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SOME TECHNOLOGICAL PROBLEMS OF CATALYTIC CONVERSION OF METHANE WITH CARBON DIOXIDE IN THE GAS PHASE WITH THE PARTICIPATION OF CATALYSTS

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Abstract

As mentioned above, the industrial application of the catalytic conversion of methane in the gas phase with carbon dioxide catalysts is hindered by the fact that the process is highly exothermic., in other words, high energy consumption; secondly, very low stability of the catalyst to coking. The development of new catalysts continues as part of the fight against coking. We have already mentioned the work of the company "Topsoe" in the field of reducing the toxicity and coking of nickel catalysts [57; pp. 44-44].

Introduction

In terms of reducing energy costs, the main way to solve this problem is to carry out the reaction (3) in combination with reactions that, in various generalizations, are accompanied by the release of heat, mainly partial oxidation of methane (2) or complete oxidation of methane to CO2 and H2O.

Attempts have also been made to separate the methane and CO2 activation stages using membrane reaction devices for the catalytic conversion of methane in the presence of carbonate catalysts [58; pp. 74-82].

In the catalytic conversion of methane in the presence of oxygen and carbonate catalysts, $Ba_{0,5}\,Cr_{0,5}\,Co_{0,8}\,Fe_{0,2}O_x$ An oxygen-permeable membrane has also been used [59; pp. 61-62]. In catalytic conversion with oxygen catalysts, temperatures of 850°C and $CH_4{:}O_2$ At high ratios, the catalytic conversion of methane to carbon dioxide in the gas phase with catalysts and the selectivity of its conversion to CO was 98%. High activity and selectivity in the catalytic conversion with carbonate catalysts were achieved at 900°C.. $CH_4+CO_2+O_2$ 90-92% for methane in which the change continued stably in the presence of catalysts for more than 100 hours in the mixture, and CO_2 for 94-96%, CO The selective effect of turning into is close to 100%. [60;259-268-б.] in is presented a reaction device whose walls can turn heat into a whole. The reaction device consists of a ceramic cylindrical tube, the outer and inner walls of which are catalysts Rh/Al_2O_3 (Fig. 1.1). This ceramic cylindrical tube is placed inside another cylindrical tube made of a metal with low thermal conductivity. The gas mixture is fed into the inner cylindrical tube; there, the combustion of methane occurs with the release of heat.

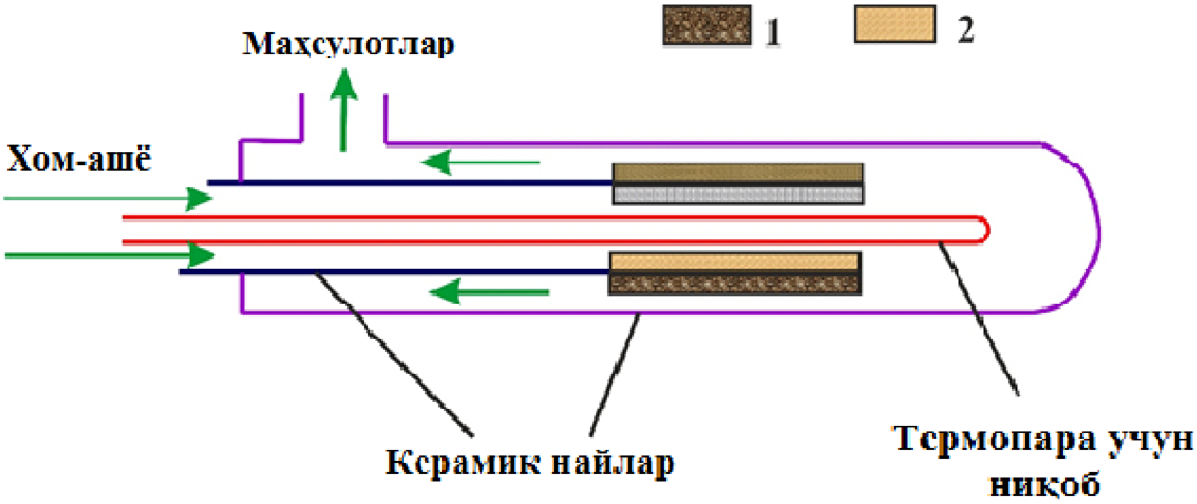

Figure 1.1. Schematic of a device for the catalytic conversion of methane with carbon dioxide in the gas phase in the presence of catalysts, which can be used to synthesize the total heat of reaction [61; 2019.]

1-burning catalyst film;
2- catalyst layer of catalytic change in the presence of catalysts.

Most of the outgoing heat passes through the wall to the outer surface of the cylindrical tube and in it CH_4+CO_2 ва CH_4+H_2O Reactions that occur with the absorption of heat. In such an apparatus, it is possible to maintain a constant temperature in the entire reaction chamber. We have used this principle of "tube within a tube" in the study of the catalytic conversion of methane with carbon dioxide in the presence of catalysts coated with manganese oxide.

In our [62;2015.] it was found that catalytic conversion of methane occurs on oxide-manganese catalysts under non-stationary conditions. This allowed us to propose a three-stage thermoneutral process; these

1) Catalytic conversion with the participation of carbonate catalysts, which is accompanied by the absorption of heat by methane;
2) Oxidative condensation, which is accompanied by the evolution of heat by methane;
3) Reoxidation of the catalyst, which is accompanied by the evolution of heat. To fully compensate for energy costs, in the third stage, a certain amount of methane was added to the oxygen in order to obtain additional heat by its deep oxidation.

New work has appeared on the catalytic conversion of methane with the participation of catalysts, the necessary heat of which is obtained by burning a part of the raw material in atmospheric oxygen. Catalytic conversion of methane with the participation of oxycarbonate catalysts Pt/ZrO_2, Pt/Al_2O_3 and Ni/Al_2O_3 at 550-800°C at [63;73-77-б.] at studied. CH_4+CO_2+O_2 for the mixture CO and H_2 (93-11%) at any temperature CH_4+CO_2 The carbon deposition was reduced and the “hot spot” on the catalyst was easier to deal with. When the O2 content in the mixture was 11%, CO and H_2 product is relevant CH_4+O_2 Close to catalytic conversion in the presence of oxygen catalysts (95% at 800°C). The reaction occurs in two stages:

1. Deep oxidation of methane;
2.Catalytic conversion of methane to CO2+H2O in the presence of catalysts.

This makes it difficult to carry out a process in which the required heat is obtained by burning part of the raw material in atmospheric oxygen. [64; pp. 259-268] $CH_4+CO_2+O_2$ and $CH_4+H_2O_2$ of mixtures Ni/MgO A decrease in carbon formation was observed in the catalytic conversion of aluminosilicate catalysts with the presence of catalysts. The process temperature effect was 800°C. $CH_4+CO_2+O_2$ = 60:16:24 is close to zero for the mixt. $2H_2$:1CO A mixture of hydrogen and carbon monoxide is formed. [58] The catalytic conversion of methane with high catalytic activity, productivity, and selectivity is achieved by the combustion of a portion of the feedstock in atmospheric oxygen, where the required heat is obtained by catalytic steam-oxygen catalysts. $2H_2$:CO The factors that contribute to catalytic conversion in the presence of catalysts, which produce a mixture of hydrogen and carbon monoxide, have been considered. As shown in [59] $CH_4+CO_2+O_2$ in mixtures La/NiO/γ/Al_2O_3 "hot spot" is preserved even when the mixture is completely thermoneutral, CO_2 it will reduce the stain. During the 100-hour test 750°C initial composition CH_4:O_2=2:1 CH_4:COand $_2$=10:1 In the presence of permanent catalysts, the catalytic conversion of methane (95%) and CO2 (97%) is preserved, with selectivity for hydrogen production of 94% and final composition of CO 100%. H_2:CO=1,7:1. Do not mix $CH_4+CO_2+O_2$ As the oxygen content increases, the catalytic conversion of methane with carbon dioxide in the gas phase in the presence of catalysts increases, while the catalytic conversion with CO2 catalysts reaches a high value. The formation of a "hot spot" on the catalyst bed in the presence of oxygen has a significant impact on the product yield..

CO_2+CH_4 a reaction that involves the absorption of heat Rh/α-Al_2O_3 ва Rh/γ-Al_2O_3 A device in which sulfur reaction is carried out on a catalyst based on silicates was proposed [65 T. 6.]. The process is under conditions 700-800°C ва 3,5 atm is the absorption power of the reaction device 200-300 kW, catalytic conversion of methane with carbon dioxide in the gas phase in the presence of catalysts -80% The problem is the accumulation of carbon in the catalyst.

The most convenient method of catalytic conversion in the presence of catalysts, the required heat of which is obtained by burning a part of the raw material in atmospheric oxygen, consists in carrying out reactions (1), (2), (3), (6) in a single reaction device and generalizing the deep oxidation of methane.

The main difficulty in creating devices for such reactions is that these reactions occur at different temperatures; therefore, it is necessary to divide the length of the catalyst bed into sections where heat is released and heat is absorbed. As a solution to the problem In the works of Japanese researchers CH_4 +CO_2+O_2 It has been proposed to carry out catalytic conversion in a fluidized bed with the participation of mixed catalysts. However, it is not always possible to obtain the desired composition of the final mixture CO+H2.

Summary

The most convenient method of catalytic conversion in the presence of catalysts, the required heat of which is obtained by burning a part of the raw material in atmospheric oxygen, consists in carrying out reactions (1), (2), (3), (6) in a single reaction device and generalizing the deep oxidation of methane

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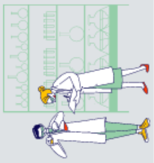

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