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CATALYTIC CONVERSION OF METHANE INTO OLEFINS

Abstract. The worldwide use of olefins in the chemical industry is growing every year. This is due to increased consumption of olefins for the production of chemically important products, such as polyethylene, ethylene glycol, acetaldehyde and vinyl chloride. In the present work, the activity of the developed heteropolyacid (HPA) catalysts based on phosphorus and tungsten in the oxidative conversion of methane to olefins was studied. The developed catalysts were applied to various natural and synthetic carriers. The process of oxidative conversion of methane was studied by varying the reaction temperature, the ratio of the reacting components, the space velocity, and the effect of the addition of water vapor to the reaction mixture. When 5% of the HPA was applied to natural carriers, ethane, ethylene, hydrogen and propylene were observed in the reaction mixture. The same activity was observed for catalysts deposited on synthetic carriers. It has been established that the optimal conditions for the oxidative conversion of methane on a catalyst of 5% HPA applied to a natural carrier are: $T = 1073\text{K}$, $W = 3900\text{h}^{-1}$, $\text{CH}_4 : \text{O}_2 = 2 : 1$. The positive effect of the addition of water vapor to the reaction mixture was determined.

Key words: catalytic oxidation, catalysts, methane, olefins.

Introduction

Chemistry of lower alkanes is one of the most rapidly developing scientific fields [1-8]. The most important source of alkanes in nature is natural gas, mineral hydrocarbon raw materials - oil and associated oil gases. Natural gas consists of 95 percent methane [9]. Therefore, in the modern petrochemical industry, saturated hydrocarbons are the basis for obtaining a variety of organic compounds, an important raw material in the processes of obtaining intermediates for the production of plastics, rubbers, synthetic fibers, detergents and many other substances.

It is estimated that over the next decades, the world situation will be when half of the existing oil reserves will be spent and the expected production come into conflict with the growing demand for oil [10]. The clash of these trends could lead to a shortage of oil, increase in the price of this kind resource and will become a powerful resource and a prerequisite for the transition to alternative energy sources. According to numerous forecasts of Russian and foreign analysts in the next 10-20 years the situation has changed in favor of the priority of gas demand. Natural, economic and political factors, which together determine the inevitability of change in the structure of world power balance in favor of growth in the share of gas are at the heart of this process. Therefore, the widespread use of gas in areas focused on the consumption of petroleum products is important program of the world economy, which is undoubtedly important for Kazakhstan. The full range of products produced from petroleum, can be synthesized by direct route from natural gas. The cost of such substances as synthesis gas, H_2 , ethylene, formaldehyde, and benzene is 10-100 times higher than the original gas. They are the basic raw material for the synthesis of methanol, polyethylene, alcohols, acids, liquid motor fuel, dimethyl ether, ammonia fertilizer and hundreds of other compounds necessary for the development of chemical industry.

The problem of processing of natural gas into organic compounds solved by steam, carbon dioxide and oxidative conversion of alkanes to synthesis gas with subsequent production a mixture of paraffin, olefins and alcohols [11,12]. Co-conversion of methane with C₃-C₄ hydrocarbons with formation of mono- and polycyclic aromatic hydrocarbons, oxidative dimerization of methane to ethylene and ethane, selective oxidation of methane to methanol can serve as example of one-step conversion of methane [13,14]. Produced hydrocarbons are readily oxidized to carbon dioxide and water in the presence of oxygen, which significantly reduces the selectivity of the reaction at high conversion of methane. This leads to a higher cost of hydrocarbons produced from methane than analogs of petroleum origin. In general, one-step methane conversion processes are at the level of laboratory research, and finding new ways of effective utilization of natural gas is an urgent task.

We have developed polyoxide catalysts based on molybdenum, chromium and gallium, applied to natural clays for catalytic oxidation of propane butane mixture into oxygenates and olefins [15-17].

Light olefins are the most important building blocks for polymers and a variety of intermediate products. The world demand for ethylene and propylene exceeds 180 MTA (about 2/3 of ethylene production) with annual growth of 4-5% in the next decade [18].

The oxidative conversion of alkanes to ethylene in place of the use of petroleum feedstock is of practical interest, since ethylene and propylene are the basis for the production of approximately 50% of all organic products in the chemical industry. At present, their annual output is one of the main indicators of the potential of industrial development. It is known that the petrochemical potential of many countries is estimated by the volume of production of ethylene and propylene, which are the basic raw materials for the production of polyethylene, polypropylene, plastics and other products. The literature reports an increase in ethylene prices and an increase in olefin production in Asia, Europe and America [19]. Expansion of production and construction of new petrochemical complexes is also in Russia and China. For Kazakhstan, which has huge reserves of natural gas, a significant part of which is flared, the development and implementation of technologies for processing alkanes is a strategic task.

There are two main ways of producing valuable chemicals from methane - indirect and direct conversion. Currently, the most commonly used method is indirect conversion, i.e. methane is first converted to a synthesis gas with various C/H ratios by either reforming or partial oxidation, and then the synthesis gas is converted to raw chemicals by Fischer-Tropsch synthesis, converting the synthesis gas to an olefin, converting the synthesis gas to gasoline, synthesis of ammonia or many other processes. However, indirect conversion of methane is always accompanied by complicated installations, high production costs and, in particular, large CO₂ emissions. Consequently, the study of the direct conversion of methane into valuable chemicals has recently attracted special attention [20].

Experimental

Catalyst preparation

The method of catalyst preparation has been previously developed in the laboratory of oxidative catalysis of JSC "D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry" [21]. The catalysts were prepared by the capillary impregnation method of mixed aqueous solutions of nitrate salts of metals, supported on carriers.

Characterization techniques

The analysis of the initial mixture and reaction products was carried out using a chromatograph "Chromos GC-1000" with the "Chromos" software and on a chromatograph "Agilent Technologies 6890N" (USA) with computer software. Chromatograph "Chromos GC-1000" is equipped with packed and capillary columns. The packed column is used for the analysis of H₂, O₂, N₂, CH₄, C₂H₆, C₂H₄, C₃-C₄ hydrocarbons, CO and CO₂. A capillary column is used to analyze of liquid organic substances, such as alcohols, acids, aldehydes, ketones and aromatic hydrocarbons. Temperature of the detector by thermal conductivity – 200°C, evaporator temperature – 280°C, column temperature – 40°C. Carrier gas velocity Ar = 10 ml/min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve $V = f(S)$ was constructed, where V - amount of substance in ml, S - peak area in cm². Concentrations of the obtained

products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was $\pm 3.0\%$.

Results and discussion

The influence of nature of carriers, as well as reaction temperature during partial oxidation of methane on catalysts supported on various natural and synthetic carriers on the basis of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ and $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ was investigated. The reaction was investigated under the following conditions: the ratio of initial reaction mixture $\text{CH}_4:\text{O}_2 = 7:1$ (36.0%: 5.0%, the rest - Ar); $V = 7800 \text{ h}^{-1}$ by varying the reaction temperature from 873 to 1173 K. The formation of hydrogen, as well as the C_2 , C_3 , and C_4 hydrocarbons occurred in this temperature range. Conversion (X) of methane was varied from 0.5 to 35.6%.

When supporting of 5% HPA on natural carriers: TC, EKC, diatomite, CC, TWC, ZE conversion of methane was varied from 2.7 to 15.6%. Selectivity (S) on the main product - ethylene varied from 6.2 to 41.9%. At 1023 K on the catalyst supported on ZE observed the formation of ethane with yield (Y) 3%, 44.4% selectivity at 6.7% conversion of methane. With further increase of reaction temperature to 1173 K the yield of ethane decreased to 1.6% (selectivity 23.9%). Starting from 1073-1123 K there was the formation of ethylene. Conversion at the same time kept constant and the selectivity of ethylene increased from 33.6 to 40.1%. Hydrogen began to form at 973 K increasing at higher temperatures, the selectivity of its grown from 15.3% to 24.7%. Propylene was also observed in small amounts in the reaction products.

Effect of synthetic carriers on the activity of 5% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst in reaction of partial conversion of methane was investigated. It was investigated a series of synthetic carriers: CaA, Siral-10, Siral-20, Siral-30, NaX, AlSi and 20% Al_2O_3 +80% H-ZSM-5. Hydrogen, C_2 , C_3 , and C_4 hydrocarbons, and CO are formed on synthetic carriers as well as on natural in this temperature range. Conversion of methane was varied from 1.3 to 19.7%.

Comparing the data obtained on 5% $\text{H}_3\text{PW}_{12}\text{O}_{40}$ catalyst supported on synthetic and natural carriers, revealed that the optimal catalyst leading ODM reaction toward the formation of C_2 hydrocarbons is 5% HPA, supported on East Kazakhstan zeolite. At 1023 K observed the formation of 3% ethane and 2.7% ethylene at 1123 K. 5.17% hydrogen at 900°C formed on the catalyst supported on TWC.

Table 1 - The influence of ratio of $\text{CH}_4:\text{O}_2$ in oxidative conversion of methane on 5.0% HPA/NC catalyst

Concentration $\text{CH}_4:\text{O}_2$, %	Ratio, $\text{CH}_4:\text{O}_2$	X_{CH_4} , %	Yield, %		
			H_2	C_2H_6	C_2H_4
50,0 : 50,0	1,0 : 1,0	significant formation of hydrogen with sparks			
67,0 : 33,0	2,0 : 1,0	14,0	28,0	2,8	10,8
75,0 : 25,0	3,0 : 1,0	22,0	-	2,75	9,12
80,0 : 20,0	4,0 : 1,0	significant formation of hydrogen with sparks			
84,0 : 16,0	5,0 : 1,0	15,0	-	1,4	5,2

Note - $T = 1073 \text{ K}$, $V = 3900 \text{ h}^{-1}$.

Series of experiments at a space velocity of reaction 3900 h^{-1} and the temperature range 973-1173 K on the investigation of reactants ratio $\text{CH}_4 : \text{O}_2$ with in 1 : 1, 2 : 1, 3 : 1, 4 : 1, 5 : 1 was performed (Table 1). It was determined that the highest yield of ethylene 10,8% is observed at ratio of $\text{CH}_4 : \text{O}_2 = 2 : 1$ at reaction temperature 1073 K.

Effect of the changes in space velocity (1000, 3900, 10000, 12000 and 15000 h^{-1}) of process on the catalytic activity in oxidative conversion of methane was investigated. It was determined experimentally that the best in the conversion of methane to 28% H_2 and 13,6% C_2 hydrocarbons is space velocity 3900 h^{-1} and contact time 0.9 s (Table 2).

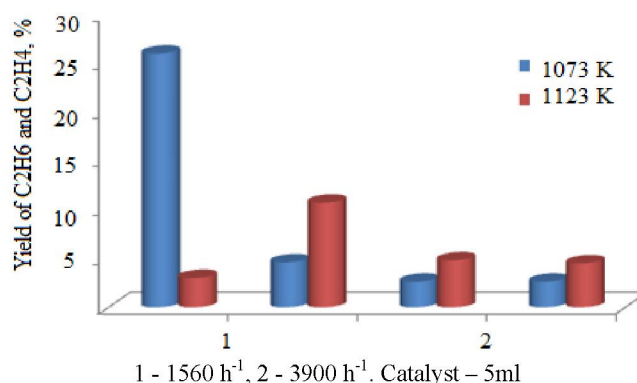
Addition of water vapor into the reaction mixture at a ratio of $\text{CH}_4 : \text{H}_2\text{O} = 1 : 0.5$, space velocity 3900 h^{-1} and the temperature range of 973-1173 K, $\text{CH}_4 : \text{O}_2 = 2 : 1$ was examined. It was shown that with the addition of water vapor into the reaction mixture ethylene yield remained constant at 10,8% at 1073 K.

Table 2 - Effect of space velocity on the performance of process of oxidative conversion of CH_4 on 5,0% HPA/NC catalyst

Space velocity, h^{-1}	X_{CH_4} , %	Yield, %		
		H_2	C_2H_6	C_2H_4
1000	13	26	1,9	8,8
3900	13,9	28	2,8	10,8
10000	6,6	4,3	3,0	3,2
12000	15,0		4,0	8,1
15000	20,0		1,0	1,2

Note - $T = 1073 \text{ K}$, $V = 3900 \text{ h}^{-1}$, $\text{CH}_4 : \text{O}_2 = 2 : 1$.

Also, we investigated the increase in the volume of catalyst to 5ml and decrease of space velocity to 1560 h^{-1} which shows that with increase of catalyst sample the yield of ethane and ethylene at 1073K was respectively 26% and 4,6% with sharp decrease of ethane up to 3% and increase of ethylene to 10,7% with increase in the reaction temperature on 50 K (Figure 1). It was shown that the yield of ethane and ethylene at 1073 K was 2,6% with slight increase in the amount of ethane to 4,8% and ethylene 4,5% at raise of reaction temperature to 1123 K with increase of space velocity up to 3900 h^{-1} .

Figure 1 - Effect of space velocity and temperature of reaction in the oxidative conversion of CH_4 on 5,0% HPA/NC catalyst

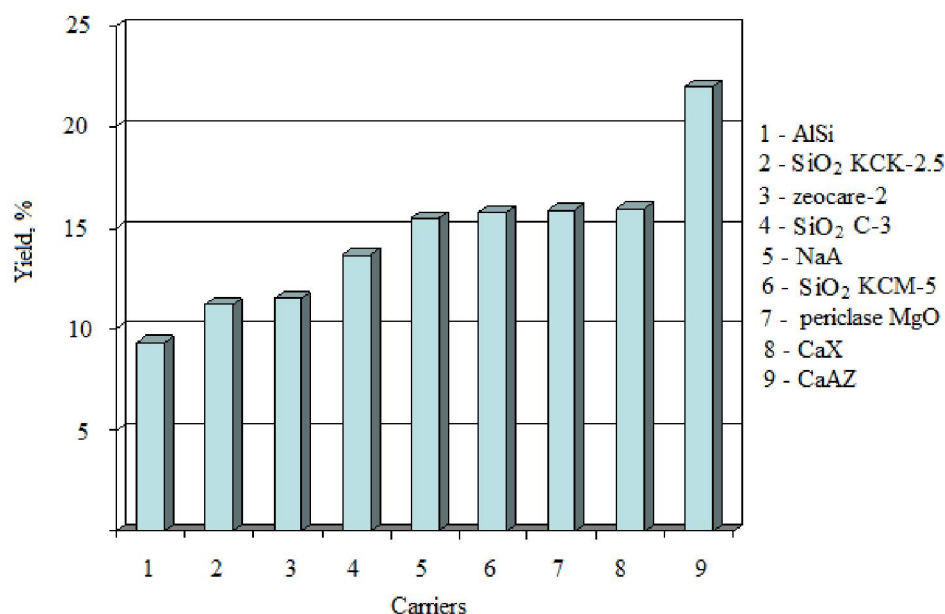
Thus, the optimal conditions for the oxidative conversion of methane on 5% HPA/TWC catalyst were determined: the ratio of reactants $\text{CH}_4 : \text{O}_2 = 2 : 1$, 1073 K temperature and space velocity 3900 h^{-1} .

On the example of 5-15% catalysts based on $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ and its salts on aluminosilicate was established the formation of C_2H_6 , C_2H_4 , CO_2 , H_2 , the ratio of which was determined by temperature of reaction in oxidative dimerization of methane (ODM). The ratio $\text{C}_2\text{H}_4 : \text{C}_2\text{H}_6$ in products increased toward the formation of C_2H_4 with increasing temperature and transition from high-percentage to low-percentage catalysts. Catalysts 5% $\text{H}_4\text{SiW}_{12}\text{O}_{40}/\text{AlSi}$ ($S_{\text{C}_2\text{H}_4} = 51.5\%$, $S_{\text{C}_2\text{-HC}} = 80.0\%$) and 15% $\text{H}_3\text{PW}_{12}\text{O}_{40}/\text{AlSi}$ ($S_{\text{C}_2\text{H}_4} = 39.2\%$, $S_{\text{C}_2\text{-HC}} = 60.2\%$) had a maximum selectivity by C_2 -hydrocarbons. CaAZ, CaX, minerals containing MgO , SiO_2 , and NaA can be recommended as a carrier. The yield of C_2H_4 from CH_4 achieved 13,5-18,5% at conversion of CH_4 23-32% and the ratio of $\text{C}_2\text{H}_4 : \text{C}_2\text{H}_6$ 3,6-7,5, Figure 2.

The studied cations as part of HPC form series on the effectiveness of influence on yield of C_2H_4 (%) from CH_4 :

-for 5% $[\text{SiW}_{12}]/\text{SiO}_2$: 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 5% $[\text{PW}_{12}]/\text{SiO}_2$: Mg (14,2) > Cs (12,7) > Pb (11,7) > Ba (10,0) > Cr (9,8).



The composition of reaction mixture, % vol.: CH₄ - 20,5; O₂ - 15,4; Ar - 64,1; water vapor.

Figure 2 – Effect of the nature of carrier of 5% [SiW₁₂] catalysts on conversion and yield of C₂ hydrocarbons in oxidative dimerization of methane

The transition from supported HPA to their salts optimized ODM process. It was shown that Y and S formation of C₂H₄ increases with increasing ratio of CH₄:O₂ from 1:1 to (1,5-30):1 on 0,5% H₄SiW₁₂O₄₀/AlSi, Table 3. The composition of mixture, mol: CH₄ - 0,0018-0,0031, O₂ - 0,0013, inert gas - 0,008-0,004 is optimal for synthesis of C₂H₄. The positive effect has introduction of water vapor (CH₄:O₂ = 1:0,21, mol) into reaction mixture.

Table 3 – Influence of CH₄ and O₂ in mixture on yield and selectivity of C₂ hydrocarbons on 0,5% H₄SiW₁₂O₄₀/AlSi

Composition of reaction mixture, mol	Yield, %		Selectivity, %	
	C ₂ H ₆	C ₂ H ₄	C ₂ H ₆	C ₂ H ₄
CH ₄ -0,0013, O ₂ -0,0013, Ar-0,006	2,2	9,5	5,9	25,7
CH ₄ -0,0018, O ₂ -0,0013, Ar-0,0056	3,4	8,8	16,6	43,0
CH ₄ -0,0031, O ₂ -0,0013, Ar-0,0042	3,1	10,2	11,2	38,6
CH ₄ -0,0044, O ₂ -0,0013, Ar-0,0030	3,0	8,9	48,0	20,9
CH ₄ -0,0018, O ₂ -0,0004, Ar-0,0065	5,1	5,2	28,4	29,0
CH ₄ -0,0018, O ₂ -0,0004, Ar-0,006	4,1	7,4	13,6	24,6

Note – T=750°C, τ=0,46s. By-products: CH₂O, H₂, CO₂.

ODM process can be intensified by additional oxidative dehydrogenation of ODM product - C₂H₆ into C₂H₄.

Conclusion

Thus, it follows from the above results that optimization of the ODM process can be achieved by rigorous selection of the process parameters of the reaction, by improving the composition of the supported catalysts, for example, by substituting the protons of the HPA for metal cations of Groups I and II, by applying GPC to silicon-containing carriers (SiO₂, pentasils, aluminosilicates, and synthetic zeolites).

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МЕТАННЫҢ ОЛЕФИНДЕРГЕ ДЕЙІН КАТАЛИТИКАЛЫҚ КОНВЕРСИЯСЫ

Аннотация. Химия өндірісінде олефиндердің әлемдік Қолданылуы жыл өткен сайын өсуде. Бұл полиэтилен, этиленгликоль, ацетальдегид және винилхлорид секілді химиялық маңызды өнімдерді өндіруге арналған олефиндерді Қолданылуының артуымен байланысты. Ұсынылған жұмыста метанның олефиндерге тотығу конверсиясында фосфор және вольфрам негізіндегі жасалынған гетерополикышқылды (ГПК)

катализаторлардың белсенділігіне зерттеулер жүргізілді. Әр түрлі синтетикалық және табиғи тасымалдағышқа отырғызылған катализаторлар жасалынды. Метанның тотыға айналу үрдісі барысында әр түрлі температура мен көлемдік жылдамдықта реакцияға түсетін компоненттердің Қатынасы, сондай-ақ реакциялық Қоспаға су буының әсері зерттелді. Табиғи тасымалдағышқа 5% ГПК енгізгенде реакциялық Қоспадан этан, этилен, сутек және пропилен түзілгені байқалды. Синтетикалық тасымалдағышқа отырғызылған катализаторлар үшін де осындай белсенділік байқалды. Метанның тотыға айналу конверсиясы үшін табиғи тасымалдағышқа отырғызылған 5% ГПК катализаторының оңтайлы жағдайының шарттары $T = 1073\text{K}$, $W=3900\text{ сағ}^{-1}$, $\text{CH}_4 : \text{O}_2 = 2 : 1$ болып табылады. Реакциялық қоспаға су буын қосқандағы әсері оң нәтиже көрсететіні анықталды.

Түйін сөздер: катализаторлар, метан, олефиндер.

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КАТАЛИТИЧЕСКАЯ КОНВЕРСИЯ МЕТАНА В ОЛЕФИНЫ

Аннотация. Мировое применение олефинов в химической промышленности растет с каждым годом. Это связано с увеличением потребления олефинов для производства химически важных продуктов, таких как полиэтилен, этиленгликоль, ацетальдегид и винил хлорид. В представленной работе проведено исследование активности разработанных гетерополикислотных (ГПК) катализаторов на основе фосфора и вольфрама в окислительной конверсии метана в олефины. Разработанные катализаторы были нанесены на различные природные и синтетические носители. Процесс окислительного превращения метана исследовался при варьировании температуры реакции соотношение реагирующих компонентов, объемной скорости, а также изучено влияние добавление паров воды в реакционную смесь. При нанесении 5% ГПК на природные носители в реакционной смеси наблюдалось образование этана, этилена, водорода и пропилена. Такая же активность наблюдалась и для катализаторов нанесенных на синтетические носители. Установлено, что оптимальными условиями окислительной конверсии метана на катализаторе 5% ГПК нанесенном на природный носитель являются: $T = 1073\text{K}$, $W=3900\text{ч}^{-1}$, $\text{CH}_4 : \text{O}_2 = 2 : 1$. Определено положительное влияние добавления паров воды в реакционную смесь.

Ключевые слова: каталитическое окисление, катализаторы, метан, олефины.

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