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Catalytic Processing of Natural Gas into Olefins

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The problem of environmentally friendly utilization of natural gas in important products is relevant. The solution to this problem will minimize environmental pollution from products of burning of natural gas. A significant part of natural and associated petroleum gas is flared during their production, polluting the environment. The rest is used for heating and a small part is processed into valuable products. This leads to irreparable losses of valuable natural raw materials, the loss of potential profit due to the price difference between expensive products and cheap raw materials and creates complex environmental problems in the mining regions. In recent years, much attention has been paid to various methods of oxidative conversion of methane. Catalysts based on heteropoly compounds supported on supports were studied by the oxidative condensation of methane into ethylene. Using a set of methods (TPR, IR spectroscopy, XRD), it was shown that the exposure of the $H_4SiW_{12}O_{40}$ heteropoly acid in the components of the air–water vapor reaction medium leads to the preservation of its secondary structure in the temperature range 20 - 400 °C, the formation of oxide-like W compounds at $T \geq 650$ °C, along with the preservation of oxygen-containing fragments W – O - W, W = O, Si – O - W heteropoly acids.

Introduction

Natural and associated gases are the most valuable alternative source for the production of valuable organic intermediates and products. Unfortunately, at present a small proportion of natural gas is used in industrial production. Large volumes of gas are consumed in the form of fuel, and the remainder is flared in "torches". This leads to an irreparable loss of valuable chemical raw materials and creates complex environmental problems in connection with the burning of huge volumes of gas. Solving the problem of such irrational use of natural gas, increasing the depth of methane processing will reduce environmental problems, raise the level of purity of the used technologies and expand the range of the obtained petrochemical products. Natural gas can be considered as an alternative source to obtain synthesis-gas by different methods: steam reforming through process modeling (Herrera-Aristizabal et al., 2018), in a membrane reactor (Kyriakides et al., 2017), dry reforming (Frontera et al., 2017), steam conversion along with partial oxidation (Gil-Calvo et al., 2017), steam conversion along with dry reforming on supported Ni catalyst with addition of Ce (Siang et al., 2017), the same process with addition of La (Singh et al., 2017), and partial oxidation of CH_4 (Ricca et al., 2016). Synthesis-gas can also be obtained from biogas with membrane cleaning (Sharifian et al., 2019) and on Ni catalysts (Palma et al., 2018). Olefins also play an important role as target products as well as intermediates in the petrochemical industry. They can be obtained from methane (Godini et al., 2014), from biogas (Penteado et al., 2017) and from shale gas (Yang et al., 2017). The prospects for the development of the gas processing industry are associated with the creation and implementation of new catalytic environmentally friendly technologies for the production of commercial products for the processing of alkanes, including the production of olefins. Based on the synthesis of olefins, the production of polymers, alcohols and motor fuel is being built. 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 transition metals, alkaline earth metals and rare earth oxides are the most studied catalysts. As a result of numerous tests, it was found that a highly efficient catalyst should contain

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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). It was investigated the layered loading of catalysts with different catalytic properties in a fixed-bed reactor. 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). New promising catalysts based on heteropoly compounds (HPC) have also appeared (Tungatarova et al., 2015). A deeper study of such catalysts is necessary. The increasing need of the C_2H_4 for industry 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. In this regard, the purpose of this study is the production of a valuable petrochemical product - ethylene from natural gas, mainly flared in the Republic of Kazakhstan, as a result of which the environmental situation at production sites is significantly deteriorating due to an increase in the maximum permissible values of carbon oxides, nitrogen oxides, hydrocarbons, sulfur-containing compounds. Selective synthesis of ethylene from natural gas will solve environmental problems and get an expensive target product in comparison with aimlessly burned raw materials. The production under development is clean enough without the formation of harmful by-products. In addition, for this process it is necessary to develop a low-temperature catalyst, the stability of which is confirmed by a set of physicochemical methods.

Experimental

Catalysts on the base of $H_4SiW_{12}O_{40}$ heteropoly acid (SiW_{12}-HPA) were prepared by impregnating of granular supports with solutions of heteropoly compounds. The concentration of active component ranged from 1 to 20%. The experiments were carried out in a flow system in a tubular quartz reactor with a fixed catalyst bed. Tests were carried out in a reaction mixture containing CH_4, O_2, an inert gas with or without water vapor at 600 – 900 °C, contact time ≤ 0.5 s and atmospheric pressure. Contact time and component ratio were varied. The crystalline phases were evaluated by X-ray diffraction (XRD) using the powder method and Fe anode operating at 28 kV and 28 mA. The diffraction patterns were recorded on XRD Siemens D500 diffractometer. The diffractograms were recorded in the range 10 – 80 °. Infrared (IR) spectroscopy research of the HPC and catalysts based on them were carried out on Specord-80 spectrometers. The method of temperature-programmed reduction (TPR) by hydrogen from an Ar + 20 % H_2 mixture stream at a flow rate of 40 mL×min^{-1} in the temperature range of 20 – 1,100 °C was used to study the nature of structural and adsorbed oxygen in catalysts on the base of HPC and its reactivity. Differential thermal analysis (DTA) was performed on a MOM-101 derivatograph of the Paulik-Paulik-Erdey system at a sample heating rate of 10 °C/min. The thermal decomposition of the catalysts was investigated by derivatography. An Agilent 6890N (Agilent Technologies, USA) gas chromatograph with computer software equipped with flame ionization and thermal conductivity detectors was employed for on-line analysis of initial substances and reaction products. The feed components and the reaction products were analyzed on copper capillary column HP-PLOT Q with 30 m long and 0.53 mm in diameter, filled with polystyrene-divinylbenze.

Results and Discussion

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 physical and chemical methods. Differential thermal analysis of silica-tungsten heteropoly acids SiW_{12}-HPA and their salts – heteropoly compounds (HPC) showed that both endo- and exo-thermic effects are present on DTA curves (Table 1). Endothermic effects (up to 150 – 250 °C) are caused by the release of crystallization water and the removal of hydroxyl coating (Misono, 1987).

Table 1: Differential thermal analysis of the 12th series W HPC

Catalysts	Endothermic effect, °C	Exothermic effect, °C
$H_4SiW_{12}O_{40}$	25, 150	480
15 % $H_4SiW_{12}O_{40}$/Al·Si	50, 150	520
$Ca_2SiW_{12}O_{40}$	125, 205	550
15 % $Ca_2SiW_{12}O_{40}$/Al·Si	50, 150	no
$Na_4SiW_{12}O_{40}$	100, 140, 230	600

The exothermic effect for SiW_{12}-HPA is close in temperature to that established by other authors and is due to the onset of structural changes that subsequently lead to its decay. As can be seen from the table, the transition from SiW_{12}-HPA to its salts or supported catalysts increases the temperature of the onset of structural transformations of the heteropoly compound in air by 40 - 120 °C and higher.

The nature of oxygen-containing fragments participating in the interaction with hydrogen in the process of temperature-programmed reduction with hydrogen was determined. According to the data of XRD analysis, the initial $H_4SiW_{12}O_{40}$ HPA is characterized by the appearance in the spectrum of the group of diffraction maxima (dm) in the region of 2θ = 5 - 10 °, which are characteristic for the phase of the Keggin structure of the SiW_{12}-HPA. The TPR spectrum shows the presence of 4 temperature absorption peaks of H_2 due to its interaction with structural oxygen with different bond strengths and nature: I – 350 - 500 °C, T_{max} = 460 °C; II – 500 - 650 °C, blurred: III – 700 - 900 °C, T_{max} = 850 °C; IV - above 900 °C. The amount of oxygen involved in the interaction with H_2 in the TPR regime in the temperature range of 20 – 1,100 °C corresponds to stoichiometry calculated on the basis of tungsten - WO_3. In the I peak of TPR, type I of structural oxygen is removed. The amount of HPA oxygen that did not react with hydrogen (TPR peaks II - IV), according to the calibration curves, corresponds to the stoichiometry of $WO_{2.90}$. After the removal of oxygen I in the temperature-programmed reduction mode, the diffraction maxima 2θ = 8 - 10 ^{o} disappear in the XRD spectrum of this sample, due to the decomposition of the $H_4SiW_{12}O_{40}$ HPA phase. New diffraction maxima corresponding to the formation of a WO_3 compound with a tetragonal lattice with parameters a_0 = 0.525 nm, c_0 = 0.391 nm (JCPDS No. 5-0388) appear. Diffraction maxima corresponding to the $WO_{2.9}$ compound have crystal lattice parameters close to WO_3 (a_0 = 0.530 nm, c_0 = 0.383 nm, tetragonal system, JCPDS No. 18-1417).

After removal of oxygen I and II from SiW_{12}-HPA in TPR mode, the stoichiometry of the remaining oxygen (by TPR) in the sample corresponds to the formation of $WO_{2.78}$ compound. The maxima corresponding to the formation of the $WO_{2.83}$ phase (JCPDS No. 36-103) with parameters a_0 = 1.931 nm, b_0 = 0.378 nm (β = 104.4 ^{o}), and c_0 = 1.707 nm appear on the diffractogram of this sample. The HPA sample after removal of structural oxygen I - III in TPR mode by hydrogen (TPR I - III peaks, T = 20 - 850 ^{o}C) has a stoichiometry of $WO_{1.99}$. In this case, the maxima corresponding to the formation of the WO_2 phase (monoclinic, a_0 = 0.558 nm, b_0 = 0.489 nm (β = 118.869°), c_0 = 0.556 nm, JCPDS No. 32-1393) with a small admixture (~ 15 %) of the phase $WO_{2.72}$ (monoclinic, a_0 = 1.771 nm, b_0 = 0,378 nm (β = 110.60 °), c_0 = 1.404 nm, JCPDS No. 36-101) appear on its diffraction pattern. The complete removal of oxygen from HPA in the TPR mode (oxygen I - IV, T = 20 – 1,100 °C), according to the XRD, leads to the formation of a metal W phase crystallized in a cubic lattice with parameters a_0 = 0.316 nm, JCPDS No. 4-806) with a small admixture of WO_2 (JCPDS No. 32-1393).

From the combination of TPR and XRD data, it follows that in the case of $H_4SiW_{12}O_{40}$, the peak of TPR I is due to the absorption of hydrogen on the oxygen reduction of the molecular structure of the HPA, accompanied by the loss of 2.4 electrons per one heteropoly anion during oxygen reduction while maintaining the Keggin lattice. The stoichiometry of $WO_{0.1}$ corresponds to this form of oxygen per tungsten or loss of I O atom per HPA.

According to the assumptions (Misono, 1987), H^+ protons are involved in the interaction with structural oxygen I, which are formed from the H_2 molecule as a result of its activation and dissociation at the proton centers of the HPA. The established absence of peak I in the TPR curves for medium salts of $Mg_2SiW_{12}O_{40}$, $Na_4SiW_{12}O_{40}$, $Ca_2SiW_{12}O_{40}$, its partial presence when shifted 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 HPA with hydrogen. After complete removal of oxygen I, an imperfect structure is formed, according to the TPR calibration curves, $WO_{2.9}$ stoichiometry. The peak of TPR II corresponds to the participation of oxygen of an oxide of imperfect structure $WO_{2.9}$ in the amount of 1 O atom per one heteropoly anion in interaction with hydrogen, accompanied by a loss of ~ 1.6 e. The process leads to the formation of oxide $WO_{2.83}$ (possibly all these are intermediate forms of degradation of HPA in H_2). Upon reduction, the structural "forms" of oxygen reduced in the I and II absorption peaks of hydrogen lose a total of –4e, which is consistent with published data (Misono, 1987).

The TPR III peak of SiW_{12}-HPA at T = 650 - 850 °C is associated with the participation of oxygen from the $WO_{2.83}$ structure in the reaction and is accompanied by the formation of the WO_2 phase, which leads to the formation of the W_{metal} phase (XRD). Apparently, the temperature-programmed hydrogen reduction curves (TPR peaks I and II) describe the behavior of the directly Keggin molecular structure of $H_4SiW_{12}O_{40}$ only in the temperature range 20 - 650 °C. The process is accompanied by the participation of 2 O atoms in the reaction and the loss of 4e per structural unit of HPA.

Figure 1 shows the TPR spectra of the initial SiW_{12}-HPA, recorded after its exposure at various temperatures in a steam - air mixture (components of reaction mixtures for partial oxidative conversion of C_1-C_2 alkanes).

Preheating of the HPA in a steam - air mixture at temperatures lower and inclusive of 250 °C does not lead to a change in the TPR spectrum as compared to the initial sample. An increase in temperature to 400 °C leads to an insignificant shift of the maxima of the TPR peaks I and II to the region of higher temperatures (by 40 °C and 70 °C). In this case, the intensity and position of the TPR peaks III and IV do not change. This may indicate that an individual $H_4SiW_{12}O_{40}$ HPA in the presence of water vapor is thermally stable in air at 400 °C. After steam-air treatment at temperature 550 °C, the peak of TPR I disappears, and peak II moves to the region of higher temperatures (T_{max} = 650 - 670 °C). Calcination of the sample at 900 °C leads to the disappearance of peak II in the TPR spectrum as well.

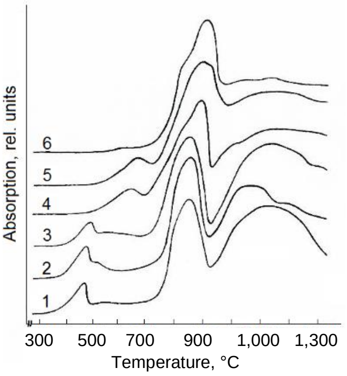

Figure 1: TPR spectra of the initial $H_4SiW_{12}O_{40}$ HPA (1) and heated in a steam - air mixture at: 2 – 250 °C, 3 – 400 °C, 4 – 550 °C, 5 – 650 °C, 6 – 900 °C

Figure 2 shows the IR spectra of the initial $H_4SiW_{12}O_{40}$ HPC and after its heating in a steam - air mixture at various temperatures.

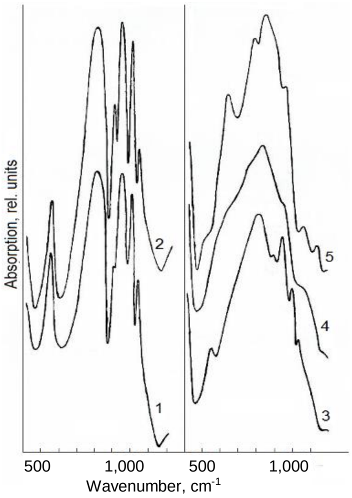

Figure 2: IR spectra of the initial $H_4SiW_{12}O_{40}$ HPA (1) and heated in a steam-air mixture at: 2 – 250 °C, 3 – 400 °C, 4 – 650 °C, 5 – 900 °C

In the IR spectrum of the initial SiW_{12}-HPA sample, there are absorption bands (a.b.) in the region of 700 – 1,100 cm^{-1}, which are characteristic of the Keggin structural form of the heteropoly anion and relate to valence bond vibrations: bridging - linear W – O - W (790 cm^{-1}) and angular – W - O - W (880 - 895 cm^{-1}) types, as well as Si – O - W (925 cm^{-1}) and W = O (980, 1,020 cm^{-1}). The result is consistent with published data (Misono, 1987). The position of the absorption bands is maintained after heating the sample in a steam - air mixture at T = 250 °C, 400 °C.

The heating of the sample in a steam - air mixture at higher temperatures leads to a gradual and significant change in the IR spectra: at 650 °C - its strong broadening with the appearance of one wide absorption region at 550 – 1,050 cm^{-1} with resolved absorption bands, at 810 cm^{-1} and “shoulders” at 550 - 560, 780, 930 and 1,040 cm^{-1}. The shoulders in the region of the bands of 780, 930, and 1,040 cm^{-1} are characteristic of the Keggin structure of the SiW_{12}-HPA and reflect the valence vibrations of the W – O – W bonds (linear), Si – O – W, W = O tetrahedral. In this case, the characteristic absorption bands for valence vibrations of the W – O – W bonds (angular, 890 cm^{-1}) and one of the doublets from W = O (980 cm^{-1}) disappear from the IR spectrum. According to published data (Misono, 1987), the presence of a doublet of absorption bands in the IR spectrum and a sharp decrease in their intensity during the dehydration of HPC are characteristic of the W = O bond.

After steam-air treatment of SiW_{12}-HPA at 900 °C, the disappearance of absorption bands from linear and angular bridges W – O - W (790, 890 cm^{-1}), as well as one absorption band from the doublet W = O (980 cm^{-1}) is observed in the IR spectrum. However, absorption bands 930 and 1,040 cm^{-1} from the Si – O - W and W = O fragments are preserved, and new bands appear that are not characteristic of the HPA structure (> 650 °C). This suggests that predominantly other, probably, fragments of the oxide type based on HPA, while saving individual elements of the HPA structure, begin to form with T ~ 650 °C in the steam - air mixture.

X-ray diffraction studies have allowed the identification of secondary high-temperature processes in reaction mixtures containing air and water vapour associated with oxide formation based on $H_4SiW_{12}O_{40}$.

From the X-ray diffraction patterns of the $H_4SiW_{12}O_{40}$ HPA under various conditions of temperature-steam-air treatment, it follows that the presence of a group of diffraction maxima in the range 2θ = 5 - 45 ° is characteristic of the initial sample. Of these, the maxima at 2θ = 8 - 10 ° are characteristic for the HPA. Diffraction peaks characteristic of HPA are observed in samples heated to 400 °C. However, according to the XRD spectra, the process of changing the structure of the HPA at 250 - 400 °C is not accompanied by the appearance of diffraction peaks characteristic of tungsten oxides. This may indicate either the X-ray amorphous nature of the tungsten oxide formed at this stage of heat treatment, or the absence of its formation. The latter is consistent with the data of TPR and IR spectroscopy.

When the temperature of the steam-air treatment increases to 550 °C, the diffraction maxima characteristic of the $H_4SiW_{12}O_{40}$ phase disappear. This probably indicates decomposition of the secondary structure of the HPA. The formation of tungsten (VI) oxide in a tetragonal crystal lattice (a_0 = 0.525 nm, c_0 = 0.391 nm, JCPDS No. 5-388) is observed from an amorphous formation when processed in a steam - air mixture. The phase transition of the tetragonal modification of WO_3 to orthorhombic (a_0 = 0.738 nm, b_0 = 0.385 nm, c_0 = 0.751 nm, JCPDS No. 20 – 1,324) begins at 750 °C, which ends at 900 °C. The formation of tungsten silicides WSi_2 and Si_3W_5 was not detected.

A study of the effect of steam-air treatment of $H_4SiW_{12}O_{40}$ HPA on its structural characteristics with the combination of IR spectroscopy, TPR, and XRD methods showed that $H_4SiW_{12}O_{40}$ is characterized by 4 types of structural oxygen: W – O - W angular, W – O - W linear, W = O, Si – O - W. They are characterized by absorption bands in the IR spectrum - 790, 890 (W – O - W angular and linear), 980 – 1,020 cm^{-1} (W = O), 930 cm^{-1} (Si – O - W), in the X-ray diffraction maxima in the range 2θ = 5 - 20 ° (8 – 9 °). In the TPR spectra, 4 types of reaction oxygen are observed. The first two of which relate directly to the reduction of the structure of the HPA. The molecular structure of HPA is stable in a steam - air medium in the temperature range of 20 – 400 °C. A change in its secondary structure is observed at T > 400 °C due to dehydration. The decomposition of HPA begins with a treatment temperature of 550 °C (TPR, IR spectroscopy, XRD) with a gradual destruction of fragments of the heteropoly anion structure: W – O - W (angular) (up to T = 550 °C), W – O - W (linear) (up to T = 650 - 700 °C). However, its fragmented formations (Si – O - W, W = O, in the IR spectra - absorption bands 930 and 1,020 cm^{-1}) are likely to remain in the temperature range of the steam - air treatment 650 – 900 °C. A partial preservation of the absorption bands characteristic of the structure of the HPA in the IR spectra indicates this. In parallel with the conservation of fragments of the SiW_{12}-HPA structure, the formation of (apparently based on the degraded fragments) sequentially phase W (VI) oxides of tetragonal and then orthorhombic coordination in the presence of O_2 and H_2O vapour at T ~ 650 - 900 °C occurs.

Conclusions

As a result of the studies, selective and thermally stable catalysts have been developed, the action of which is confirmed by physicochemical methods. The process in which these samples are used makes it possible to obtain an expensive and sufficiently pure product. Thermal stability of the 12th series molecular structure of $H_2SiW_{12}O_{40}$ HPA was investigated by complex of physical and chemical methods (TPR, IR spectroscopy, XRD). It was installed that HPA preserves the secondary structure at the conditions of reaction medium for oxidative conversion of light alkanes (hydrocarbons, air, water vapour) at 20 – 400 °C. At the temperatures $>$ 650 °C the oxide-similar W compounds are formed together with preserving the fragments of HPA structure.

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