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Selective Polyoxide Catalysts for Synthesis of Ethylene from Natural Gas

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Processing of the methane of natural gas into important hydrocarbons, oxygen-containing products and motor fuels has become one of the major problems of chemistry. The degree of chemical processing of natural gas in valuable products remains at a low level, and a significant portion of associated petroleum gas is burned in flares in the fields. This leads to an irreparable loss of valuable raw materials and generates complex environmental problems in the mining regions. Oxidative condensation of methane, steam and steam-oxygen conversion, dry reforming and tri-reforming of methane attract a great attention in recent years. Catalysts based on Si-W heteropoly compounds supported on carriers were investigated in oxidative condensation of methane to ethylene. Determination of the effect of reaction parameters, the nature of catalyst on composition and distribution of products were carried out. Supporting of Si-W heteropoly compounds on aluminosilicate does not destroy the Keggin molecular structure and increases its thermal stability. Thus, effective catalysts for the production of ethylene from methane have been developed.

1. Introduction

Natural gas is the most important alternative source for the production of valuable organic products. Unfortunately, at present natural gas is mainly burned in "torches". This leads to an irreparable loss of valuable raw materials and generates complex environmental problems. Natural gas can be considered as an alternative source to obtain synthesis-gas by dry reforming (Siang et al., 2017) and partial oxidation of CH_4 (Ricca et al., 2016), olefins (Godini et al., 2014). Olefins can also be obtained from biogas (Penteado et al., 2017). Prospects for the development of gas processing industry are associated with the creation and implementation of new catalytic environmentally friendly technologies for the production of olefins, on the basis of which the production of polymers, alcohols, and motor fuel is based. The oxidative coupling of CH_4 (OCM) to C_2H_6 or C_2H_4 is a reaction, which has received a lot of attention since the work of Keller and Bhasin (Aseem et al., 2018). However, the yields of C_2-hydrocarbons were small. The highest yield to date is 20 - 26 % (Arndt et al., 2012). Oxides of alkaline earth metals, transition metals and rare earth oxides are the most studied catalysts. The results of long studies have suggested that a high-performance catalyst should consist of a strongly basic oxide (for example, Mg, La) with an additive that promotes both selectivity (for example, Cs, Na, Sr, Ba) and catalyst activity (for example, Mn, W, Cl). Rare earth oxides are more active in a number of cases than basic oxides and allow the production of C_2-hydrocarbons at lower temperatures (Elkins et al., 2016). Catalysts containing Cs, Sr, Ba, Li, Mn, Ca supported on MgO, La_2O_3, Al_2O_3, CaO were studied. In recent years, these catalysts have been compared to Na_2WO_4-Mn/SiO_2, which is considered the most promising catalyst for OCM (Sarsani et al., 2017). Layered loading of catalysts with different catalytic properties in a fixed-bed reactor was investigated. It was shown that a layered sample containing a more active Ag-Mn-Na_2WO_4/SiO_2 catalyst, loaded before a more selective Ce-Mn-Na_2WO_4/SiO_2 sample, increased the overall selectivity and lowered the reaction temperature compared to the Mn-Na_2WO_4/SiO_2 catalyst (Liang et al., 2018). In recent years, new promising catalysts based

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on heteropoly compounds (HPC) have also appeared (Tungatarova et al., 2015). A deeper study of such catalysts is necessary. The increasing need for industry in C_2H_4 make the OCM process especially attractive. Additional opportunities are opened at embedding the process in the technological chain of production of valuable products from natural gas.

2. Experimental

Experiments were carried out in flow type system with remove of products from cooling zone. Tubular quartz reactor with fixed bed of catalysts was used for investigation. The catalysts were prepared by impregnation of granulated carriers. Catalytic activity of supported catalysts prepared with using of Mo and W HPA and HPC was investigated in OCM process. Tests were realized in reaction mixture, containing CH_4, O_2, inert gas with or without water vapor at the temperature of reaction 600 – 900 °C, contact time (τ) $\leq$ 0.5 s, and atmospheric pressure. The catalysts were prepared by impregnation of different carriers (aluminosilicate, alumina, cordierite, active carbon, zeolites, clinoptilolite, etc.) by HPC solutions. The concentration of active component is varied from 1 to 20 %. The contact time and relationship of components are varied widely. XRD and thermo-programmed reduction (TPR) were used for physical-chemical investigation.

3. Results and Discussion

The reaction of OCM to C_2-hydrocarbons is the most rapidly developing among the various pathways of CH_4 oxidation. Publications on this problem are much higher than the publication of other possible pathways of partial oxidation. The mechanisms of this process are proposed, 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 %, $S_{C2\text{-}HC}$ = 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 %, $S_{C2\text{-}HC}$ = 80.0 %) and 15 % $H_3PW_{12}O_{40}$/AlSi (S_{C2H4} = 39.2 %, $S_{C2\text{-}HC}$ = 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 ΣC_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).

Effect of the nature of carrier containing of Al, Si, Mg and Ca oxides on the OCM process into C_2-hydrocarbons was studied on 5 % $H_4SiW_{12}O_{40}$ supported catalysts. Carriers form series with respect to increasing influence on S_{C2H4} at 800 °C, %: 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). The effect of carriers on the conversion and yield of C_2-hydrocarbons is shown in Figure 1.

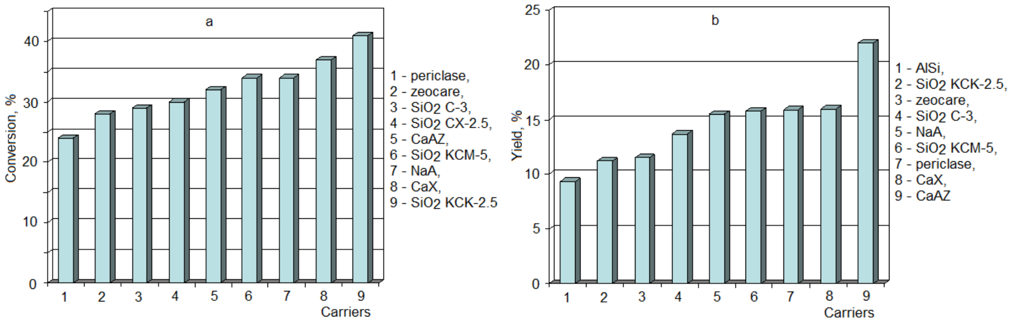

Figure 1: Influence of the nature of carrier of the 5 % [SiW_{12}] catalysts on conversion and yield of C_2-hydrocarbons in the process of oxidative condensation of CH_4. Reaction mixture, vol.%: CH_4 - 20.5; O_2 - 15.4; Ar - 64.1; water vapor

The yield of C_2H_4 from CH_4 reaches 13.5 - 18.5 % at the conversion of CH_4 to 23 – 32 % and the ratio of C_2H_4 : C_2H_6 in products - from 3.6 to 7.5 in the case of using the optimal carriers. Similar results were obtained for catalysts based on [PW_{12}]-HPC. The possibility of using the modified natural zeolite of the Republic of Kazakhstan with the content of clinoptilolite up to 80 % as a carrier was shown by special studies. Effect of the cation - substituent of proton in HPA on efficiency of the OCM process has also been studied over supported 12th series W HPC with the P as a central atom. The studied cations form the following series in terms of efficiency on the yield of C_2H_4 (%) from CH_4:

- for 5 % [SiW_{12}]/SiO_2: Na (13.7) > Mg (11.9) > Ce (11.1) > Cd (10.7) > Ni (10.0) > Pb (9.7) > Ca (6.9) > Cr (8.1) > Fe (7.3) > Bi (7.0);
- for 15 % [SiW_{12}]/SiO_2: Cd (15.1) > Mg (12.2) > Ca (7.8) > Na (7.1) ~ Fe (7.1);
- for 5 % [PW_{12}]/SiO_2: Mg (14.2) > Cs (12.7) > Pb (11.7) > Ba (10.0) > Cr (9.8) > Cu (4.4);
- for 15 % [PW_{12}]/SiO_2: Cs (14.8) > Pb (12.5) > Cr (11.3) > Mg (11.0) > H > Ba (10.0).

It can be seen that Cd, Mg and Na, where the ethylene yield reaches 15.1 - 13.7 %, are optimal in the case of the salts of silicotungstic acid.

For [PiW_{12}] acid, the optimal yield of C_2H_4 (14.2 - 14.8 %) on HPC with Mg and Cs as cations was observed on 5-15 % supported catalysts. Thus, the 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 C_2H_4 from CH_4. The optimal content of C_2H_4 in the composition of C_2-hydrocarbons or the ratio of $C_2H_4 : C_2H_6$ is observed on supported [PW_{12}]-HPC modified with Cr ($C_2H_4 : C_2H_6 = 6.5 : 1$), Ba ($C_2H_4 : C_2H_6 = 5.6 : 1$), Cs ($C_2H_4 : C_2H_6 = 9.3 : 1$) cations, as well as in other HPC systems containing Mg (5.1), Cd (7.9), Na (6.4), Ce (5.6) cations, and silicon as the central atom. Transition from the supported heteropoly acids to their salts optimizes the OCM process.

The influence of reaction mixture on the formation of C_2-hydrocarbons 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 (Table 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.

Table 1: Effect of the concentration of CH_4 and O_2 in mixture on the yield and selectivity of the C_2-hydrocarbons formation over 0.5 % $H_4SiW_{12}O_{40}$/AlSi

Composition of the reaction mixture, %	Conversion, %	Yield, %		Selectivity, %	
		C_2H_6	C_2H_4	C_2H_6	C_2H_4
CH_4 – 0.0013 O_2 – 0.0013 Ar – 0.006	37.0	2.2	9.5	5.9	25.7
CH_4 – 0.0018 O_2 – 0.0013 Ar – 0.0056	20.5	3.4	8.8	16.6	43.0
CH_4 – 0.0031 O_2 – 0.0013 Ar – 0.0042	26.4	3.1	10.2	11.2	38.6
CH_4 – 0.0044 O_2 – 0.0013 Ar – 0.0030	18.6	3.0	8.9	48.0	20.9
CH_4 – 0.0018 O_2 – 0.0004 Ar – 0.0065	17.9	5.1	5.2	28.4	29.0
CH_4 – 0.0018 O_2 – 0.0004 Ar – 0.006	30.0	4.1	7.4	13.6	24.6

Note: T = 750 °C, GHSV = 7,800 h^{-1}, $\tau = 0.46$ s

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, nature of carrier, ratio of components of reaction mixture and reaction temperature were established. [PW_{12}]-HPA at replacement of proton to the Na and Cs as well as [SiW_{12}]-HPA at replacement of proton to the Na, Mg and 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, $\tau = 0.38 - 0.46$ s.

Thermal stability of supported catalysts based on the 12th series W-HPC in a high temperature gas phase OCM process was examined by XRD and TPR methods under influence of the medium ($O_2 + H_2O + Ar + CH_4$) at T = 20 – 800 °C. It is caused by preservation of fragmented formations of HPC at temperatures up to 800 – 850 °C on a carrier, light renewability under the action of reaction medium containing water vapor, or vapor-air treatment of reactive oxygen-containing fragments of HPA.

The process of OCM into ethylene can be intensified by creating a technology that is close to non-waste technology by additional oxidative dehydrogenation of the product of OCM - ethane to ethylene, and by adding additives to CH_4 of other alkanes in order to increase the conversion of CH_4 to C_2H_4 and C_2H_6.

On the proposed supported catalysts based on 12th series W-HPC (their compositions are close to those used in the OCM) for the concomitant process of oxidative dehydrogenation of C_2H_6 (ODE), the C_2H_4 yield in the presence of water vapor is 41.6 - 51.3 % or 527 - 641 g C_2H_4/m^3 C_2H_6, selectivity for C_2H_4 reaches 86 – 94 % (Table 2).

Table 2: Optimum results obtained in the process of oxidative dehydrogenation of C_2H_6

Catalysts	Conversion, %	Yield of C_2H_4, %	Productivity, g C_2H_4/m^3 C_2H_6	Selectivity by C_2H_4, %
15 % $Cs[PW_{12}]/SiO_2$	59.7	51.3	640.9	85.8
5 % $Mg[PW_{12}]/SiO_2$	46.8	41.6	527.0	88.4
15 % $Ca[SiW_{12}]/AlSi$	54.2	48.6	607.2	89.6
15 % $Mg[SiW_{12}]/AlSi$	46.5	43.8	547.5	94.2
15 % $Ba[PW_{12}]/AlSi$	49.9	44.1	551.3	88.4
5 % $Ca[SiW_{12}]/AlSi$	49.6	43.7	546.3	88.2

Note: T = 725 °C, GHSV = 6,920 h^{-1}, $\tau = 0.53$ s

40 % content of C_2H_4 in exhaust gases (Table 3) and production of 1 t of C_2H_4 can be achieved from 1.8 - 2.1 t of ethane by varying the concentration of water vapor in reaction mixture. The process retains high selectivity for the target product.

Table 3: Influence of the content of water vapor and oxygen in the reaction mixture on the synthesis of C_2H_4 from C_2H_6

Initial mixture, %				C_{C2H6}, %	Y_{C2H4}, %	S_{C2H4}, %
C_2H_6	O_2	N_2	H_2O			
22.2	2.8	32.4	42.6	54.9	46.4	89.5
19.7	2.5	34.1	37.8	47.6	39.5	83.0
19.7	2.5	28.1	49.2	47.5	38.8	81.6
16.7	2.1	0	81.3	44.6	36.0	80.9
42.9	5.4	0	51.7	59.6	14.0	23.5
68.9	8.6	0	22.8	20.4	10.4	50.0
27.6	3.4	0	69.0	46.5	36.2	80.8

Note: T = 725 °C, $\tau = 0.53$ s

It was found that the C_2H_4 yield was raised to 18.5 - 34.5 %, productivity was up to 1.43 kg C_2H_4/l Catalyst × h, and the optimal temperature of the OCM process was decreased by 100-200 °C in the case of using a mixture of CH_4 with C_3 - C_4 alkanes for oxidation. In parallel, the appearance of C_3H_6, C_4H_{10} and C_1 - C_4 alcohols is observed in reaction products. The developed catalysts for the process of oxidative conversion of CH_4 to C_2H_4 are thermostable for operation for more than 120 h (T = 800 °C). The process retains high selectivity for the target product.

Taking into account the established factor of the positive effect of steam on the yield, selectivity and productivity of the OCM process on the main products of CH_4 conversion (C_2-hydrocarbons, CH_2O), the method of catalyst regeneration and stabilization of its activity during long-term high-temperature operation by periodic treatment with steam-air mixtures was developed.

Thus, the Implementation of OCM process on heteropoly acid systems allowed to increase the conversion of CH_4 and yield of C_2H_4. 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. It 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 t of ethylene per day from 1 t of catalyst.

The initial structure of $H_4SiW_{12}O_{40}$ HPA was studied by a combination of TPR and XRD methods. The nature of its oxygen-containing fragments involved in the interaction with H_2 in the process of TPR by H_2 was determined.

According to X-ray diffraction data, the appearance in the spectrum of the group of diffraction maxima (dm) in the region of 2θ = 5 - 10 °, is characteristic for the phase of the Keggin structure of SiW_{12}-HPA. The TPR spectrum shows the presence of four temperature absorption peaks of H_2 due to its interaction with various structural oxygen in terms of bond strength and nature: I – 350 – 500 °C, T_{max} = 460 °C; II – 500 – 650 °C, diffuse: III – 700 – 900 °C, T_{max} = 850 °C; IV - above 900 °C. The amount of oxygen involved in interaction with H_2 in TPR regime in the temperature range 20 – 1,100 °C corresponds to the stoichiometry calculated on tungsten - WO_3, Figure 2.

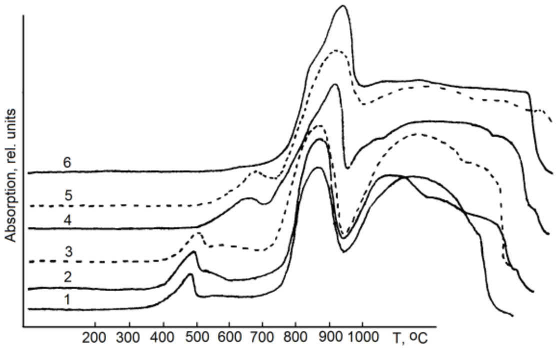

Figure 2: Curves of the TPR of $H_4SiW_{12}O_{40}$ after steam-air treatment at various temperatures. 1 – 20 °C, 2 – 250 °C, 3 – 400 °C, 4 – 450 °C, 5 – 650 °C, 6 – 900 °C, processing for 1 h.

In the I peak of TPR, the removal of structural oxygen of the I type is observed. In this case, the amount of unreacted oxygen of HPA (II-IV peaks of TPR) with H_2, according to the calibration curves, corresponds to the stoichiometry of $WO_{2,90}$. D.m. 2θ = 8 – 10 ° disappear in the X-ray spectrum of this sample after removing of oxygen I in the mode of thermo-programmed reduction due to the decomposition of the $H_4SiW_{12}O_{40}$ HPA phase and new diffraction maxima corresponding to the formation of the WO_3 with tetragonal lattice with the parameters a_0 = 5.25 Å, c_0 = 3.91 Å (JCPDS No 5-0388) appear. The diffraction maxima corresponding to $WO_{2.9}$ have lattice parameters close to WO_3 (a_0 = 5.30 Å, c_0 = 3.83 Å, tetragonal system, JCPDS No 18-1417).

After removing of the I and II oxygen forms from SiW_{12}-HPA in the TPR mode, the stoichiometry of the remaining oxygen (according to TPR) in the sample corresponds to the participation in interaction with H_2 of the oxygen of oxide of the imperfect $WO_{2.9}$ structure in the amount of 1 O atom per 1 heteropoly anion and is accompanied by a loss of ~ 1.6 e. The process results in the formation of an oxide with the stoichiometry $WO_{2.83}$ (it is possible that all these forms are intermediate at the destruction of the HPA in H_2).

Thus, the structural "forms" of oxygen, reduced in the I and II absorption peaks of H_2 in the process of reduction, lose in the sum of 4 e, which agrees with the literature data (Misono, 1987). The maxima corresponding to the formation of the $WO_{2.83}$ (JCPDS No 36-103) phase with the parameters a_0 = 19.31 Å, b_0 = 3.78 Å (β = 104.4°), c_0 = 17.07 Å, appear on the diffractogram of this sample.

The III peak of the TPR of SiW_{12}-HPA at T = 650 – 850 °C is associated with participation of oxygen of the $WO_{2.83}$ structure in reaction and is accompanied by the formation of the $WO_{1.99}$ phase. Thus, the HPA sample has a stoichiometry of $WO_{1.99}$ after removing of the I-III forms of structural oxygen (I-III TPR peaks, T = 20-850 °C) in the TPR mode by hydrogen. In addition, the maxima corresponding to the formation of the WO_2 phase (monoclinic, a_0 = 5.575 Å, b_0 = 4.8995 Å (β = 118.869°), c_0 = 5.5608 Å, JCPDS No 32-1393) with a small admixture (~ 15 %) of $WO_{2.72}$ phase (monoclinic, a_0 = 17.713 Å, b_0 = 3.784 Å (β = 110.60°), c_0 = 14.035 Å, JCPDS No 36-101) appear on its diffractogram.

The complete removing of oxygen from HPC in TPR mode (I-IV oxygen, T = 20 – 1,100 °C), according to XRD, leads to formation of a phase of the metal W, crystallized in a cubic lattice with the parameters a_0 = 3.1648 Å, JCPDS No 4-806) with a small admixture of WO_2 (JCPDS No 32-1393). Thus, apparently, the curves of thermo-programmed reduction by hydrogen (I and II TPR peaks) describe behavior of the Keggin molecular structure of the $H_4SiW_{12}O_{40}$ HPA only in the temperature range 20 – 650 °C. The process is accompanied by the participation of two O atoms in reaction and loss of the 4e to the structural unit of HPC.

Thus, from the combination of TPR and XRD data, it follows that in the case of $H_4SiW_{12}O_{40}$, the I TPR peak is due to the absorption of H_2 for reduction of oxygen directly to the molecular structure of the HPA. This process is accompanied by the loss of 2.4 electrons per heteropoly anion during the reduction of oxygen while maintaining the Keggin lattice. The $WO_{0.1}$ stoichiometry or loss of the I O atom per one HPA corresponds to this oxygen form per tungsten. According to the assumptions (Misono, 1987), H+ protons, formed from the H_2 molecule as a result of its activation and dissociation at the proton centers of the HP, participate in the interaction with the structural oxygen I. The established absence of the I peak on TPR curves for $Mg_2SiW_{12}O_{40}$, $Na_4SiW_{12}O_{40}$ and $Ca_2SiW_{12}O_{40}$ salts, its partial presence when shifting to the high temperature region for the $CaHSiW_{12}O_{40}$ acid salt and the presence in $H_4SiW_{12}O_{40}$ can also indicate the above mechanism of the interaction of oxygen I from the HPA with H_2.

It has been shown that the treatment of SiW_{12}-HPA at various temperatures in a water vapor-air mixture or supporting on a carrier promotes an increase in the temperature of the start of structural changes in the HPA and its stabilization on the carrier. These catalysts proved to be highly effective and thermal stable for the processes of oxidative condensation of CH_4 to C_2H_4 during long-term operation. Analysis of the results showed that the initial HPA partially decomposes into constituent oxides, but the structure of the HPA is preserved fragmentarily as the temperature of the vapor-air treatment increases.

4. Conclusions

The optimal reaction conditions by varying the composition of HPC, nature of carrier, ratio of components of reaction mixture and reaction temperature were established. [PW_{12}]-HPA at replacement of proton to the Na and Cs as well as [SiW_{12}]-HPA at replacement of proton to the Na, Mg and 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, $\tau = 0.38 - 0.46$ s. It was shown the preservation of fragmented formations of HPC at temperatures up to 800 – 850 °C on a carrier and light renewability under the action of reaction medium containing water vapor.

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