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**B.K.Massalimova[1], G.D.Jetpisbayeva, D.T.Altynbekova,**
**S.M.Nauruzkulova, A.A.Atakozhaeva[1], V.A.Sadykov[2]**

[1]M.Kh. Dulaty Taraz State University, Taraz, Kazakhstan;
[2] Novosibirsk State University, Novosibirsk, Russia;
[2]Institute of Catalysis named after G.K. Boreskov, Novosibirsk, Russia

# LOW-PERCENTAGE Co/CLAY CATALYSTS IN THE PROCESS OF OXIDATIVE CONVERSION OF C3-C4 SATURATED HYDROCARBONS

**Abstract.** Oxidative conversion of $C_3$-$C_4$ hydrocarbons by air to oxygen-containing compounds at T = 400-550°C and space velocity of 7500 $h^{-1}$, 9000$h^{-1}$ on monoxide catalysts containing 1-, 3-, 5% Co supported on natural red clays was studied. The reaction temperature, contact time, change in the space velocity in the process of partial oxidation of $C_3$-$C_4$ hydrocarbons have been studied.

Acid treatment of the sorbents contributed to the development of the surface area and the enlargement of pore radius, which led to an increase of oxygen-containing compounds in the final product. The $SiO_2/Al_2O_3$ ratio (silica modulus) was increased after acid treatment too.

**Key words:** catalysts, hydrocarbons, natural clay.

**Introduction.** The rational use of hydrocarbons and environmental protection are of the most important goals of the fuel and energy complex. Incineration of associated gas is a national problem which leads to environmental and economic damage of our country [1-3]. When burning gas without maintaining the optimal mode of combustion, about 250 harmful chemicals are released into the atmosphere, namely, non-combustible hydrocarbons; oxides of carbon, nitrogen and sulfur; hydrogen sulfide, heavy metals (mercury, chromium), arsenic compounds, aromatic hydrocarbons, including polycyclic compounds [3-5].

These substances pollute the atmosphere, water and soil. Associated gas can be used as a fuel for power generation, as well as hydrocarbons for the production of petrochemical products as a raw material. Efficient use of hydrocarbon resources is one of the most relevant sectors of the oil and gas industry. Associated gas as an unconventional source of hydrocarbons is still not used effectively [5-7].

In recent years, many researchers and manufactures have been interested in the technological processes of converting natural gas into liquid chemicals. Natural gas is a perspective energy source for the needs of mankind in the energy and hydrocarbon raw materials for over hundred years. About 5% of world natural gas is still used as a motor fuel or raw material for petrochemical production. Petrochemical natural gases $C_2$-$C_4$ and natural gas are underutilized [1-5].

**Methods.** Today, about 80-85% of the various processes occurring in the chemical, petrochemical, and oil refining industries are implemented with the participation of the catalysts. The temperature impact on the process of partial oxidation of the propane-butane gas mixture is discussed. The experiments were carried out at atmospheric pressure in a continuous-flow unit with a fixed-bed quartz-tube reactor [7].

To conduct the experiment, the catalysts with different Co content supported on the natural red clay were used. The experiment were carried out at a temperature of 400°C-550°C with a change of space velocity of 7500 $h^{-1}$, 9000 $h^{-1}$.

The natural red clay was used as a carrier. Catalysts with 1 -, 3 -, 5% of cobalt supported on the natural red clay (NRC) were produced. The carrier was pretreated with 4 different methods: adjustment of active phase at constant atmospheric pressure in different temperature ranges.

In the case of partial oxidation of C3-C4 hydrocarbons initial and final gaseous products $C_2H_4$, $H_2$, CO, $CH_4$, $CO_2$ as well as liquid organic substances were detected by the chromatographic method.

Partial oxidation of C3-C4 hydrocarbons was carried out on 1% Co/NRC catalyst, at atmospheric pressure, under the following conditions: C3-C4=33.33%; $0_2$=7.0%; $N_2$=26.34%: Ar=33.33%; space velocity of 7500$h^{-1}$.

When the temperature rises to 300-350°C, liquid organic compound is not formed. In the gas phase, only traces of $C_2H_4$, $H_2$, CO, $CH_4$ and $CO_2$ are observed.

With gradual increase of temperature to 400°C the following products formed on catalyst are preferably formed: acetaldehyde, 26.6%; acetone - 23.0%; methanol - 20.7%. Aromatic compounds and carboxylic acids are not fully formed. When the reaction temperature reaches 500°C, the reaction selectivity for acetaldehyde and acetone gradually decreases and the selectivity for methanol reaches 41.8%. The conversion of propane is 9.8%, the conversion of butane is 25.4%.

At this temperature, it can be seen that the selectivity for acetaldehyde and methanol gradually increases, and the selectivity for ketone decreases. Conversion of gases contained in compressed petroleum gas at 450°C was equal to: $C_3H_8$=7.4%; $C_4H_{10}$=25.4%. Table 1 demonstrates the conversion increase of the propane-butane gas mixture in the following sequence: $C_3H_8$=4.6-10.2%; $C_4H_{10}$=17.3-30.0%. With the gradual increase of temperature in the gas-phase product the number of components $C_2H_4$, $H_2$, CO, $CH_4$ and $CO_2$ increases (table 1).

Table 1 - The effect of temperature on the yield of products
in the liquid phase resulting from the partial oxidation
of C3-C4 hydrocarbons. State of the reaction: C3-$C_4$:$O_2$:$N_2$=7:1:4; W=7500$h^{-1}$. Catalyst 1Co/ NRC

| T, °C | V, % $C_3H_8$/ $C_4H_{10}$ | **Selectivity, %** | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Acetaldehyde | acetone | methanol | MEK | ethanol | benzene | propanol | crotonaldehyde | butanol | H- butanol | Acetic acid | Acrylic acid | Propionic acid |
| 400 | 4,6<br>17,3 | 26,6 | 23,0 | 20,7 | 21,0 | 6,4 | 0 | 0 | 1,1 | 0 | 0 | 0,7 | 0 | 0 |
| 450 | 7,4<br>21,5 | 26,0 | 22,6 | 25,8 | 18,7 | 5,0 | 0 | 0 | 1,0 | 0 | 0 | 0,7 | 0 | 0 |
| 500 | 9,8<br>25,4 | 18,0 | 16,0 | 41,8 | 21,0 | 3,2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| 550 | 10,2<br>30,0 | 11,2 | 27,8 | 22,8 | 27,1 | 4,3 | 1,7 | 0 | 3,6 | 0 | 0 | 0,8 | 0 | 0 |

The NRC carrier used in the experiment was analyzed by physical and chemical methods: BET, elemental analysis.

The main factor determining the catalytic properties is the chemical composition. However, even while maintaining the chemical composition, the catalytic characteristics of the catalysts, depending on the state and method of preparation, undergo changes in surface area as a result of dispersion, porous structure, nature of the interaction of the constituent parts of the catalyst and crystal chemical changes, which ultimately significantly affects the passage of catalytic reactions [7].

The catalytic system 1, 3-, 5% Co/NRC for the reaction of partial oxidation of C3-C4 hydrocarbons was studied. The content of the products formed as a result of partial oxidation reaction carried out in stable state in the temperature diapason of 400°C-550°C on the NRC and other catalytic systems is given in table 2.

According to table 2, the oxidation product obtained on 3% Co/NRC contains acetaldehyde, acetone, methanol, MEK, benzene, crotonaldehyde, propanol, and acetic acid, which were determined by chromatography.

Table 2 - The influence of the contact time of hydrocarbons C3-C4 on the flow of products formed in the process of partial oxidation. State of the reaction: $C_3$-$C_4$=33,3%; $O_2$=7,0%; $N_2$=26.4%; Ar=33.3%7. 3%Co/ NRC; V=2cm$^3$

| W, $h^{-1}$ | τ, c | T, °C | V, % $C_3H_8$/ $C_4H_{10}$ | yield , % | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | aldehyde | ketone | alcohols | Carboxylic acid | Gas phase |
| 9000 | 0,4 | 500 | 26,6<br>48,3 | 29,2 | 5,4 | 9,0 | 0 | 12,0 |
| | | 550 | 40,0<br>58,7 | 21,4 | 8,0 | 6,6 | 0 | 19,6 |
| 7500 | 0,5 | 500 | 32,3<br>55,7 | 32,0 | 19,8 | 14,1 | 1,3 | 20,8 |
| | | 550 | 41,8<br>82,5 | 34,4 | 20,3 | 14,2 | 3,1 | 35,6 |

The experiment on 3% Co/NRC catalyst, was conducted at atmospheric pressure, at temperatures of 500-550 °C, at a space velocity of 7500 h$^{-1}$, 9000 h$^{-1}$. As it is shown in table 2, 29.2% of aldehyde, 5.4% of ketone and 9.0% of alcohols are formed in the process of liquid catalysis at a temperature of 500 °C on 3% Co/NRC catalyst. The conversion of propane is 26.6%, and the conversion of butane - 48.3%. When the temperature exceeds 550°C, the content of acetaldehyde in the catalyst decreases to 21.4%. In the ranges of these temperatures, the yield of ketone increase to 8.0%. The formation of ketone is increased by 34.4% at a temperature of 600$^0$C at space velocity of 7500 h$^{-1}$. Carboxylic acids are not formed at temperatures of 500°C-550°C at space velocity of 9000 h$^{-1}$, but at space velocity of 7500 h$^{-1}$ at this temperature interval 1.3-3.1% of Carboxylic acids are formed. In the gas phase, ethylene and hydrogen yield is 10-19% (table 2).

**Results and discussion.** During partial oxidation of C3-C4 the hydrocarbons were processed with cobalt catalysts. The catalysts were investigated by physicochemical methods: X-ray diffraction, BET, elemental analysis.

The phase composition of the catalyst was determined on X-ray diffractometer DROH-4 -07. Comparison of refractometric reflexes was performed using powder paper (standard JCPDS). Natural red clay is X-ray morphic mineral (4.20°) consisting of -α-quartz / 3.33; 2.28 / (JCPDS 5-490) - and kaolinite (JCPDS 29-1488). The diffractogram of the initial catalysts 1,3-, 5% Co/NRC correspond to the clay. Since it is dispersed, due to different doses of metal, the structural elements are not detected.

The determination of the specific surface area and porosity of solids is based on the determination of isothermal adsorption of gas phase molecules on the surface. The adsorption isotherm takes shape on the dependance of the number of adsorbed molecules on pressure at moderate temperatures.

The textural and adsorption characteristics of the catalyst were measured by the American "micrometritics Accusorb" using the BET method for low-temperature nitrogen adsorption.

Table 3 - The surface area of the catalyst, the volume of porosity and changes in the main volume

| № | Catalyst composition | results | | |
|---|---|---|---|---|
| | | Surface, m$^2$/g | Pore volume $V_{ADSmax}$,ml/g | Vист, (ml)= $V_{ADSmax}$·K(0,001558) |
| 1 | NRC | 15,39 | 221,69 | 0,345 |
| 2 | 1%Co/ NRC | 29,90 | 221,74 | 0,345 |
| 3 | 3%Co/ NRC | 51,35 | 467,63 | 0,729 |
| 4 | 5%Co/ NRC | 58,12 | 328,19 | 0,511 |

The catalysts shown in table 3 also have different porosity volumes. The porous volume of NRC is 221.69 ml/g; 1% Co/NRC - 221.74 ml/g; 3% Co/NRC - 467.63 ml/g; 5% Co/NRC- 328.19 ml/g. The main volume of catalysts is as follows: the pore volume of the NRC is 0.345 ml; 1% Co/ NRC - 0.345 ml; 5% Co/ NRC - 0.729 ml; 5% Co/NRC - 0.511 ml.

It has been shown that the surface area of the catalyst and the porosity affect the selectivity of hydrocarbons in the liquid and gas phase resulting from the partial oxidation of hydrocarbons. Natural red clay was treated in four different ways. Elemental analysis of 1-, 3-, 5% catalysts which were used as catalysts for the oxidation process was performed using an Agilent 4200 atomic emission spectrometer. The catalysts were investigated on the Australian apparatus Agilent 4200 MP-AES which is located in Taraz State University named after M.Kh. Dulati at the Department of Chemistry and Chemical Technology. In the new spectrometer, the electromagnetic microwave field excites plasma in nitrogen, which is generated from the air. The concentration of the analyte was determined by the AES method. All measurements were performed using an Agilent 4200 MP-AES equipped with an Agilent 4107 nitrogen generator. The sample introduction system consisted of a two-pass cyclone spray chamber, OneNeb sprayer, Solvaflex pump tube (orange / green) and an Easy-fit burner for sample introduction. Used multi-element calibration standards containing elements with a concentration of 50 mg $L^{-1}$. The standard was prepared in an environment of 5% $HNO_3$ / 0.2% HF (v / v).

Table 4 - Results of elemental carrier analysis

| elements | NRC | 1Co/ NRC | 3%Co/ NRC | 5%Co/ NRC |
|---|---|---|---|---|
| | % | % | % | % |
| Sr | 0.0005 | 0.0005 | 0.0005 | 0.0004 |
| Ce | | 0.003 | 0.002 | 0.003 |
| Zn | 0.002 | 0.002 | 0.002 | 0.0015 |
| Cu | 0.001 | 0.004 | 0.002 | 0.002 |
| Sn | 0.0003 | 0.0003 | 0.0003 | 0.0003 |
| Mo | 0.00015 | 0.00015 | 0.00015 | 0.00015 |
| Ba | 0.003 | 0.0033 | 0.0025 | 0.0025 |
| Ni | 0.008 | 0.005 | 0.01 | 0.01 |
| Mn | 0.015 | 0.015 | 0.015 | 0.015 |
| V | 06 | >1 | 06 | 06 |
| Tl | 0.0015 | 0.0025 | 0.0025 | 0.0025 |
| Pb | 0.006 | 0.01 | 0.008 | 0.01 |
| Cr | 0.000005 | 0.000008 | 0.000005 | 0.000005 |
| Ag | 0.03 | 0.03 | 0.02 | 0.03 |
| Nb | 0.0015 | 0.0015 | 0.0010 | 0.001 |
| Be | 0.00015 | 0.00015 | 0.00015 | 0.00015 |
| Ge | 3 | 6 | 9 | 12 |
| Bi | 0.0001 | 0.0001 | 0.0001 | 0.0001 |
| Ga | 0.00008 | 0.0008 | 0.0008 | 0.0008 |
| P | - | - | 0.003 | - |
| CaO | <01 | <01 | <01 | <01 |
| MgO | 01 | 015 | <01 | <01 |
| $Fe_2O_3$ | 21 | 15 | 20 | 19 |
| $Al_2O_3$ | 45 | 47 | 48 | 42 |
| $Na_2O$ | 015 | <01 | 015 | 02 |
| $K_2O$ | - | - | - | - |
| $SiO_2$ | 25 | 30 | 25 | 30 |

According to elemental analysis, all the elements in table 4 are common in the catalyst used, but the difference lies in the amount of these elements. Also, the main distinguishing feature is the change in the content of oxides in the composition of the carrier. For example, oxide of 3 valence iron is up to 21% of NRC, 1% Co/NRC - 15%, 3% Co/NRC - 20% and 5% Co/NRC - 19%. $Al_2O_3$ ranges from 42 to 48% in all catalysts. And in the composition of all catalysts 25-30% of $SiO_2$ was found.

**Conclusion.** For the development of the petrochemical industry, Kazakhstan has large reserves of hydrocarbon raw materials - natural and associated gases, oil and products of its processing, as well as oil bituminous rocks. The main deposits are developed in the western regions of Kazakhstan. According to the forecast geological exploration data, hydrocarbon reserves in the northern, central and eastern regions are insignificant [6-7].

To ensure the processing of natural resources of hydrocarbon raw materials in the republic, an important issue is the creation of petrochemical complex for the final stages of processing hydrocarbon raw materials to marketable products via the modernization of the existing capacities of oil refining industries to obtain basic products for the oil and gas industry.

The process of partial oxidation of hydrocarbons $C_3$-$C_4$ was carried out on catalytic systems 1-, 3-, 5% Co/NRC supported on the NRC.

The influence of temperature, space velocity (750 and 7500 $h^{-1}$), the effect of the active phase dose were tested, the optimal ways to conduct the $C_3$-$C_4$ hydrocarbon partial oxidation process (300°C-600°C) and to obtain the reaction products were determined for the catalytic systems studied.

In the process of oxidation of hydrocarbons $C_3$-$C_4$, the following results were obtained:

1) The oxidation process of $C_3$-$C_4$ hydrocarbons occurs in a mild state at atmospheric pressure.

2) At 1% Co/NRC catalyst at a ratio of 500°C, $C_3$-$C_4$ HC: $O_2$: $N_2$: Ar = 5: 1: 4: 5 at a space velocity of 7500 $h^{-1}$, 41.8% methanol is formed.

It is necessary to conduct a study of catalysts for partial oxidation of $C_3$-$C_4$ hydrocarbons on an electronic scanning microscope.

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**Б.К.Масалимова[1], Г.Д.Джетписбаева[1], Д.Т.Алтынбекова[1],**
**С.М.Наурузкулова[1], АА.Атакожаева[1], В.А.Садыков[2]**

[1]М.Х. Дулати атындағы Тараз мемлекеттік университеті, Тараз, Қазақстан;
[2]Новосибирск мемлекеттік университеті, Новосибирск, Ресей;
[2]Г.К. Боресков атындағы катализ институты, Новосибирск, Ресей

## $C_3$-$C_4$ ҚАНЫҚҚАН КӨМІРСУТЕКТЕРДІҢ ТОТЫҒА АЙНАЛУ ПРОЦЕСІНДЕГІ ТӨМЕНГІ ПАЙЫЗДЫҚ Co/САЗБАЛШЫҚ КАТАЛИЗАТОРЫ

**Аннотация.** С3-С4 көмірсутектерін оттек құрамды композиттерге дейін ауамен тотықтыру кезінде Т = 400-550°С-та және табиғи қызыл сазбалшыққа қондырылған 1-, 3-, 5% Со бар моноксидті катализаторлардағы 7500 $сағ^{-1}$, $9000сағ^{-1}$ көлемдік жылдамдығы зерттелді. С3-С4 көмірсутектердің жартылай тотығу процесіне реакция температурасы, жанасу уақыты, көлемдік жылдамдықтың өзгерісі зерттелді.

Сорбенттерді қышқылдық өңдеуде бетінің пайда болуына және кеуек радиусының ұлғаюына ықпал етті, бұл катализатта оттегі бар қосылыстардың көбеюіне әкелді. $SiO_2/Al_2O_3$ қатынасы (силикатты модуль) қышқылдық өңдеуден кейін де артады.

**Түйін сөздер:** катализатор, көмірсутектер, табиғи сазбалшық.

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**Б.К.Масалимова[1], Г.Д.Джетписбаева[1], Д.Т.Алтынбекова[1],**
**С.М.Наурузкулова[1], А.А.Атакожаева[1], В.А.Садыков[2]**

[1]Таразский государственный университет им.М.Х. Дулати, Тараз, Казахстан;
[2]Новосибирский государственный университет, Новосибирск, Россия;
[2]Институт катализа им. Г.К.Борескова

## НИЗКОПРОЦЕНТНЫЕ Co/ГЛИНОВЫЕ КАТАЛИЗАТОРЫ В ПРОЦЕССЕ ОКИСЕНИЯ НАСЫЩЕННЫХ С3-С4 УГЛЕВОДОРОДОВ

**Аннотация.** Исследовано окислительное превращение С3-С4 углеводородов воздухом в кислородсодержащие композиции при Т=400-550°С и объемной скорости $7500ч^{-1}$, $9000ч^{-1}$ на монооксидных катализаторах, содержащих 1-, 3-, 5% Со, нанесенных на природные красные глины. В процессе полуокисления С3-С4 углеводородов исследовались температура реакции, время контакта, изменение объемной скорости. Кислотная обработка сорбентов способствовала разработке поверхности и увеличению радиуса пор, что приводило к увеличению кислородсодержащих соединений в катализате. $SiO_2/Al_2O_3$ соотношение (силикатный модуль) также увеличивался после кислотной обработки.

**Ключевые слова:** катализатор, углеводороды, природная глина.

**Information about authors:**

Massalimova Bakytgul Kabykenovna – candidate of chemical sciences, associated professor, manager of the department of “Chemistry and chemical technology”, M.Kh. Dulaty Taraz state university, e-mail: massalimova15@mail.ru **ORCID ID** https://orcid.org/0000-0003-0135-9712

Jetpisbayeva Gulim Danebaevna - PhD student of 6D060600- Chemistry of the department of “Chemistry and chemical technology”, M.Kh. Dulaty Taraz State University, e-mail: gulim_86@mail.ru

Altynbekova Dinara Tansykovna - PhD student of 6D060600- Chemistry of the department of “Chemistry and chemical technology”, M.Kh. Dulaty Taraz State University, e-mail: altynbekova.1985@inbox.ru

Naurzkulova Symbat Muratbekovna- PhD student of 6D060600- Chemistry of the department of “Chemistry and chemical technology”, M.Kh. Dulaty Taraz State University, e-mail: simbat_3@mail.ru

Atakozhaeva Aygul Amalbekovna – 1st year master student of the department of “Chemistry and chemical technology”, M.Kh. Dulaty Taraz State University. e-mail: ataqojaeva_aigul@tarmpu.kz

Sadykov Vladislav Aleksandrovich - doctor of chemical sciences, professor, Novosibirsk State University, Institute of Catalysis named after G.Boreskov. E-mail: sadykov@catalysis.ru

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