

Research Article

Carbonate Conversion of Methane in Membranal Catalyses

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Annotation

Based on the concept of the nature of the membrane catalyst as a form of heterogeneous catalyst, it was found that the intensification of the heterogeneous catalytic process is possible in the absence of the effect of the reaction mass splitting on the membrane. It was found that the effect of the membrane catalyst is related to the increase in the porosity level of the catalyst. The shape of the kinetic model of the reaction showed that the rate and selectivity of the conversion of methane to carbon dioxide are characterized by a membrane in the reactor-contactor for all studied types of catalyst and traditionally a general system of differential equations. The change in the parameters of the catalytic reactor and model in which the catalyst layer is installed corresponds to the change in the penetration level of the inner surface of the pores. The difference in the kinetic properties of methane carbon dioxide conversion and the difference in the porous structure of the membrane catalyst does not preclude the manifestation of the membrane effect, regardless of the method of its preparation.

Keywords: *methane, carbon dioxide, catalyst, reaction product, conversion, synthesis gas.*

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Introduction

The process of converting methane to carbon dioxide and obtaining a "synthesis gas" has not yet been introduced into industry due to the lack of a long-lasting stable catalyst, but it is important in terms of CO₂ loss. Carbonate conversion of methane is also a promising method with the simultaneous use of two different gases (methane and carbon dioxide) that evoke the "greenhouse effect" and has significant environmental and economic significance. Another advantage of this method is that the process of carbonate conversion of methane is carried out at normal atmospheric pressure (0.1 MPa), at 650-800⁰C [1-6]. Therefore, it is important to develop new, cost-effective, waste-free methods and environmentally friendly technologies for the production of import-substituting, export-oriented products from natural gas, as well as to increase the country's export potential for chemicals and new technologies and protect the environment.

Methane carbonate is a conversion synthesis gas and the methanol production reaction based on it takes place in the presence of a zeolite-containing catalyst.

Based on the above, the aim of this work is to synthesize environmentally friendly liquid fuels by direct catalytic conversion of the two gases methane and carbon dioxide, which cause the “greenhouse effect”.

Currently, the only and most sensible way to process natural gas is to synthesize it by catalytically converting it into a gas and obtaining methanol on its basis. It has been more than 30 years since the catalytic carbonation reaction of methane was discovered, but this reaction has not yet been introduced into the industry due to the lack of a stable catalyst with high activity and efficiency. The catalytic carbonation reaction of methane has the following advantages [7-11]:

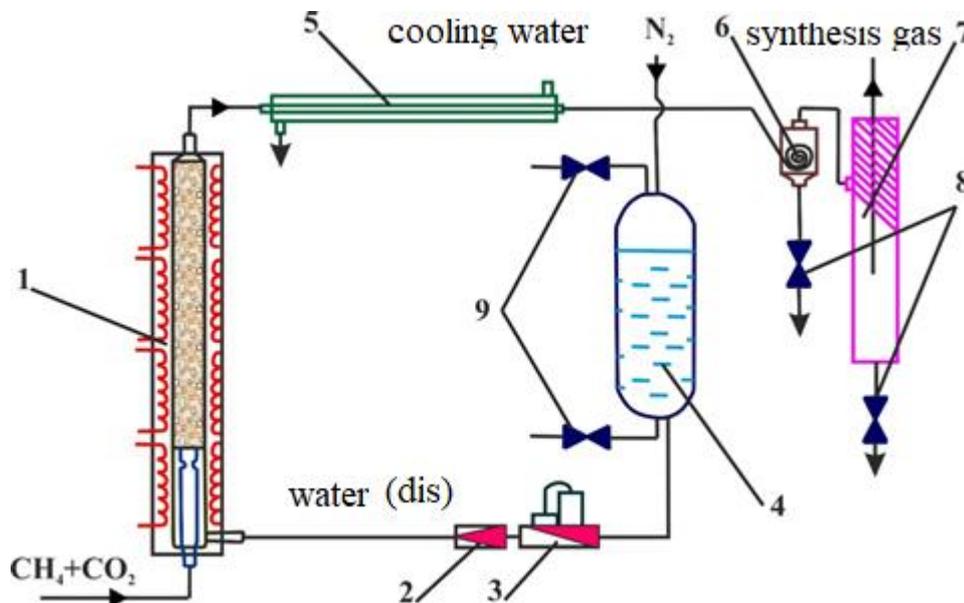
- The process of carbonation of methane takes place in one technological stage. According to the Fisher-Tropsch reaction, the synthesis-gas production by converting methane with water vapor is a multi-step process [12-16].

- Synthesis gas is the main product of petrochemical synthesis, from which many substances can be synthesized [17-21].

- The catalytic carbonation reaction of methane takes place at normal atmospheric pressure, unlike the Fisher-Tropsch synthesis. Fisher-Tropsch synthesis proceeds under high pressure. This, in turn, is costly [22-25]. An analysis of the literature [26-33] shows that the specific features of the methane catalytic carbonation process are the high temperature and the relatively low selectivity in all known catalysts. A number of works have been carried out on the synthesis of methane from methanol and the production of methanol on its basis, which is distinguished by its economic efficiency [34-39]. However, work in this area is still insufficient. It is important to study the mechanism of the process of catalytic carbonation of methane, to create its mathematical model, to optimize the process by assessing the adequacy of the models, to create an automated control system of kinetic processes. Therefore, it is expedient to study the thermodynamic laws of the carbonation process for the simultaneous production of synthesis gas and methanol, which are valuable raw materials from methane, the selection of specific active and efficient catalysts, modeling and optimization of the process in differential reactors. These are relevant in terms of developing a method of synthesis of methane carbonation process based on kinetic laws, its improvement and the creation of an automated system of the process. Selection of cheap and active catalysts for methane catalytic carbonation reaction with high efficiency and selectivity, high temperature stability, stable, strong, thorough and extremely stable and evaluation of kinetic results based on them, full study of the mechanism of the process and its thermodynamic substantiation. The creation of energy and resource-saving technologies is one of the most important and topical issues facing professionals. In this study, membrane catalysts were considered as one of the types of heterogeneous catalysts characterized by the possibility of forced transport of reagents through the hole structure. This approach allows the use of preparation methods known in heterogeneous catalyst technology, as well as the use of traditional classification in heterogeneous catalysis (dividing them into massive and supported ones). It should be noted that a solid membrane catalyst is a catalyst in which the active component is somehow deposited directly on the substrate (microfiltration corundum membrane), in which it is located in the form of an independent layer. In a membrane catalyst, the reactive component is distributed in a

special catalyst base layer, which is a layer of γ -Al₂O₃ deposited to increase the substrate surface area and narrow the hole size.

Experimental part. The schematic diagram of the laboratory unit for steam-carbon dioxide conversion of methane is shown in Picture-1, and the general view of the installation is shown in Picture-1.



Picture 1. Diagram of the block of steam-carbonate conversion of methane: 1 - conversion reactor, 2 - check valve, 3 - flow meter, 4 - water bottle, 5 - refrigerator, 6 - cyclone, 7 - separator, 8, 9 - valves.

The analysis of the composition of the resulting synthesis gas was carried out using a Chromatograph "Kristalluks-4000M". We used columns 3 m long and 3 mm in inner diameter. Helium was used as a carrier gas. The phases in the columns are molecular sieves 5A and Haysep Q. Determination of the quantitative composition of gas mixtures was carried out by an external standard method (chromatograph was pre-set for each component of the gas mixture) [40-47]:

$$C_i = k_i * S_i,$$

Where S_i is the concentration of the i -th component in the gas mixture (vol.%), the calibration coefficient for the k_i -th component (vol.% : (mV-min)), S_i is the peak area of the i -th component in the chromatogram (mV-min).

Processes are carried out in a flow reactor in the absence of water vapor at atmospheric pressure (carbonate conversion of methane) and in the presence (methane vapor carbonate conversion) in a ratio of 1: 1 CH₄: CO₂, volumetric feed rate 1000 -1 (V0) and process temperature 300 to 1050 Was carried out by modifying to °C. The analysis of the initial and final products of the reaction was carried out on-line using gas chromatography. The volume of the catalyst was 6 ml, the duration of the process was 10-12 hours.

Contact time τ_{contact} (in seconds) is calculated according to the following formula:

$$\tau_{\text{kont}} = \frac{V_{\text{kat}} * 273}{F * (T_p + 273)} * 60$$

Where V_{catalyst} is the volume of the catalyst sample (ml), F is the volume (molar) flow rate of the reaction mixture, and T_r is the reaction temperature ($^{\circ}\text{C}$).

The volume of the V_{catalyst} was determined according to the following formula.

$$V_{\text{cat}} = \frac{\pi * (D^2 - d^2)}{4} * h,$$

Where D is the outer diameter of the catalyst (cm), d is the inner diameter of the catalyst (cm), and h is the length of the catalyst (cm).

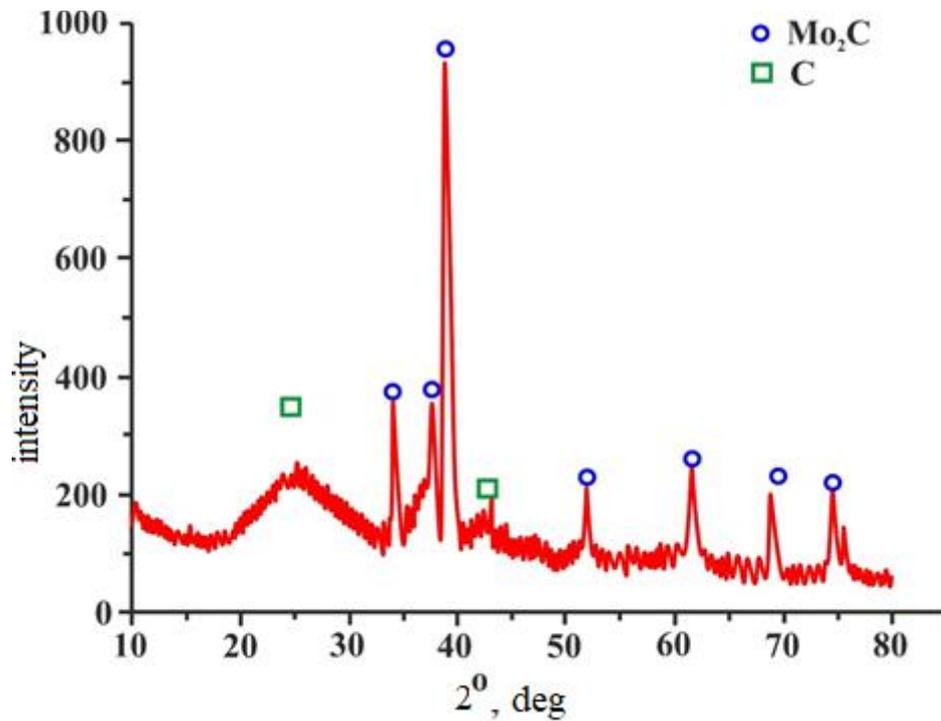
The main parameters of the process of conversion of methane to carbon dioxide were determined by the following formulas:

$$X(\text{CH}_4) = \frac{F(\text{CH}_4)_0 - F(\text{CH}_4)}{F(\text{CH}_4)_0} * 100\%, \quad X(\text{CO}_2) = \frac{F(\text{CO}_2)_0 - F(\text{CO}_2)}{F(\text{CO}_2)_0} * 100\%,$$

where $X(\text{CH}_4)_0$ and $X(\text{CO}_2)$ are the conversion rates of methane and carbon dioxide (%), $F(\text{CH}_4)_0$ and $F(\text{CH}_4)$ are the volumetric (molar) consumption of methane at the inlet to the reactor and at the outlet, respectively (ml: min), $F(\text{CO}_2)_0$ and $F(\text{CO}_2)$ - volumetric (molar) flow rate of carbon dioxide at the entrance and exit of the reactor (ml: min), $F(\text{CO})$ is the flow rate of carbon dioxide at the outlet of the reactor (ml: min), $F(\text{H}_2)$ - volumetric (molar) hydrogen consumption at the output.

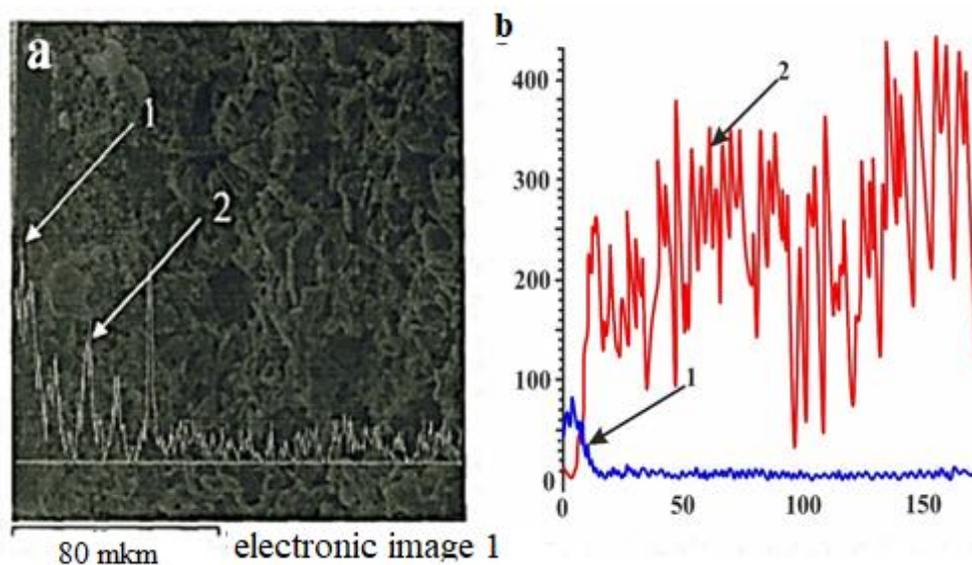
Experimental results and their discussion. Catalyst samples were obtained by the sol-gel method using a highly dispersed mixture of particles consisting of non-stoichiometric molybdenum compounds with oxidation states ranging from 5 to 6 - layers called "molybdenum blue". The molybdenum faces themselves were synthesized by the reduction of ammonium pentamolybdate in an acidic medium; glucose solution was used as a reducing agent.

The advantage of these colloidal systems is that the catalytic active phase is molybdenum carbide, which is formed immediately after their calcination in an inert atmosphere. This is confirmed by XRD data obtained during the analysis of "molybdenum blue" powder calcined at 800°C in a very pure nitrogen medium (picture 2). It can be seen from the X-ray diffraction scheme presented that a sample consisting of a hexagonal crystal lattice of molybdenum carbide Mo_2C also contains free amorphous carbon. In the X-ray diffraction scheme of membrane catalyst samples, the carbide phase becomes unrecognizable due to the very small thickness of the deposited layers (several tens of microns).



Picture 2. X-ray powder diffraction scheme obtained by burning molybdenum blue in an inert atmosphere at 800 ° C.

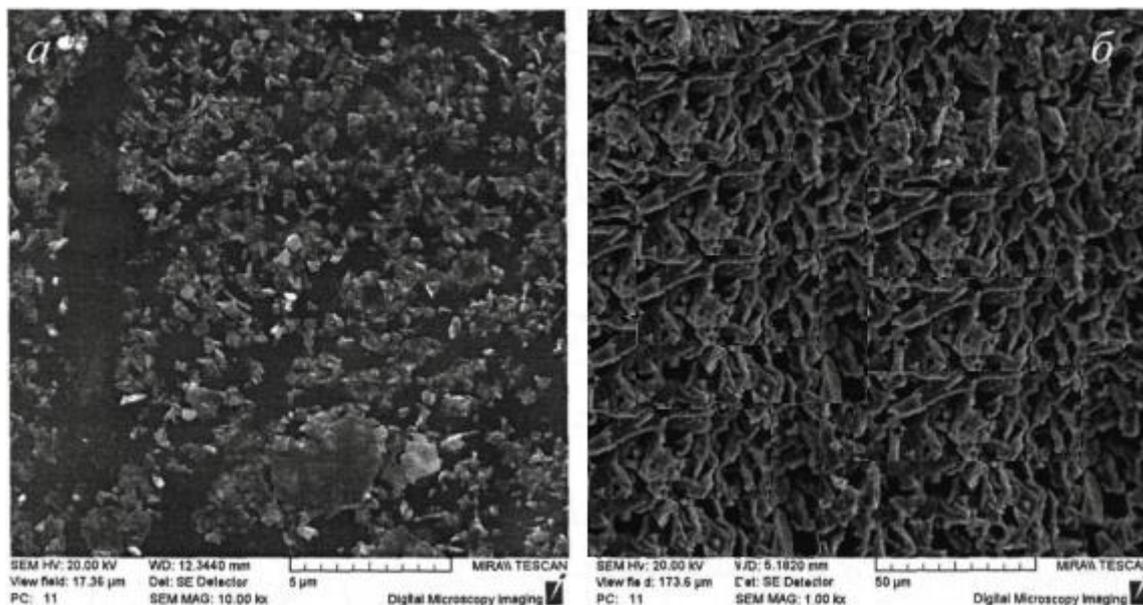
Large molybdenum-carbide catalyst. The sample was obtained by applying “molybdenum blue” to the original corundum substrate, which was then calcined in a nitrogen stream at 800 ° C. The fact that the catalytic layer of these membranes consists mainly of molybdenum carbide is indirectly confirmed by MPCA data (Fig. 2a). It can be seen that the intensity of the signals from depth for molybdenum (1) and carbon (2) is symbolically placed in the cross section of the membrane catalyst. Figure 106 allows you to estimate the observed depth of the signal from molybdenum and aluminum. On the outer surface of the sample, the signal from aluminum has a minimum value and molybdenum has a maximum value. From this, it can be concluded that the molybdenum compounds deposited on the substrate (corundum microfiltration membrane) are partially located on its outer surface. As the distance from it increases, the signal from aluminum increases and molybdenum decreases. That is, the amount of molybdenum decreases. Its concentration reaches background values at a depth of about 15 microns. Such a narrow distribution can be considered as a layer.



Picture 2. Active membrane molybdenum-carbide catalyst (a-Mo (1) and C (2); b-Mo (1) and X-ray diffraction scheme of element distribution by cross section of A1 samples (2).

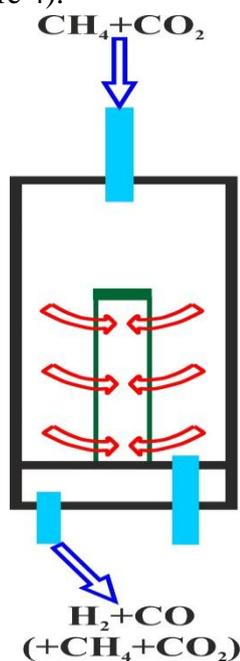
The content of the active component (indicating the weight of the original substrate) was 0.85%. A comparison of the total specific surface area of the activation with the surface of the membrane catalyst shows that this value changes significantly when the active component is applied to the base. Before testing in a membrane reactor, the total specific surface area of the membrane catalyst is almost five times that of the substrate. For him, this value is determined by the inactive inner surface of the corundum particles. After testing the membrane catalyst under conditions of carbon dioxide conversion of methane, its specific surface area decreases to $10.5 \text{ m}^2/\text{g}$; external - up to $7.1 \text{ m}^2/\text{g}$, internal - up to $2.3 \text{ m}^2/\text{g}$. Such a change on the surface of the membrane catalyst can occur, for example, as a result of sintering the active component material or removing free amorphous carbon from it. The size of the pores of the membrane catalyst undergoes similar changes. The values of the specific surface area of the active component obtained were found to be close to the corresponding values for the membrane catalyst obtained by the CVD method. The micrography of the surface (Pic. 11a) shows that the catalyst layer is a flat and almost clean [47].

In addition, the plates of molybdenum carbide particles are clearly visible, the molybdenum blue color is distributed in the carbon matrix formed during heat treatment. All components of a given catalyst are clearly visible in the cross section.



Picture 3. Surface (a) and cross-section (b) micrographs of the active membrane molybdenum-carbide catalyst sample.

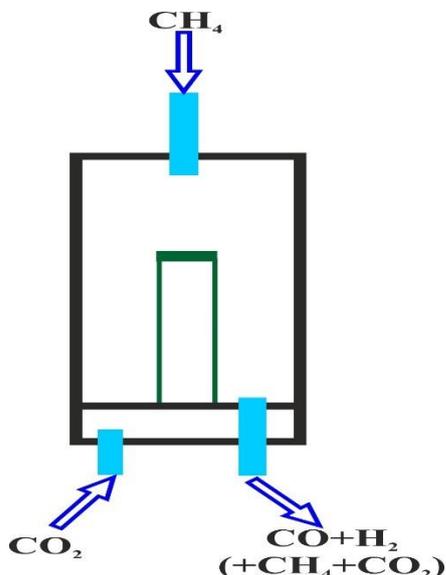
According to the principle of operation, the membrane reactor-contactor is the closest to a conventional catalyst of all other membrane reactors. In it, due to the pressure difference ("pushed" through the catalyst), the entire reaction mixture passes through the porous structure of the catalyst and, together with the products obtained, is discharged from the reactor via the permeate line (Picture 4).



Picture 4. Flow diagram in a membrane catalytic reactor-contactor.

As for the distributor reactor, the mechanism of interaction of the reagents with the catalyst is less clear in it than in the contactor reactor. On one side of the membrane catalyst (the side of the catalytic layer) the starting material A is fed (in our experiment it is methane) (Pic. 5). It penetrates deep into the catalytic layer due to diffusion, as there is a difference in concentration on the outer surface of the membrane catalyst and inside it. On the other hand, the initial substance B is transported through the porous structure of the substrate due to the pressure difference (in our experience it is carbon dioxide), the

concentration of reaction products in its reaction zone must be limited or its interaction prevented. In the holes of the catalyst (and not at the entrance to them), these two streams - methane and carbon dioxide - mix and react with each other, after which the products are desorbed and removed from the reactor. That is, the high-concentration bond of the starting materials at the entrance to the catalyst holes in the membrane reactor-distributor is also eliminated.

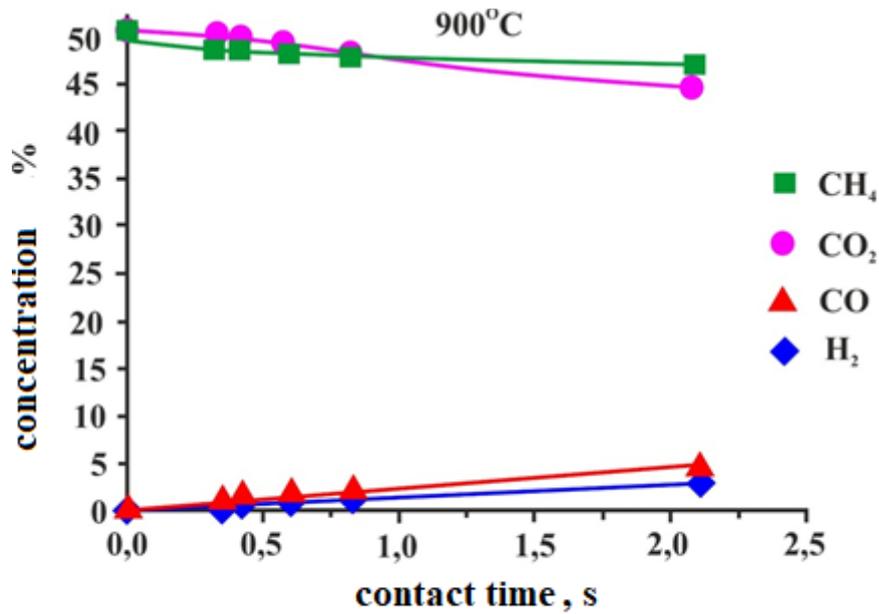


Picture 5. Flow diagram in a membrane catalytic distributor reactor.

Thus, in each reactor discussed, the flow of substances moves differently relative to the catalyst layer. To compare the effect of the process, the reaction rate in each case under consideration must be set experimentally, i.e., a kinetic experiment must be carried out. In this case, it is necessary to evaluate the difference in the internal properties of the catalysts. Therefore, in the experiment, we used mass and activated membrane catalysts with the same activating component.

In this work, the change in the concentration of starting materials and reaction products, as well as the dependence of the conversion rates on the contact time at different temperatures in membrane reactors (reactor-contactor and reactor-distributor) were experimentally established. The same dependencies but for the fragmented membrane catalysts and the powder active component (Mo_2C) it was set in a solid-cell conventional catalytic reactor.

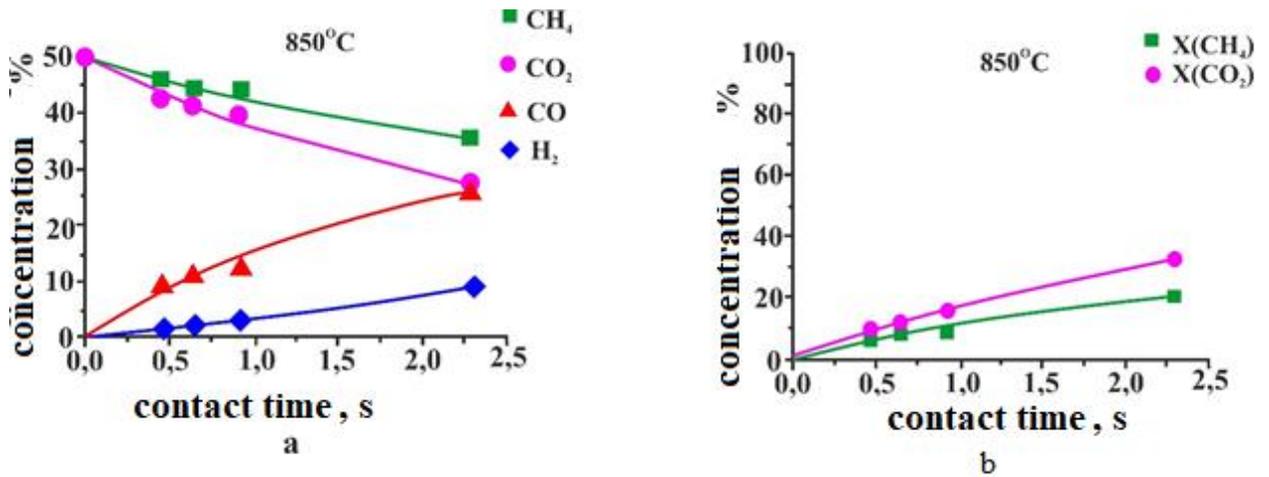
An increase in the conversion temperature of methane to carbon dioxide to 800°C (Pic. 6), although this process led to a slight increase in the rate, but the conversion rate of the starting materials exceeded 10 per cent.



Picture 6. Changes in the active membrane catalysis of the reaction mixture in the UKM reaction from the time of bonding at 800 ° C in a conventional catalytic reactor.

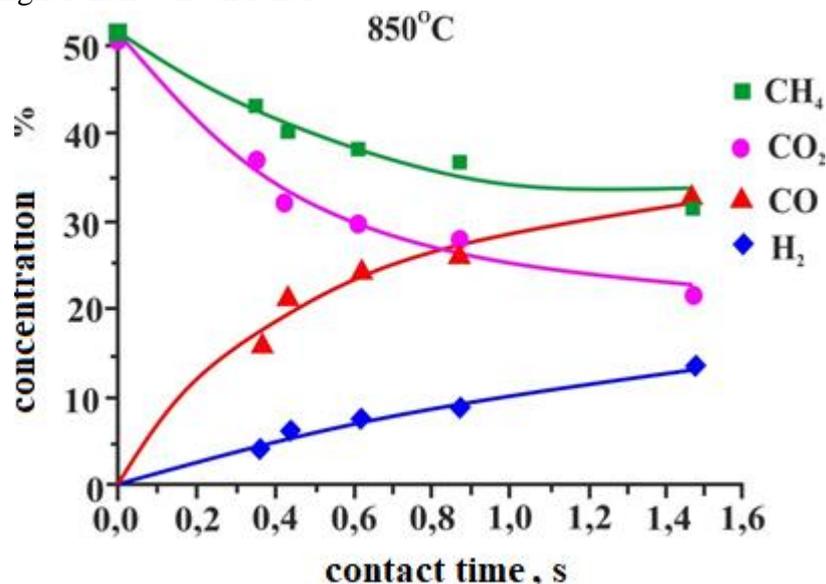
Low concentration variations in crushed catalysts may have the following explanation. As a result of milling the membrane catalyst for testing in a conventional stationary catalytic reactor, a membrane catalyst layer containing the active component is formed on only one side of the particle (1: 6 of this outer surfaces per cube). This reduces the possibility of complete contact of the starting materials with the clear catalytic surface, as there is a possibility of bypassing ("sliding") of gases through the layer without contact with the active component, resulting in a decrease in the conversion rate of the starting materials.

To dispel doubts about the accuracy of the results obtained, it was decided to study the UKM flow process in Mo₂C powder. True, in this case the content of the active component in the conventional reactor layer was almost 120 times higher than in the study of the crushed mass membrane catalyst and almost 67 times higher than in the study of the crushed activated catalyst. Figure 7 shows the test results of the same molybdenum carbide powder obtained from the same molybdenum blue used in the preparation of membrane catalysts (bulk and supported). 7a shows that in pure molybdenum carbide, the concentrations of both the initial compounds and the reaction products vary significantly, exceeding the same values for the crushed membrane catalyst. Conversion rates at 850 ° C (Pic. 7b) exceed 20%. In this case, the H₂: CO ratio increased from 0.21 to 0.35 as the contact time increased.



Picture 7. The change in the composition of the reaction mixture (a) and the conversion rate of the starting materials (b) depend on the contact time of the powder in the UKM reaction at 850 ° C in a conventional catalytic reactor. Mo₂C (active component of membrane catalysts).

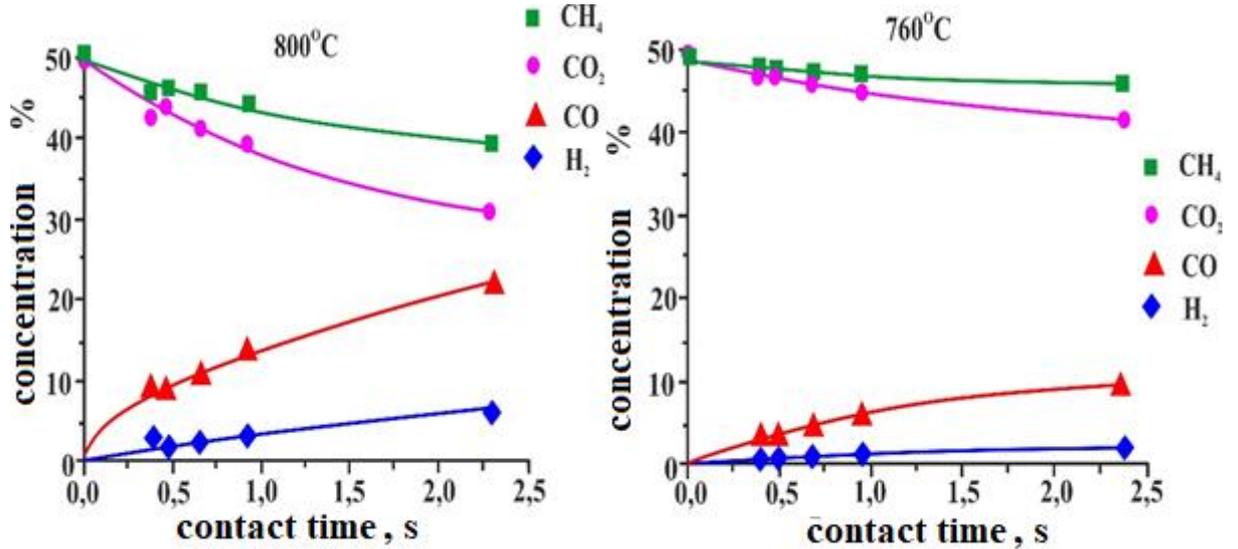
An increase in the mass of the active component of the catalyst in a conventional catalytic reactor with a fixed bed leads to an increase in its specific capacity (productivity per unit volume of the bed). The low conversions in the pulverized membrane catalysts are probably due to the low active ingredient content in them. Active membrane catalysts. Figure 8 shows the experimental kinetic curves (dependence of concentration on contact time) on a massive membrane catalyst at 850 ° C in a membrane catalytic reactor-contactor. The nature of the connections between a reactor-contactor and a conventional reactor is the same. However, the conversion rate of starting materials in a membrane catalytic reactor is significantly higher than conventional.



Picture 8. The change in the mass of the reactive mixture from the contact time in the UKM reaction at a temperature of 850 ° C in the reactor-contactor in the membrane catalyst.

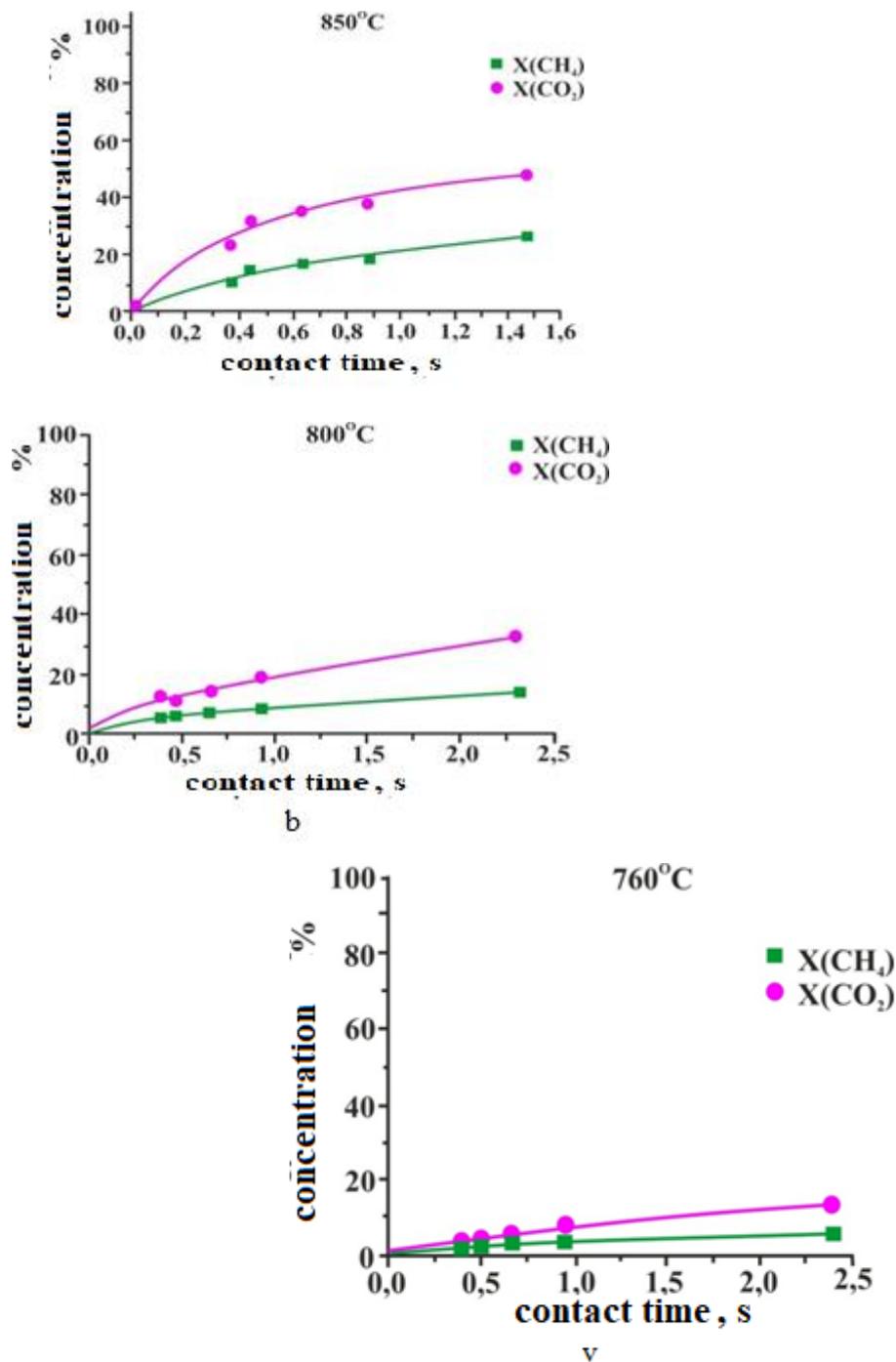
The graph provided shows that the concentration of starting materials and reaction products depends on the contact time. The starting materials are consumed at different rates

- the methane concentration decreases more rapidly with increasing contact time than the carbon dioxide concentration. The accumulation of reaction products in the reaction mixture also occurs at different rates - carbon monoxide accumulates faster than hydrogen.



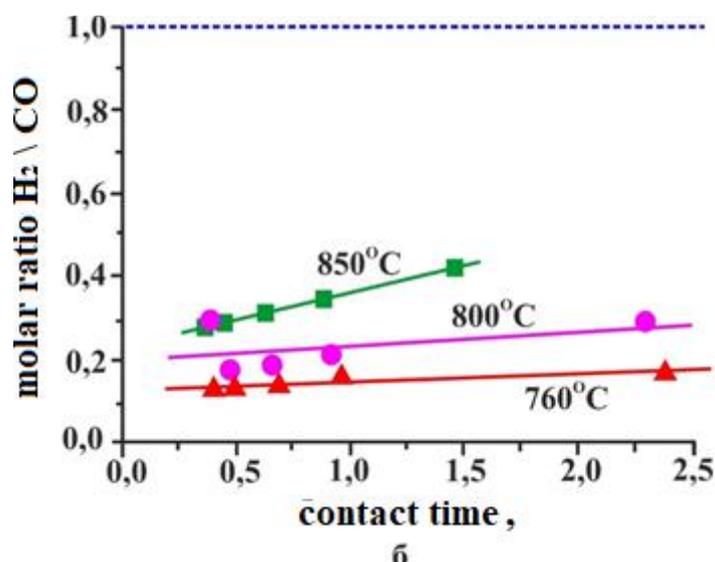
Picture 9. The change in the concentration of starting materials and reaction products at the temperatures of 800 ° C and 760 ° C in the reactive contactor relative to the contact time in the massive membrane catalyst.

Picture 9 shows the change in the concentration of starting materials and products in the conversion of methane to carbon dioxide in a contactor reactor with an active membrane catalyst at 800 ° C and 760 ° C. Comparing these results with the data presented in Figure 8, it can be noted that the nature of the change in the concentration of starting materials and products in the membrane catalytic reactor remains the same throughout the studied temperature range. As the process temperature decreases, the starting materials are absorbed at a lower rate. The level of accumulation of products also decreases. This is confirmed by the fact that the conversion rates shown in Figure 10 depend on the contact time at different temperatures of the process.



Picture 10. The rate of transfer of starting materials to the active catalyst in the membrane reactor-contactor at different temperatures from the time of contact: a - 850 ° C; b - 800 ° C; v - 760 ° C.

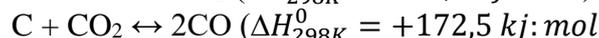
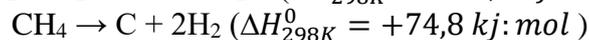
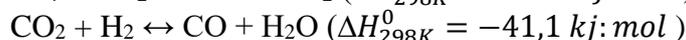
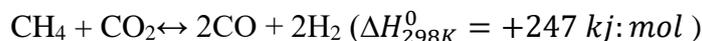
Picture 11 shows the molar ratio of carbon dioxide conversion products at different process temperatures. An analysis of the presented dependencies shows that an increase in temperature and contact time leads to an increase in this ratio, which reflects the selectivity of this catalytic process. In this case, the effect of temperature on the H₂: CO ratio under experimental conditions was greater than the effect of contact time.



Picture 11. H_2 ; The molar ratio of CO depends on the contact time in the reactor-contactor at different temperatures in the active membrane catalyst.

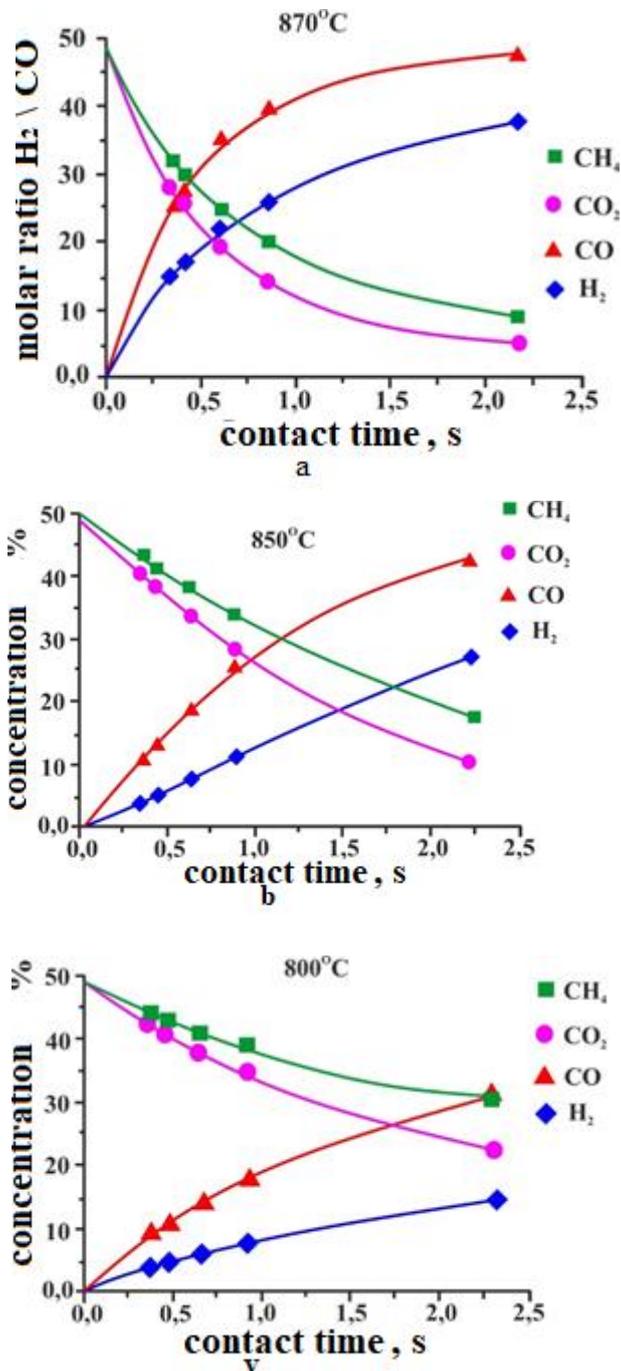
However, the value of H_2 : CO is far from unity, i.e., the consumption of starting materials and the accumulation of products do not correspond to the stoichiometry of the reaction of methane to carbon dioxide. This provides a basis for predicting the occurrence of side reactions, which leads to deviations from the stoichiometric ratios of the starting materials and reaction products.

It is known that in this process, serial and parallel side conversions can occur simultaneously with the main reaction of the interaction of CH_4 with CO_2 (1) (for the direct reaction) 298K shown):



These reactions explain the results of the above experiment very well. Obviously, the observed difference in the concentration of starting materials and products is primarily due to the interaction of carbon dioxide and hydrogen. Reactions 3 and 4 are unlikely to cause a difference in the concentration of starting materials and products in the reaction mixture because the products formed in them are in the same proportion as the main reaction. The difference in the results obtained in the reactor-contactor and in a conventional catalytic reactor with a stationary layer is, in our opinion, explained by the difference in the different forms of the mass transfer mechanism in the catalyst. The active component in the membrane catalyst is in the form of a tubular porous base layer and in the fragmented membrane catalyst in the form of a particle layer. In a conventional catalytic reactor, the delivery of the initial compounds to the catalytic surface and the removal of the products from it occur due to molecular diffusion. In a membrane reactor, raw materials and products are forcibly transported due to the pressure difference on both sides of the membrane catalyst. Obviously, we can talk about convective mass transfer in the case of a membrane catalyst. In the crushed catalyst particles, the phenomenon of interdiffusion inhibition, which is characteristic of rapid chemical reactions, including reactions that occur at high temperatures, is observed.

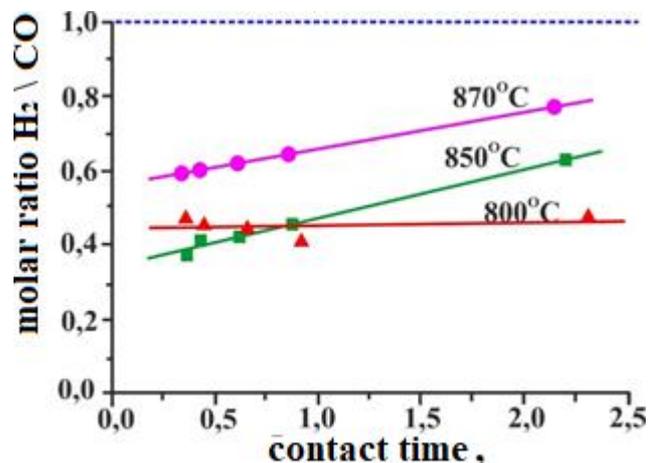
Activated membrane catalyst. Picture 12 shows the dependence of the composition of the reaction mixture on the membrane reactor-contactor on the supported membrane catalyst.



Picture 12. The change in the concentration of the starting materials and products of the conversion of methane to carbon dioxide to the activated catalyst in the membrane reactor-contactor: a - 870 ° C; b - 850 ° C; s - 800 ° C.

The graphs show that the carbon dioxide conversion of methane in the contactor reactor proceeds according to the laws observed in the active membrane catalyst in the supported membrane catalyst. The concentration of carbon dioxide in the reaction mixture is lower than that of methane and that of hydrogen is lower than that of carbon monoxide. the

difference between carbon dioxide conversion in the activated catalyst and the active process is that the absolute changes in concentrations are greater in the activated catalyst if all else is equal. That is, the deposited membrane catalyst turned out to be more active than the mass.



Picture 13. Dependence of the molar ratio of H₂: CO on the contact time in the reactor-contactor at different temperatures of carbon dioxide conversion in the supported membrane catalyst.

This is confirmed by the data in Picture 13. When these results are compared with the massive membrane catalyst data (Pic. 11), it can be seen that the molar ratio at the same temperature and contact time is high. in an activated catalyst. As with the active membrane catalyst, an increase in the process temperature leads to an increase in the molar ratio of the reaction products. It can be assumed that during the operation of the membrane reactor in the contactor mode, side reactions occur in the activated membrane catalyst, which prevents the products from achieving a stoichiometric ratio under these experimental conditions. Thus, a comparison of the characteristics of the carbon dioxide conversion process in a membrane reactor-contactor and in a conventional reactor in conventional Mo₂C powder shows that the basic laws are the same in both reactors. The values of the concentration of the components of the reaction mixture and their variation with the contact time and temperature are different.

The product ratio in the reactor-contactor in both membrane catalysts and in the conventional reactor in Mo₂C powder turned out to be less than 1: 1 from the required stoichiometric value. In a massive membrane catalyst crushed during short contact times, it is close to unity, which is probably due to errors in determining the concentration of the low conversion and reaction mixture components. When testing Mo₂C powder in a conventional reactor, it was found that the active ingredient was 25 times more than the larger membrane catalyst (0.85% Mo₂C) and 16.5 times more than the supported membrane. Kidding is very important. catalyst (Mo₂C content - 1.26% by weight).

When testing Mo₂C powder in a conventional reactor, it was found that the active ingredient was 25 times more than the larger membrane catalyst (0.85% Mo₂C) and 16.5 times more than the supported membrane. Kidding is very important. catalyst (Mo₂C content - 1.26% by weight).

It should also be noted that the use of a membrane reactor-contactor allows to achieve the process parameters recorded at low temperatures in a conventional reactor.

A comparison of the results of the study of catalysts in a conventional catalytic reactor and a membrane catalytic reactor-contact or allows us to draw the following conclusions. Since the conditions in the reactors differ only in the components of the reaction mixture on the catalyst surface and in the transport mechanism from it, it can be assumed that this is the main reason for such a large difference in the behavior of the same catalysts. this is observed in catalytic reactors.

Conclusion

Thus, since membrane catalysts are one of the types of heterogeneous catalysts, this allows them to apply most of the rules of catalysis theory and practice, as well as methods for obtaining and studying their behavior in different chemical reactions.

1. Based on the concept of the nature of the membrane catalyst as a form of heterogeneous catalyst, it was found that the intensification of the heterogeneous catalytic process is possible in the absence of the effect of the reaction mass splitting into a membrane.

2. It was found that the effect of the membrane catalyst is related to the increase in the porosity level of the catalyst.

3. The shape of the kinetic model of the reaction showed that the rate and selectivity of the conversion of methane to carbon dioxide are characterized by a membrane in the reactor-contactor for all studied types of catalyst and traditionally a general system of differential equations. the change in the parameters of the catalytic reactor and model in which the catalyst layer is installed corresponds to the change in the penetration level of the inner surface of the pores.

4. The difference in the kinetic properties of methane carbon dioxide conversion and the difference in the porous structure of the membrane catalyst does not preclude the manifestation of the membrane effect, regardless of the method of its preparation.

Literature

- M. T. Ravanchi, T. Kaghazchi, A. Kargari, Application of membrane separation processes in petrochemical industry: a review // *Desalination*. 2009; No235. P. 199-244.
- T. Westermann, T. Melin, Flow-through catalytic membrane reactors - principles and applications // *Chemical Engineering and Processing*. 2009. No48'. P. 17-28.
- H. Weyten, J. Luyten, K. Keizer, L. Willems, R. Leysen, Membrane performance: the key issues for dehydrogenation reactions in catalytic membrane reactor // *Catalysis Today*. 2000. No56. P. 3-11.
- R. Schafer, M. Noack, P. Kolsch, M. Stohr, J. Caro, Comparison of different catalysts in the membrane-supported dehydrogenation of propane // *Catalysis Today*. 2003. No82. P. 15-23.
- J. P. Collins, R. W. Schwartz, R. Sehgal, T. L. Ward, C J. Brinker, G. P. Hagen, C. A. Udovich, Catalytic dehydrogenation of propane in hydrogen perm selective membrane reactors // *Ind. Eng. Chem. Res*. 1996. No35. P: 4398-4405/
- J.-S. Chang, H.-S. Roh, M. S. Park, S.-E. Park, Propane dehydrogenation over hydrogen perm selective membrane reactor // *Bull. Korean Chem. Soc*. 2002. No23-5. P. 674-678.
- Y. Yildirim, E. Gobina, R. Hughes, An experimental evaluation of high-temperature composite membrane systems for propane dehydrogenation // *Journal of Membrane Science*. 1997. No135. P. 107-115.

- B. N. Lukyanov, D. V. Andreev, V. N. Parmon; Catalytic reactors with hydrogen membrane separation // *Chemical Engineering Journal*. 2009. doi: 10.1016/j.cej.2009.04.023.
- M. E. Adrover, E. Lopez, D. O. Borio, M. N. Pedernera, Simulation of a membrane reactor for the WGS reaction: pressure and thermal effects // *Chemical Engineering Journal*. 2009. doi: 10.1016/j.cej.2009.04.057.
- Y. Wang, F. Gao, W. T. Tysoe, Interaction of molybdenum hexacarbonyl with hydroxylated alumina thin. films at high temperatures: formation and removal of surface carbides // *Journal of Molecular Catalysis A: Chemical*. 2006; No248. P. 32-41,
- M. Kmetz, B. J. Tan, W. Willis, S. Squib, F. S. Galasso, CVT) Mo; W and; Cr ox carbide, carbide, and silicide coatings on Sic yarn // *Journal of Materials Science*: 199 1. No26. P: 2107-2110:
- T. Ivanova; K. A. Gesheva, A. Szekeres,. Structural and optical properties; of CVD. molybdenum oxide films^for electrochromic. application // *J. Solid State Electrochemist*. 2002. No7. P. 21-24
- A. Szekeres-. T. Tvanova, K. Gesheva;, Spectroscopic; ellipsometry study of CVD molybdenum oxide films: effect of temperature//*J- Solid State Electrochemist*. 2002: No7. P^ 17-20.'
- R. E. Tanner., A. Szekeres, D: Gogova, K. Gesheva, Study of the surfaces of CVD-WO₃ films, by atomic; force microscopy and spectroscopic ellipsometry // *Journal of Materials Science: Material sim Electronics*: 20031 NoM,P: 769-770
- RLE. Tanner; A.. Szekeresj D:Gogova; K. Gesheva,' Study of the surface roughness of CVD-tungsten oxide thin films // *Applied Surface Science*. 2003. No218. P. 162-168;
- K. A. Gesheva, T. Ivanova; G. Popkirov, F. Himmelman Optoelectronic properties of CVD M003 and M003-WO₃ films and their application in electrochromic cells // *Journal of Optoelectronics and Advanced Materials*. 2005. Vol. 7. No1.P: 169-175. .
- A.-M Alexander,..J. S. J: Flargreaves, Alternative catalytic materials: carbides, nitrides, phosphides and amorphous boron alloys // *Ghem: Soc. Rev*. 2010. No39. P. 4388-4401.
- Flakan W. Hugosson, Theoretical studies of phase stabilities and electronic structure in molybdenum carbide, Uppsala University, Uppsala 1999. PI 32.
- Tiancun Xiao, Andrew P. E. York, Karl S: Coleman, Effect of carburizing agent on the structure of molybdenum carbides // *J: Mater. Chem*. 2001. No11. P. 3094-3098:
- M. Lewandowski, P. Da Costa, D. Benichou, C. Sayag, Catalytic performance of platinum doped tungsten carbide in simultaneous hydro denitrogenating and hydrodesulphurization // *Applied Catalysis B: Environmental*. 2010. No93. P. 241-249.
- Hua-Min Wang, Xiao-Hui Wang, Ming-Hui Zhang, Synthesis of bulk and supported molybdenum carbide by single-step thermal carburization method // *Chem. Mater*. 2007. No19. P. 1801-1807.
- P. M. Patterson, T. K. Das, B. H. Davis, Carbon monoxide hydrogenation over molybdenum and tungsten carbides // *Applied Catalysis A: General*. 2003. No251. P. 449-455.
- Changhai Liang, Pinliang Ying, Can Li, Nanostructured p-Mo₂C prepared by carbothermal hydrogen reduction on ultrahigh surface area carbon material // *Chem. Mater*. 2002. No14. P. 3148-3151.
- Ch. Ma, N. Brandon, G. Li, Preparation and formation mechanism of hollow micro spherical tungsten carbide with mycoparasite // *J. Phys. Chem. C*. 2007. No111. P. 9504-9508.
- Ch. Liang, F. Tian, Z. Li, Z. Feng, Z. Wei, C. Li, Preparation and adsorption properties for

- thiophene of nanostructured W_2C on ultra-surface-area carbon materials // Chem. Mater. 2003. No15. P. 4846-4853.
- J. P. Bosco, K. Sasaki, M. Sadakane, W. Ueda, J. G. Chen, Synthesis and characterization of three-dimensionally ordered microporous (3DOM) tungsten carbide: application to direct methanol fuel cells // Chem. Mater. 2010. No22. P. 966-973.
- J. B. Claridge, A. P.E. York, A. J. Brungs, M. L. H. Green, Study of the temperature-programmed reaction synthesis of early transition metal carbide and nitride catalyst materials from oxide precursors // Chem. Mater. 2000. No12. P. 132-142.
- P. Arnoldy, J. C. M. Jonge, J. A. Moulijn, Temperature-programmed reduction of MoO_2 and MoO_3 // J. Phys. Chem. 1985. No89. P. 4517-4526.
- Kyung Tack Jung, Won Bae Kim, Chang Houn Rhee, Effects of transition metal addition on the solid-state transformation of molybdenum trioxide to molybdenum carbides // Chem. Mater. 2004. No16. P. 307-314.
- OV Krylov, Carbon dioxide conversion of methane into synthesis gas // Ross. Chem. magazine. 2000. Vol. 44. No1. S. 19-33.
- D. San-Jose-Alonso, J. Juan-Juan, M. J. Illan-Gomez, M. C. Roman-Martinez, Ni, Co and bimetallic Ni-Co catalysts for the dry reforming of methane // Applied Catalysis A: General. 2009. No371. P. 54-59.
- L. Guczi, G. Stefier, O. Geszti, Methane dry reforming with CO_2 : A study on surface carbon species // Applied Catalysis A: General. 2010. No375. P. 236-246. 34. MI
- M. M. Quiroga, A. E. C Luna, Kinetic analysis of rate-data for dry reforming of methane // Ind. Eng. Chem. Res. 2007. No46. P. 5265-5270. 95. U.
- J. M. Ginsburg, J. Pina, T. E. Solh, H. I. de Lasa, Coke formation over a nickel catalyst under methane dry reforming conditions: thermodynamic and kinetic models // Ind. Eng. Chem. Res. 2005. No44. P. 4846-4854.
- D. C LaMont W. J. Thomson, Dry reforming kinetics over a bulk molybdenum carbide catalyst // Chemical Engineering Science. 2005. No60. P. 3553-3559.
- T. Christofolletti, J. M. Assaf, E. M. Assaf, Methane steam reforming on supported and non-supported molybdenum carbides // Chemical Engineering Journal. 2005. No106. P. 97-103.
- P. Liu, J. A. Rodrigues, Water-gas-shift reaction on molybdenum carbide surfaces: essential role of the ox carbide // J. Phys. Chem. B. 2006. No110. P. 19418-19425.
- M. L. Pritchard, R. L. McCauley, B. N. Gallaher, W. J. Thomson, The effect of sulfur and oxygen on the catalytic activity of molybdenum carbide during dry methane reforming // Applied Catalysis A: General. 2004. No275. P. 213-220.
- Demidov DV, Rosenkevich M.B., Sakharovsky Yu.A. Steam carbon dioxide conversion of methane as a method for producing synthesis gas of a given composition for small-scale production of methanol and synthetic hydrocarbons: Innovations in science: collection of articles. Art. by mater. VIII int. scientific-practical conf. Part I. - Novosibirsk: SibAK, 2012.
- Bobomurodova, S.Y., Fayzullaev, N.I., Usmanova, K.A. Catalytic aromatization of oil satellite gases // International Journal of Advanced Science and Technology, 2020, 29(5), стр. 3031–3039.
- Tursunova, N.S., Fayzullaev, N.I. Kinetics of the reaction of oxidative dimerization of methane // International Journal of Control and Automation, 2020, 13(2), стр. 440–446
- Fayzullaev, N.I., Bobomurodova, S.Y., Avalboev, G.A. Catalytic change of c1-c4-alkanes // International Journal of Control and Automation, 2020, 13(2), стр. 827–835
- Mamadoliev, I.I., Fayzullaev, N.I., Khalikov, K.M. Synthesis of high silicon of zeolites

- and their sorption properties//International Journal of Control and Automation, 2020, 13(2), стр. 703–709
- Sarimsakova, N.S., Fayzullaev, N.I., Musulmonov, N.X., Atamirzayeva, S.T., Ibodullayeva, M.N. Kinetics and mechanism of reaction for producing ethyl acetate from acetic acid//International Journal of Control and Automation, 2020, 13(2), стр. 373–382
- Fajzullaev, N.I., Yusupov, D., Shirinov, Kh.Sh., ...Keremetskaya, L.V., Umirzakov, R.R. Catalytic vapor-phase hydration of acetylene and its derivatives//Khimicheskaya Promyshlennost', 2002, (7), стр. 34–37
- Shuxrat Chorievich Aslanov, Abdurazzoq Qobilovich Buxorov, Normurot Ibodullaevich Fayzullayev. Catalytic synthesis of C2-C4-alkenes from dimethyl ether//International Journal of Engineering Trends and Technology Volume 69 Issue 4, 67-75, April 2021ISSN: 2231 –5381 /doi:10.14445/22315381/IJETT-V69I4P210©
- Samadov S.Zh. Nazarov F.S. Beknazarov E.M. F.F. Nazarov Biological activity of the synthesized compounds of derivatives of N, N-polymethylene bis [(no-aromatic-cycloalkanolylo) carbamates]. // Universum Journal: March 3 (84), 2021