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CATALYTIC CONVERSION OF METHANE INTO SYNGAS AND ETHYLENE

Abstract. The object of research is development technology of the new composite materials synthesis for the processing of light alkanes into syngas and ethylene. The study varying technological parameters of the reaction (temperature, volumetric rate, reaction mixture composition) oxidative conversion of methane into syngas and ethylene. Paper presents data of developed methods of synthesis were developed and the catalysts physicochemical characteristics were established. Optimized technological parameters of the process in an integrated automated laboratory setup. It has been established that the active in syngas and ethylene formation in mixture oxidative transformation of $\text{CH}_4 + \text{O}_2 + \text{Ar}$ on 10%K-30%Mn-10%Nb/50% glycine catalyst prepared by the SHS (solution combustion synthesis) method and 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation method.

Key words: methane, catalytic oxidation, syngas, ethylene.

Introduction

The world's oil reserves are decreasing every day due to the continuous production and their processing using the most modern technologies. Scientists all over the world are looking for various raw materials and methods to use the vast resources of natural gas as a substitute for petrochemicals. In this regard, great attention is drawn to natural gas as an alternative source of raw materials for petrochemical industries.

According to the annual Statistical Review of World Energy – 2018, published by British Petroleum (BP) at the end of 2017 proven natural gas reserves in the world are estimated at 193.5 trillion cubic meters.

Kazakhstan ranks 15th in the world and 4th in the CIS of natural gas reserves. The prospects for the development of the global gas processing industry are associated with the creation and introduction of new catalytic environmentally friendly technologies for producing of olefins, based on production of polymers, alcohols and motor fuels. Gas processing plants in Kazakhstan are currently engaged mainly in the purification of gases from water, impurities of carbon dioxide and hydrogen sulfide for their use for domestic purposes. This situation is associated with the lack or absence of new catalytic technologies for the directed processing of light $\text{C}_1\text{-C}_4$ alkanes. There are no production facilities for the production of olefins, plastics, motor fuels and other products whose demand is met by imports. Therefore, an important task is the intensive development of the industrial processing of light hydrocarbon raw materials, the reserves of which far exceed oil reserves.

It is known that natural gas is 90% methane. Oxidative dimerization of methane to ethylene, which allows to obtain a number of petrochemical products, such as polyethylene, polystyrene and many other chemical products, is of considerable interest. This is primarily due to the low cost of methane compared to other hydrocarbons [1]. Development of new efficient catalysts for the selective oxidation of light alkanes is still at the research and development stage [2-8].

In the work of Karakaya [9] the $\text{Mn}/\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalyst was studied for the oxidative dimerization of methane. The catalyst was prepared by impregnation methods. The influence of temperature, volume velocity and the ratio of reaction gases were investigated. It is determined that methane conversion is 38% at a volume rate of 390 h^{-1} . The maximum ethylene yield was 16% at 750°C and a gas ratio of $\text{CH}_4/\text{O}_2 = 2$.

In [10] Sr-Al, La-Sr-Al and $\text{Na}_2\text{WO}_4\text{-Mn}/\text{SiO}_2$ series of catalysts were prepared by solution combustion synthesis (SCS). The activity of catalysts was investigated at $450\text{-}850^\circ\text{C}$ and $\text{CH}_4:\text{O}_2:\text{N}_2 = 32:8:10$ ratio, the linear velocity of gases was 50 ml/min . During the experiments it was determined that catalysts were not active in the temperature range of $450\text{-}600^\circ\text{C}$. The Sr-Al series of catalysts, where $\text{Sr}/\text{Al} = 1.25$, were active. It was found that the maximum yield of C_2 hydrocarbons on the $\text{Sr}/\text{Al} = 1.25$ catalyst was 11.5% at $\sim 800^\circ\text{C}$ and $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 = 4.5$ ratio. For each catalyst of the La-Sr-Al series, the C_2 hydrocarbons yield and ethylene/ethane ratio were measured over a wide temperature range. The highest ethylene yield of 12.3~13.0% was achieved at 720°C , and the $\text{C}_2\text{H}_4/\text{C}_2\text{H}_6 = 1.7$ and 1.6 ratio, respectively. It was found that the 10% $\text{Na}_2\text{WO}_4\text{-}5\%$ Mn/SiO_2 catalyst providing the maximum yield of C_2 hydrocarbons $\sim 21\%$ at 750°C and the ethylene / ethane = 2 ratio is the most highly active and selective.

In [11] the Mn-Ce- $\text{Na}_2\text{WO}_4/\text{SiO}_2$ catalysts prepared by the impregnation method were investigated for oxidative dimerization of methane. In particular, due to the double advantages of the tubular membrane reactor, a high methane conversion of 60.7% with selectivity of C_{2+} 41.6%, ethylene/ethane ratio of 5.8% and ethylene yield of 19.4% at a space velocity of $\text{GHSV} = 6050 \text{ ml}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ was achieved.

We have developed polyoxide catalysts based on molybdenum, chromium and gallium, applied to natural clays for catalytic oxidation of propane butane mixture into oxygenates and olefins [12-14] and developed of composite materials by combustion synthesis method for catalytic reforming of methane to synthesis gas [15-17].

Methods for synthesis of catalysts were presented in paper the physicochemical characteristics of catalysts were established, as well as the optimization of technological parameters for the process of synthesis of syngas and ethylene from methane in an integrated automated installation.

Experimental

Catalyst preparation

Paper presents results of the study of activity of developed following catalysts:

1.5% K - 3.5% Mn/AlSi;

10% K - 30% Mn - 10% Nb/50% glycine;

10% K - 30% Mn - 10% Nb/ceramic block;

The catalytic systems were synthesized by the method of impregnation in air and by solution combustion synthesis.

The developed compositions of catalysts were prepared by capillary impregnation of mixed aqueous solutions of metal nitrate salts supported on carriers by moisture capacity, followed by drying at $T = 473 \text{ K}$ for 2 h. Calcinations of samples at $T = 773 \text{ K}$ for 2 h in air was carried out for decomposition of supported metal salts and corresponding volatilization of nitrates from the catalyst surface.

The catalysts with using the SCS method were prepared [18-20]. Thus, certain amounts of nitrates of the corresponding salts were weighed to prepare a catalyst. These salts are pre-ground in an agate mortar and then mixed in a porcelain dish. Then 10 ml of distilled water is gradually added to this mixture of salts, the mixture is stirred in air for several minutes until complete dissolution.

The muffle furnace was previously turned on to the required temperature (in our case, up to 500°C). The prepared mixture from a porcelain cup is transferred to a 200 ml heat-resistant glass beaker and placed in a heated muffle furnace. After 2-3 minutes with an incomplete opening of the door of the muffle furnace, it is visually possible to observe burning in the solution, at which this mixture rises along the walls of the glass during rapid boiling. Urea and glycine were added to the composition of SCS catalysts to improve the combustion process. The presence of glycine or urea in the composition of catalyst contributes to a change in the color of solution into brown color during combustion. Then the glass is cooled in air and the finished catalyst is placed in glass cups.

The specific surface area and measurement of the pore distribution of the developed catalysts were studied by the BET method (Bronauer-Emmett-Teller) on a GAPP V-Sorb 2800 analyzer (China). Nitrogen with helium was used as carrier gas. BET method was carried out at Advanced Ceramics and

Composites Laboratory, Institute of Nanoscience and Nanotechnology NCSR "Demokritos" (Athens, Greece).

Characterization techniques

The 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 – $200^\circ C$, evaporator temperature – $280^\circ C$, column temperature – $40^\circ C$. Carrier gas velocity $Ar = 10$ ml/min. The chromatographic peaks were calculated from the calibration curves plotted for the respective products using the "Chromos" software for pure substances. Based on the measured areas of the peaks corresponding to the amount of the introduced substance, a calibration curve $V = f(S)$ was constructed, where V - amount of substance in ml, S - peak area in cm^2 . Concentrations of the obtained products were determined on the basis of the obtained calibration curves. The balance of regulatory substances and products was $\pm 3.0\%$.

Results and discussion

The paper presents data of activity of 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation for the oxidative conversion of the 34% CH_4 +17% O_2 +49% Ar mixture at $6500\ h^{-1}$ space velocity. As can be seen from figure 1, the yield of the reaction products also increases with increasing the reaction temperature from 650 to $900^\circ C$. The formation of products of partial oxidation - H_2 and CO , complete oxidation - CO_2 , and the target reaction products - C_2H_6 and C_2H_4 are observed in the oxidative conversion of methane.

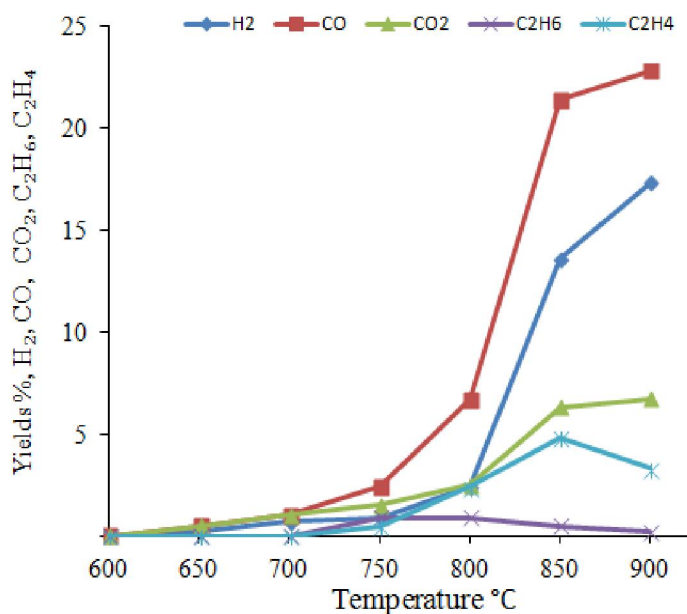


Figure 1 - Effect of a reaction temperature on the product yield of the oxidative conversion of methane on 1.5 % K - 3.5 % Mn/AlSi catalyst

It should be noted that the process goes towards the formation of H_2 and CO . The yields of products increase with increasing reaction temperature. CO_2 is produced in smaller amounts, the yield of which also increases with increasing temperature. The yield of ethylene does not exceed 5% at all temperatures.

Data on the activity of the developed three-component 10%K-30%Mn-10%Nb/50%glycine catalyst prepared by the SCS method for oxidative conversion of 41.8% CH_4 + 16.2% O_2 + 42.% Ar mixture at a space velocity of $3500\ h^{-1}$ and $CH_4:O_2 = 2.5:1.0$ ratio will be given. As can be seen from figure 2, the three-component composition with the addition of niobium showed good activity in relation to the

formation of ethylene compared with the two-component compositions of catalyst. The yield of ethylene also increases with an increase in the reaction temperature from 600 to 800°C. At a temperature of 800°C, the ethylene yield passes through a maximum and decreases again with increasing temperature to 900°C. The yields of H₂, CO and CO₂ slightly change with increasing temperature and vary within 2-3%.

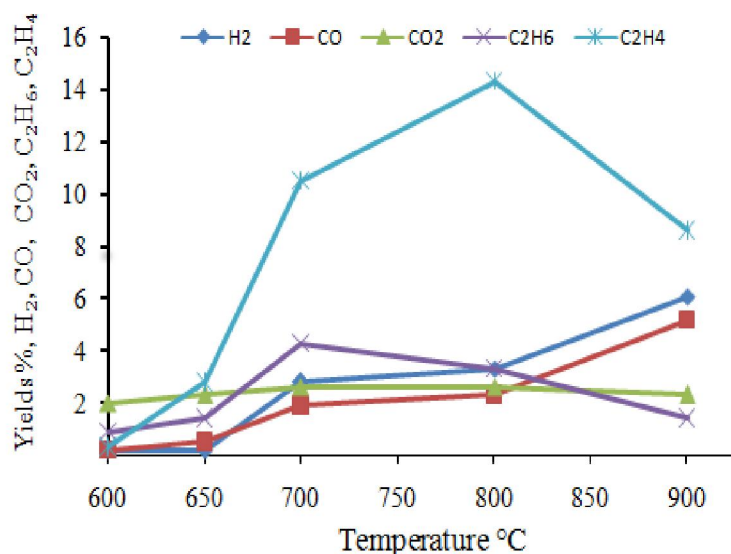


Figure 2 - Effect of reaction temperature on the product yield of oxidative conversion of methane on 10%K-30%Mn-10%Nb/50% glycine catalyst

Thus, the optimal temperature for the formation of ethylene is 800°C at which the ethylene yield is 14.3%.

Developed active phase of 10% K -30% Mn - 10% Nb of catalyst was supported on ceramic block (Fig. 3). The activity of this catalyst composition

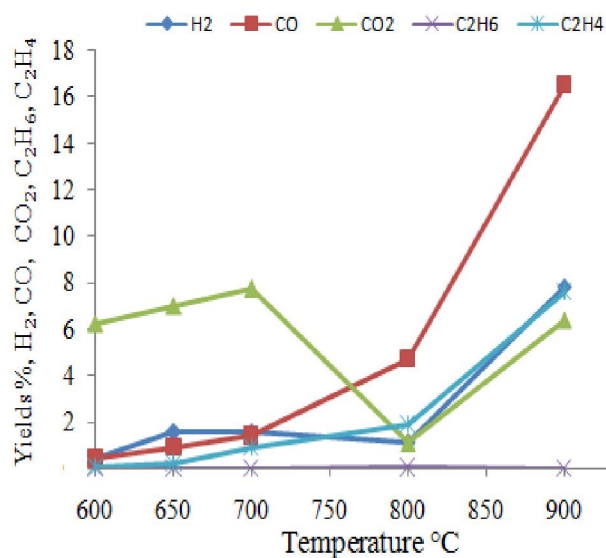


Figure 3 - Effect of reaction temperature on the product yield of the oxidative conversion of methane on 10 % K – 30 % Mn – 10 % Nb/ceramic block

CH₄ + 16.2% O₂ + 42% Ar mixture with a ratio of CH₄:O₂ = 2:1.5 and at 6500 h⁻¹ space velocity. Under these conditions, the catalyst was less active with respect to the formation of both ethylene and H₂. As the temperature rises, only the yield of CO increases.

Thus, the activity of the developed two- and three-component catalytic systems prepared by impregnation and SCS method in the oxidative conversion of the methane of natural gas was investigated.

It was established that 10%K-30%Mn-10%Nb/50%glycine catalyst prepared by the SCS method is the most active in formation of ethylene and 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation for the oxidative conversion of methane into syngas.

In addition, the methods for synthesis of the developed catalysts were determined and the physicochemical characteristics of the catalysts were established. Developed applied K-Mn catalyst was studied by G. Kaumenova, a 3-year doctoral student at al-Farabi Kazakh National University during an overseas internship (Fig. 4,5). Nitrogen with helium was used as carrier gas.

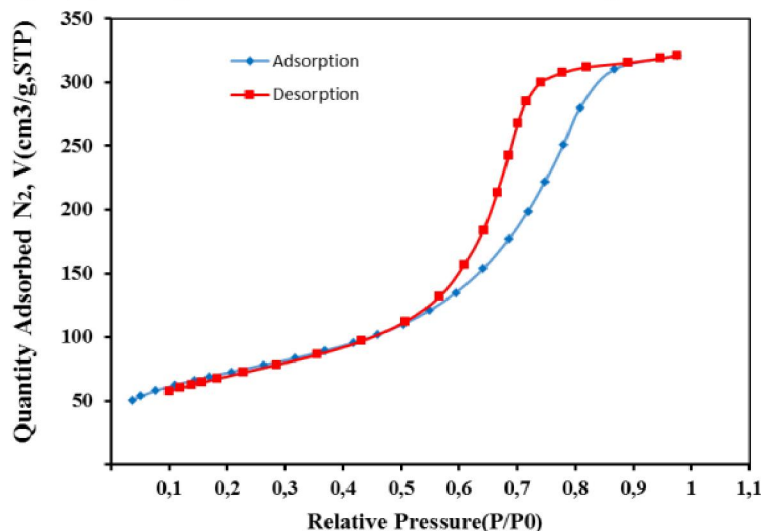


Figure 4 – Isotherm of adsorption and desorption of applied K-Mn catalyst

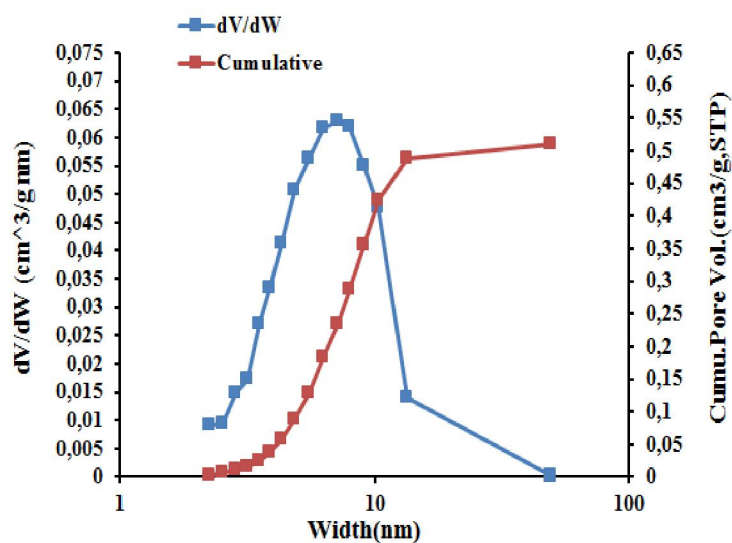


Figure 5 – Differential dependence of pore size distribution on applied K-Mn catalyst

From the data of Figure 5, it can be seen that a significant amount of pores have a size of up to 10 nm. This, in turn, is an important characteristic of catalyst, on the basis of which it can be concluded that the developed catalyst is nanoscale.

Thus, the influence of technological parameters of reaction on the yield of target products was established. The study of catalytic oxidative conversion of the main components of natural gas is methane was carried out on the developed catalytic systems by varying the reaction temperature, space velocity and ratio of the main gases in reaction mixture in order to obtain the optimal amount of desired reaction products. Process parameters on an effective catalyst in an integrated plant were optimized.

Conclusion

Thus, synthesis methods were developed and physicochemical characteristics of catalysts were established. Technological parameters of the process in an integrated automated laboratory setup were optimized.

It was established that 10% K - 30% Mn - 10% Nb/50% glycine catalyst prepared by SCS method is active for production of 14.3% C₂H₄ in oxidative conversion of 41.8% CH₄ + 16.2% O₂ + 42% Ar at 800°C and space velocity of 3500 h⁻¹ and 1.5%K - 3.5%Mn/AlSi catalyst prepared by impregnation method is active for obtaining of 17.3% H₂ and 23.8% CO in the oxidation of 34% CH₄+17% O₂+49% Ar at space velocity of 6500 h⁻¹.

From the above results, it follows that it is possible to optimize the process of oxidative conversion of methane by selecting the reaction technological parameters and improving the composition of inserted catalysts.

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МЕТАННЫҢ СИНГАЗ ЖӘНЕ ЭТИЛЕНГЕ ДЕЙІН КАТАЛИТИКАЛЫҚ КОНВЕРСИЯСЫ

Аннотация. Зерттеу нысаны табиғи газ метанды олефиндерге қайта өңдеуде жаңа композитті материалдарды синтездеу болып табылады. Олефиндерге тотыға айналу реакциясының технологиялық параметрлерінің (температура, көлемдік жылдамдық, реакциялық қоспаның құрамы) өзгерістері зерттелінді.

Мақалада дайындалған катализаторлардың синтездеу әдістері мен физика-химиялық қасиеттері ұсынылған. Автоматтандырылған зертханалық қондырғыда үрдістің технологиялық параметрлері оңтайландырылған.

Ерітіндіде ӨЖС әдісімен 10%K-30%Mn-10%Nb/50% глицин дайындалған катализаторда және сіңіру әдісімен дайындалған 1,5%K-3,5%Mn/AlSi катализаторы бастапқы реакциялық қоспа CH₄+O₂+Ar сингаз және этилен түзуде белсенділігі анықталынды.

Түйін сөздер: метан, каталитикалық тотығу, сингаз, этилен.

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КАТАЛИТИЧЕСКАЯ КОНВЕРСИЯ МЕТАНА В СИНГАЗ И ЭТИЛЕН

Аннотация. Объектом исследования является разработка технологии синтеза новых композиционных материалов для переработки природного газа метана в олефины. Было изучено варьирование технологических параметров реакции (температура, объемная скорость, состав реакционной смеси) окислительного превращения метана природного газа в олефины.

В статье представлены данные разработанных методов синтеза и установлены физико-химические характеристики катализаторов. Оптимизированы технологические параметры процесса в автоматизированной лабораторной установке.

Установлено, что активным по образованию сингаза и этилена при окислительном превращении смеси $\text{CH}_4 + \text{O}_2 + \text{Ar}$ являются 10%K-30%Mn-10%Nb/50%глицин катализатор, приготовленный методом СВС в растворе и 1,5%K-3,5%Mn/AlSi катализатор приготовленный методом пропитки.

Ключевые слова: метан, каталитическое окисление, сингаз, этилен.

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REFERENCES

- [1] Gambo Y, Jalil AA, Triwahyono S, Abdulrasheed AA (2018) Journal of Industrial and Engineering Chemistry 59:218-229. DOI: 10.1016/j.jiec.2017.10.027
- [2] Dury F, Gaigneaux EM, Ruiz P (2003) Applied Catalysis A: General 242:187-203. DOI: [10.1016/S0926-860X\(02\)00516-1](https://doi.org/10.1016/S0926-860X(02)00516-1)
- [3] Ozkan US, Watson RB (2005) Catalysis Today 100:101-114. DOI: [10.1016/j.cattod.2004.12.018](https://doi.org/10.1016/j.cattod.2004.12.018)
- [4] Dimitratos N, Vadrine JC (2006) Journal Mol Catal A Chem, 255:184-192. DOI: [10.1016/j.molcata.2006.03.075](https://doi.org/10.1016/j.molcata.2006.03.075)
- [5] Routray K, Reddy KRSK, Deo G (2004) Applied Catalysis A: General, 265:103-113. DOI: [10.1016/j.apcata.2004.01.006](https://doi.org/10.1016/j.apcata.2004.01.006)
- [6] Wang J, Chou L., Song H., Yang J., Zhao J., Li S. (2006) Catal. Commun, 7:59-63. DOI: <https://doi.org/10.1016/j.catcom.2005.08.013> (in Eng)
- [7] Aubakirov YA, Sassykova LR, Starikov EB (2016) International Journal of Biology and Chemistry DOI: 10.26577/2218-7979-2016-9-2-45-50
- [8] Aubakirov YA, Sassykova LR, Nalibayeva AM, Dossumov KD, Tashmukhambetova ZK, Zhumakanova AS (2017) Oriental journal of chemistry DOI: <http://dx.doi.org/10.13005/ojc/330655>
- [9] Karakaya C, Zhu H, Loebick C, Weissman JG, Kee RJ (2018) Catalysis Today 312:10-22. DOI: [10.1016/j.cattod.2018.02.023](https://doi.org/10.1016/j.cattod.2018.02.023)
- [10] Ghose R, Hwang HT, Varma A (2013) Applied Catalysis A: General 452:147-154. DOI: [10.1016/j.apcata.2012.11.029](https://doi.org/10.1016/j.apcata.2012.11.029)
- [11] Liu K, Zhao J, Zhu D, Meng F, Kong F, Tang Y (2017) Catalysis Communications 96:23-27. DOI: [10.1016/j.catcom.2017.03.010](https://doi.org/10.1016/j.catcom.2017.03.010)
- [12] Baizhumanova TS, Tungatarova SA, Xanthopoulou G, Zheksenbaeva ZT, Kaumenova G.N, Erkibaeva MK, Zhumabek M, Kassymkan (2018) News of the NAS RK. Series chemistry and technology, 431:132-138 <https://doi.org/10.32014/2018.2518-1491.17> (in Eng).
- [13] Massalimova BK, Jetpisbayeva GD, Altynbekova DT, Nauruzkulova SM, Atakozhaeva AA, Sadykov VA (2019) News of the NAS RK. Series chemistry and technology, 434:5-11. <https://doi.org/10.32014/2019.2518-1491.11> (in Eng).
- [14] Baizhumanova T, Tungatarova S, Kaumenova G, Zhumabek M, Kassmkhan K (2019) Oriental journal of chemistry, 35:404:408. <http://dx.doi.org/10.13005/ojc/350151> (in Eng).
- [15] Tungatarova SA, Xanthopoulou G, Kaumenova GN, Zhumabek M, Baizhumanova TS, Grigorieva VP, Komashko LV, Begimova GU (2018) News of the NAS RK. Series chemistry and technology, 432:6-15. <https://doi.org/10.32014/2018.2518-1491.20> (in Eng).
- [16] Xanthopoulou G, Karanasios K, Tungatarova S, Baizhumanova T, Zhumabek M, Kaumenova G, Massalimova B, Shorayeva K (2019) Reaction Kinetics, Mechanisms and Catalysis 126: 645-661. <https://doi.org/10.1007/s11144-019-01541-9> (in Eng).
- [17] Tungatarova S, Baizhumanova T, Zheksenbaeva Z, Zhumabek M, Kaumenova G, Aubakirov Y, Begimova G. (2019) Chemical Engineering and Technology, 42: 918:924. <https://doi.org/10.1002/ceat.201800522> (in Eng).
- [18] Tungatarova SA, Xanthopoulou G, Karanasios K, Baizhumanova TS, Zhumabek M, Kaumenova G (2017) Chemical Engineering Transactions 61:1921-1926. DOI: 10.3303/CET1761318
- [19] Tungatarova SA, Zheksenbaeva ZT, Baizhumanova TS, Zhumabek M, Sarsenova RO, Kaumenova G, Massalimova B, Shorayeva KA (2018) Chemical Engineering Transactions 70:1927-1932. DOI: 10.3303/CET1870322
- [20] Xanthopoulou G, Karanasios K, Tungatarova S, Baizhumanova T, Zhumabek M, Kaumenova G, Massalimova B, Shorayeva K (2019) Reaction Kinetics, Mechanisms and Catalysis DOI: 10.1007/s11144-019-01541-9.