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THE CATALYTICAL OXIDATION OF PROPAN-BUTANE MIXTURE ON THE HYDROGEN AND HYDROGEN CONTENT COMPOUNDS

Abstract. Oxidative conversion of the propane-butane mixture by air into oxygen-containing compositions was studied. It were determined the optimum reaction temperature, contact time, change in the space velocity in the process of partial oxidation of C3-C4 hydrocarbons. The physicochemical studies of the initial and treated catalysts were carried out under experimental conditions. When changing the content of the active component from 1 to 10% on the carrier, it was found that the most optimal is 1% MoCrGa/TC catalyst, on which up to 89.92% of hydrogen is obtained. As a result of varying the composition of the catalyst, the content of the active phase, the ratio of reactants, up to 70% of ethylene was obtained. In addition, in some cases, CH₃OH was obtained, the maximum yield of which is 22%, and also up to 35% of methyl ethyl ketone. As a result of EM and XRD studies, it was shown that under reaction conditions, a new Cr₂O₃ phase is formed on the catalyst surface (corresponding to the Cr²⁺ and Cr³⁺ transition to Cr⁵⁺), as well as joint Mo phases with Cr in different valence states, the physical meaning and role of which are to be determined.

Key words: catalysts, propan-butane mixture, natural clay.

Introduction. It requires the creation of large chemical industries on the basis of gas and oil resources to strengthen its economic status concerned to the strategic program of the Republic of Kazakhstan [1-3]. Today Kazakhstan has large reserves of raw materials, which have not been put into production [4-7]. Recently, environmental attention has been focused on reducing their harmful effects by incorporating hydrogen and hydrogen-based additives into fuels used in heat centers as well as for gasoline and diesel fuels. It is known that the use of catalysts for the production of hydrogen and hydrogen-based additives from the alkanes is a progressive and scientifically developed course of research [8-12].

Methods. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor. Analysis of the reactants and products was carried out chromatographically with an “Agilent Technologies 6890N” instrument. The catalysts were investigated by X-ray diffraction (XRD), electronic microscopy (EM), infra-red spectroscopy, and their surface area, porosity, and elemental composition were determined [1,5].

Figure 1 shows the effect of temperature on the hydrogen emissions generated by partial oxidation of the propane-butane mixture with the catalysts. It was determined that the yield of H₂ gradually increased as the temperature increased from 623K to 873K.

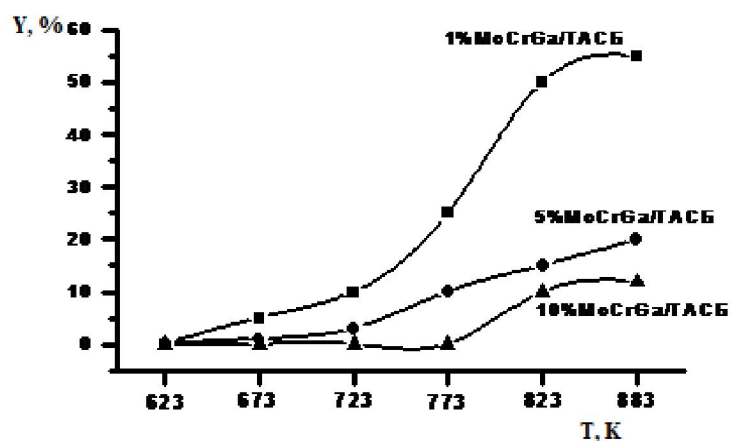


Figure 1 - The effect of temperature on the hydrogen product generated in partial oxidation of propane-butane mixture.
Reaction: $C_3-C_4:O_2:N_2:Ar=1:1:4:1$

As seen from the Figure 2, the change of the active phase between 1 and 10% has a direct impact on the yield of product. It was obtained 89,92% hydrogen from the 1%MoCrGa/NWC three-component catalyst by changing the active phase composition into the supporter.

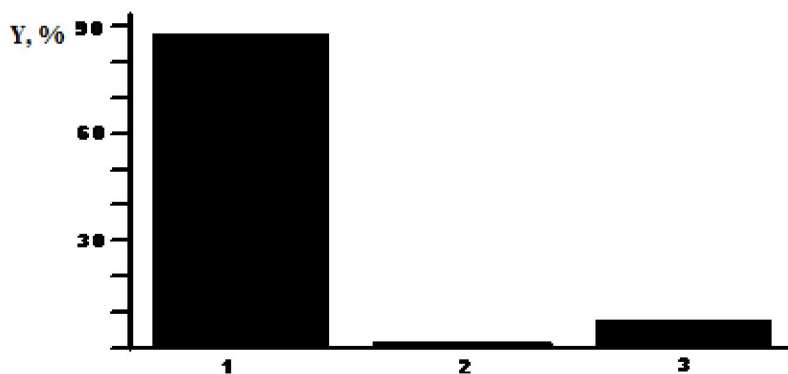


Figure 2 - Influence of active phase composition on hydrogen output. Reaction: C_3-C_4 KC: $O_2:N_2:Ar=0,95:1:3,76:0,95$; $T_p=873K$; $W=3150 h^{-1}$; 1-1%MoCrGa/NWC; 2-10% MoCrGa/ NWC; 3-5% MoCrGa/ NWC +ZSM-5+ $Al_n(OH)_{3n-1}NO_3$.

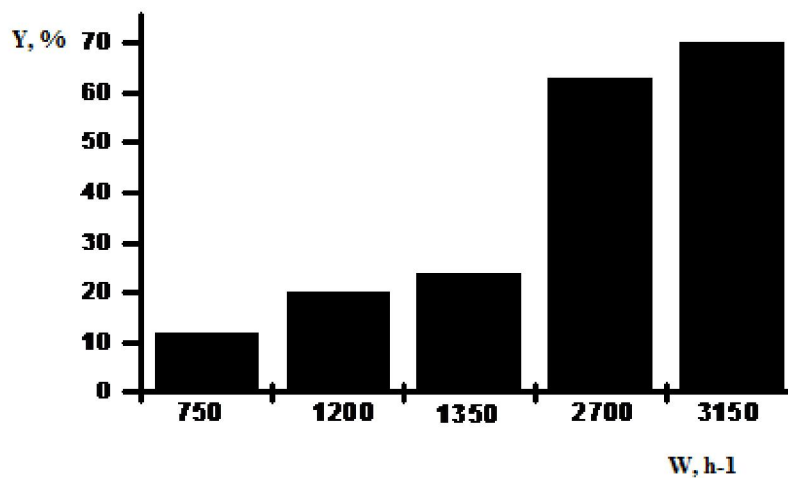


Figure 3 - Influence of volume velocity on the yield of hydrogen in 1%MoCrGa/ NWC catalyst. Reaction: C_3-C_4 KC: $O_2:N_2:Ar=0,95:1:3,76:0,95$; $T_p=823K$

The change in 1%MoCrGa/(NWC) of catalyst at 330-15000 h⁻¹ speed directly influence the reaction product. The most suitable volume velocity is 3150 hr⁻¹ for 1% MoCrGa/NWC catalyst for hydrogen removal 70,0% (Figure 3).

A favorable composition of the process was studied by modifying the starting reactions. It has been determined that by changing O₂ concentration in mixture 89,92 of % hydrogen is formed in 1%MoCrGa/NWC catalyst at a temperature of 873K at a range of 3,8-18,0 %; 71,4% of ethylene is formed in 1% MoCrGa/NWC catalyst at 723K and 450 hr⁻¹ of volume velocity, when the reaction mixture is C₃-C₄:O₂:N₂:Ar=5:1:4:5.

Results and discussion. According to the results of the above study, it was found out that the product of the oxidation of propane-butane mixture in the molybdenum, chromium, gallium catalyst placed on the natural white clay has a direct effect on the temperature, reaction mixture, contact time, catalyst composition.

The phase composition and surface area of 1%MoCrGa/NWC catalyst were studied by x-ray amorphous and Brunagoer Emmet-Taylor methods. It has been found that natural white clay is composed of α -quartz, kaolinite and roentgenomorphous composition. In the reaction, the content of raw and processed catalysts corresponds to the natural white clay diffractogram. Due to the dispersion of catalysts, no structural elements corresponding to metals were found. The whole sample consists of α -quartz SiO₂ x-ray amorphous. Cr₂O₃, Cr₃O₁₂ structures were observed only during 723K processing. However, the structures corresponding to Ga, Mo are not found in all models. Also, if the surface area of 1% MoCrGa/NWC catalyst is 14,51 m²/g, hollow volume is 155,53 ml/g then the surface area of 1%MoCrGa/NWC catalyst is 16,80 m²/g, hollow volume is 303,61 ml/g grows.

According to the results of the electron microscope, the ring-shaped phases Mo₃O₅ and Mo_{0,42}C_{0,58} consist of ring-shaped phases Cr₃O₄, α -Ga₂O₃, Mo₅O₈, γ -MoC in size of 10-20 nm containing the large composition of accumulated thick particles, Ga and MoC mixture in the form of symmetrical reflexes in size of 20 nm of individual particles, CrO, Ga₂O₃, MoO₃ and Mo₂C of thick particle composition of a small aggregate of 10-12nm, particle groups in size of 5-20 nm during the reaction processed at a temperature of 723K on the surface of 1% MoCrGa/NWC catalyst.

In addition to the phase shrinkage, it was determined that the formation of Mo₂C, γ -MoC phases, as well as the change of Mo³⁺ to Mo⁵⁺ have a positive effect on the growth of hydrogen and ethylene outputs generated during the dehydration of the propane-butane mixture.

Thus, it have been determined the favorable conditions to obtain the appropriate product: 71,4% of ethylene is formed in 1% MoCrGa/NWC catalyst at 723K and 450 hr⁻¹ of volume velocity, when the reaction mixture is C₃-C₄:O₂:N₂:Ar=5:1:4:5; 89,92 of % hydrogen is formed in 1%MoCrGa/NWC catalyst at a temperature of 873K and 1350 h⁻¹ of volume velocity, when the reaction mixture is C₃-C₄:O₂:N₂:Ar=1:1:4:1. It was studied that oxidation, dehydration and cracking processes are carried out during the research of polyoxide catalysts, which are supported in natural white clay.

Conclusion. Suggested in this research work catalytic reactions can be base for creation of industrial C₃-C₄ mixture utilization process and for production of valuable oxygen-containing compounds.

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ПРОПАН-БУТАН ҚОСПАСЫНЫҢ СУТЕГІ ЖӘНЕ СУТЕКҚҰРАМДАС ҚОСЫЛЫСТАРҒА КАТАЛИТИКАЛЫҚ ТОТЫҒУЫ

Аннотация. Пропан-бутан қоспасын оттегі құрамды композицияларға дейін тотықтыру бойынша зерттеулер жүргізілді. Тотығу процесінің оңтайлы температурасы, реакциялық қоспаның бастапқы компоненттерінің коэффициенттері, тасымалдағыштағы белсенді фаза және көлемдік жылдамдық анықталды. Эксперименттік жағдайларда бастапқы және өңделген катализаторлардың физика-химиялық зерттеулері жүргізілді. Белсенді компоненттің құрамын 1%-дан 10%-ға өзгерткен кезде ең оңтайлы катализатор 1% MoCrGa/ТСБ, нәтижесінде сутегінің 89,92%-алынды. Катализатордың құрамын, белсенді фазаның мөлшерін, реагенттердің қатынасын өзгерту нәтижесінде этилен 70%-ға дейін алынған. Сонымен қатар, кейбір жағдайларда CH₃OH алынды, оның максималды шығыны 22%, сондай-ақ 35% метилэтилкетон алынды. Реакция жағдайында катализатордың бетінде жаңа Cr₂O₅ фазасы (Cr²⁺ және Cr³⁺ -ға Cr⁵⁺ -ке көшу), сондай-ақ әртүрлі валентті Cr-мен бірге Мо-фазалары пайда болатынын ЭМ және РФА зерттеулерінің нәтижесі көрсетті, келешекте физикалық мағынасы мен рөлін анықтау керек.

Түйін сөздер: катализатор, пропан-бутанды қоспа, табиғи сазбалшық

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КАТАЛИТИЧЕСКОЕ ОКИСЛЕНИЕ ПРОПАН-БУТАНОВОЙ СМЕСИ НА ВОДОРОД И ВОДОРОДСОДЕРЖАЩИХ СОЕДИНЕНИЙ

Аннотация. Проведены исследования по окислительному превращению пропан-бутановой смеси воздухом в кислородсодержащие композиции. Определены оптимальные температуры процесса, соотношения исходных компонентов реакционной смеси, содержания активной фазы на носителе и объемные скорости. Проведены физико-химические исследования катализаторов исходных и обработанных в условиях эксперимента. При изменении содержания активного компонента от 1 до 10% на носителе установлено, что наиболее оптимальным является 1%MoCrGa/ТГ катализатор, на котором получено до 89,92% водорода. В результате варьирования состава катализатора, содержания активной фазы, соотношения реагирующих компонентов было получено до 70% этилена. Кроме того, в ряде случаев получен CH₃OH, максимальный выход которого составляет 22%, а также до 35% метилэтилкетона. В результате ЭМ и РФА исследований показано, что в реакционных условиях на поверхности катализаторов образуется новая фаза Cr₂O₅ (соответствует переходу Cr²⁺ и Cr³⁺ в Cr⁵⁺), а также совместные фазы Мо с Cr в различных валентных состояниях, физический смысл и роль которых предстоит определить.

Ключевые слова: катализатор, пропан-бутановая смесь, природная глина

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