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Article

Catalytic oxidation of C_3-C_4 mixture into industrially important chemical products

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Abstract: The processing of alkanes (the main components of natural gas) for obtaining of industrially important chemical products is one of the most urgent environmental problems, because the major share of raw materials are burned in torches. Therefore, the main goal of the work is the development of catalysts and conditions for obtaining of important petrochemical products from light alkanes. For the preparation of catalysts, Mo, Cr and Ga oxide catalysts as well as catalysts based on heteropoly compounds, supported on natural materials were used. The catalysts were prepared by the capillary impregnation method and used in oxidative conversion in a flowing unit while varying the process conditions. It has been determined that 5 and 10% MoCrGa catalysts are optimal for obtaining of liquid and gaseous products, and 1% catalyst is more favorable for the synthesis of gaseous products. Supported catalysts from heteropoly acid $H_3PW_{12}O_{40}$ are highly active in oxidative dehydrogenation and cracking processes, which are concurrent. High activity is caused by dispersity of catalysts, formation of crystal hydrates and amorphous phase of heteropoly acid in a condition of interaction with carrier. Maximum yield of C_2H_4 - 35.2% at 973 K, C_3H_6 – 20.0% and C_4H_8 – 14.3% at 773 K were observed.

Keywords: catalytic oxidation, oxide catalysts; C_3-C_4 mixture; ethylene, propylene, butylenes, heteropoly compound

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1. Introduction

Natural and oil gases are the most important alternative sources of raw materials, capable in the long term to compete with oil. The problem of rational use of C_1-C_4 alkanes, included in their composition, is particularly relevant in countries rich in this type of raw materials. Despite the huge reserves of hydrocarbons in the Republic of Kazakhstan, it is mainly used in the form of domestic, industrial and motor fuel, and the remaining raw materials are burned or re-injected into oil tanks. In this regard, the processing of alkanes (the main components of natural gas) for obtaining of industrially important chemical products is one of the most urgent environmental problems in Kazakhstan.

Formation of synthesis gas, unsaturated hydrocarbons, aldehydes, acids and alcohols should be expected at incomplete oxidation of methane, ethane, propane and butane. Only the optimal selection of catalysts can purposefully to carry out the process with preferential formation one of the listed products. However, the development of new effective catalysts for selective oxidation of light alkanes is still at the stage of research and development [1-11].

In the process of oxidative conversion of propane-butane mixture on various types of catalysts is possible to obtain a range of products such as oxygenates [12-16], olefins [16-20], hydrogen [21,22], synthesis gas [23-25] and $CO_2 + H_2O$ [26].

W and Mo heteropoly compounds (HPC) supported on carriers are widely investigated as catalysts for reactions of selective oxidative conversion of C_1-C_4 alkanes. Special interest to them is caused by unique combination of the acid-basic and red-ox active centers inside complex molecules. Catalytic reactions of the oxidative type which has been carried out at T = 593-673 K in conditions of their stability in liquid-phase and vapor-phase processes on HPC in solutions, on films, solid oxides are more investigated owing to low heat stability of compact heteropoly acids (HPA, 623-773 K) [27, 28].

Catalysts based on Si-Mo heteropoly compounds supported on carriers were investigated in oxidative dehydrogenation of ethane to ethylene. Determination of the effect of reaction parameters and the nature of catalyst on composition and distribution of products was carried out. The optimal reaction conditions: C_2H_6 – 20.0%, O_2 – 2.5%, N_2 – 57.5%, H_2O – 20.0%, space velocity – 8000 h^{-1}, contact time – 0.45 s were installed. Ethylene yields exceeding 42% with selectivity above 87% were obtained over novel Pb-Si-Mo heteropoly compound catalysts under oxidative dehydrogenation of ethane at 1023 K [29].

In case of compact HPC, their use in oxidative processes for synthesis of oxygen-containing compounds from C_3-C_4 alkanes, mainly acids, aldehydes, ketones, (meth)acrylic acids, (meth)acrolein, acetic, propionic acids and others are more widely known. 12 series HPA: $H_3PMo_{12}O_{40}$ modified by Ce, V, Sb, Cs, Fe, Cu, W, Bi, Cr in the form of acid-forming elements or counter-cations were used as catalysts. The investigations on influence of the nature of carrier including zeolites on process are well known. The investigations of catalytic activity in reaction of oxidative conversion of C_3-C_4 alkanes into oxygen-containing compounds (alcohols, aldehydes, acids, and ketones), C_2-C_4 olefins and H_2 over W-, Mo-HPC with P and Si as central atoms supported on Si-containing oxide carriers are developed [27-36].

2. Experimental

2.1. Catalyst preparation

Preliminary preparation was carried out for the preparation of catalysts on natural carriers (clays). The natural carriers were dried at 473 K for 2 h, calcined at 773 K for 2 h and then treated in a solution of 10% HCl and calcined again at 773 K for 2 h. The catalysts were prepared by the capillary impregnation method of mixed aqueous solutions of nitrate salts of metals, supported on preformed natural clays. A sequential and combined method of introducing the active components into the composition of the developed catalysts was studied. It has been determined that the sequential introduction of one or two components negatively influence on the efficiency of catalyst. It is assumed that the metals begin to react with each another (as observed visually during preparation of catalysts) and eliminates the additional separate drying and calcination of each supported subsequent element separately at co-supporting process of active phase of catalyst on carrier. It was determined that the simultaneous introduction of all components into the impregnating solution is optimal.

Supported catalysts on the base of $H_3PW_{12}O_{40}$ HPA and its salts were prepared by impregnation with following drying on air at 383 K during 4 h. 15% is the content of HPC over carrier. Synthetic aluminosilicate (Si/Al = 10, S = 320 m^2/g) and clinoptilolite – natural Sary-Ozek sorbent (Si/Al = 5, S = 9.8 m^2/g) processed by 10% HCl and washed by distilled water up to pH = 6-7 were used as carriers.

2.2. Characterization techniques

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 H_2, O_2, N_2, CH_4, C_2H_6, C_2H_4, C_3-C_4 hydrocarbons, CO and CO_2. 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 – 473 K, evaporator temperature – 553 K, column temperature – 313 K. Carrier gas (Ar) velocity = 10 ml/min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. A calibration curve V = f (S), where V - amount of substance in ml, S - peak area in cm^2, was constructed based on the measured areas of the peaks corresponding to the amount of the introduced substance. Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was ± 3.0%.

2.3. Physico-chemical research

The phase composition of catalysts was determined on X-ray diffractometer DRON-4-7 with Co-anode (25 kV, 25 mA, $2\theta = 15\text{-}80°$). Determination of the surface was conducted by low-temperature adsorption of nitrogen by the BET method on the "Accu Sorb" installation from Micromeritics produced in the USA. Morphology, particles size, chemical composition of initial and worked out catalysts were performed on transmission electron microscope TEM-125K with enlargement up to 66000 times by replica method with extraction and micro diffraction. Carbonic replicas were sputtered in vacuum universal station, and carrier of catalysts was dissolved in HF. Identification of micro diffraction patterns were carried out by means of ASTM cart index (1986).

3. Results and discussion

The results of a study of activity of the MoCrGa catalysts supported on natural clays of different content in the process of partial oxidation of propane-butane mixture at C_3-C_4 : O_2 : N_2 : Ar = (33.33 : 7.0 : 26.34 : 33.33, %), GHSV = 450 h^{-1} and a temperature range of 673-823 K are presented. As can be seen from Figure 1, the formation of C_2H_4, H_2, and CO_2 was observed at oxidative conversion of propane-butane mixture on the developed 1% MoCrGa catalyst. A 39.2% yield of ethylene passed through a maximum at 773 K. The formation of 1.0 – 2.6% H_2 was also observed. 39.5% of CO_2 is formed by raising the reaction temperature to 773 K and up to 823 K in reaction mixture. With increasing temperature, the process proceeds towards the formation of a deep oxidation product (CO_2) along with oxidative dehydrogenation (C_2H_4, H_2).

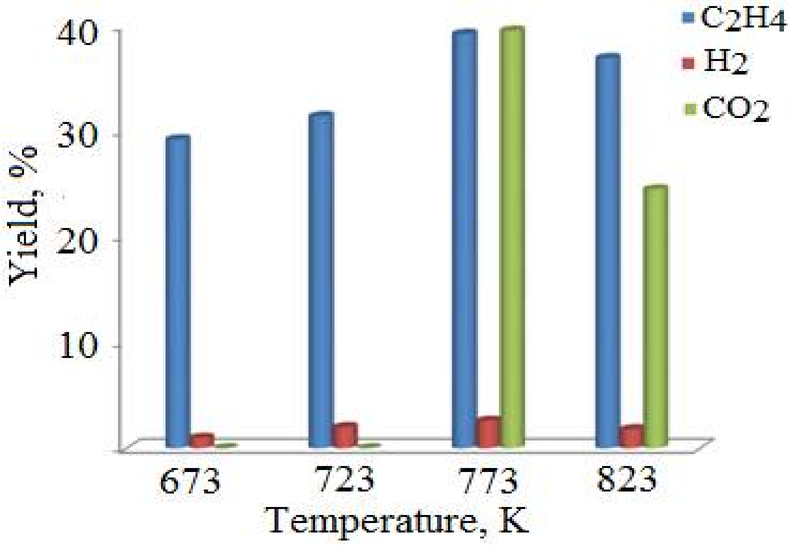

Figure 1. Oxidative conversion of C_3-C_4 mixture on 1% MoCrGa catalyst.

Figure 2 shows the activity of 5% MoCrGa/natural clay catalyst at oxidative conversion of propane-butane mixture. The greatest yields of acetaldehyde and methanol were obtained at relatively low temperatures of 673-723 K. The yield of acetaldehyde decreased from 33.3% to 11.5% with an increase of temperature from 673 K to 823 K, and methanol - from 13.8% to 10.7% at 773 K. Methanol was not detected in product at higher temperatures. A different picture was observed for acetone and methyl ethyl ketone. The maximum yields for these products were observed at 823 K. The yield of acetone at this temperature was 50.9%, and methyl ethyl ketone - 37.6%. It was determined that content of ethylene at all temperatures decreased compared with 1% catalyst.

However, the yield of hydrogen increased from 5.7 to 18.8%. The formation of products of deep oxidation was not observed.

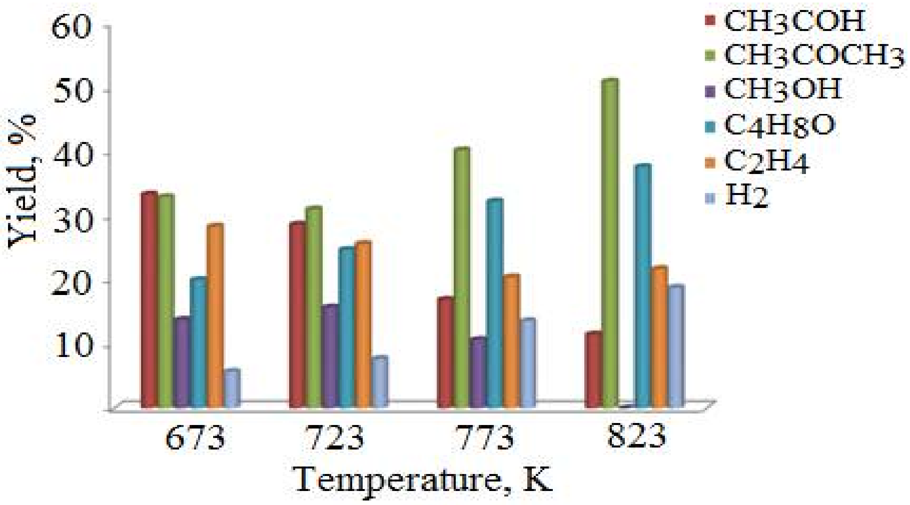

Figure 2. Oxidative conversion of C_3-C_4 mixture on 5% MoCrGa catalyst.

The same trend of reduction of gaseous substances in reaction products was observed at a further increase in the content of MoCrGa on the carrier to 10%. The yield of ethylene did not exceed 8.6%. A new product - ethanol appeared in the liquid phase, the yield of which was 66.0% at 823 K.

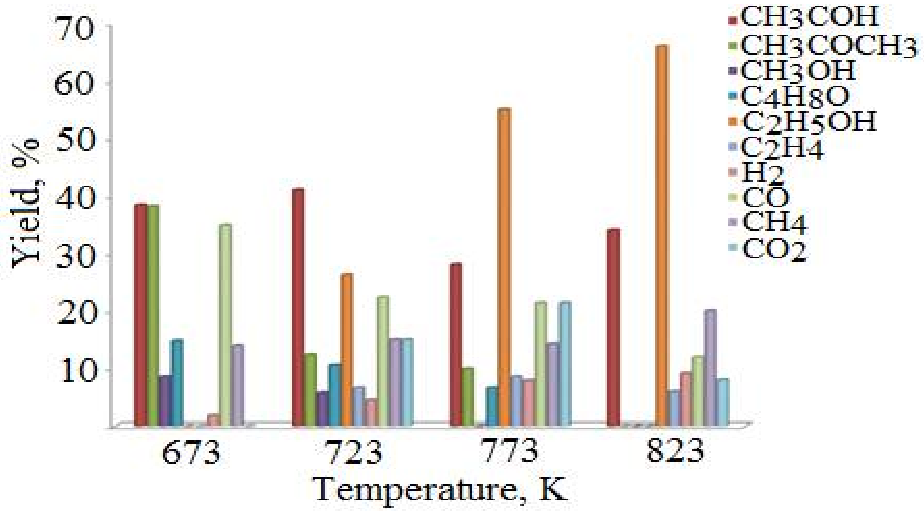

Figure 3. Oxidative conversion of C_3-C_4 mixture on 10% MoCrGa catalyst.

It can be seen from the data in Figure 3 that the decrease in the formation of acetaldehyde, acetone, methanol, MEK, ethylene and hydrogen was observed on this catalyst composition compared to the 5% catalyst composition.

Thus, the production of a number of products with high yields: acetaldehyde - at 673-723 K, acetone - at 823 K, methanol - at 673-723 K, MEK - at 773-823 K, ethanol - at 823 K, ethylene - at 673-723 K, H_2 - at 823 K is possible during the oxidative conversion of propane-butane mixture at GHSV = 450 h^{-1} on 1-10% MoCrGa catalysts. It was determined that 1% MoCrGa/natural clay catalyst is more suitable for the synthesis of gaseous products. It has been established that 5% MoCrGa catalyst is an optimal for obtaining of high yields both liquid products of partial oxidation and oxidative dehydrogenation products (33.3% acetaldehyde, 50.9% acetone, 15.7% methanol, 37.6% MEK, 28.3% ethylene and 18.8% H_2).

The polyoxide MoCrGa catalysts supported on natural clays and investigated in the oxidative conversion of propane-butane mixture were studied by physical-chemical methods. The specific surface and porosity of the studied sorbent samples were determined by the BET method for low-temperature nitrogen adsorption. It was established that the clay surface is 10-16 m^2/g, and the change in the optimum pore radius was observed from 20 to 50 Å. Elemental analysis of the initial and processed samples of sorbents with 10% HCl showed that the oxide compounds of Si, Al, as well as Ca, Mg, Fe, and Na are predominantly present in clay samples. The ratio of SiO_2/Al_2O_3 (silicon module) was 5-0.4. The silicon module increased after acid treatment, but the phase composition remained practically unchanged. In the course of work, it was determined that the yields of target products on the catalysts pretreated with 10% HCl exceed analogous yields on the untreated catalysts. It is assumed that acid treatment of sorbents contributed to development of surface and increase in the pore radius, which led to increase in the yield of target products of the oxidative conversion of propane-butane mixture.

It was established by the XRD method that the kaolinite $Al_2[OH]_4Si_2O_5$ (JCPDS-29-1488), α-quartz SiO_2 (JCPDS 5-490) and X-ray amorphous component (short-range order 4.20 Å) are the main phase of natural clay. The diffractograms of spent catalysts under reaction conditions at 573 and 773 K are identical. The 3.62, 2.66, and 2.48 reflexes, relating to the phase of Cr_2O_3 (JCPDS 6-504) and the 3.52, 2.67, 2.38 reflexes, relating to the phase of Cr_3O_{12} (JCPDS 18-390) were detected. The 3.52 reflex refers, perhaps, to textured kaolinite. The structural elements relating to Ga and Mo were not detected because of their dispersity.

Transmission electron microscopic studies have shown that the presence of a large number of insoluble components, which make it difficult to decipher the deposited phases is characteristic for carrier, Figure 4.

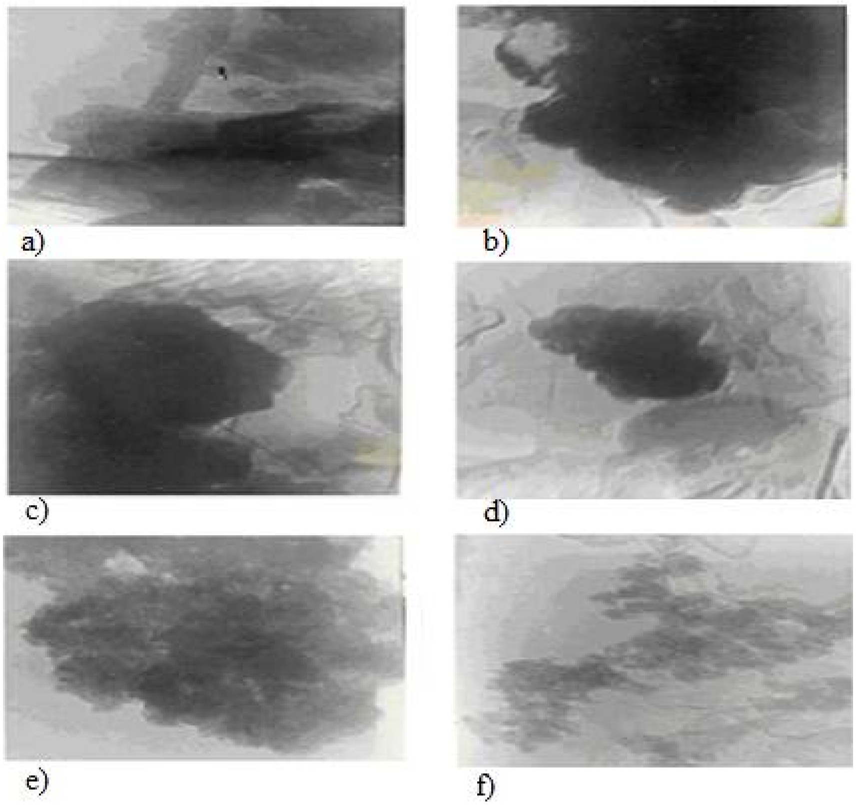

Figure 4. Transmission electron microscopic images of the 5% MoCrGa (× 66000); a) $CrMoO_4$ and $CrMoO_6$, 30-50 Å; b) $Cr_{0.17}Mo_{0.83}O_2$ and CrO, 200 Å; c) $Cr(MoO_4)_3$, MoO_2 and ε-Ga_2O_3 > 100 Å; d) Ga, ϕ-Ga_2O_3, 100-120 Å; e) ε-Ga_2O_3 ~ 50 Å; f) Cr_2O_5 ~ 30 Å.

Large particles and aggregates from large dense particles are characteristic for the initial samples of MoCrGa. Their microdiffraction pattern is represented by separate rare reflections attributed to Cr_2O_3 (JCPDS, 6-508) and CrO (JCPDS, 6-532), as well as to semitransparent plate-like particles, the micro diffraction pattern from which is represented by reflexes located on a hexagonal motif referred to $CrMoO_4$ (JCPDS, 34-474). The presence of combined chromium-molybdenum-gallium phases is characteristic for samples processed under experimental conditions.

Figure 4a shows small clusters composed by particles with a size of 30-50 Ǻ and big plate-like particles. A mixture of rings and separate reflexes presents the microdiffraction. The rings correspond to $CrMoO_4$ phase (JCPDS, 29-452) - dispersed particles. The big plate crystals correspond to $CrMoO_6$ (JCPDS, 33-401).

Figure 4b shows an aggregate of dense particles with signs of cutting with a minimum dimension of ~ 200°. The microdiffraction pattern is presented by reflexes arranged along the rings, and corresponds to mixtures of $Cr_{0.17}Mo_{0.83}O_2$ (JCPDS, 34-473) and CrO (JCPDS, 6-532).

The microdiffraction pattern of aggregate (Figure 4c) is presented by rings and reflexes, which are located by series and corresponds to a mixture of $Cr(MoO_4)_3$ (JCPDS, 20-309), MoO_2 (JCPDS, 9-209) and, possibly, ε-Ga_2O_3 (JCPDS, 6-503) phases, where there are aggregates with a size more than 100 Ǻ and individual large particles. A small aggregates (Figure 4d) with particle sizes of 100-120 Ǻ are presented in the microdiffraction pattern by separate reflexes and correspond to ϕ-Ga_2O_3 (JCPDS, 20-426) in a mixture with Ga (JCPDS, 31-539). The extensive aggregation (Figure 4e) from dispersed particles of size ~ 50 Å corresponds to ε-Ga_2O_3 (JCPDS, 6-509). More small-dispersed particles (Figure 4f) with sizes of ~ 30 Å are assigned to Cr_2O_5 (JCPDS, 36-1329).

Comparison TEM images of the 1-10% MoCrGa samples showed that the set of phases is significantly reduced at simultaneous enlargement of particles with increasing the content of active component on carrier.

$CrMoO_2$ + CrO spinels with a particle size of 600 Å and Ga_2O_3 of various modifications (α and ϕ) as well as Cr^{5+} remain on the surface of the 5% MoCrGa sample treated at 623 K. The Cr^{5+}, CrOOH phases disappear on the surface. The phases corresponding to Ga^{3+} and Cr^{3+} are present in all catalysts, becoming somewhat larger in size. The appearance of spinel ($CrMoO_6$) with a size of 500 Å, which was absent at 573 K, and also Cr^{2+} is a distinguishing feature of the highly active optimal 5% MoCrGa catalyst heated at 823 K. This facilitates the process both towards partial oxidation and towards oxidative dehydrogenation with optimum production of the desired reaction products.

Figure 5 shows the activity of developed 15% $H_3PW_{12}O_{40}$/clinoptilolite catalyst in the oxidative conversion of C_3-C_4 mixture at $\tau = 0.29$ s and C_3-$C_4 : H_2O = 1 : 0.21$ by varying the reaction temperature and the C_3-$C_4 : O_2$ ratio. The formation of oxygenates (C_3H_7OH, C_4H_9OH-1, C_4H_9OH-2, i-C_4H_9OH, CH_2O), olefins (C_2H_4, C_3H_6, C_4H_8), and cracking reaction products (CH_4, CO_2, H_2) observed at varying the ratio of the C_3-$C_4 : O_2$ and the reaction temperature.

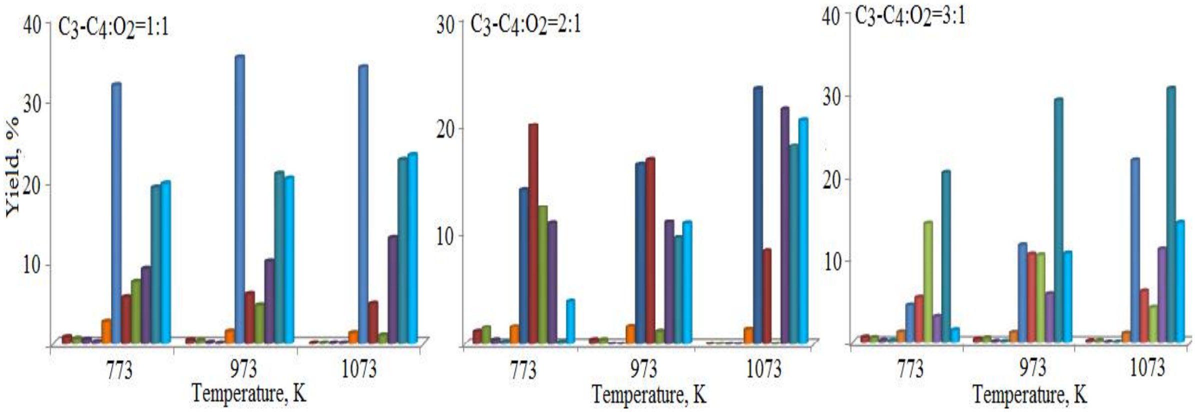

Figure 5. Influence of the reaction temperature and C_3-$C_4 : O_2$ ratio on yield of products of partial oxidation of C_3-C_4 mixtures over 15% $H_3PW_{12}O_{40}$/clinoptilolite catalyst.

Thus, the yield of cracking products increased due to the growth of the reaction temperature at all ratios of the C_3-$C_4 : O_2$ mixture in reaction mixture. For all variations the yield of oxygenates does not exceed 5%. Formation of C_2-C_4 olefins was determined by the reaction temperature. Maximum for formation of C_2H_4 -35.2% at 973 K (C_3-$C_4 : O_2 = 1 : 1$), C_3H_6 – 20.0% at 773 K (C_3-$C_4 : O_2 = 2 : 1$), C_4H_8 – 14.3% at 773 K (C_3-$C_4 : O_2 = 3 : 1$) were installed at these conditions. The $C_3 : C_4 = 1 : 1$ ratio was optimal for the formation of C_2H_4, $C_3 : C_4 = 2 : 1$ - for C_3H_6 and $C_3 : C_4 = 3 : 1$ for C_4H_8.

According to IRS, XRD, TPR-TPO results [37] it was proposed that high activity of 15% $H_3PW_{12}O_{40}$/clinoptilolite catalyst in oxidative dehydrogenation of the propane-butane mixture in comparison with more high-percentage catalysts on carriers (> 20 % mas. of HPA) is caused by presence in the catalyst both crystallites of HPA (2Ɵ = 8-11°) and amorphous phase (2Ɵ = 3.14 – 4.45°) due to interaction in the system the HPA-carrier. It was installed that HPA preserves the secondary structure at the conditions of reaction medium for oxidative conversion of C_1-C_4 alkanes (hydrocarbons, air, water vapor). At the temperatures > 923 K the oxide-similar W compounds are formed together with preserving the fragments of HPA structure, which promotes the activity of catalysts.

4. Conclusions

Thus, developed three-component catalytic systems based on Mo, Cr and Ga showed catalytic activity in gas-phase oxidation of linear hydrocarbons to aldehydes, alcohols, ketones and olefins. The research of oxidative conversion of propane-butane mixture on polyoxide catalysts based on molybdenum, chromium and gallium supported on natural clay allowed to determine that preferential composition of products is determined by temperature of process. It was found that 5% MoCrGa catalyst in which by varying the reaction temperature was obtained up to 33% acetaldehyde, 50.9% acetone, 38% MEK, 15.7% methanol, 28.3% ethylene and 18.8% hydrogen is most active when the content of active phase of catalyst varies from 1 to 10% on a carrier.

It was found that the total greatest 46% yield of olefins (C_2H_4, C_3H_6, C_4H_8) was obtained at oxidative conversion of the C_3-C_4 mixture on 15% $H_3PW_{12}O_{40}$/clinoptilolite catalyst at optimum C_3-C_4 : O_2 = 1 : 1 ratio at 973 K. The processes of oxidative dehydrogenation and cracking are concurrent in formation of olefins. High activity is caused by dispersity of supported catalysts (XRD, IRS) both formation of crystal hydrates and an amorphous phase of heteropoly acid in a condition of interaction with the carrier.

Author Contributions: T. Baizhumanova and S. Tungatarova designed and the experiments, Z. Zheksenbaeva contributed to scientific discussions, D. Abdukhalykov supervised the study, R. Sarsenova, K. Kassymkan and G. Kaumenova performed the experiments and wrote the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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