DEEP PROCESSING OF METHANE OF NATURAL GAS INTO IMPORTANT PRODUCTS OF PETROCHEMICAL SYNTHESIS

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Abstract

Catalytic methods for oxidative conversion of the methane of natural gas into the product of organic synthesis: formaldehyde, ethylene, synthesis-gas, hydrogen, hydrogen-containing fuel mixtures, and catalytic combustion of methane to CO_2 for production of heat were discussed. Content of polyoxide catalysts and optimal conditions for synthesis organic compounds were developed.

Key words: *methane, petrochemical synthesis, catalysts, oxidation, polyoxide catalyst, heteropoly compounds, alkanes*

1. INTRODUCTION

Natural and oil gases is the most important alternative sources of raw materials that could in the future compete with oil because oil reserves on Earth are not unlimited. The problem of rational use of alkanes that are part of natural gas is particularly relevant in countries rich in this kind of raw material. Kazakhstan has significant reserves of oil and gas, which, unfortunately, now mostly burned in a "torch". Space imaging in recent years as well as ground studies suggest that the major oil fields near the shores of the Caspian Sea are just the "margin" of powerful oil deposits, the core of which is in the northern Caspian Sea, where total reserves are estimated very impressive sizes - 3-3.5 billion tons of oil and 2-2.5 trillion m^3 gas [1]. According to experts, the widespread use of gas in areas focused on consumption of petroleum products is an important program of the world economy. Organization of large-scale production of important products based on natural gas during its production could significantly reduce the cost of final products and reduce environmental pollution. Regulations on environmental protection in the future will dramatically limit the combustion of gas in "torches." In recent geological exploration for oil and gas in some countries does not begin before develop a more attractive plan for the use of gas overlying in a new oil reservoir than incineration or re-pumping into the reservoir. The volume of ineffectively used natural gas, i.e. gas which is burned in "torches", dumped into the atmosphere or re-injected into the reservoir in 1996, for example, was 439 billion m^3 which is equivalent to the annual production of 222 million tons of synthetic oil. Thus, studies on the development of catalysts and methods for producing of useful products from alkanes for developing organic synthesis industry of Kazakhstan are relevant both from an environmental and economic points of view. Researchers in many countries developed the catalytic oxidative methods for processing of the alkanes of natural gas into products of industrial organic synthesis [2-8]. Much attention is paid to the processes of oxidative conversion of saturated hydrocarbons, particularly methane, also in Kazakhstan [9-13]. On the example of supported catalysts based on molybdenum

polyoxometalates has been established formation of CH_2O, CH_3OH, C_2H_6, C_2H_4, C_2H_2, C_3H_6, C_6H_6, H_2, in oxidative conversion of CH_4. Their ratio is determined by the temperature of reaction. It was installed the sequence and discreteness of formation of products with increasing of temperature: CH_2O (600-700°C), C_2H_6 (700-850°C), C_2H_4 (750-900°C), C_2H_2 (850-950°C), C_3H_6, C_6H_6, H_2 (higher than 850°C). The method of catalytic oxidation of CH_4 to CO_2 in order to generate heat is a promising way for utilization of mine, vent and flared CH_4. Catalytic combustion is fundamentally different from thermal combustion, as occurs on the surface of solid catalysts without formation of flame selectively up to CO_2 at much lower temperatures which prevents the formation of NO_x and other harmful substances [14-16]. The production of synthesis gas by direct oxidation of CH_4 in oxygen deficiency and short contact time is a new approach to finding the ways to activate and involve methane in the new chemical reactions. A mixture of $CO+H_2$ can be used for various syntheses: production of methanol, high-molecular hydrocarbons (Fischer-Tropsch synthesis) [17]. Hydrogen, which is formed in the oxidative conversion of alkanes, has an independent interest as a commercial product. Much attention is paid to the synthesis of hydrogen and hydrogen-containing mixtures for the production of hydrogen fuels. Even 20 years ago it seemed that this scientific imagination which will be implemented in the distant future. But the distant future comes quickly: about thousand companies in the world dealing with this problem seeing in hydrogen energy good alternative to oil and gas. In this report we present results on the oxidative conversion of methane of natural gas in various products.

2. EXPERIMENTAL

The studies were conducted in flow-type installation at atmospheric pressure in a tubular quartz reactor with a fixed bed reactor. The gas mixture containing hydrocarbon and O_2, diluted with an inert gas Ar in the presence or absence of water vapor was used for oxidation. Ratio of the components of reaction mixture was varied widely. Catalysts were prepared by incipient wetness impregnation of the different carriers, followed by drying at 20-250°C for 3 hours in air and calcination at 500°C for 2 hours. The concentration of the active phase on the carrier varied from 0.1 to 20.0%. An Agilent 6890N gas chromatograph equipped with a flame ionization detector and thermal conductivity detector was employed for the on-line analysis of the products. Physical-chemical properties of catalysts have been investigated by complex methods: XRD, IRS, TEM, TPD, TPR, TPO methods.

3. RESULTS AND DISCUSSION

3.1. The synthesis of formaldehyde by oxidation of methane

The problem of selective production of formaldehyde from methane is less studied, although in recent years have seen growing interest to this reaction in Western Europe, America and China. From the standpoint of availability and low cost of raw materials as well as the simplicity of technology to obtain of formaldehyde by direct oxidation of natural gas by oxygen is preferred to relatively complex and multi-step synthesis of CH_2O through synthesis-gas and CH_3OH, which is evident from the scheme, although attempts to implement this route are encountered with problem of low selectivity due to high strength of chemical bonds in CH_4 molecule:

$CH_4 \rightarrow$ synthesis-gas $\rightarrow CH_3OH \rightarrow CH_2O$

In addition, at high temperatures required for the activation of CH_4 its partial oxidation products are more active and more easily undergo to further deep oxidation than CH_4. Stop the process at an intermediate stage is the actual problem, whose solution will solve the problem of selective obtaining of CH_2O from CH_4. At present maximum yields of CH_2O not exceed 2-3% per pass.

Catalysts based on 12 series Mo heteropoly compounds (HPC) supported on different carriers were investigated in the process of partial oxidation of methane to formaldehyde (POMF) in different conditions. The highest yields of CH_2O were obtained on low-percentage catalysts (1-2.3%). The formation of structures of interaction "fragment of HPA-carrier" is due to the finely dispersed distribution of heteropoly acid (HPA) on carrier in the low-percentage catalysts (samples are X-ray amorphous). This can be seen 1) by the absence of the DTA curves of exo-effect at 360°C corresponding to decay of individual HPA, 2) by coincidence of a.b. of low-percentage HPA and carrier at shift of characteristics on 10-30cm^{-1} to higher frequencies absorbance area of IR spectra, and 3) by the shift of TPR peaks in low-percentage samples to higher temperature area due to increase of bond strength of structural reactive oxygen [18,19].

Bidisperse of active HPC is characteristic for high-percentage catalysts (>10% HPA) which confirmed the presence of crystallized HPC (IRS – a.b. 780, 865, 915, 960 cm^{-1}) together with the structure of interaction "fragment of HPA-carrier". It follows that the activity in POMF determined by the presence on the surface of the HPA, which has acidic properties and exists in the pH range 1-4. It was found that the yield of CH_2O is correlated with the content of acid centers in catalyst with strength 7.4-8.12 eV and varies symbatically with variation of the 1 and 2 forms of oxygen determined by TPR curves of hydrogen [20,21]. These data indicate that the nature of carrier has a decisive importance for obtaining of highly active and selective catalysts. Catalysts supported on Si-containing carriers were the best. This is due to the large number of hydroxyl groups on their surface causing the high proton acidity as well as the presence of Si both in the carrier and active phase, which determines the "crosslinking" at interaction of HPA with surface OH groups of carrier. This follows from the data about decrease of Si-OH groups' concentration at supporting of HPA. Thus there is a distortion of HPA structure at interaction with carrier. It is assumed that the sorption of HPA on hydroxylated surface should be a "multipoint", that is strong enough.

It was shown that the presence of water vapor in mixture greatly increases the yield (Y) of CH_2O and reduces the optimum temperature. The presence of H_2O in reaction mixture stabilizes the structure of HPC catalyst resulting in a "development" of its activity after steam-air treatment between experiments for 20 minutes at 250°C and increasing the duration of operation of catalyst in presence of water vapor, in contrast to the similar composition of oxide catalyst [22,23]. Studies of the role of concentration of water vapor in reaction mixture allowed to develop optimal conditions for obtaining the products of POMF. By using the method of isotope exchange was found that water vapor is not just a diluent in the reaction of POMF, but act as a mild oxidant and prevent coke formation [23].

The test of POMF process in a cascade of two series-connected flow reactors showed that on 2.3% $H_4SiMo_{12}O_{40}$/AlSi catalyst at a ratio of $CH_4 : H_2O : O_2 = 1 : 0{,}53 : 0{,}45$ was obtained up to 6-8% CH_2O in a single pass with capacity 10-14 kg CH_2O/kg HPC·h at 60-85% selectivity by CH_2O. The catalyst was stable for 120 h at periodic regeneration of catalyst in water vapor-air mixture at 650°C which is confirmed by the IRS and ESDR methods, Fig. 1. The presence of water vapor is a stabilizing factor, as it is known that a massive HPA decomposes at 360°C. Method for separating of CH_2O from gas phase was developed. There has been CH_2O concentration resulting from the partial oxidation reaction, as well as its transfer into a solid white precipitate - urotropine.

The high stability of low-percentage catalysts based on HPC due to the fact that surface of carrier is covered with HPA, or dehydrated, or anhydride-like form of its (close to the monolayer, fine dispersed coating). Massive HPA blocking the carrier is formed in addition on the surface in high-percentage catalysts. Probably, the samples with high content of HPA are destroyed with the formation of oxides on the surface at high temperature treatment under the experimental conditions, as in this case the stability of the catalyst depends on the properties of massive, thermally unstable HPA. Low-percentage catalysts, as shown by IRS, DTA, ESDR, TPR methods, and emission analysis, are

thermally stable due to the interaction of HPA-carrier. Regeneration in the steam-air mixture returns catalyst to its original state. Thus, the activity of low-percentage catalysts at high temperatures under the reaction conditions caused by:

- the acidity of catalysts (HPA and carrier). In low-percentage samples even after a possible decomposition of HPA into components due to the high acidity of carrier is probably re-synthesis of HPA (it is known that not only oxide phase, but HPA are formed on the surface at supporting of MoO_3 on silica gel as pH of carrier is sufficient for synthesis of HPA on the sample surface), especially in processing by water vapor. High-percentage catalysts are difficult to regenerate because decomposed HPA, located on the surface, forms a significant amount of oxides. The acidity of carrier for the regeneration of HPA in water vapor, apparently, is not sufficient, although on the surface are likely to be small amounts of HPC but the content of decomposition products will prevail. Hence it is clear that the stabilizing influence of carrier has a significant effect only on low-percentage samples;
- the preservation of structural fragments of HPA in steam-air treatment up to 600-650^{o}C, as can be judged by the constancy of the bands in IR and ESDR spectra;
- the finely dispersed distribution of HPA on carrier, which facilitates on the one hand, the interaction of HPA-carrier, on the other hand - the formation of small crystallites of HPA, thermal decomposition of it is absent in DTA regime up to 600^{o}C;
- the finely dispersed distribution of HPA on carrier up to 2.3-10% supporting that provides hardening of connection of structural fragments of HPA (shift of TPR peaks to the high area compared to the TPR of pure HPA), which apparently causes thermal stability of catalysts during prolonged high-temperature operation.

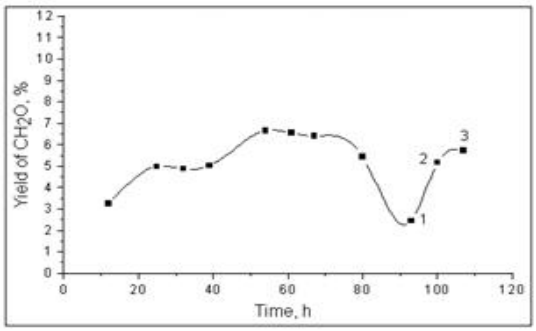


Fig.1. Effect of duration of experiment on oxidative conversion of CH_4 to CH_2O on 2.3% $H_4SiMo_{12}O_{40}$/AlSi in mixtures in the presence of water vapor. CH_4 – 39.0%, O_2 – 17.6%, CH_4 : H_2O : O_2 = 1 : 0.53 : 0.45. W = 8000 h^{-1}. T = 650^{o}C, 1-3 - yield of CH_2O after regeneration in the vapor-air mixture: 1 – 200^{o}C, 2 – 400^{o}C, 3 – 650^{o}C.

3.2. Oxidative condensation of methane to C_2 hydrocarbons

The reaction of oxidative condensation of methane (OCM) to C_2-hydrocarbons (C_2-HC) is the most rapidly developing among the various pathways of methane oxidation. Publications on this problem are much higher than the publication of other possible pathways of partial oxidation [24,25]. The mechanisms of this process are proposed [25], but the processes that are embedded in the production do not exist yet. The maximum yield and selectivity of C_2-HC formation from CH_4 ($Y_{C2\text{-}HC}$ = 9.6% and

10.0%, S_{C2-HC} = 80.0% and 57.6 % S_{C2H4} = 51.5% and 39.2%, respectively) were achieved on the 5% and 0.5% $H_4SiW_{12}O_{40}$/AlSi catalysts. C_2H_4/C_2H_6 ratio in the products increases sharply toward the formation of C_2H_4 for each of the investigated catalysts with increasing of reaction temperature from 600 to 900°C and the transition from high-percentage to low-percentage catalysts. In some cases it was possible to obtain only C_2H_4 from CH_4 (at T = 800-900°C) and at T = 600°C - only C_2H_6.

The most active catalysts show the highest selectivity for C_2-hydrocarbons: 5% $H_4SiW_{12}O_{40}$/AlSi (S_{C2H4} = 51.5%, S_{C2-HC} = 80.0%) and 15% $H_3PW_{12}O_{40}$/AlSi (S_{C2H4} = 39.2%, S_{C2-HC} = 60.2%). Catalysts based on W-HPC with P as central atom in all cases are similar in activity, but less selective in OCM reaction to $\sum C_2$-hydrocarbons compared to HPC with Si as central atom. The yield of C_2-hydrocarbons on Mo-containing catalysts are lower than on the W-containing catalysts (2.3% sample – 7.8%, 5.0% sample – 9.3%, 10.0% sample – 9.7%, T = 750-900°C). Carriers form series with respect to increasing influence on Y_{C2H4} and S_{C2H4} at 800°C: S_{C2H4}, %: SiO_2 KSK-2,5 (23,3) < zeocare-2 (37,1) < zeolite NaA (37,2) < zeolite CaX (38,9) < SiO_2 KSM-5 (43,4) < AlSi (49,0) < periclase MgO (57,9) < pentasile CaAZ (58,5). Elements of the I and II groups of the Periodic System (Na, Mg, Cd, Cs) are optimal substituents for the proton in HPC of synthesis of ethylene from methane.

The influence of reaction mixture on the formation of C_2-HC was studied. The yield and selectivity of formation of C_2H_4 increases with the ratio of CH_4 : O_2 from 1 : 1 to (1.5-30) : 1. The composition of mixture (mol: CH_4 – 0.0018-0.0031, O_2 – 0.0013, inert gas – 0.008-0.004) is optimal for synthesis of C_2H_4 from CH_4. Introduction of water vapor (CH_4 : O_2 = 1 : 0,21, mol) in the reaction mixture has a positive effect on reaction. The results show that the OCM process can be optimized through a rigorous selection of process parameters of reaction and improvement the composition of supported catalysts. The optimal reaction conditions by varying the composition of HPC, the nature of carrier, the ratio of components of reaction mixture and reaction temperature were established. [PW_{12}]-HPA at replacement of proton to the Na, Cs as well as [SiW_{12}]-HPA at replacement of proton to the Na, Mg, Cd possess the highest activity at 750-850°C and when using the Si-containing oxides as carrier, such as pentasile, SiO_2, or AlSi at supporting of 0,5-15% HPC on carrier and carrying out the experiment in the reaction mixtures: CH_4 – 0.0018-0.0031, O_2 – 0.001, mol, CH_4 : H_2O = 1 : 0,21, Ar is residual, τ = 0,38-0,46 c. Implementation of OCM process on polyoxide systems in installations with one or two reactors (Table 1), as well as on polyoxide catalysts of the complex composition allowed to increase the conversion of CH_4 to 46.0%, the yield of C_2H_4 - up to 18.5% at $\sum Y_{C2-HC}$ to 22,0% [26-29].

Preliminary mathematical analysis of the kinetic results of reaction was conducted with a view to recommending the optimal design of an industrial reactor for the developed OCM process and optimal conditions for the realization of the industrial process on catalysts. Was offered the presumed optimal model of the industrial reactor. Analysis of results showed that the use of industrial-scale multi-shelf (5-7 layers) adiabatic reactor is the best. Productivity of the process according to preliminary estimates may be up to 3.2-3.4 tons of ethylene per day from 1 ton of catalyst.

3.3. Catalytic combustion of methane to CO_2

Development of catalysts for the complete combustion of CH_4 aimed to improve the thermal stability of oxide contacts by modifying the carrier or by the synthesis of perovskites have special relevance. The use of additions of elements of the II (Ba, Sr) and III (Ce, La) groups to obtain of highly dispersed mixed oxides of perovskite-type ABO_3 or solid solutions of oxides was the basic to improve of supported Mn and Ni-Cu-Cr catalysts. Regularities of formation and changes in the structure, morphology of polyoxide catalysts of complete combustion using physical and chemical methods have been studied. On the catalysts were observed 90-100% oxidation of CH_4 at 700-800°C to CO_2, which is little changed at varying the concentration of CH_4 (0.2-4.0%) and O_2 (2-20%) at a space velocity of $10 \cdot 10^3$ h^{-1}. Comparison of thermal stability of selected contacts as they heating up to 900-1000°C

showed that both catalysts does not change its activity at 700°C, especially at promotion by Pt and Pd. The specific rate of oxidation of CH_4 on Mn-REE-AEE remains constant at 1100-1200°C in contrast to the Ni-Cu-Cr catalyst, for which it is reduced on 20% at 700°C.

Table 1. The yield, selectivity and productivity of OCM by C_2-HC on complex oxide systems in installations with one or two reactors.

Catalyst	T,°C	Yield, %		Selectivity,%		gC_2H_4/m^3CH_4		C_2H_4/C_2H_6	Note (reactor)
		C_2H_6	C_2H_4	C_2H_6	C_2H_4	on transmitted CH_4	on converted CH_4		
1	750	6.0	11.6	20.1	38.9	145.0	486.7	1.9	R-1
	800	3.5	18.5	11.0	58.5	231.3	731.8	4.5	R-1
	850	1.9	16.3	4.8	41.0	203.8	514.5	8.0	R-1
2	800	1.9	13.9	5.9	43.4	173.8	543.0	7.3	R-1
	850	0	12.9	0	34.7	161.3	434.6	100%	R-1
3	700	4.6	6.6	34.5	49.6	82.5	620.3	1.4	R-1
	750	3.3	10.5	17.0	54.1	131.3	676.5	3.2	R-1
	800	1.6	14.4	4.3	38.1	180.0	486.5	9.0	R-1
4	800	2.4	13.5	10.3	57.9	168.8	724.3	5.6	R-1
5	800	3.7	17.8	8.6	41.4	222.5	517.0	4.8	R-1
	800	3.0	15.7	8.6	45.2	196.3	565.0	5.2	R-2
						∑419.8			

In the synthesis of both catalysts after heating at 600°C on the support surface by XRD and EM methods was reported the presence of CeO_2 crystallites and X-ray amorphous clusters (d = 20-100Å) of transition metal oxides Mn_2O_3, CuO, NiO, and solid solutions of metal oxides CuO (NiO), perovskites based on manganese with REE. The presence of super-stoichiometric oxygen in catalyst dissolved in the structure of mixed oxides and released during heating in Ar at form of weakly bound oxygen (O_2^-, O^-) at low temperatures (327-527°C) with an activation energy of desorption of 88-95 kJ/mol was found. Decomposition of oxides takes place at 700-727°C with E_{des} = 98 for Mn_2O_3 to Mn_3O_4; Mn_3O_4 and perovskites to MnO - 115-142, for CuO (NiO) - Cu_2O - 128, NiO to Ni_2O - 120 and mixture of CuO (NiO) -140 - 144 kJ/mol.

The interaction of H_2 in TPR experiments with these oxygen structures proceeds easily, starting from 200 up to 400°C. Adsorption of O_2 re-occurs at low temperatures (52°C) on the catalysts after the decomposition of oxides both on Ni-Cu-Cr, and Mn-REE-AEE/Ce/θ-Al_2O_3. This indicates on high reactivity of adsorbed O_2^-, O^- and lattice oxygen of dispersed oxides and their mixtures and their ability to easy re-activation.

According to XRD and EM at temperatures above 1000°C in air phase transformations occur in the catalysts: metal oxides react with aluminum oxide. In the case of Ni-Cu-Cr contact aluminates $MeAl_2O_4$ type with d = 200-1000Å formed, the surface is drastically reduced to 2-5 m^2/g. In TPD

spectra of such catalyst weakly adsorbed oxygen is absent, and H_2 begins to oxidize only at high temperatures (T = 800°C) due to decomposition of Ni and Cu aluminates. Adsorption of O_2 on Ni-Cu-Cr catalyst (heated at 1200°C) in TPO experiments occurs in the smaller quantities and at higher temperature than on standard catalyst heated at 600°C. These factors reduce the degree of oxidation of CH_4 up to 60% at 700°C and the specific reaction rate.

According to TPD, XRD and EM the content of oxide Mn_2O_3 and solid solutions with rare earth elements and alkaline earth elements on the catalyst surface Mn-REE-AEE/2%Ce/θ-Al_2O_3 is significantly reduced, as well as the adsorption of oxygen on it with T_{des} from 300 to 600°C after heating at high temperature (1200°C). This is not due to volatilization of manganese oxide catalyst, but a result of interaction of Mn_2O_3, oxides of REE, oxides of AEE with θ-Al_2O_3 to form a first perovskites, and then the hexa-aluminates of manganese. The processes occurring during heating of Mn-REE-AEE catalysts have positive character: to 1000°C the REE interacting with θ-Al_2O_3 to Ce(La)Al_2O_3, prevent the formation the aluminates of $MnAlO_4$. There is additional dispersion of clusters of Mn_2O_3 and formation of Mn perovskite with REE and AEE at 600-900°C. Hexa-aluminates of $MnLaAl_{11}O_{19}$, whose content increases with heating and promotion by Pt and Pd, are formed in the catalyst along with clusters of Mn_2O_3 and perovskites at 1100-1200°C. All three types of formed manganese compounds are active in the oxidation of CH_4 to CO_2. This is an obvious reason for stable activity of Mn catalyst at heating to 1100 1200°C. According to TPD of oxygen in Mn_2O_3 and solid solutions of Mn-REE-AEE has low activation energy of desorption (80.2-98.2 kJ/mol) and easily reacts with reducing agents. Heating the mixed Mn catalysts at 900°C reduces the activation energy of break processes of the M-O bond on 10-20 kJ/mol. The concentration of oxygen vacancies increased in this case in bulk Mn perovskites $LaMnO_3$, which contributes to increase of activity in oxidation reaction.

Thus, significant contribution to activity make generated hexa-aluminates of $LaMnAl_{11}O_{19}$ after high-temperature (> 1100°C) processing of Mn-REE-AEE catalyst on 2%Ce/θ-Al_2O_3 due to the ease of oxidation-reduction reactions $Mn^{3+} \leftrightarrow Mn^{2+}{}_{octa}$ and low binding energy of oxygen detected by TPD and TPR data. High stability in the conversion of CH_4 to CO_2 at high-temperature treatment in air for 100 h is explained by formation of hexa-aluminates. The results indicate on real possibility of practical use of Mn-REE-AEE catalyst on 2% Ce/θ-Al_2O_3 thermo stable up to 1200°C for utilization of poor CH_4 mixtures in catalytic heat generators. The developed catalyst is not conceding in activity and thermal stability the known analogues, in which are used perovskites and hexa-aluminates of manganese. This catalyst has passed pilot tests in oxidation of propane-butane in catalytic heat generator at the Research Institute of Agriculture of MES RK, used for heating of greenhouses and additional fertilizing of plants by formed carbon dioxide and recommended to implementation [16,30].

3.4. Production of synthesis gas by direct oxidation of methane

Production of synthesis gas by direct oxidation of CH_4 at deficiency of oxygen and short contact time is a new approach to finding the ways of activating and involve of methane to the new chemical reactions. We have investigated the partial oxidation of CH_4 to synthesis gas on 9% Ni-Cu_3-$Cr_{0,1}$ oxide catalyst supported on 2% Ce/(θ+α)-Al_2O_3, reduced in mixture of H_2 + Ar (H_2 : Ar = 40 : 60) at 900°C for 1 hour, as well as catalysts promoted by Pt, Ru, Pd. Experiments were carried out in quartz micro reactor by passing the initial reaction mixture CH_4 : O_2 : Ar = (1.2 ÷ 1.6) : (0.7 ÷ 0.8) : (97 ÷ 98) (vol.%), varying the temperature from 800 to 950°C, the ratio of CH_4 : O_2 from 1.38 to 4.0, the contact time (τ) from 2.0 to 3.27 ms, and space velocity from 1.8 to 1.17 10^6 h^{-1} [31-35].

The best results were obtained at stoichiometric ratio CH_4 : O_2 = 2 in the whole range of space velocities: the degree of conversion of methane - 77 ÷ 100%, selectivity by CO and H_2 is close to

100%. In the interval $\tau = 2 \div 2.49$ ms was not observed formation of any products, except for H_2 and CO in the ratio $H_2 : CO = 2$ (the ideal ratio for methanol synthesis).

In Fig. 2 presents the results of tests of the reduced Ni-Cu-Cr catalyst for 180 minutes of experiment at ratio $CH_4 : O_2 = 2.79$, $\tau = 2$ ms. It is seen that the conversion of methane into a mixture of CO and H_2 with high selectivity of products that are stable for 3 hours, occurs on the catalyst. Ratio of H_2/CO in the resulting mixture was $1.85 \div 1.93$. By reducing the space velocity from $1.44 \cdot 10^6$ h^{-1} to $1.02 \cdot 10^6$ h^{-1} (τ from 2.49 to 3.5 ms) the degree of conversion of CH_4 increased to 97-100%, while maintaining high selectivity for CO and H_2 (S_{CO} = 96.6-100% S_{H2} = 79.3-99.7%) and the ratio of H_2/SO in resulting mixture ~ 2.0. Further reduction of space velocity up to $4.5 \cdot 10^5$ h^{-1} resulted in the appearance in resulting mixture of 0.03% CO_2 and reduction selectivity by H_2 to 75.9%. Low percentage Pd-Co-catalyst also conducted complete oxidation of CH_4 to CO_2 with low conversion of CH_4. Pt-Ru catalysts supported on 2% Ce $(\theta+\alpha)$-Al_2O_3, provided high conversion of methane to synthesis gas with high selectivity by CO and H_2 (~ 96%). A small amount of CO_2 (S_{CO2} = 3.85%) was observed in the products. H_2/CO ratio in the synthesis gas is equal 2, as in the case of Ni-Cu-Cr/2% Ce/$(\theta+\alpha)$-Al_2O_3 [36].

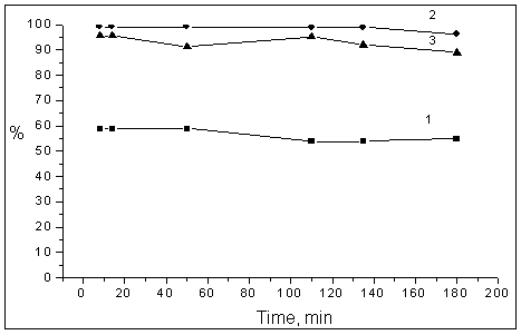


Fig.2. Changing the methane conversion, selectivity by CO and hydrogen on the reduced 9% Ni-Cu-Cr/2% Ce/$(\theta+\alpha)$-Al_2O_3 catalyst during the experiment. $\tau = 2$ ms, $CH_4 : O_2 = 2.79$, T = 900°C. 1 - conversion of CH_4, 2 - selectivity by CO, 3 - selectivity by H_2.

Using of X-ray diffraction, electron microscopy with electron micro diffraction, and BET to study the structure and morphology of Ni-Cu-Cr catalyst showed that after the initial process of oxidation in air, then reduction in H_2 at 900°C and in reaction process $CH_4 + 1/2O_2 \rightarrow CO + 2H_2$ catalyst is a mixture of dispersed nanoparticles of Cu, Ni and Ce (3-20 nm) in the reduced and partially oxidized state, surrounded by larger particles of aluminates and chromates (20-30 nm) on a carrier $(\theta+\alpha)$-Al_2O_3 (S = 43-49 m^2/g), Fig. 3 [36-37].

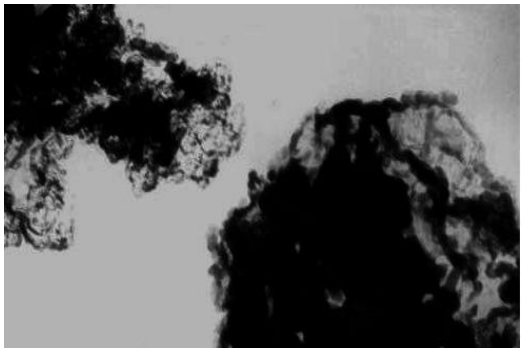


Fig.3. Electron-microscopic photo of 9% NiCuCr/2% Ce/(θ+α)-Al_2O_3 after 56 h in a reaction of partial oxidation of methane to synthesis gas.

3.5. Production of hydrogen-containing fuel mixtures

Rapid reduction of oil and gas resources forces the humanity to engage seriously by search of environmentally clean energy sources. Experts believe that hydrogen will save the world - almost inexhaustible renewable source of energy. It should be noted that hydrogen by power consumption exceeds all compounds that can serve as a fuel: 2.6 times - natural gas, 3.3 times - liquid petroleum hydrocarbons, 5 times - coal, 6.6 times - methanol, 8.5 times - cellulose, etc. [38]. Hydrogen is the only environmentally clean fuel and reagent, product of oxidation of which is the water vapor or liquid water. There was a high efficiency of introduction of hydrogen as an addition to motor fuels. It was shown that the addition of 5-15 wt. % of hydrogen from flow of gasoline reduces the concentration of CO, NO_x and hydrocarbons in exhaust gases of vehicles, and reduces fuel consumption by 20-30%. This increases the efficiency of fuel combustion and cleanliness of exhaust gases of vehicles and industrial production by CO, NO_x, C_mH_n which is important. Air pollution of cities with a large number of mobile and stationary sources the emissions of harmful substances is a key factor in negative impacts on the natural environment of the city. Annually into the air, for example, Almaty released about 180 thousand tons of pollutants, over 80% of which are motor vehicle emissions. Their number has increased over the past decade to 250 thousand units. Almaty remains among the most environmentally unfriendly cities of the Republic of Kazakhstan.

The influence of some technological parameters on the yield and selectivity of formation of products for selection of optimum conditions of synthesis of hydrogen from methane was studied. Data on the effect of the composition of active component are shown in Fig. 4. It was shown that samples of $(NH_4)_4NiMo_6O_{24}$ and $Mg_2SiMo_{12}O_{40}$ exhibit the best performance. Varying the conditions of oxidative dehydrogenation of methane on the catalysts from HPC supported on aluminosilicate has allowed to reveal reaction parameters that provide maximum yields of H_2 in mixture with C_2-hydrocarbons: τ = 0.45-0.9 s, T = 800 900°C at the content of O_2 with respect to CH_4 43-10% vol. and content of minimum amount of water vapor in the mixture. Catalysts in the synthesis of H_2 on the effectiveness form the following series: [$BiSiMo_{12}$] (Y = 2.5%, S = 44%) < [$ZnSiMo_{12}$] (Y = 12.3%, S = 43.6%) < [$MgSiMo_{12}$] (Y = 19.4%, S = 61%) < [NH_4NiMo_6] (Y = 56.9%, S = 84.8%).

Development of supporting technology of polyoxy-complex compounds of Mo and W on porous blocks from cordierite was carried out for the oxidative conversion of CH_4 of natural gas into H_2-containing mixtures. As HPC were used $Mg_2SiMo_{12}O_{40}$, $Na_5PV_6W_5O$, and $(NH_4)_4NiMo_6O_{24}$. From the presented results of the oxidative conversion of CH_4 on the effect of supporting method by varying the secondary carrier, binder, and protective layer of HPC at 600-900°C and the ratio of CH_4 : O_2 = 7 : 3, W = 3200 h^{-1} in the presence of water vapor can be seen that the catalyst prepared from

$(NH_4)_4NiMo_6O_{24}$ has optimal properties. Under optimal conditions (900°C) yield of H_2 from CH_4 reaches 34.3% vol. per CH_4, or 11.5% per total flow of components.

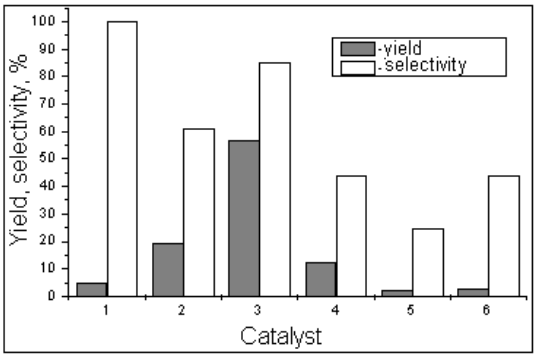


Fig.4. Effect of the composition of 10% Mo-containing catalysts supported on aluminosilicate on the yield and selectivity by hydrogen. W = 4000 h^{-1}, τ = 0,9 s, CH_4 : O_2 : Ar = 70 : 30 : 100, vol. 1 – $Fe_2Mo_6O_x$, 2 - $MgSiMo_{12}O_x$, 3 - $NH_4NiMo_6O_{24}$, 4 - $ZnSiMo_{12}O_{40}$, 5 – $Na_6PV_3Mo_9O_{40}$, 6 - $BiSiMo_{12}O_x$.

As stated earlier, obtaining of 19-57% H_2 is possible on the salts of Mo-containing acid. Prolonged tests for 100-120 hours demonstrated that the catalyst works steadily with a slight decrease in activity by about 10%. Enlarged tests the effectiveness of granulated catalysts in the synthesis of H_2 from CH_4 (catalyst volume – 15.0 cm^3, in contrast to previously studied (1.5 cm^3)) as well as on block carriers from cordierite (volume of the block – 40.5 cm^3) were conducted. Previously have been tested block carriers with volume 3.7 cm^3. The increase in the volume of granulated catalyst, while maintaining the other process parameters decreased yield of hydrogen to 50.3% (56.9% at catalyst volume 1.5 cm^3). Studying the process of oxidative conversion of CH_4 into H_2-containing mixtures on the W-HPC of different composition supported on granulated carrier containing Al and Si oxides was conducted in a series of experiments, Table 2.

Table 2. Oxidative conversion of CH_4 to H_2 on the W-containing catalysts supported on granulated aluminosilicate. W = 8000 h^{-1}, T = 850°C, τ = 0,45 s, CH_4 : O_2: Ar = 70 : 30 : 100, vol.

Catalyst	Yield of hydrogen,%
$Ni_x[SiW_{11}Ni]$	68.7
$Ni_x[SiW_{11}Cr]$	63.1
$K_x[SiW_{11}Cr]$	71.4
$Na_x[SiW_{11}Fe]$	14.3
$Na_x[PW_{11}Fe]$	34.2
$Ba_x[PW_{11}Ni]$	80.8

The results indicate that there are reserves to increase the yield of H_2 for granulated catalysts. The catalyst containing $[Ba_xPW_{11}Ni]$ in the active phase has optimal properties. The yield of H_2 is 80.8% [39-41].

4. CONCLUSION

Due to the projected decrease in oil reserves and increases the importance of natural gas the interest to its conversion increases. The coming reorientation in the source of raw materials is inevitable, so prepare for it - this is a serious strategic problem. Since the 80s of the XX century the chemists are working intensively on the processes of "C1 chemistry." Attention to this problem to enable a smooth transition from the generally accepted technologies for producing of fuels and organic compounds from oil to new technology for production of the same products from the raw gas is also paid in Kazakhstan. The article deals with various areas of oxidative conversion of methane of natural gas to the strategically important products of organic synthesis.

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