STUDY OF NON-HYDROGEN TRANSFORMATION OF MODEL n-ALKANES AND A DIESEL FRACTION OVER La-Zn-Mn/Al₂O₃+ZSM-CATALYST

Aizhan Omarova, Larissa Sassykova, Marat Tulepov, Nurbubi Zhakirova

Faculty of Chemistry and Chemical Technology Al-Farabi Kazakh National University, 71, Al-Farabi str., 050040, Almaty, Kazakhstan E-mail: larissa.rav@mail.ru Received 03 December 2018 Accepted 08 March 2018

ABSTRACT

This work presents the study of the conversion of model mixtures of C_6 -, C_{14} -alkanes and a diesel fraction over ZSM-containing catalyst modified with manganese, lanthanum and zinc additives. Physico-chemical methods, including TEM and IR, are applied for the characterization of the catalysts used. The presence of Brönsted and Lews acid centers as M^0 - or M^{n+} -metal centers is identified. It is found that the structure of the acid centers can include $MnSiO_3$, La_5Si , $Mn_{15}Si_{26}$, $LaMn_2Si_2$, $La Al_{11}O_{18}$, $La_2Si_2O_7$, La_3Si_2 , functioning as Lewis acid centers. The results of the study show that the degree of conversion of hexane and tetradecane as well as the composition of the resulting compounds are determined by the length of the hydrocarbon chain and the conditions of the process.

<u>Keywords</u>: catalytic cracking, modified zeolites, C_6 - alkanes, C_{14} - alkanes, high - octane gasoline.

INTRODUCTION

The development of the catalytic cracking processes has been recently paid attention in respect to the processing of heavy hydrocarbon raw materials. The catalytic cracking is one of the most common processes in the oil refining industry. It contributes to a significant increase of the oil refining degree and is used for the production of high-octane gasolines and diesel fuels from heavy oil fractions, as well as for the production of petrochemical synthesis products [1 - 5]. The paraffins are the main component of many oil fractions. They are thermally and thermodynamically stable organic compounds. Their cracking requires high activation energy even in presence of catalysts, and hence, it proceeds with a significant rate only at elevated temperatures. The transformations of the paraffinic hydrocarbons reflect most fully the reaction conditions of cracking and, therefore, we pay great attention to the research. The determination of the primary cracking products and the simple low molecular paraffins is difficult because the olefins participate in rapid secondary transformations [6 - 8].

The important factor affecting the degree of conversion, the direction of the alkane cracking and transformation refers to the length of its hydrocarbon chain. Nanoscale catalysts based on high-silica zeolites are used in oil refining and petrochemical processes. Their activity is mainly determined by their unique acid-base properties [9, 10]. One of the possible ways to regulate the catalytic properties is the introduction of modifying additives into the catalyst composition [11]. Typically, the catalytic cracking is carried out in a vapor phase at a temperature of 450° - 520°C. The contact time of the feedstock with the catalyst is within a few seconds. Aluminum silicates, both natural and synthetic (zeolites), are used as catalysts of cracking [12, 13]. The application of various zeolite-based catalysts is an integral part of the modern oil refining and petrochemical industries. The analysis of the patent and the scientific literature shows that catalysts based on high-silica zeolites are very promising for various processes including catalytic cracking and synthesis of high-octane gasoline [14-16].

This paper presents the results of an investigation of the dependences of conversion of model C_6 - and C_{14} -

alkanes and a diesel fraction in absence of hydrogen by using Al_2O_3 +ZSM as a catalyst. The latter is modified by manganese, lanthanum and zinc additives.

EXPERIMENTAL

The decationization of zeolite NaZSM was carried out by treatment with 15 % NH_4NO_3 solution. One volume of zeolite is poured into a threefold volume of NH_4NO_3 solution. The mixture was maintained at a temperature of 60°C and constant stirring for 2 h. Then, after settling, the solution was discharged and a new portion of NH_4NO_3 solution was added. Then the zeolite was washed ten times the volume of the distilled water aiming to reach pH = 7.0. Following the washing, the zeolite was dried at a room temperature and in a water bath. It was subjected to further calcination in a muffle furnace at 500°C for 10 h.

The catalysts were prepared by impregnating a mixture of aluminum hydroxide $Al(OH)_3$ with HZSM-5 decationized zeolite with water-soluble salts of nitrate salts of the modifying elements: lanthanum, zinc and manganese [17, 18]. The ratio of Al_2O_3 : ZSM was 7:3, the zeolite module was equal to 35.5. A catalyst of a composition of 1 % La - 3 % Zn - 1 % Mn/65 % Al_2O_3 + 30 % ZSM-5 was synthesized and tested. The crystallinity of the zeolite was 92-93%. After molding, the catalyst samples were dried, calcined at a temperature of 500°C for 5 h.

The catalyst was tested during the processing of $C_6^$ and C_{14}^- paraffins and a diesel fraction in a flow installation in an inert atmosphere (argon) in the temperature range 300°C - 500°C, at pressure = 0.1 MPa and a feed rate of 1.5 h⁻¹.

The analysis of the starting and forming compounds was carried out by GLC using Chromatograph Chrom-5 (a column 3.5 m x 0.05 m filled with Al_2O_3 (Supelco)). A complex of physicochemical methods was used to study the structure and the state of the catalyst surface: EM, BET, IR spectroscopy using ammonia as a probe molecule [19 - 21]. The X-ray diffraction analysis was performed on DRON-4-0.7 X-ray diffractometer with a copper anode and parameters referring to 25 kV, 25 mA, 20 ranging from 5 ° to 80°. The samples were prepared by mechanical destruction of the catalyst. The crushed part of the catalyst was ground in an agate mortar up to 100 μ m and used for an analysis.

The surface of $Al_2O_3 + ZSM$ composition was 338.3

cm²/g, the pore volume = 0.39 ml/g, the pores of d_{average} of ca 1.0 nm and d_{average} of ca 6.5-7.5 nm predominated. The surface of La-Zn-Mn/Al₂O₃ was 264.5 m²/g. There were two types of pores - of d_{average} \approx 1.5 - 2.5 nm and 6.0 nm. The total pore volume was ca 224.23 ml/g.

RESULTS AND DISCUSSION

Researching hydrogen-free conversion of model nalkanes and diesel fraction

The degree of hexane conversion (T = 300° C - 500° C) on La-Zn-Mn/Al₂O₃ + ZSM catalyst during its hydrogen-free processing and the yields of the main products formed are presented in Table 1. As can be seen from the data in Table 1, the temperature increase in the range of 320° C - 500° C results in significant increase of the degree of conversion of C₆H₁₂ to La-Zn-Mn/Al₂O₃ + ZSM from 29.1% to 96.9 %. Under these conditions, increase of the yield of light hydrocarbons and decrease of the amount of the liquid phase are observed: from 66.7 % to 89.3 % and 33.3 % to 10.7 %, respectively.

The liquid part of the final sample at 320°C contains 77.6 % of naphthenic hydrocarbons C_4-C_{14} , 13.5 % of iso-alkanes C_4-C_6 , 2.2 % of C_4-C_{10} olefins, 3.7 % of aromatic hydrocarbons, 2.9 % of naphthenic hydrocarbons and 0.1 % of benzene. With increase of temperature to 500°C, the yields of components decrease: up to 4 % for C_4-C_6 paraffins, to 0.2 % - for C_4-C_6 olefins while the yield of naphthenic hydrocarbons decreases also up to 1.9 %. The concentration of the aromatic compounds and benzene increases up to 66.6 % and 14.1 %, respectively. The maximum yield of C_4-C_{10} iso-alkanes (20.1% - 20.8 %) is observed at 350 °C - 400°C.

The molecular mass of the initial alkane affects significantly the qualitative changes of the composition of the resulting compounds obtained with temperature increase. The cracking of tetradecane is also studied to identify the behavior of heavier n-alkanes in the process of non-hydrogen processing. It is revealed that the conversion of tetradecane varies little with increase of the temperature from 350 °C to 500°C, from 86.5% to 87.6 % (Figs. 1, 2). Under these conditions, the yield of the liquid-phase products decreases from 80.0% to 57.5 %, but the gas-phase products yield increases from 20.0 % to 42.7 %.

It is evident from the data presented in Figs. 1 and 2 that the amount of light C_1 - C_4 alkanes formed in the

| Table 1. Influence of temperature on the process of hydrogen-free conversion of hexane at $P = 0.1M$ | MPa |
|--|-----|
| and $V = 1.5 h^{-1}$. | |

| Yield of components, % | Process temperature, °C | | | | | | | |
|--|-------------------------|------|------|------|-------|--|--|--|
| | 320 | 350 | 400 | 450 | 500 | | | |
| Composition of a gas phase, % | | | | | | | | |
| Paraffins C ₁ -C ₄ | 75.9 | 76.9 | 76.5 | 82.2 | 89.2 | | | |
| Olefins C ₂ -C ₇ | 1.9 | 1.1 | 0.6 | 0.4 | 0.3 | | | |
| Isoparaffins C4-C7 | 21.3 | 21.1 | 21.5 | 11.1 | 2.1 | | | |
| Naphthenic hydrocarbons C ₅ -C ₇ | 0.3 | 0,3 | 0.2 | 0.1 | 0.07 | | | |
| Aromatic hydrocarbons C ₆ -C ₇ | 0.08 | 0.1 | 0.1 | 1.2 | 2.8 | | | |
| Hydrogen | 0.4 | 0.5 | 1.0 | 5.0 | 5.6 | | | |
| Yield of a gas phase | 66.7 | 80.0 | 82.7 | 86.7 | 89.3 | | | |
| Yield of a liquid phase | 33.3 | 20.0 | 17.3 | 13.3 | 10.7 | | | |
| Conversion | 29.1 | 50.1 | 82.2 | 86.1 | 96.9 | | | |
| Composition of a liquid phase, % | | | | | | | | |
| \sum Paraffins C ₄ -C ₆ | 77.6 | 60.7 | 20.6 | 15.2 | 4.0 | | | |
| \sum Iso-alkanes C ₄ -C ₆ | 13.5 | 20.8 | 20.1 | 18.1 | 13.1 | | | |
| \sum Olefins C ₄ -C ₆ | 2.2 | 0.9 | 0.6 | 0.6 | 0.2 | | | |
| \sum Aromatic hydrocarbons | 3.7 | 14.4 | 54.0 | 57.8 | 66.6 | | | |
| Benzene | 0.1 | 0.4 | 19 | 5.6 | 14.1 | | | |
| | 0.1 | 0.4 | 1.7 | 5.0 | 17.1 | | | |
| ∑ Naphthenic hydrocarbons | 2.9 | 2.8 | 2.7 | 2.6 | 1.9 | | | |
| Octane number (research method) | 39.9 | 55.1 | 85.2 | 92.3 | 101.6 | | | |
| Octane number (motor method) | 49.3 | 57.9 | 75.9 | 79.8 | 85.4 | | | |

gas phase at 350°C is 57.7 %, that of C_4-C_7 iso-alkanes amounts to 22.3 %, while that of C_2-C_{10} -olefins is equal to 17.8 %. There is an insignificant amount of aromatic and naphthenic hydrocarbons. Under these conditions 23.7 % of C_4-C_{14} paraffins, 19.9 % of C_4-C_{10} iso-alkanes, 13.1 % of C_4-C_{10} olefins, 21.6 % of aromatic hydrocarbons, 20.9 % of naphthene hydrocarbons and 0.8 % of benzene are formed in the liquid part of the final sample. With temperature increase up to 500°C, the transformations of tetradecane proceed predominantly in direction of aromatic derivatives formation: the amount of aromatic hydrocarbons and benzene formed increases to 61.9 % and 11.4 %, respectively. The content of C_4 - C_{14} paraffins, C_4 - C_{14} isoalkanes and C_5 - C_{10} olefins decreases to 12.8 %, 12.1 % and 0.5 %, respectively.

The temperature dependence of the activity of La-



Fig. 1. Composition of the gas phase for hydrogen-free conversion of tetradecane at P = 0.1 MPa, V = 1.5 h⁻¹: 1 - paraffins C_1 - C_4 , 2 - olefins C_2 - C_7 , 3 - isoparaffins C_4 - C_7 , 4 - naphthenic hydrocarbons C_5 - C_7 , 5 - aromatic hydrocarbons C_6 - C_7 , 6 - Hydrogen, 7 - yield of a gas phase, 8 - yield of a liquid phase, 9 - conversion.

Zn-Mn/Al₂O₃+ZSM catalyst during the non-hydrogen processing of alkanes is probably connected with variation of the structure and the state of the active sites of the catalyst.

Thus, it is found that in case of hydrogen-free transformation of hexane and tetradecane on a La-Zn-Mn/ Al_2O_3 + ZSM catalyst their molecular mass affects significantly the qualitative changes of the composition of the resulting compounds. They occur with increase of the temperature from 320°C to 500°C and affect especially the yield of C₄-C_n-alkanes. In case of hexane processing, their amount varies from 77.6 % to 4.0 %, while in that of tetradecane their yield varies within the limits of 23.7 % - 12.8 %. The amount of C₄-C₁₀-olefins formed during the cracking of tetradecane is 13.1 % - 0.5 %. In case of hexane, their yield is lower and equals 2.2 % - 0.2 %. The maximum yield of aromatic compounds in the processing of hexane is higher than that of tetradecane: 66.6 % and 61.9 %, respectively.

The refining of the diesel fraction is also investigated (Table 2). It is shown that the yield of the liquid phase decreases from 53.3 % at 350°C to 27.0 % at 450°C. The yield of the diesel fraction hydrocarbons increases under these conditions from 28.0 % to 62.0 %, while



Fig. 2. Composition of the liquid phase for hydrogen-free conversion of tetradecane at P = 0.1 MPa, V = 1.5 h⁻¹: 1 - Σ Parafins C₄-C₁₄, 2 - Σ Iso-alkanes C₄-C₁₄, 3 - Σ Olefins C₄-C₁₀, 4 - Σ Aromatic hydrocarbons, 5 - Benzene, 6 - Σ Naphthenic hydrocarbons, 7 - Octane number (research method), 8 - Octane number (motor method).

the octane number changes from 79.8 to 74.6 (according to the motor method) and from 97.0 to 109.7 (according to the research method). It should be noted that a significant amount of hydrogen is formed when the diesel fraction is processed in absence of hydrogen but using the catalyst developed. It should be noted that the olefinic hydrocarbons in the catalytic cracking process are primarily subjected to reactions of cleavage of the C-C bond, isomerization of the double bonds, skeletal isomerization, hydrogen transfer, disproportionation, cyclization and polymerization [22 - 24].

Determination of the physicochemical characteristics of the synthesized catalysts

The structure and the state of the La-Zn-Mn/Al₂O₃ + ZSM catalyst active sites are studied using TEM and IR spectroscopy. The X-ray diffraction analysis is used for determination of the phase content of the developed catalysts (the phase composition).

The TEM studies of the dispersity, the structure, and the states of La-Zn-Mn/Al₂O₃+ZSM active centers (Fig. 3) show a significant inhomogeneity of the catalyst surface. It is associated with the formation of surface structures of heteronuclear nanoscale particles that differ

| Yield of components, % | Pro | Process temperature, °C | | | |
|--|--------------------|-------------------------|-------|--|--|
| | 350 | 400 | 450 | | |
| Composition | of the gas phase, | ,%, | | | |
| Paraffins | 63.9 | 74.1 | 85.0 | | |
| Olefins | 1.9 | 1.8 | 1.1 | | |
| Iso-paraffins | 30.5 | 17.6 | 3.3 | | |
| Naphthenic hydrocarbons | 0.2 | 0.05 | - | | |
| Aromatic hydrocarbons | 0.2 | 0.2 | 0.2 | | |
| Hydrogen | 3.0 | 6.0 | 9.5 | | |
| Yield of a gas phase | 46.7 | 56.0 | 73.0 | | |
| Yield of a liquid phase | 53.3 | 44.0 | 27.0 | | |
| Hydrocarbon comp | osition of gasolin | e fraction | | | |
| \sum Parafins C ₄ -C ₁₄ | 5.0 | 3.1 | 2.9 | | |
| \sum Iso-alkanes C ₄ -C ₁₄ | 1.1 | 1.2 | 8.8 | | |
| \sum Olefins C ₄ -C ₁₀ | 32.7 | 24.5 | 25.6 | | |
| \sum Aromatic hydrocarbons | 8.5 | 5.2 | 1.5 | | |
| Aromatic hydrocarbons | 52.4 | 63.9 | 59.2 | | |
| Octane number (research method) | 97.0 | 101.0 | 109.7 | | |
| Octane number (motor method) | 79.2 | 82.2 | 74.6 | | |
| Yield of a liquid phase | 28.0 | 45.8 | 62.0 | | |

Table 2. Effect of temperature on the process of diesel fraction hydrogen-free transformation at P = 0.1MPa, V = 1.5 h⁻¹.

in their structure.

The X-ray diffraction analysis and TEM show that on the surface of La-Zn-Mn/Al₂O₃+ZSM catalyst there are:

- non-uniformly distributed aggregates of large dense particles of cut features and d \approx 150.0-300.0 nm; they are identified by X-ray diffraction analysis as a complex mixture of LaMn₂Si₂, LaMnO_{3'15}, LaSi₂, ZnO and β -MnO₂.

- small formations of d of ca 7.0 nm -10.0 nm, which include Mn_2O_3 , Mn_3O_4 , $La_2Si_2O_7$, La $Al_{11}O_{18}$ and Mn

(OH)₂ (according to X-ray diffraction analysis).

- extensive clusters of particles of d of ca 3.0 nm - 4.0nm; the microdiffraction studies show that they consist of La₂O₃, Mn₂O₃, La Al₁₁O₁₈ La₃Si₂ and ZnO.

The TEM and X-ray diffraction data reveal also small accumulations of particles consisting of oxidized and reduced forms of lanthanum - La_2O_3 , LaO and LaO of d of ca 3.0 nm, structures of d of ca 5.0 nm - 7.0 nm formed by La_2O_3 , La_5Si , $Mn_{15}Si_{26}$ and single particles MnSiO₃ of d of ca 10.0 nm -20.0 nm.

The TEM results show the presence of strong inter-



Fig. 3. TEM- images of La-Zn-Mn/Al₂O₃ + ZSM catalyst at zoom 80,000.

action in La-Zn-Mn/Al₂O₃ + ZSM system: lanthanum, zinc and manganese are introduced to Al₂O₃ crystal lattice and the zeolite. According to data in refs. [25 - 27] the structures of MnSiO₃, La₅Si, Mn₁₅Si₂₆, LaMn₂Si₂, La Al₁₁O₁₈, La₂Si₂O₇, La₃Si₂, La₃Si₂ can function as Lewis-acid centers. A good agreement of this data with that of the IR spectroscopic studies using ammonia as a molecular probe is observed. The IR spectrum of ammonia adsorbed on the surface of La-Zn-Mn/Al₂O₂ + ZSM-catalyst recorded at 250°C shows peaks at 3,500 cm⁻¹, 3,300 cm⁻¹, 3,200 cm⁻¹ and 1,630 cm⁻¹ which are indicative of the presence of Lewis acid sites. There are also peaks characteristic of Brönsted acid sites (1,570 cm⁻¹; 850 cm⁻¹). The results of the IR spectroscopic studies indicate a shift to the low-frequency region (to 1,650 cm⁻¹; 1,400 cm⁻¹; 3,400 cm⁻¹). There is obviously strengthening of NH,-an active center bond). Peaks appear here at 362 cm⁻¹ and 1,200 cm⁻¹ [28 - 30]. The intensity of the peaks of ammonia chemisorbed at the Brönsted acid sites of La-Zn-Mn/Al₂O₂ + ZSM catalyst is higher than that of the Lewis acid sites. The adsorption of ammonia on the latter at 350°C is prevailing at La-Zn-Mn/Al₂O₃ + ZSM catalyst. A broad absorption band is observed in the in the IR spectrum in the range of 3,700 cm⁻¹-3,000 cm⁻¹ with maxima at 3,450 cm⁻¹, 3,355 cm⁻¹, 1,645 cm⁻¹ and 1,525 cm⁻¹. Ammonia under these conditions is strongly chemisorbed on the surface of the catalyst.

The catalysts characteristics defined in this work are in good agreement with the data of the scientific literature [31 - 34].

CONCLUSIONS

The effectiveness of a catalyst on ZSM base modified by La-Zn-Mn in the reaction of hydrogen-free conversion of alkanes and a diesel fraction is studied. The length of the hydrocarbon chain and the technological parameters of the process affect the degree of alkanes conversion as well as the type and the composition of the compounds formed. The structure and the composition of the products formed during the processing of C₆- and C_{14} - n-alkanes in presence of La-Zn-Mn/Al₂O₃ + ZSM catalyst indicates the development of several paraffinconverting directions on the catalysts. At the same time, several reactions occur: cracking and dehydrogenation with formation of intermediate activated complexes of a decreased content of carbon atoms and adsorbed states of olefins, isomerization, dehydrocyclization and alkylation. Depending on the nature of the active center of the catalyst, different directions of the transformation proceed with the participation of the intermediate activated complexes.

REFERENCES

- 1. P. O'Connor, Chapter 15 Catalytic cracking: The Future of an Evolving Process, Studies in Surface Science and Catalysis, 166, 2007, 227-251.
- A. Scott, LG develops catalytic naphtha cracking process, J. Chemical Week, 164, 21, 2002, 24.
- L.R. Sassykova, Technology of heterolytic and homolytic oil refining processes: Educational manual, Qazaq University, Almaty, 2018.
- Zh.Kh. Tashmukhambetova, N.K. Zhakirova, L.R. Sassykova, K.A. Kadirbekov, Y.A. Aubakirov, A.S. Zhumakanova, Synthesis and Study of Catalysts of Cracking on the Basis of Heteropolyacids, Orient J. Chem., 33, 6, 2017, 2803-2809.
- K. Wada, K. Tada, N. Itayama, T. Kondo, T. Mitsudo, Preparation of microporous acidic oxides from aluminum-bridged silsesquioxanes and catalytic activities for the cracking of hydrocarbons, Journal of Catalysis, 228, 2, 2004, 374-385.
- G. Moretti, XPS, Studies of characterized Cu/Al₂O₃, Zn/Al₂O₃ and Cu/Zn/Al₂O₃, catalysts, J. Surface and Interface analysis, 17, 10, 1991, 745-750.
- V.R. Choudhary, S. Mayadevi, D.B. Akolekar, Influence of Coke Deposition on Acidity, Intercrystalline Mass Transfer, and Catalytic Properties of Pt•H-ZSM-5•Al₂O₃ Catalyst, Journal of Catalysis, 144, 1, 1993, 16-29.
- L. Dai, Y. Hashimoto, H. Tominaga, T. Tatsumi, Reforming of hexane with Pt/zeolite catalysts, Catalysis Letters, 45, 1997, 107-112.
- M.A. Abul-Hamayel, Effect of Feedstocks on High-Severity Fluid Catalytic Cracking, Chemical Engineering & Technology, 25, 1, 2002, 65-70.
- M. Jacoby, Nanosized Catalysts, Chemical & Engineering News, 70, 37, 2002, 30.
- N. Viswanadham, G. Muralidhar, T.S.R. Prasada Rao, Cracking and aromatization properties of some metal modified ZSM-5 catalysts for light alkane conversions, Journal of Molecular Catalysis A: Chemical, 223, 1–2, 2004, 269-274.
- H. Itoh, C.V. Hidalgo, T. Hattori, M. Niwa, Y.J. Murakami, Role of acid property of various zeolites in the methanol conversion to hydrocarbons, Journal of Catalysis, 85, 2, 1984, 521-526.
- 13. F.N. Guerzoni , J. Abbot, Catalytic Cracking of a Hydrocarbon Mixture on Combinations of HY and

HZSM-5 Zeolites, Journal of Catalysis, 139, 1, 1993, 289-303.

- L. Sassykova, Y. Aubakirov, Catalytic hydrogenation of gasoline fractions under elevated pressure, Chiang Mai J. Sci.; 45, 1, 2018, 474-483.
- 15. H. van Bekkum, E.M. Flanigen, P.A. Jacobs, J.C. Jansen, Introduction to the Zeolite science and practice, Elsevier, 2001, 747-819.
- W.M. Meier, D.H. Olson, C.E. Bacrlocher, Atlas of zeolite structure types, Elsevier, 1996.
- 17. S.M. Rigutto, R. Veen, H. Laurent, Zeolites in hydrocarbon processing, Studies in Surface Science and Catalysis, 168, 2007, 855-913.
- I.E. Maxwell, W.H.J. Stork, Chapter 17 Hydrocarbon processing with zeolites, Studies in Surface Science and Catalysis, Studies in Surface Science and Catalysis, 137, 2001, 747-819.
- 19. M. Lassinantti, Synthesis, characterization and properties of zeolite films and membranes, Micropores and Mesopores Materials, 2001, 25-63.
- 20. K. Bhaskar, S. Sendilvelan, L.R. Sassykova, Effect of premix and exhaust gas recirculation on the emission characteristics of biodiesel fueled engine, News of the National Academy of Sciences of the Republic of Kazakhstan, Series of Geology and Technical Sciences, 428, 2, 2018.
- 21. M. Stocker, Gas phase catalysis by zeolites, Microporous and Mesoporous Materials, 82, 2005, 257–292.
- J.H. Chen, J.N. Lin, Y.M. Kang, W.Y. Yu, C.N. Kuo, B.Z. Wan, Preparation of nano-gold in zeolites for CO oxidation: Effects of structures and number of ion exchange sites of zeolites, Applied Catalysis A: General, 291, 1-2, 2005, 162-169.
- 23. E. Derouane, D.J. Vanderveken, Structural recognition and preorganization in Zeolite catalysts: Direct aromatization of n-hexane on Zeolite L-based catalysts, Applied Catalysis, 45, 1988, 15.
- L.R. Sassykova, Development of Catalysts for the Hydrogenation of the Aromatic Ring in Gasolines, Chemical and biochemical engineering quarterly, 31, 4, 2017, 447-453.
- 25. Y.A. Aubakirov, L.R. Sassykova, A.M. Nalibayeva, K. Dossumov, Z.K. Tashmukhambetova, A.S. Zhumakanova, A.K. Zhussupova, N.K. Zhakirova, Synthesis and testing of catalysts for decrease of toxic emissions of vehicles, Orient. J. Chem., 33,

6, 2017, 3130-3137.

- L.R. Sassykova, A.M. Nalibayeva, Sh.A. Gil' mundinov, Development of technology of synthesis of catalysts for neutralization of emissions of the industry and motor transport, Bulg.Chem.Com., 49, 3, 2017, 583-588.
- L.R. Sassykova, Theory and technology of catalytic petrochemical productions: Educational manual, Qazaq University, Almaty, 2018.
- T.R. Brueva, I.V. Mishin, G.I. Kapustin, Distribution of acid-site strengths in hydrogen zeolites and relationship between acidity and catalytic activity, Thermochimica Acta, 379, 2001, 15-23.
- A.V. Vosmerikov, G.V. Echevsky, L.L. Korobitsyna, Acidic and Catalytic Properties of Mo-Containing Zeolite Catalysts for Non-Oxidative Methane Conversion, Eurasian Chemico-Technological Journal, 6, 3, 2004, 201-206.
- 30. E.N. Coker, L.V.C. Rees, Kinetics of ion exchange in quasi-crystalline aluminosilicate zeolite precur-

sors, Microporous and Mesoporous Materials, 84, 2, 2005, 171-178.

- Y. Zhang, Y. Zhou, M. Tang, X. Liu, Y. Duan, Effect of La calcination temperature on catalytic performance of PtSnNaLa/ZSM-5 catalyst for propane dehydrogenation, Chemical Engineering Journal, 181–182, 2012, 530-537.
- 32. B.T. Tuktin, N.N. Nurgaliyev, A.S. Tenizbayeva, A.A. Shapovalov, Catalytic Conversion of Light Hydrocarbons Into Aromatic Hydrocarbons over Modified Zeolite Catalysts, Orient J Chem, 33, 4, 2017, 1799-1804.
- 33. G. Yang, Y. Wang, D.H. Zhou, J.Q. Zhuang, X.C. Liu, X.W. Han, X.H. Bao, On configuration of exchanged La³⁺ on ZSM-5: a theoretical approach to the improvement in hydrothermal stability of La-modified ZSM-5 zeolite, J. Chem. Phys. 119, 2003, 9765-9770.
- C.D. Wagner, J.F. Moulder, L.E. Davis, W.M. Riggs, Handbook of X-ray photoelectron Spectroscopy, Perkin-Elmer Corp., Minnesota, USA, 1992.