MODIFIED ZEOLITE CATALYSTS FOR EFFICIENT PROCESSING OF N-HEXANE AND GASOLINE FRACTION

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ABSTRACT

In this work hydrogen-free processing (in the absence of hydrogen) and hydrotreating of n-hexane and straight-run petrol fraction on the catalysts samples “C-1” (La-ZSM-Al₂O₃) and “C-2” (Ni-Mo-La-P-ZSM-Al₂O₃) were studied. “C-2” catalyst has high activity in both studied processes. The conversion of n-hexane during hydrogen-free processing on the “C-2” catalyst in the range of 350-500ºC increased from 58.8 to 90.7%; the octane rating of the final product in the temperature range of 350-500 ºC was within 55.1-87.9 according to the research method (RM), and from 61.4 to 84.9 according to the motor method (MM). The octane rating of hydrotreating products increases mainly due to an increase in the content of isoalkanes. The octane rating of the resulting gasoline is significantly higher than that of the original straight-run gasoline (73.1 (RM), 54.1 (MM)), and it reaches 92.1 (RM) and 81.7 (MM). The surface of the developed catalysts is within 201.10-252.20 m²/g of the catalyst. The catalysts have pores with d ≈ 1.5–3.65 nm. The highest concentration of acid sites with medium binding energy is typical for the “C-2” catalyst and determines its high hydroisomerizing activity in the processes of hydrotreating of n-hexane and gasoline fraction. Thus, multifunctional modified zeolite-containing catalysts for hydrotreating gasoline fractions have been developed, which make it possible to simultaneously carry out the processes of hydrotreating, hydroisomerization, and hydrocracking in one stage, as well as to obtain environmentally friendly high-octane gasoline.

Keywords: Hydrotreating, Hydrogen-Free Processing, N-Hexane, Gasoline Fraction, Zeolite, Catalyst.

INTRODUCTION

More than 80% of the processes of chemical technology including oil refining, thanks to which countries can receive up to 30% of national income, are catalytic.¹ ⁴ Therefore, the development of technologies for the synthesis of new effective selective stable catalysts is a promising direction worldwide, since the further intensification of production is directly related to the development of catalysts.⁵ ¹³ According to international standards, which are tightened from year to year the world, the content of sulfur, olefins, and aromatic hydrocarbons in gasoline should be significantly limited.¹⁴,¹⁵ In conditions of increasing demand for the production of commercial gasoline, an urgent task is to improve the technology of catalytic purification processes, such as catalytic cracking, reforming, hydrotreating, and synthesis of new effective catalysts. The implementation of this direction is associated with the creation of new multifunctional catalysts for effective hydrotreating of petroleum gasoline fractions in one stage, including the processes of removal of sulfur, nitrogen-containing compounds, hydrogenation of unsaturated, and aromatic compounds, hydroisomerization and selective hydrocracking of n-paraffin hydrocarbons.¹⁶ ²² It is known that a constant deficiency of H₂ is observed during oil refining. Today, a very important issue is the creation of new efficient catalysts for processing low-octane petrol fractions of oil into high-octane ones without the use of hydrogen.¹³ Hydrogen-free processing of low-octane petrol fractions on zeolite-based catalysts, which have high activity and selectivity in the reactions of isomerization, dehydrogenation, and dehydrocyclization of hydrocarbons is considered one of the most perspective methods for producing high-octane motor gasoline. The issue of developing catalysts for the obtaining of high-octane gasoline from straight-run gasoline fractions without the use of hydrogen is of great theoretical and practical importance due to the growing
shortage of hydrogen. Catalysts based on high-silica zeolites are widely used in many oil refining and petrochemical processes. Their activity and selectivity are determined by their unique properties.

This article presents the results of processing n-hexane and straight-run petrol on the modified zeolite-based catalysts in the absence of hydrogen and during hydrotreating.

**EXPERIMENTAL**

For experiments, the laboratory flow units with a fixed catalyst layer were used (Fig.-1). Composition of the initial gasoline fraction, %: alkanes \( \text{C}_4 - \text{C}_{10} \) - 33.2; iso-alkanes - \( \text{C}_4 - \text{C}_{10} \) - 28.8; olefins \( \text{C}_2 - \text{C}_{10} \) - 0.3; aromatic hydrocarbons - 4.5; naphthenic hydrocarbons - 33.1. The octane rating of the initial petrol is 73.1 (RM) and 54.1 (MM). In all experiments, modified zeolite-containing catalysts were used: sample “C-1” (La-ZSM-Al\(_2\)O\(_3\)) and sample “C-2” (Ni-Mo-La-P-ZSM-Al\(_2\)O\(_3\)). The catalysts were prepared by mixing aluminum hydroxide with zeolite ZSM-5 (SiO\(_2\)/Al\(_2\)O\(_3\)=35) and impregnating with aqueous solutions of salts of nickel nitrate, lanthanum, ammonium para-molybdate, and phosphoric acid.

![Experimental setup](image)

Fig.-1: The Laboratory Flow Installations with a Fixed Bed for the Hydrogen-Free Processing (a) and Hydrotreating (b) of n-Hexane and Gasoline Fraction: 1-Burette, 2 – Pump; 3, 7, 12, 14-Valves; 4, 8-Pressure Gauges; 5-Argon (Hydrogen) Cylinder; 6-Reducer; 9-Reactor made of a Metal Tube; 10-Refrigerator, 11-Rotameter; 13-Separator; 15-Flask for the Final Product.

The procedure for the preparation of modified catalysts based on zeolites and the reaction procedure are described in our previous articles. The analysis of the initial compounds and reaction products was carried out by gas-liquid chromatography (GLC) on chromatographs Chromatic-Crystal 5000.2 and Agilent. The physicochemical characteristics of the synthesized catalysts were studied by BET methods on the Accusorb installation of Micromeritics manufactured in the USA. The acidic properties of zeolite-containing catalysts have been determined by the method of thermo programmed desorption (TPD) of NH\(_3\). The dispersion of metal particles in the catalysts was studied by Transmission Electron Microscopy (TEM) method (“EM-125K”) using microdiffraction.

**RESULTS AND DISCUSSION**

Testing the Activity of Catalysts in the Hydrogen-Free Processing of Model N-Hexane and Gasoline Fraction

The results of the experiment showed that the hydrogen-free conversion of n-hexane on catalysts “C-1” and “C-2” proceeds with the formation of \( \text{C}_1 - \text{C}_4 \) and \( \text{C}_5 - \text{C}_6 \) iso- and n-alkanes, olefinic, aromatic, and naphthenic hydrocarbons. The degree of conversion of n-hexane on the catalyst “C-1” with an increase in temperature from 350 to 500ºC increases within 17.7-74.5% (Fig.-2). At 350ºC, the yield of light hydrocarbons \( \Sigma \text{C}_1 - \text{C}_4 \) is 8.9%, \( \Sigma \text{C}_5 \) - 2.1%, \( \Sigma \text{C}_5 - \text{C}_6 \) - 3.5%, cyclohexane - 5.1%. As the temperature rises, the qualitative and quantitative composition of the compounds formed changes. At 500ºC, the amount of \( \text{C}_1 - \text{C}_4 \) - hydrocarbons increases from 8.9% to 45.9%, \( \Sigma \text{C}_5 \) - from 2.1% to 5.2%, cyclohexane - from 5.1% to 16.2%, heptane-
0.8%, benzene - 2.7% and octane - 2.1%. The total yield of C₂-C₈ olefins increases from 1.8 to 23.2%, and isoalkanes - from 3.5 to 8.4% with an increase in temperature within 350-500°C.

Conversion of the original product, n-hexane, at different temperatures was (in %): 17.7 (350°C), 45.0 (400°C), 63.0 (450°C), and 74.5 (500°C). The conversion of n-hexane during hydrogen-free processing on the “C-2” catalyst in the range of 350-500°C increases from 58.8 to 90.7%. At a temperature of 350 °C, 11.6% of liquid-phase products are formed. As the temperature rises, the cracking direction of n-hexane transformations increases. The amount of liquid products drops to 6.7% at 450 °C, and at 500 °C only gaseous compounds are formed. The yield of gaseous compounds under these conditions varies from 80.8 to 100.0% (Fig.-3). C₁-C₁₀ n-paraffins, C₄-C₁₀ iso-alkanes, C₆-C₇ aromatic hydrocarbons, a small amount of C₄-C₈ olefins, and naphthenic compounds are formed. In addition, hydrogen is formed. At 350°C, 53.6% of C₅-C₁₀ paraffins, 11.4% of C₄-C₁₀ isoalkanes, and 35.0% of aromatic hydrocarbons were found in the liquid final product. When the temperature rises to 500°C, the yield of n-paraffin decreases to 22.8%, and aromatic hydrocarbons increases to 51.7%. The content of C₄-C₁₀ isoalkanes changes extremely with increasing temperature, reaching a maximum value (27.1%) at 400°C, and then decreasing to 15.7% at 500°C. Naphthenic hydrocarbons appear at 380°C, their yield ranges from 4.5-5.4%. The yield of hydrogen increases from 0.5 to 6.5%. The octane number of the final product in the temperature range of 350-500 °C varies from 55.1 to 87.9 according to RM, and from 61.4 to 84.9 according to MM. It was established that the process of n-hexane conversion on the studied catalysts proceeds simultaneously and in parallel in several directions: cracking, cyclization, dehydrogenation, and dehydrocyclization. In the case of hydrogen-free processing of straight-run petrol fraction on the “C-2” catalyst, with an increase in the reaction temperature from 350 to 500°C, the yield of the liquid product decreases from 77.0 to 20.0% (Fig.-4). Under these conditions, in the final liquid product, the content of isoalkanes increases from 21.9 to 29.9%, olefins from 1.9 to 4.8%, and aromatic hydrocarbons from 4.5 to 20.7%. In addition, olefins were found in the final product (1.9–4.8%), which are probably formed as a result of the dehydrogenation of paraffin. Obviously, the presence of these compounds in the products of gasoline processing indicates the simultaneous and parallel occurrence of dehydrocyclization, dehydrogenation, isomerization, and cracking reactions. With increasing process temperature, the rate of such reactions increases significantly. The results of the experiment show that the conversion of n-hexane and gasoline fraction on the studied catalysts at the hydrogen-free processing occurs simultaneously and in parallel in several directions: cracking, cyclization, dehydrogenation, and dehydrocyclization.

The Hydrotreating of Model N-Hexane and Straight-Run Gasoline Fraction
The main products of hydrotreating of n-hexane on the catalyst “C-2” (at T=400 °C, P=3.5 MPa) are C₁-C₄ alkanes-43.5%, C₅-C₇-alkanes-23.6%, iso-alkanes C₄-C₆-30.5%, and aromatics-2.4% (Fig.-5). The influence of temperature on the degree of conversion of alkanes and the composition of products after their hydrotreating on the “C-2” catalyst was studied. The degree of conversion of hexane on “C-2” at 320°C, V_{volumetric}= 4 h⁻¹, and P_{H₂} = 3.5 MPa is 27.1%. The reaction products contain light C₁-C₄ alkanes (7.7%), C₅-C₇ n-alkanes (73.3%), C₄-C₆ isoalkanes (17.8%) and a small number of aromatic hydrocarbons (1.2 %).
When varying the temperature in the range of 320-400ºC, the degree of conversion of n-hexane increases to 85.1%. At T=400ºC, the cracking direction of the process intensifies, as evidenced by an increase in the yield of light C1-C4-alkanes to 43.5% and a decrease in the amount of C5-C7 hydrocarbons of a normal structure to 23.6%. Under these conditions, the yield of C4-C6 iso-alkanes increases - up to 30.5, i.e., almost 1.5 times. The amount of aromatic hydrocarbons at T=400ºC is 2.4%. The reaction products contain light C1-C4 alkanes (7.7%), C5-C7 n-alkanes (73.3%), C4-C6 isoalkanes (17.8%), and a small number of aromatic hydrocarbons, 1.2% (Fig.-5).

Catalyst “C-2” was tested in the process of hydrotreating of straight-run petrol fraction (Fig.-6). After hydrotreating of straight-run petrol fraction on a “C-2” catalyst at 320ºC, the yield of liquid product is
98.0%, it contains 24.1% C_{2}-C_{10} paraffin; 36.1% C_{4}-C_{10} isoalkanes; 1.0% C_{2}-C_{10} olefins; the amount of aromatic and naphthenic hydrocarbons is 4.7 and 34.2%, respectively.

![Fig.-6: Hydroprocessing of Straight-Run Petrol Fraction on a Modified “C-2” Catalyst at Temperature 320-400ºC, Pressure 3.5 MPa, \( V_{\text{volumetric}} \) = 4 h^{-1}; (a) the Content of Hydrocarbons in the Final Product; (b, c) Change in Octane Number, b-RM, c-MM](image)

The octane number of the resulting gasoline is significantly higher than that of the original straight-run gasoline (73.1 RM and 54.1 MM, respectively), and it reaches 92.1 (RM) and 81.7 (MM). With an increase in the temperature of the hydrotreating of the original straight-run gasoline from 320ºC to 400ºC, the yield of refined gasoline remains practically unchanged - 97.0%. In the reaction products, the amount of C_{4}-C_{10} isoalkanes increases significantly - up to 45.1%, and the share of C_{4}-C_{10} kinds of paraffin and naphthenic hydrocarbons decreases to 18.4 and 31.0%, respectively. The yield of olefins and aromatic compounds in the range of 320-400ºC practically does not change and fluctuates between 0.9-1.0% and 4.6-4.7%, respectively. The octane number of refined gasoline reaches 92.1 (RM) and 81.7 (MM). Thus, the main direction of the processes of hydrotreating the gasoline fraction on the “C-2” catalyst, as well as the hydrotreating of n-hexane, is the isomerization of n-alkanes. Liquid phase yield at different temperatures was, in %: 98.0 (320 ºC); 97.7 (350°C); 97.3 (380°C); 97.0 (400ºC). The high content of isoalkanes in the composition of the final product determines the high octane number of hydro-refined gasoline and reaches 91.9 (RM) and 80.6 (MM).

**Determination of Physicochemical Characteristics of Catalysts**

It has been established by the BET method that the surface of the developed catalysts ranges from 201.10-252.20 m^{2}/g of the catalyst. The catalysts have pores with \( d \approx 1.5–3.65 \) nm. (Fig.-7).

![Fig.-7: Pore Distribution Curves in Catalysts According to Their Effective Radii: a) Catalyst “C-1”; b) Catalyst “C-2”](image)

Studies have shown that NH_{3} is adsorbed on the “C-2” catalyst in three forms with \( T_{\text{max}} \) equal to 155ºC, 230ºC, and the most strongly bound NH_{3} is desorbed at \( T_{\text{max}}=460ºC \). Their number is 16.79; 3.79, and \( 7.07 \cdot 10^{-4} \) mol/g of catalyst (Table-1). The total content of acid sites is equal to \( 27.73 \cdot 10^{-4} \) mol/g of the catalyst. Catalyst “C-2” is characterized by the presence of mainly acid sites with NH_{3} desorption temperature of 195-230ºC. The highest concentration of acid sites with medium binding energy (desorption
temperature $T_{\text{max}}=210^\circ\text{C}$) is typical for the “C-2” catalyst and determines its high hydroisomerizing activity in the processes of hydrotreating of n-hexane and gasoline fractions.

### Table-1: Results of the Study of TPD of Ammonia

| Catalyst | $T_{\text{max}}, ^\circ\text{C}$ | Amount of NH$_3$ desorbed, $10^{-4}$ mol/g of catalyst | $\Sigma$NH$_3$, $10^{-4}$ mol/g of catalyst |
|----------|-------------------------------|------------------------------------------------------|------------------------------------------|
| “C-1”   | 155 230 460                   | 16.79 3.79 7.07                                       | 27.73                                    |
| “C-2”   | 160 230 470                   | 2.73 28.85 1.12                                       | 32.70                                    |

Metals of different oxidation states, which are fixed inside and outside the cavities of the zeolite, can be in acid sites, and the combination of two or more metals determines the multifunctionality of the catalysts. In the study by TEM (Fig.-8) on the surface of a catalyst “C-1”, small evenly spaced nanosized particles of lanthanum oxide with $d \approx 2.95-3.95$ nm, clusters of translucent hexagonal particles with a size of 4.0-5.0 nm and small aggregates of loose particles were found with $d \approx$ from 5.0 to 10.0-20.0 nm, including a mixture of two modifications of lanthanum oxide. In addition, there are aggregates ($d \approx 20.05$ nm) consisting of loose, smaller particles, which are identified as lanthanum hydroxide mixed with its oxide. The highly dispersed structures AlNi, Ni$_2$O$_3$, Mo$_3$O$_5$, and Mo$_5$Si$_3$ with $d \leq 1.95$ nm and 0-4.95 nm and accumulations of Ni$_2$O$_3$ particles with an average size of 6.8-10.05 nm predominate on the surface of a catalyst “C-2”. Translucent aggregates ($d \approx 19.50$ nm) were revealed, consisting of loose, smaller particles, which were identified as a mixture of states, including a rare earth element: LaO$_2$, La$_2$O$_3$, La (MoO$_4$), MoP, SiP, and NiOOH. The presence of clusters of composition MoSi, SiP, and MoNiSi probably indicates the direct interaction of matrix atoms with modifying metal additives. Such clusters can act as Lewis acid sites, which is consistent with the TPD of NH$_3$ results. Uniformly distributed small MoNiSi, Ni$_2$O$_3$, MoSi$_2$, and Mo$_6$O$_{11}$ with $d \approx 5.9-9.9$ nm were found. It has been established that Ni$_2$O$_3$ particles form single islands with sizes of 4.9–9.9 nm.

![Fig.-8: TEM- Images of Catalysts](a, b) Catalyst “C-1”, magnification 100,000; (c, d) Catalyst “C-2”, magnification 120,000

The results obtained during the study of the hydrotreating process of the straight-run gasoline fraction on the catalysts “C-1” and “C-2” show that the conversion process proceeds by a complex mechanism. This mechanism includes hydrocracking by C-H and C-C bonds with the formation of low molecular weight n- and iso-alkanes and olefins, which on the surface of the catalyst enter into secondary processes of hydrogenation, cyclization (naphthene), dehydrocyclization (aromatic hydrocarbons), alkylation, etc.

### CONCLUSION

The modified zeolite-containing catalysts sample “C-1” (La-ZSM-Al$_2$O$_3$) and sample “C-2” (Ni-Mo-La-P-ZSM-Al$_2$O$_3$) were used at the hydrotreating and hydrogen-free processing of n-hexane and gasoline fraction. The hydrogen-free conversion of n-hexane on both catalysts proceeds with the formation of C$_1$-C$_4$ and C$_5$-C$_6$ iso- and n-alkanes, olefinic, aromatic, and naphthenic hydrocarbons. A comparative analysis of the processes of hydro- and hydrogen-free processing of hydrocarbon raw materials shows that during hydrogen-free processing, especially at high temperatures, the cracking direction prevails. The octane rating of the final products of the hydrotreatment process increases mainly due to an increase in the content of isoalkanes.
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REFERENCES

1. M.A. Alabdullah, A.R. Gomez, J. Vittenet, A. Bendjericou-Sedjerari, W. Xu, I.A. Abba and J. Gascon, *ACS Catalysis*, 10(15), 8131 (2020), [https://doi.org/10.1021/acscatal.0c02209](https://doi.org/10.1021/acscatal.0c02209)

2. B.T. Tuktin, N. N. Nurgaliyev, A. S. Tenizbayeva and A. A. Shapovalov, *Oriental Journal of Chemistry*, 33(4), 1799 (2017), [https://doi.org/10.13005/ojc/330424](https://doi.org/10.13005/ojc/330424)

3. A. G. Okunev, E. V. Parkhomchuk, A. I. Lysikov, P. D. Parunin, V. S. Semeikina and V. N. Parmon, *Russian Chemical Reviews*, 84(9), 981 (2015), [https://doi.org/10.1070/rcr4486](https://doi.org/10.1070/rcr4486)

4. O. F. Glagoleva and V. M. Kapustin, *Petroleum Chemistry*, 60(11), 1207 (2020), [https://doi.org/10.1134/s0965544120110092](https://doi.org/10.1134/s0965544120110092)

5. Z. S. Qureshi, P. Arudra, M. A. Bari Siddiqui, A. M. Aitani, G. Tanimu and H. Alasiri, *Heliyon*, 8(3), e09181 (2022), [https://doi.org/10.1016/j.heliyon.2022.e09181](https://doi.org/10.1016/j.heliyon.2022.e09181)

6. A. Tanimu, G. Tanimu, H. Alasiri and A. Aitani, *Energy & Fuels*, 36(10), 5152 (2022), [https://doi.org/10.1021/acs.energyfuels.2c00567](https://doi.org/10.1021/acs.energyfuels.2c00567)

7. M. Marafi and E. Furimsky, *Energy & Fuels*, 31(6), 5711 (2017), [https://doi.org/10.1021/acs.energyfuels.7b00471](https://doi.org/10.1021/acs.energyfuels.7b00471)

8. T. V Shakiyeva, L. R. Sassykova, A. A. Khamlenko, U. N. Dzhatkambayeva, A. R. Sassykova, A. A. Batyrbayeva, Z. M. Zhaxibayeva, A. G. Ismailova and S. Sendilvelan, *Chimica Techno Acta*, 9(3), 20229301 (2022), [https://doi.org/10.15826/chimtech.2022.9.3.01](https://doi.org/10.15826/chimtech.2022.9.3.01)

9. H. D. Velázquez, R. Cerón-Camacho, M. L. Mosqueira-Mondragón, J. G. Hernández-Cortez, J. A. Montoya de la Fuente, M. L. Hernández-Pichardo, T. A. Beltrán-Oviedo and R. Martínez-Palou, *Catalysis Reviews*, 1-221 (2022), [https://doi.org/10.1080/01614940.2021.2003084](https://doi.org/10.1080/01614940.2021.2003084)

10. T. V Shakiyeva, L. R. Sassykova, U. N. Dzhatkambayeva, A. A. Khamlenko, N. K. Zhakirova, A. A. Batyrbayeva, R. N. Azhigulova, Sh. N. Kubekova, Zh. M. Zhaxibayeva, M. A. Kozhaisakova, L. A. Zhusupova, S. Sendilvelan and K. Bhaskar, *Rasayan Journal of Chemistry*, 14(2), 1056 (2021), [https://doi.org/10.31788/rjc.2021.1426152](https://doi.org/10.31788/rjc.2021.1426152)

11. M.A. Samborskaya, E.A. Laktionova, A.V. Wolf, V.V. Mashina and A.A. Syskina, *Procedia Chemistry*, 10, 332 (2014), [https://doi.org/10.1016/j.proche.2014.10.056](https://doi.org/10.1016/j.proche.2014.10.056)

12. M.C. Kerby, T.F. Degnan, D.O. Marler and J. S. Beck, *Catalysis Today*, 104(1), 55 (2005), [https://doi.org/10.1016/j.cattod.2005.03.028](https://doi.org/10.1016/j.cattod.2005.03.028)

13. S. Soltanali, S. R. S. Mohaddecy, M. Mashayekhi and M. Rashidzadeh, *Journal of Environmental Chemical Engineering*, 8(6), 104548 (2020), [https://doi.org/10.1016/j.jece.2020.104548](https://doi.org/10.1016/j.jece.2020.104548)

14. L. R. Sassykova, S. Sendilvelan, K. Bhaskar, A. S. Zhumakanova, Y. A. Aubakirov, T. S. Abildin, Sh. N. Kubekova, Z. T. Mataeva and A. A. Zhakupova, *News of National Academy of Sciences of the Republic of Kazakhstan*, 434(2), 181 (2019), [https://doi.org/10.32014/2019.2518-170x.53](https://doi.org/10.32014/2019.2518-170x.53)

15. L. Sassykova, V. Bunin, A. Nalibayeva and M. Nurakhmetova, *Journal of Chemical Technology and Metallurgy*, 53(3), 537 (2018)

16. P. Dufresne, *Applied Catalysis A: General*, 322, 67 (2007), [https://doi.org/10.1016/j.apcata.2007.01.013](https://doi.org/10.1016/j.apcata.2007.01.013)

17. Z.S. Qureshi, M. A. Siddiqui, A. Tanimu, A. Aitani, A. Akah, Q. Xu and M. AlHerz, *SSRN Electronic Journal*, [https://doi.org/10.2139/ssrn.4129096](https://doi.org/10.2139/ssrn.4129096)

18. M. Ghashghaee, *Journal of Analytical and Applied Pyrolysis*, 115, 326 (2015), [https://doi.org/10.1016/j.jaap.2015.08.013](https://doi.org/10.1016/j.jaap.2015.08.013)

19. A. Usman, M. A. B. Siddiqui, A. Hussain, A. Aitani and S. Al-Khattaf, *Chemical Engineering Research and Design*, 120, 121 (2017), [https://doi.org/10.1016/j.cherd.2017.01.027](https://doi.org/10.1016/j.cherd.2017.01.027)

20. L.R. Sassykova, N.K. Zhakirova, Y.A. Aubakirov, S. Sendilvelan, Z.K. Tashmukhambetova, T. S. Abildin, B. D. Balgyshsheva, A. A. Omarova, M. A. Sarybayev and L. K. Beisembaeva, *Rasayan Journal of Chemistry*, 13(3), 1444 (2020), [https://doi.org/10.31788/rjc.2020.1335822](https://doi.org/10.31788/rjc.2020.1335822)
21. A. V. Vosmerikov, B. Ulzii, Ya. E. Barbashin, L. L. Korobitsina, M. Tuya and L. N. Vosmerikova, *Petroleum Chemistry*, 51(2), 143(2011), https://doi.org/10.1134/s0965544111020149
22. G. P. Belov and P. E. Matkovsky, *Petroleum Chemistry*, 50(4), 283(2010), https://doi.org/10.1134/s0965544110040055
23. B. Tuktin, E. Zhandarov, N. Nurgaliyev, A. Tenizbayeva and A. Shapovalov, *Petroleum Science and Technology*, 37(15), 1770(2019), https://doi.org/10.1080/10916466.2019.1590403
24. G. D. Zakumbaeva, L. B. Shapovalova, B. T. Tuktin and A. A. Omarova, *Petroleum Chemistry*, 50(2), 135(2010), https://doi.org/10.1134/s096554411002009x
25. B. T. Tuktin, A. S. Tenizbayeva, A. A. Omarova, L. R. Sassykova and Zh. A. Sailau, *Rasayan Journal of Chemistry*, 12(3), 1478(2019), https://doi.org/10.31788/RJC.2019.1235236
26. E. Rodriguez-Castellon, A. Jimenez-Lopez and D. Eliche-Quesada, *Fuel*, 87(7), 1195(2008), https://doi.org/10.1016/j.fuel.2007.07.020
27. R. Kh. Ibrasheva, V. S. Yemelyanova, L. R. Sassykova, U. N. Dzhatkambayeva, T. V. Shakiyeva, B. T. Dossumova, N. K. Zhakirova, S. Sendilvelan and T. M. Seilkhanov, *Rasayan Journal of Chemistry*, 13(4), 2370(2020), https://doi.org/10.31788/rjc.2020.1345948
28. N. Rahimi and R. Karimzadeh, *Applied Catalysis A: General*, 398, 1(2011), https://doi.org/10.1016/j.apcata.2011.03.009
29. P. A. Jalil, M. A. Al-Daous, A.-R. A. Al-Arfaj, A. M. Al-Amer, J. Beltramini and S. A. I. Barri, *Applied Catalysis A: General*, 207(1–2), 159(2001), https://doi.org/10.1016/s0926-860x(00)00670-0
30. Z. Diao, Di Rong, X. Hou, Y. Chen, P. Zheng, Y. Liu and D. Sun, *Energy & Fuels*, 33(12), 12696(2019), https://doi.org/10.1021/acs.energyfuels.9b03458
31. L. Zhao, J. Gao, C. Xu and B. Shen, *Fuel Processing Technology*, 92(3), 414(2011), https://doi.org/10.1016/j.fuproc.2010.10.003
32. P. Liu, Z. Zhang, M. Jia, X. Gao and J. Yu, *Chinese Journal of Catalysis*, 36(6), 806(2015), https://doi.org/10.1016/s1872-2067(14)60311-9
33. G. Vassilina, K. Umbetkaliyeva, A. Abdassilova, T. Vassilina and Z. Zakirov, *Open Chemistry*, 20(1), 225(2022), https://doi.org/10.1515/chem-2022-0134
34. T. F. Degnan, *Topics in Catalysis*, 13(4), 349(2000), https://doi.org/10.1023/a:1009054905137

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