

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

<https://doi.org/10.32014/2019.2518-1491.27>

Volume 3, Number 435 (2019), 38 – 43

UDC 544.478

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LIQUEFIED PETROLEUM GAS AS RAW MATERIALS FOR THE PRODUCTION OF LIQUID OXYGEN-CONTAINING ORGANIC COMPOUNDS

Abstract. Studies on the air oxidative transformation of the propane-butane mixture to oxygen-containing compositions have been carried out. The optimum temperatures of the process, as well as the ratios of the initial components of the reaction mixture and the content of the active phase on the carrier and volumetric rates have been determined. Physical and chemical studies of the initial and treated catalysts under experimental conditions were carried out. When changing the content of the active component on the carrier from 1 to 10%, it was found that the most optimal is the catalyst 5% MoCrGa/TC, on which up to 22% acetone was obtained. As a result of varying the composition of the catalyst, the content of the active phase, the ratio of reactants, up to 35–40% of acetone was obtained. In addition, in some cases, CH₃OH was obtained, with the maximum yield 22%, as well as 35% of methyl ethyl ketone. As a result of EM and XRD studies, it was shown that under reaction conditions a new Cr₂O₅ phase (corresponding to the Cr²⁺ and Cr³⁺ transition to Cr⁵⁺) is formed on the catalyst surface, as well as joint phases of Mo and Cr in various valence states, the physical meaning and role of which are to be determined.

Key words: natural clay, acetone.

Introduction. Natural and petroleum gases are the most important alternative sources of raw materials that can in the long run compete with oil. Of particular relevance for countries rich in this type of raw material is the problem of the rational use of alkanes in their composition [1-5]. Kazakhstan has significant oil and gas reserves. Unfortunately, there is currently no industrial organic synthesis based on alkanes in Kazakhstan, with the exception of gas processing plant in Zhanauzen, the nitrogen-fertilizer plant in Atyrau (which uses the low-profitable process of steam reforming of methane into synthesis gas) and ethylene production in Aktau (by non-catalytic pyrolysis of ethane with the addition of other hydrocarbons and petroleum fractions). Kazakhstan is entering a new era in hydrocarbon processing. Gas processing is the most promising direction of petrochemistry is. This sphere will help Kazakhstan to integrate faster in the world market. The partial oxidation of liquefied petroleum gas to ketones and aldehydes is relevant from the of ecological and economical point of view, since about 100 billion cubic meters of associated petroleum gas are burned annually and pollutant emissions to the atmosphere amount to thousands of tons [6-11]. The combustion process due to oxygen consumption and heat release contributes to the greenhouse effect. In addition, the economy is suffering losses due to the combustion of far from cheap petroleum gas, especially if we consider that it would be possible to get petrochemical products from the liquefied petroleum gas which are much more expensive than the original product.

A large number of studies have been carried out on the oxidation of propane and butane to unsaturated aldehydes and acids /12-16/, but there are few works on the production of ketones /17-20/.

Methods. This paper presents the results of oxidative transformation study of liquefied petroleum gas (propane-butane mixture) by air into oxygen-containing compositions in reaction mixtures with a propane-butane content 14- 80% and oxygen 4-18% at $T = 300-600\text{ }^{\circ}\text{C}$ and $W=330-15000\text{ h}^{-1}$. Polyoxide catalysts of different composition, containing 1-10% Mo, Ga, Cr in various proportions, deposited on natural Torgai clay (TC), having the structure of kaolinite (in some cases with the addition of hematite and α -quartz) were tested. Automated analysis of initial materials and reaction products were carried out on Agilent Technologies 6890N chromatograph. Physical and chemical studies of the initial and treated catalysts under experimental conditions (XRD, EM, elemental analysis, determination of acidity) were carried out [9-10].

It is established that the main reaction products are acetone, methanol, acetaldehyde, methyl ethyl ketone (MEK). The optimum process temperature is $350-400\text{ }^{\circ}\text{C}$. C_2H_4 , H_2 , CO , and CO_2 were detected in the reaction products when temperature increased. It was shown that the yield of oxygen-containing products on catalysts pretreated with 10% HCl exceeds similar yields on untreated catalysts. Acid treatment of sorbents contributed to the development of the surface and an increase in the pore radius, which led to an increase in oxygen-containing compounds in catalyzate [8-9]. Varying the reaction conditions on a number of catalysts (two-component - CrGa/TC and three-component - MoCrGa/TC) leads to a change in the content of the active phase and has a significant impact on the yield of the main products. When varying the content of the active component on the carrier from 1 to 10%, it was shown that the most optimal was 5% MoCrGa/TG catalyst, on which up to 22% acetone was obtained, the three-component catalyst being more active than the two-component catalyst (Figure 1).

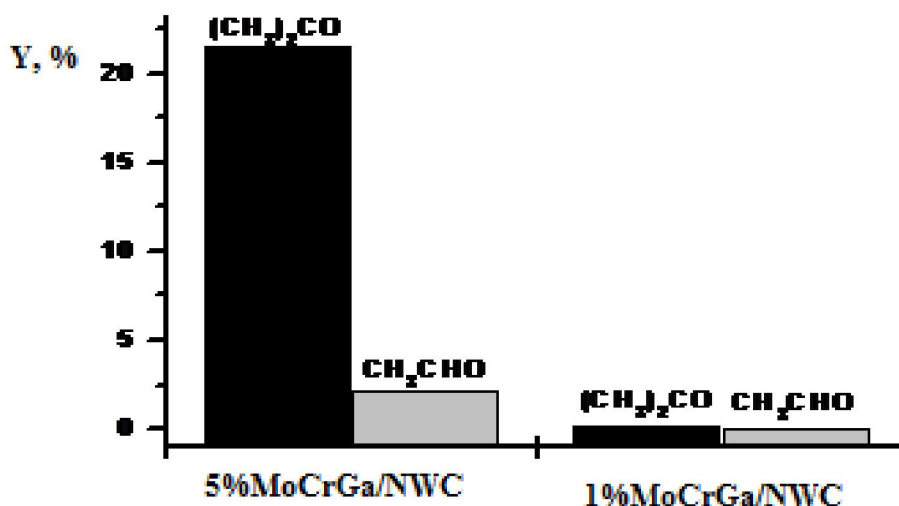


Figure 1 - The effect of active phase content of the catalysts on the yield of acetone and acetaldehyde.

Tests of the above catalysts at space velocities from 330 to 15000 h^{-1} showed that for the synthesis of acetaldehyde and acetone on the 1% CrGa / TC catalyst, the optimal rate is $W = 1200\text{ h}^{-1}$, and for the 5% CrGa/TC catalyst - 9000 h^{-1} for acetaldehyde and 330 h^{-1} for acetone (acetone yield is 32%), Figure 2 and 3. Optimal space velocities were also determined for three-component MoCrGa/TC catalysts with different content of the active phase on the carrier. At $W=1350\text{ h}^{-1}$, up to 23% of acetone and 35% of methyl ethyl ketone on 5% MoCrGa/TC were produced, whereas 22% of acetone on 5% MoCrGa/TC catalysts was produced.

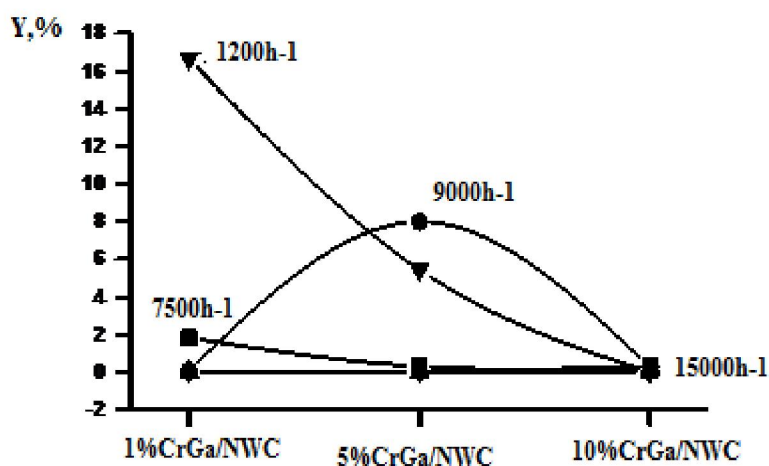


Figure 2 - The effect of space velocities on the yield of acetaldehyde on 1% -, 5% - and 10% CrGa/TC catalyst at 400 °C

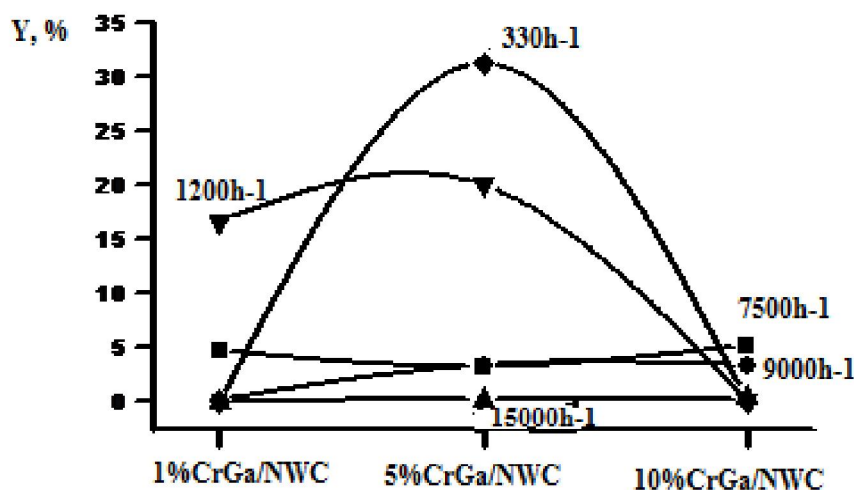


Figure 3 -The effect of space velocities on the yield of acetone on 1% -, 5% - and 10% CrGa/TC catalyst at 400 °C

Studies on variation of the initial components ratio in the reaction mixture allowed to determine the most optimal compositions for the process implementation. By varying the concentration of O₂ from 3.8 to 8.4% in the mixture, it was shown that when the content of O₂ is 5.3% and the propane-butane mixture is ~ 60-66%, the yield of acetone is 23% and methanol is 22%. When the content of the propane-butane mixture is 33-36% with the same O₂ content, 31% acetone and 35% MEK are obtained. By varying the composition of the catalyst, the content of the active phase, the ratio of reactants up to 31% acetone and 35% MEK were produced. In addition, in some cases CH₃OH was produced with the maximum yield 22%.

The microstructure and morphology of the catalysts were determined by X-ray phase analysis and electronic microscopy (EM) [14].

Results and discussion. The experiment was carried out on the electron microscope EM-125K by single-stage coal replicas method with extraction, using microdiffraction, as well as the method of survey through the lumen (suspension preparations). The survey was carried out at different magnifications depending on the particle size [1]. The carrier was dissolved in concentrated HF. The X-ray phase analysis was performed on a DRON-4-07 X-ray diffractometer. EM method provides observation of electron diffraction on individual crystals and accumulation of particulate matter, while the XRD method gives the total diffractogram of all phases [8-9].

In addition, for the manifestation of the phase in XRD it must have a large enough size. Therefore, many phases detected by EM method may not be observed in X-ray phase analysis, but this does not mean their absence in the catalyst.

For microdiffraction in electron microscopy, the transparency of the material for the electron beam is important. Sometimes well crystallized phases stably observed in XRD may be not transparent to the EM.

Both methods complement each other and provide a more complete picture of the catalyst changes under the influence of the environment.

The presence of a large number of insoluble components that make it difficult to decipher the deposited phases is characteristic of the carrier (Torgai clay). For the original clay sample MoCrGa / Torg. large particles and aggregates of large dense particles are characteristic, the microdiffraction pattern of which is represented by individual rare reflexes attributed to Cr₂O₃ (JCPDS, 6-508) and CrO (JCPDS, 6-532), as well as translucent particles of lamellar type, the microdiffraction image from which reflexes, located on the hexagonal motif, referred to CrMoO₄ (JCPDS, 34-474).

The phase related to Ga, were not detected. Mo-containing phase is characterized by dense large crystals of 500–1000 Å with signs of a rectangular motif of cut, corresponding to Mo₄O₁₁ (JCPDS, 13-142). For the Cr-containing phase, large semitransparent lamellar particles α-Cr₂O₃ (JCPDS, 6-503), small clusters made up of dispersed particles ~ 30 Å in size, referred to Cr₂O₅ (JCPDS, 36-1329), aggregates of translucent particles with minimal size 200-400 Å and larger, characteristic for CrO₂ (JCPDS, 9-332), a cluster of translucent lamellar particles Cr₅O₁₂ (JCPDS, 18-390) 300-600 Å in size with a rectangular cut motif.

Furthermore, we detected small clusters characteristic for joint phases consisting of particle 30-50 Å in size and large plate-type particles. Microdiffraction is represented by a mixture of rings and individual reflexes. The rings correspond to the phase of disperse particles CrMoO₄ (JCPDS, 29-452), and large plate crystals correspond to Cr₂MoO₆ (JCPDS, 33-401). Ga-containing phase is characterized by different phases of Ga oxidation up to the metal phase: α-Ga₂O₃ (JCPDS, 6-503), φ-Ga₂O₃ (JCPDS, 20-426), ε-Ga₂O₃ (JCPDS, 6-509) mixed with Ga (JCPDS, 31-539), Ga (JCPDS, 25-345).

Comparison with the EM pictures of the initial samples of catalysts allowed to state that as a result of their treatment under the reaction conditions, a new Cr₂O₅ phase appears, corresponding to the Cr₂ + and Cr₃ + transition to Cr₅ +, as well as the combined Mo- Cr phases in different valence states, the physical meaning and role of which are to be determined

Conclusion. Source of research funding. Initiative project "Conversion of hydrocarbon raw materials of Kazakhstan" Department of «Chemistry and Chemical Technology" of M.Kh.Dulaty Taraz State University.

ӨОК 544.478

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СЫҒЫЛҒАН МҰНАЙ ГАЗЫ - СҰЙЫТЫЛҒАН ОТТЕКҚҰРАМДАС ОРГАНИКАЛЫҚ ҚОСЫЛЫСТАР ӨНДІРІСІ ҮШІН ШИКІЗАТ РЕТІНДЕ

Аннотация. Пропан-бутан қоспасының құрамында оттегі бар органикалық қосылыстарға катализаторлық тотығуы бойынша зерттеулер жүргізілді. Сондай-ақ үрдістің оптимальді технологиялық температуралары, бастапқы компоненттердің жәнәтасымалдағыштың белсенді фаза құрамы жәнәкөлемдік жылдамдықтары анықталды. Бастапқы жәнә реакциядан кейінгі (өңделген) катализаторларға физика-химиялық зерттеулер жүргізілді. Зерттеулер нәтижесі бойынша тасымалдағыштағы белсенді компоненттердің құрамын 1% -дан 10% дейін өзгерту нәтижесінде ең тиімді катализатор 5% MoCrGa / ТСБ екені анықталып, 22% ацетон алынды. Катализатордың жәнә тасымалдағыштағы белсенді заттардың құрамын, әрекеттесуші реагенттердің қатынасын өзгерту нәтижесінде 35-40% дейін ацетоналынды. Сонымен қатар, кейбір жағдайларда CH₃OH максималды 22% шығымы жәнә 35% метилэтилкетон алынды. ЭМ жәнә РФА зерттеулерінің

нәтижесінде реакция жағдайында катализатордың бетінде жаңа Cr_2O_5 фазасы (Cr^{2+} және Cr^{3+} -ға Cr^{5+} -ге көшу), сондай-ақ әртүрлі валенттік күйлердегі Мо және Cr біріккен фазалары пайда болатыны анықталды.

Түйін сөздер: табиғи сазбалшық, ацетон, .

УДК 544.478

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СЖИЖЕННЫЙ НЕФТЯНОЙ ГАЗ КАК СЫРЬЕ ДЛЯ ПРОИЗВОДСТВА ЖИДКИХ КИСЛОРОДСОДЕРЖАЩИХ ОРГАНИЧЕСКИХ СОЕДИНЕНИЙ

Аннотация. Проведены исследования по окислительному превращению пропан-бутановой смеси в кислородсодержащие компоненты, а также определены оптимальные температуры, пропорции исходных компонентов, содержание активной фазы носителя и объемные скорости процесса. Были проведены физико-химические исследования исходных и обработанных катализаторов в условиях эксперимента. Было обнаружено, что при изменении содержания активных фаз в носителе от 1 до 10%, наиболее эффективным катализатором является 5% $\text{MoCrGa}/\text{ТГ}$, при котором было получено 22% ацетона. В результате варьирования состава катализатора, содержания активной фазы, соотношения реагентов, было получено до 35-40% ацетона. Кроме того, в некоторых случаях были получены CH_3OH с максимальным выходом 22%, а также 35% метилэтилкетона. В результате исследований ЭМ и РФА было показано, что в условиях реакции на поверхности катализатора образуется новая фаза Cr_2O_5 (соответствующая переходу Cr^{2+} и Cr^{3+} в Cr^{5+}), а также совместные фазы Мо и Cr в разных валентных состояниях, физический смысл и роль которых должны быть определены.

Ключевые слова: природная глина, ацетон.

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