability of cerium to vary in its oxidation state.

Deposition of the mixture of lanthanum and cerium oxides on fused magnesium oxide (periclase) resulted in obtaining a mechanically strong catalyst that is capable of carring out the methane condensation in an enlarged reactor with the catalyst load of 100 mL [1, 2]. ODM process in this reactor can be carried out in the autothermal mode. After heating the methane-oxygen mixture up to 600–650°C in the catalyst bed temperature started to increase, this indicated the occurrence of oxidative transformations of methane. The oxidation of methane did not occur at temperatures lower than 600°C. The temperature increase in the catalyst bed after the external heating had been switched off indicated the process occurred in the autothermal mode.

The experiments on the preparation of porous membranes that had a La–Ce/MgO system introduced into their structure, and their examination in catalysis were conducted for the purpose of searching for new approaches to selectivity control oxidative transformations of methane.

EXPERIMENTAL

A procedure for preparing the La–Ce/MgO catalyst and a setup for oxidative transforming of methane on the fixed bed of the catalyst were described in [1, 2].

Produced by SHS synthesis ceramic membranes, which consisted of titanium oxide and carbide or intermetallic compounds Ni_xAl_y [5], were used for preparation of the catalyst (0.9 wt % of La_2O_3 + 0.1 wt % of CeO_2/MgO that was located inside the pores of a ceramic membrane. The size of the membrane channels was in the range of 1 to 3 μm, and the wall was 4 mm thick.

The estimation of the porosity of the ceramic membrane showed that each 1cm^2 of the geometric surface contained up to 10^7–10^8 channels. This allows considering the membrane system as the “ensemble” of microreactors. The catalytic system that had the composition La–Ce/MgO was obtained by the zol-gel method based on colloidal solutions of organic derivatives of metals that were used as the precursors for the catalytically active phase.

The La–Ce/[ZrO_2–Y_2O_3] system, in which the mixture of zirconium and yttrium oxides had been introduced instead of magnesium oxide, was prepared to be used for composition. Oxygen ions of the crystal lattice of the ZrO_2–Y_2O_3 system, which has a cubic structure, display an enhanced mobility. This can be an additional factor for increasing the activity of the system in oxidation reactions.

The prepared colloidal solutions of the precursors were pumped through the membrane pores followed by thermal treatment at 600°C. The amount of the catalyst applied was evaluated gravimetrically. 0.05 g of MgO or ZrO_2–Y_2O_3 and 5×10^{-4} g of the La and Ce oxide mixture were introduced into 1 cm^3 of the membrane. The composition and morphology of the prepared membranes were determined using the methods of X-ray phase analysis and scanning electron microscopy and X-ray microanalysis. A schematic image of the pore of the catalyst-containing membrane is presented in Fig. 1.

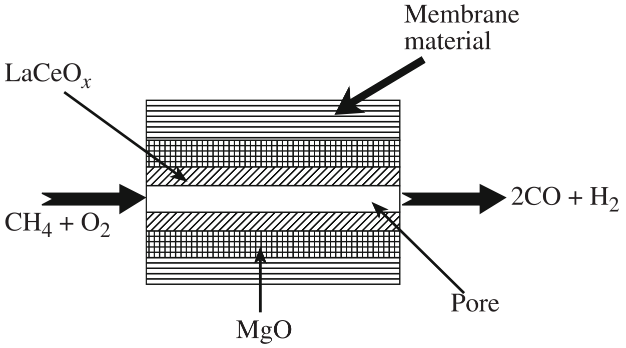

Fig. 1. Schematic diagram of the membrane pore containing the catalyst.

The transformations of methane were performed on a specially designed laboratory setup for membrane catalysis [6] in the filtration mode of reactant feeding through the membrane pores, which had been modified with highly dispersed catalysts of metal oxide. The gaseous reactants were fed into the internal volume of the membrane module (with finger-like configuration) at various temperatures, feed rates of raw mix, and the composition of starting reactants being varied.

The mixtures diluted Ar that contained 8.6% of methane and 4% or 2.2% of air oxygen were fed into the reactor. The flow rate of the reaction mixture varied from 180 to 370 cm^3/h. At the studying of carbon dioxide conversion of methane the mixture that contained methane and carbon dioxide at the ratio of 0.75 : 1 was supplied into the reactor with the feed rate of 0.72 L/h. The reaction products were analyzed using methods of gas chromatography in the on-line mode.

RESULTS AND DISCUSSION

The results of carrying out the autothermal process in an enlarged reactor that contained the fixed bed of La–Ce/MgO catalyst between the layers of quartz packing are shown in Table 1. These data demonstrate that the conversion of the mixture of CH_4 and O_2 at the

Table 1. The results of on the transformation of methane-oxygen mixture in the reactor that contained La–Ce/MgO fixed bed*

Experiment no.	t, °C		$CH_4 : O_2$, mol/mol	Degree of conversion, %		Selectivity towards C_{2+}, %	Yield of C_{2+}, %
	input	max		O_2	CH_4		
1	600	600	4	5	2	1	0.02
2	692	950	4	99	25	53	13.5
3	662	855	3	400	28	51	14.2
4	703	892	3	100	28	51	14.3
5	687	888	3	100	29	50	14.6

* The catalyst load was 100 cm^3, the feed rate of methane-oxygen mixture was 1620 h^{-1}.

Table 2. The oxidative conversion of methane in presence of membrane catalytic systems*

Catalyst	T, °C	Methane conversion, %	Selectivity of methane conversion into synthesis gas
La–Se/MgO	550	25	90
La–Se/MgO	650	35	95
La–Se[ZrO_2–Y_2O_3]	550	60	22
La–Se[ZrO_2–Y_2O_3]	650	70	20

* The flow rate of the reaction mixture (8.6% of CH_4, 2.2% of air oxygen, Ar balance) was 180 cm^3/h.

ratio of 4 : 1 in the fixed bed of the catalyst occurred to a negligible extent at temperatures lower than 600°C. Only with the temperature rising up to 690°C was the reaction occurrence detected, which was attended by the temperature increase up to 950°C. When the mixture of CH_4 and O_2 at the ratio of 3 : 1 was fed into the reactor the temperature within the catalyst bed reached 855–890°C and a mixture of ethylene and ethane (2 : 1) was formed with the yield more than 14%. Carbon dioxides were formed in comparable amounts, with the oxide prevailing. The data obtained were used for comparison with the results that had been obtained with using the membrane reactor.

The experiments on the conversion of the methane-oxygen mixture in the presence of the membrane that contained no supported catalysts have demonstrated that the original membrane made of titanium oxide and carbide did not exhibit activity towards methane transformation within the temperature range of 500–700°C. After the catalytic system La–Ce/MgO had been introduced into the membrane the oxidation process of methane into synthesis gas was observed starting from the temperature of 550°C. At 650°C, the methane conversion reached 35–40% with the selectivity between 90 and 95% towards the formation of synthesis gas that contained 1.5 to 2 CO + H_2. Therefore, in the membrane module the La–Ce/MgO catalyst appreciably increases its activity towards the oxidative transformations of methane and promotes the selective generation of synthesis gas.

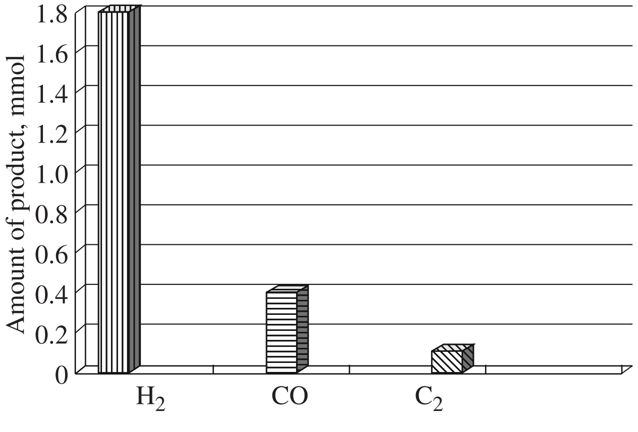

Fig. 2. The products of interaction between methane and lattice oxygen of the catalyst (La–Ce/MgO membrane, the absence of oxygen, 300 min duration).

The data in Table 2 shows that the substitution of magnesium oxide in the membrane's catalytic system for the mixture of zirconium and yttrium oxides resulted in formation of a more active but less selective catalyst. The main amount of methane (approximately 80%) was spent for the formation of carbon deposits. It is important to note that carbon dioxide was either absent or present in traces among the reaction products even when there was excess oxygen against methane in the starting mixture. Thus, it has been established that the oxidative transformations of methane within the pores of the ceramic membrane that contained the La–Ce/MgO catalyst run with a high selectivity, which had not been previously observed, and are completed by the formation mainly of synthesis gas (the mixture of carbon monoxide and oxygen) at temperatures as low as 550°C.

In a specially performed series of experiments on methane conversion under an argon atmosphere without feeding molecular oxygen into the membrane's catalytic module, a capability of selective conversion of methane into synthesis gas for 5 h at the expense of structural oxygen of oxide catalyst was revealed (Fig. 2). In this case, analogously to the experiments with the oxygen feeding the formation of carbon dioxide was not observed.

The absence of CO_2 among the reaction products was also registered during the transformation in the membrane's catalytic module of the mixtures that contained CH_4 and O_2 at the ratios of 0.7 and 3.05, respectively (Fig. 3).

The data presented in Figs. 2 and 3 allowed for an assumption that the radical chain processes that lead to the deep oxidation with the formation of CO_2 or the recombination of methyl radicals with the formation of dimerization products did not develop in the catalytic channels of the membrane. The increase in the amount of oxygen in the reaction zone resulted only in a drop of hydrogen content due to its oxidation to H_2O.

In a prolonged 10-h experiment on methane oxidation the selectivity of the total process of the formation of synthesis gas was 98%.

The set of the obtained results allows proposing that the lattice oxygen of the catalytic system participated in methane oxidation (scheme (4)). The oxygen that was additionally supplied into the reactor along with the oxidation of the hydrogen reacted with the oxygen vacancies of the catalytic system (scheme (5)). An increased hydrogen content probably resulted from transformation of methane according to reactions (6) and (7), which caused the formation of the reaction products in the observed amounts. The heat that was released in the exothermic reaction (6) enabled the possibility of reaction (7), an occurrence that led to the formation of the carbon deposits.

$$\text{Me–O} + CH_4 \longrightarrow \text{Me}[v] + CO + 2H_2; \quad (4)$$

$$2\text{Me}[v] + O_2 \longrightarrow 2\text{Me–O}, \quad (5)$$

where [v] is the oxygen vacancy;

$$CH_4 + 1/2O_2 \longrightarrow CO + 2H_2, \quad \Delta H = -35.6 \text{ kJ/mol}; \quad (6)$$

$$CH_4 \longrightarrow C + 2H_2, \quad \Delta H = +74.8 \text{ kJ/mol}. \quad (7)$$

The absence of CO_2 among the reaction products can be explained by the occurrence of reactions (8) and (9):

$$C + O_2 \longrightarrow (CO_2), \quad (8)$$

$$(CO_2) + C \longrightarrow 2CO. \quad (9)$$

The specially performed experiments on feeding CO_2 into a module of a carbonized membrane at 550–650°C demonstrated that carbon dioxide interacts with the carbon deposits with a high rate according to the known reverse Buduar reaction (9) yielding two moles of carbon monoxide. The gross rate of carbon dioxide reduction at 650°C was 1.37 mol/dm^3 of a membrane per hour. The treatment of the surface of the carbonized membrane's catalyst can be recommended as a method for its regeneration, which results in the recovery of the initial activity.

The revealed capability of the membrane-catalytic system of involving carbon dioxide into the catalytic transformations stimulated studying the possibility of performing the process of carbon dioxide conversion of methane (10) in the membrane reactor:

$$CH_4 + CO_2 \longrightarrow 2CO + 2H_2, \quad \Delta H = +\,247 \text{ kJ/mol}. \quad (10)$$

A membrane prepared on the basis of titanium carbide appeared to be practically inactive during the carbon dioxide reforming of methane. After La–Ce/MgO had been deposited to the surface of the internal pore of this system the conversion of the mixture of methane and carbon dioxide into synthesis gas with the H_2/CO ratio of approximately 1 was observed at temperatures as low as 450°C. At 600°C, the specific yield of the synthesis gas was 35L per dm^3 of the membrane per hour.

A membrane prepared with nickel–aluminum intermetallides appeared to be active towards carbon dioxide conversion of methane even without a supported catalyst (Fig. 4). After La–Ce/MgO had been supported on the internal pore's surface the performance of the membrane's catalytic system towards synthesis gas appreciably increased (Fig. 4). Fig. 4 also demonstrates that the conduction of carbon dioxide reforming methane in the nonmembrane mode (on a fixed layer of the milled modified membrane in a conventional flow reactor) substantially lowers the process efficiency.

By decreasing the contact time between the mixture of methane and carbon dioxide with the membrane's catalytic system we were able to significantly raise the process performance towards synthesis gas up to 2000 L/dm^3 h (Fig. 5).

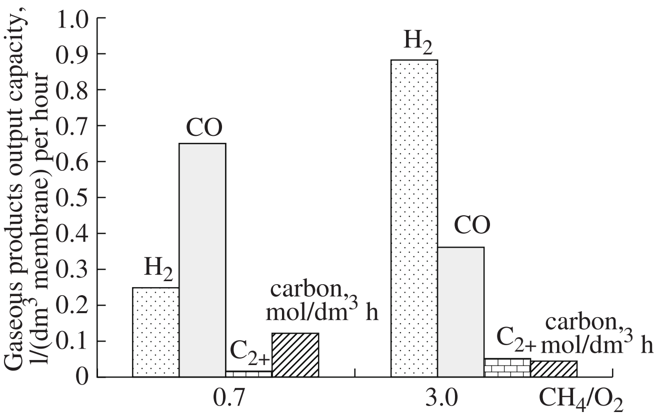

Fig. 3. The composition of the products of methane oxidation under various CH_4/O_2 ratios (La–Ce/MgO membrane as a catalyst; T = 550°C, the flow rate of the reaction mixture was 180 cm^3/h).

Our attempts to increase the performance at the expense of the subsequent growth of the rate of the gas feed resulted in destruction of the membrane. For this reason a new, more durable membrane module was designed, the presence of which enabled the performance towards synthesis gas to reach 6500 L/dm^3 of membrane per hour.

Adding oxygen into the mixture of methane and carbon dioxide that was fed into the $(Ni_7Al_{12\pm x})$ + La–Ce/MgO membrane's catalytic system led to the formation of an appreciable amount of an ethane-ethylene fraction together with the synthesis gas. At 700°C, an excess pressure of 3 atm and feed rate of the mixture of 67.9 L/h ($CH_4/CO_2/O_2$ ratio was 1/0.94/0.39), the performance was 700 and 150 l/dm^3 of the membrane per hour towards syn-

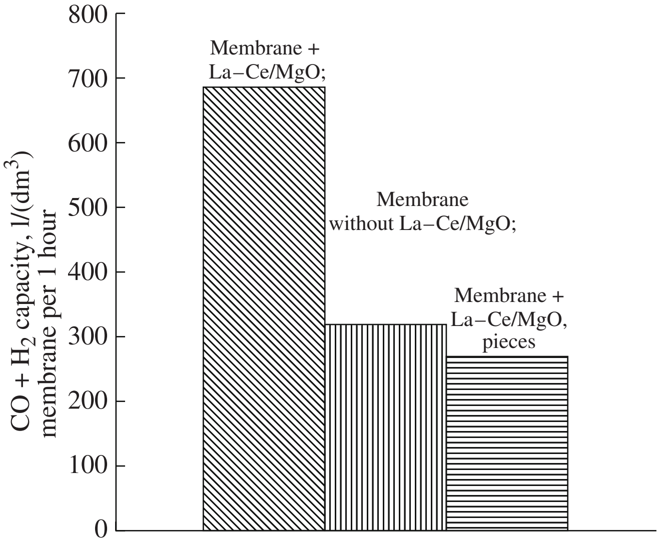

Fig. 4. The membrane effect during carbon dioxide reforming of methane $(Ni_7Al_{12\pm x})$ intermetallide (T = 600°C; contact time 2.2 s; CH_4/CO_2 = 0.75).

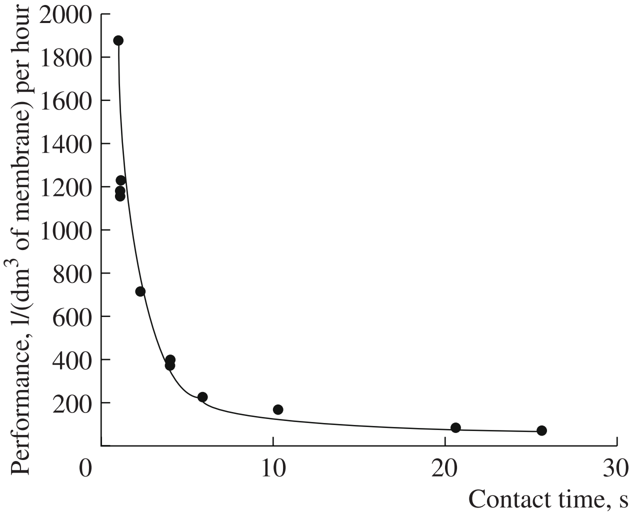

Fig. 5. The influence of the conventional contact time on the performance of nanoreactors ($Ni_7All_{12 \pm x}$) + La–Ce/MgO towards CO + H_2 during carbon dioxide reforming of methane (T = 600°C; CH_4/CO_2 = 0.75).

thesis gas and C_2 products, respectively. Such result indicate the possibility of simultaneous carrying out of the exothermic process of methane dimerization and the endothermic process of carbon dioxide reforming of methane in the membrane's catalytic module.

Thus, the results obtained demonstrate that the allocation of the La–Ce/MgO catalyst within the system of membrane nanoreactors changes both the rate and the selectivity of the oxidative transformation of methane. The mixture of methane and oxygen selectively transforms into synthesis gas. Meanwhile, the La–Ce/MgO catalyst that functions in a standard flow type reactor promotes the formation of the comparable amounts of products of both methane condensation and deep oxidation (carbon dioxide and monoxide).

Different reaction routes can be interpreted using the theoretical analysis of the diffusion features of substrate molecules inside the membrane microchannels [7]. The analysis of gasodynamics inside the channels of porous media demonstrate that inside the membrane pores the possibility of a Knudsen flow, which is characterized by the non-isotropic stochastic reflection of the molecules from the wall, appreciably increases.

The distribution fraction of the gas flow in the transverse direction significantly increases comparied to the isotropic distribution (hollow accommodation). It can be assumed that the features of the reaction occurrence in the membrane are connected with the increase in the frequency factor of collisions between substrate molecules and the active surface within the internal pore's volume. On the one hand, it leads to the growth of the performance of the membrane module, but on the other hand, it impedes development of the gaseous fraction of primary intermediates (methyl radicals).

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