

**PROCESSING OF METHANE OF NATURAL GAS TO C₂-HYDROCARBONS
AND HYDROGEN-CONTAINING COMPOUNDS**

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Abstract

It was determined the effect of the nature of carrier and active phase of catalyst on the efficiency in the reaction of partial oxidation of methane to desired products. It was found that H₂, C₂-hydrocarbons, hydrogen-containing mixtures, as well as propane and propylene in trace amounts are formed on the catalysts with desired catalytic properties in the study of oxidative conversion of methane.

Key words: methane, catalysts, oxidation, polyoxide catalyst, hydrogen, C₂-hydrocarbons

1. INTRODUCTION

Throughout the last century, oil was and still remains the main source of raw material for production of motor fuels and products of organic synthesis. Currently, however, the situation is changing. Growth rates of explored oil reserves has not kept pace with consumption. The coming end of the "oil era" is already perceived as inevitable to which to prepare now. The use of natural gas as an alternative raw material to oil is one of the most promising directions in hydrocarbon processing. Explored natural gas reserves exceed those oil reserves. The degree of chemical processing of natural gas into valuable products remains low, and most associated gas is flared, leading to irreversible loss of valuable raw materials and generates a complex environmental problems in mining regions. Production of C₂-hydrocarbons and hydrogen-containing mixtures from methane could be a promising alternative to this, because, in contrast to oil, natural gas, the main component of which is methane, is considered as a renewable source of raw material. Unfortunately, the problem of obtaining of chemically important products from methane is complicated by the fact that the methane molecule contains extremely strong C-H bond by which a carbon atom of methane is able to enter in the reaction of formation of C-C bonds only in extremely harsh conditions, and in this case the reaction proceeds with a very low selectivity leading to the formation of product mixture. Systematic analysis of the results of research on the main one step process and catalysts of catalytic processing of methane of natural gas into useful products was conducted by N.M. Popova and K. Dossumov [1]. It was shown that methane conversion processes occur at relatively high temperatures using different catalyst compositions and conditions. O₂, H₂O and CO₂ are used as oxidants. Currently, however, methane is mainly used as a fuel (home and car) or flaring in gas compressor stations. CH₄ will be used to generate energy in gas turbines. Finding the ways of activation of CH₄ and its involvement in the new chemical reaction to targeted produce of hydrogen-containing compounds and intermediates of organic synthesis is important problem [2-4]. This paper presents the results on the activity of the developed catalysts in oxidative conversion of CH₄ to hydrogen-containing mixtures and C₂-hydrocarbons.

2. EXPERIMENTAL

Setup of a flow type for the oxidative conversion of methane in a tubular quartz reactor is shown in Figure 1. The reaction gases: oxygen of air, air (from a compressor), or oxygen or oxygen-argon mixture (from the cylinder), methane or methane-argon mixture (from the cylinder) argon (from the cylinder), hydrogen, or hydrogen-argon mixture (from the cylinder) are fed into the mixer.

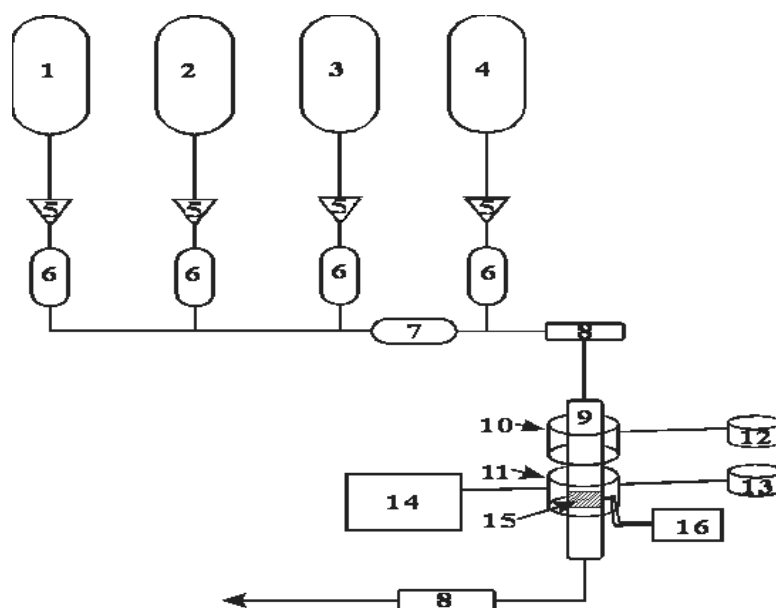


Fig. 1. The scheme of the flow laboratory setup for the catalytic oxidative conversion of methane by oxygen. 1 - O_2 of air, O_2 , $O_2 + Ar$; 2 - CH_4 , $CH_4 + Ar$; 3 - Ar ; 4 - H_2 , $H_2 + Ar$; 5 - cranes for fine control; 6 - rheometer; 7 - mixer; 8 - sampler; 9 - reactor; 10 - preheating furnace; 11 - main heating furnace; 12 - millivoltmeter; 13 - millivoltmeter; 14 - temperature controller; 15 - catalyst; 16 - thermocouple.

Their speed is adjustable via reducers, valves for fine adjustment and rheometers and then fed into the mixer. Gas is transferred from the mixer into a tubular flow reactor with a catalyst. The reactor is heated by two furnaces, one furnace to preheat of gases, followed by the other - for heating to the reaction temperature. Oven temperature for the reaction is controlled by two thermocouples: regulating and recording, located in the catalyst bed. Provides regulated supply of water vapor to the reaction gas mixture. Supply of multichannel tubular water cooler with length of 100-120 mm which ends by common cavity with adapter to remove the reaction products is provided to the reactor bottom. Refrigerator with a reactor is one. Inside the reactor there is a pocket for a thermocouple dipped in the catalyst bed. The furnace is wound on the reactor to keep the temperature in the catalyst bed. If the reaction proceeds in excess of the hydrocarbon then for shut down the reactor in an emergency is necessary to provide an initial shutdown of oxygen in order to avoid getting to explosive area. Thermocouples and rheometers for conducting of gases must be calibrated. It is necessary to provide a system of cleaning in case of air filling by oil compressor.

In the present paper, we report on the development of the composition and methods of synthesis of oxide catalysts for the oxidative conversion of methane by oxygen. New compositions of oxide catalysts based on transition metals Ni, Ni-K, Ni-K-W, Mn, La, Cu and IK-30 supported on CuO, CaX, 80% H-ZSM-5 + 20% Al₂O₃, ZSM-5 + Al₂O₃, montmorillonite as well as low-percentage 1% Pt, Ru and Pt-Ru catalysts supported on 2% Ce/($\theta + \alpha$)-Al₂O₃ were developed. The catalysts were prepared by a joint and consistent impregnation. Preliminary drying of carriers at 300°C for 2 hours was carried out for this purpose, then was determined their moisture capacity and conducted calcination at 450°C for 3 hours. Then the active phase of the catalyst was supported by joint and consistent impregnation. Activity of developed catalysts in the oxidative conversion of methane by atmospheric oxygen was determined in a flow installation at atmospheric pressure in quartz reactor. Unreduced samples of catalyst heated on air were tested. The initial reaction mixture was supplied at a ratio of CH₄ : O₂ = 2 : 1 and varying the content of CH₄, O₂ of air and Ar in the initial reaction mixture, %: 1 - 36.0 : 80.0, 2 - 5.0 : 20.0, 3 - 59.0 : 0 with a gradual increase of temperature from 600 to 900°C and the change of space velocity (V) from 3900 to 7800 h⁻¹ at the contact time (t) 0,46 - 0,92 s.

3. RESULTS AND DISCUSSION

3.1. Activity of polyoxide supported catalysts in the partial oxidation of methane

Catalysts based on Ni, Ni-K, Ni-K-W, Mn, La, Cu and IK-30 supported on CuO, CaX, 80% H-ZSM-5 + 20% Al₂O₃, ZSM-5 + Al₂O₃ and montmorillonite were investigated. The active phase of catalyst was 5.0%. The oxidative conversion of methane to desired products generally begins from 700°C to form hydrogen and ethane. Then ethylene and CO are formed in the reaction products with a gradual increase in temperature reaction to 800°C. Yields of above-mentioned of products reaction are stabilized at 850 and 900°C. It was determined that X_{CH₄} increases with the reaction temperature from 6 to 12% for 5% Mn catalysts supported on natural carrier montmorillonite, a small amount of hydrogen from 0.1 to 0.3% is formed in this case. Formation of 3.0% ethane occurs at 750°C, the amount of which is reduced to 1.3% with increasing of temperature. Formation of ethylene observed at 800°C, the amount of which also increases with increase of temperature from 0.66% to 2.61%. Also propane and propylene were found in small amounts in the reaction mixture. It was shown that X_{CH₄} increased from 2.5 to 8.7% with increasing reaction temperature from 700°C to 900°C on 5% Mn/CuO catalyst. The formation of hydrogen from 0.7 to 7.0% was observed. But the formation of C₂-hydrocarbons is observed only when the temperature rises up to 850°C. Thus, the formation of 1.0 and 1.1% ethane and ethylene is carried out. It was determined that X_{CH₄} increased from 2.7 to 16.6% with increasing reaction temperature from 600°C to 900°C on the catalyst 10% CuO/80% H-ZSM-5+20% Al₂O₃. The formation of hydrogen from 0.5 to 11.5% was observed in the reaction mixture. But the formation of C₂-hydrocarbons is observed only with increasing temperature of reaction to the 900°C on this catalyst. Thus, the formation of 0.9% ethane and ethylene in an amount 2.2% implemented Study of oxidative conversion of methane on 5% Ni supported on ZSM-5 + Al₂O₃ showed that with increasing the reaction temperature from 600°C to 900°C the X_{CH₄} increased from 6 to 29%, while there is the formation of hydrogen at the reaction temperature 600°C in an amount of 20.0% further increase to 47.0%. In this case, C₂-hydrocarbons are formed during the reaction temperature 800°C, namely, 2.9% ethane and 0.8% ethylene. The formation of ethane is reduced to 0.4%, and ethylene increased to 2,0% with rise in temperature of reaction. Also, 14.0% of CO were found in the products of reaction at 750°C, the amount of which is reduced to 9.2% with increasing of temperature. At the study of 5% Ni-K/ZSM-5 + Al₂O₃ has been determined that with increasing of reaction temperature from 600°C to 900°C the X_{CH₄} increases from 1.3 to 13%. The formation of hydrogen is observed at the reaction temperature 600°C in trace amounts of 0.1% and further change from 54.0 to 46.6 at 800°C and increase to 51.5%. In this case, C₂ hydrocarbons begin to form only at the reaction

temperature 850°C, namely, 2.4% ethane, the amount of which is reduced to 0.9%, and 1.8% ethylene is formed only at 900°C. A further modification of the 5% Ni-K catalyst supported on ZSM-5 + Al₂O₃ by addition of small amounts of W did not increase X_{CH₄} the indicators of which ranged from 11 to 13% with increasing of reaction temperature from 600°C to 900°C; and the formation of hydrogen decreases from 1 to 0.1%. C₂-hydrocarbons (1.3% ethane) begin to form at 750°C. Ethane content sharply increased to 8.2% at 800°C and further reduced to 1%. Formation of 1.9% ethylene was also observed at the reaction temperature 750°C. With increasing of temperature it is increased to 2.4%. The study of oxidative conversion of methane on 5% La/CaX showed that with increasing of temperature from 600°C to 900°C conversion of methane increases from 1.6 to 11.2%, while there is formation of a small amount of hydrogen from 0.1 to 0.2%. 2.9% ethane is formed at 700°C, the amount of which is reduced to 0.8% and when the temperature rises to 900°C increases to 1.3%. Along with the decrease in the amount of ethane in the reaction products at 800°C is formed 2.5% ethylene. On the catalyst IK-30 was determined that conversion of methane increased from 1.2 to 10.5% with increasing of reaction temperature from 600°C to 900°C. The hydrogen content increases from 0.2 to 24.4%. On this catalyst formation of C₂-hydrocarbon is observed at the reaction temperature 700°C. Thus, formation of 2.2% ethylene and 1.1% ethane is carried out. Propylene was detected in the reaction mixture in small quantities.

Thus, H₂ and C₂-hydrocarbons were detected in reaction products at all studied catalyst compositions in the study of catalytic activity based on Ni, Ni-K, Ni-K-W, Mn, La, Cu and IK-30 supported on CaX, CuO, 80% H-ZSM-5 + 20% Al₂O₃, ZSM-5 + Al₂O₃ and montmorillonite in the oxidative conversion of methane into desired products. The reaction products begin to form at the reaction temperature 600°C. Ni catalysts were the most active among the investigated samples at 700°C leading the transformation of methane to formation of H₂. La-containing catalysts promote the implementation of process mainly toward the formation of C₂-hydrocarbons.

3.2. Activity of the supported low percentage catalysts based on noble metals in the process of partial oxidation of methane

Low-percentage 1% Pt, Ru and Pt-Ru catalysts over carrier 2% Ce/(θ+α)-Al₂O₃ were prepared for study. The catalysts were prepared by sequential supporting of elements on (θ+α)-Al₂O₃ (100-200 μm, S_{sp} = 70.2 m²/g) from aqueous metal salt solutions at first Ce(NO₃)₃ × 6H₂O, then Ru(OH)Cl₃, and H₂PtCl₆ × 6H₂O by capillary impregnation by incipient wetness, followed by heating in air at 600°C for 3 hours. Unreduced samples of catalysts heated in air were tested. The oxidative conversion of methane to hydrogen-containing mixture on the 1% Pt catalyst over carrier with determining the effect of reaction temperature on the methane conversion, selectivity by H₂ and CO at millisecond contact times τ = 0,004 s and V = 9·10⁵ h⁻¹ was investigated. It was determined that with the increase of temperature from 700 to 900°C conversion of CH₄ and selectivity by CO increased from 75 and 85% to 87 and 95%, respectively, and the selectivity by H₂ at all temperatures up to 100%. In the reaction system is not observed the formation of carbon dioxide. Under these conditions, we studied the oxidative conversion of methane to hydrogen-containing mixture on 1% Ru catalyst over carrier c determining the effect of reaction temperature on the methane conversion, selectivity by H₂, CO and CO₂. It was found that with increasing of temperature from 700 to 900°C the conversion of CH₄ is reduced from 44 to 25% and the selectivity by CO and H₂ change insignificantly from 71 to 82 and 87%, respectively. Carbon dioxide was detected in the reaction mixture, and the selectivity of its formation increased with increasing of temperature. Investigation of the influence of process temperature on the activity of bimetallic 1,0% Pt-Ru catalyst over carrier showed that with increasing of reaction temperature the degree of conversion increases, and starting from 800°C carried out sharp increase conversion and selectivity by products. Methane conversion was 98.4% at similar increase in the selectivity by CO to 97.6%. With further increase in temperature to 850°C the methane conversion increased to 98.7% at selectivity by CO up to 98.0%. Methane conversion and selectivity reached

100% after increasing the temperature to 900°C. 100% selectivity by hydrogen is observed from 800 to 900°C.

Thus, it was found that the use of bimetallic catalysts in comparison with monometallic samples on the carrier is the best on the major indicators of oxidative conversion of methane into the desired products with increasing of reaction temperature from 700 to 900°C. In 1992, American scientists have studied the reduced Pt, Pd, and Rh supported catalysts in the reaction of partial oxidation of methane, and showed that the synthesis gas is formed with high selectivity ~ 80% by H₂ and CO at $\tau = 10^{-2} - 10^{-4}$ s in excess of CH₄ at high temperature [5-8]. A detailed analysis of published data on the new process of selective catalytic oxidation of CH₄ in the mixture with insufficient quantity of oxygen indicates that the reaction takes place at high space velocities (up to $10^6 - 10^7$ h⁻¹) in the absence of secondary reactions, i.e. with great performance when receiving a mixture of CO and H₂ at a ratio ideally suitable for the production of methanol, ammonia, and higher molecular weight hydrocarbons (Fischer-Tropsch synthesis), as a reducing mixtures in the industry. Effect of space velocity on the oxidative conversion of CH₄ was investigated on 1,0% Pt-Ru/2% Ce/($\theta + \alpha$)-Al₂O₃ catalyst in the initial reaction mixture CH₄ : O₂ : Ar = 1.6 : 0.8 : 97.6 %, T = 900°C, V = $1 \cdot 10^6 - 6 \cdot 10^5$ h⁻¹. Table 1 shows that 95.0 - 100% conversion of CH₄ and high selectivity (78.1 - 100%) by H₂ are observed with a decrease of space velocity from $1560 \cdot 10^3$ to $630 \cdot 10^3$ h⁻¹. Selectivity by CO increased from 80.0 to 100% at increasing of space velocity of $630 \cdot 10^3$ to $1050 \cdot 10^3$ h⁻¹, reaching 100% and then slowly decreased to 63.4% at $1560 \cdot 10^3$ h⁻¹.

Table 1. Effect of space velocity on the performance of SCO of methane on 1,0% Pt-Ru (2:1)/2%Ce/($\theta + \alpha$)-Al₂O₃ catalyst. Experimental conditions: initial reaction mixture CH₄ : O₂ : Ar = 1,6 : 0,8 : 97,6 %, T = 900°C, V = $1 \cdot 10^6 - 6 \cdot 10^5$ h⁻¹

Space velocity, h ⁻¹	The content of the reaction products at the output, %				X _{CH₄} , %	S _{H₂} , %	S _{CO} , %	H ₂ /CO
	C _{CH₄}	C _{H₂}	C _{CO}	C _{CO₂}				
$1560 \cdot 10^3$	0,07	2,39	0,97	0,01	95,62	78,10	63,39	2,46
$1530 \cdot 10^3$	0,07	2,39	1,08	0,02	95,62	78,10	70,58	2,21
$1500 \cdot 10^3$	0,08	3,04	1,38	0,02	95,0	100	90,78	2,20
$1350 \cdot 10^3$	0,08	3,04	1,42	0,02	95,0	100	93,42	2,14
$1200 \cdot 10^3$	0,07	3,06	1,49	0,02	95,62	100	97,38	2,05
$1050 \cdot 10^3$	0	3,20	1,60	0	100	100	100	2,0
$900 \cdot 10^3$	0	3,20	1,60	0	100	100	100	2,0
$750 \cdot 10^3$	0	2,81	1,32	0,01	100	87,81	82,5	2,12
$660 \cdot 10^3$	0	2,76	1,28	0,01	100	86,25	80,0	2,15
$630 \cdot 10^3$	0	2,72	1,28	0,01	100	85,0	80,0	2,12

With increasing of space velocity from $630 \cdot 10^3$ to $1560 \cdot 10^3$ h⁻¹ CO₂ content in the reaction mixture ranges from 0.01 to 0.02, and H₂/CO ratio - from 2.12 to 2.46. However, conversion of the initial methane, selectivity by H₂ and CO are equal to the maximum 100% value at $1050 \cdot 10^3$ and $900 \cdot 10^3$ h⁻¹. CO₂ is absent in product and the ratio of H₂/CO = 2, i.e. the optimal value of the process of partial oxidation of methane to synthesis gas. It was found experimentally that the space velocity of $1 \cdot 10^6 -$

$9 \cdot 10^5 \text{ h}^{-1}$ is optimal for the partial oxidation of methane into synthesis gas on supported low-percentage Pt-Ru catalyst.

Thus, it was determined that the use of bimetallic 1% Pt-Ru/2% Ce/($\theta + \alpha$)-Al₂O₃ catalysts in comparison with monometallic samples on the carrier is the best on the basic parameters of the process (X_{CH_4} , S_{H_2} , S_{CO} = 98 - 100%) with increasing the reaction temperature from 700 to 900°C, contact time 0.004 s and space velocity $9 \cdot 10^5 \text{ h}^{-1}$.

4. CONCLUSION

Thus, at the study of catalysts with desired catalytic properties based on Ni, Ni-K, Ni-K-W, Mn, La, Cu, IK-30 supported on CaX, CuO, 80% H-ZSM-5+20% Al₂O₃, ZSM-5+Al₂O₃ and montmorillonite, as well as low-percentage Pt-Ru (2:1)/2% Ce/($\theta + \alpha$)-Al₂O₃ catalysts, it was found that C₂-hydrocarbons, hydrogen-containing mixtures and trace amount of propane and propylene detected on all studied catalysts in the reaction products. Study of oxidative conversion of methane on developed catalysts to desired products showed that the H₂ produced from 600°C and higher, for the formation of C₂-hydrocarbons is optimal temperature range of 750-800°C, space velocity 3900 h⁻¹ and the ratio of the main components of the reaction mixture CH₄ : O₂ = 4.0 : 1.0 without dilution of system by inert gas (Ar). We can assume that ethylene is formed not only from the initial methane, but also as a result of subsequent synthesis from C₂H₆ with increasing of temperature. It was determined that initial conversion of methane into hydrogen and hydrogen-containing mixtures is carried out, respectively, on 5,0% Ni/ZSM-5 + Al₂O₃ and 1% Pt-Ru/2% Ce/($\theta + \alpha$)-Al₂O₃ catalysts; and IK-30 and 5% La/CaX catalysts are optimal for the formation of olefins.

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