ABSTRACT
thesis for the degree of Doctor of Philosophy (PhD)
on specialty «6D073900 – Petrochemistry»
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«Development of the new class catalysts for the production of low pour point diesel fuels»

General description of the work. The dissertation work is devoted to the development of bifunctional catalysts based on mesoporous aluminosilicates and natural bentonite for the production of low pour point diesel fuels with improved performance.

Relevance of the study. Today, due to the decrease in the reserves of medium and light oils, the amount of which, according to forecasts, will be insufficient to meet the required demand by 2035, the scientific community is faced with the issue of high-quality processing of heavy crude oil and its derivatives. This is especially true for Kazakhstan due to the predominance of reserves of highly paraffinic oils.

One of the valuable fractions of paraffinic oils is the diesel fraction, which can be used as commercial fuel. However, the high content of normal alkanes (~10-40%) in the composition of the diesel fraction leads to a deterioration in the performance characteristics of the fuel and, as a result, the inability to use the diesel fraction without additional processing in the cold season at lower temperatures, which is critical for many regions of Kazakhstan with cold winters. In this regard, the process of hydroisodewaxing of the diesel fraction is increasingly used, as a result of which n-alkanes in the presence of catalysts are converted into branched alkanes and, as a consequence, the performance characteristics of diesel fraction are improved. Bifunctional catalysts based on zeolites and mesoporous materials promoted with transition metals have become widely used in this process.

In connection with the foregoing, this work is devoted to the study of the activity of promoted catalysts based on mesoporous aluminosilicates and natural bentonite in the process of hydroisodewaxing of diesel fractions. The implementation of the study consists in the synthesis of bifunctional catalysts, the study of their physicochemical characteristics and testing their activity in the process of dewaxing diesel fractions, as well as the study of the hydrocarbon composition and performance characteristics of diesel fractions before and after the process.

Purpose of the work: development of active and selective bifunctional catalysts based on mesoporous aluminosilicates and bentonite for the process of hydroisodewaxing of diesel fractions.

To achieve this goal, the following tasks were set:

– Synthesis of mesoporous aluminosilicates with a highly developed specific surface area and large pore volumes.

– Synthesis of bifunctional catalysts based on mesoporous aluminosilicate and activated bentonite of the Tagan field.

– The study of the physicochemical characteristics of the synthesized aluminosilicates and bifunctional catalysts based on them.

– Study of the effect of the nature and content of promoting additives on the activity of bifunctional catalysts based on mesoporous aluminosilicate and activated bentonite in the process of hydroisodewaxing of diesel fraction in a flow reactor in the temperature range of 260-340 °C, pressure of 1-3 MPa, feed space velocity of 0.5-2 $h^{-1.}$

– Determination of the optimal parameters of diesel fractions hydroisodewaxing process in the presence of synthesized catalysts.

– Obtaining diesel fuels with low-temperature characteristics.

– Compilation of a probable mechanism for the conversion of higher n-paraffins in the process of hydroisodewaxing of diesel fractions in the presence of synthesized catalysts based on mesoporous aluminosilicates and activated bentonite.

The object of the study: mesoporous aluminosilicate, activated bentonite, supported catalysts, bifunctional mono- and bimetallic Ni, Mo, Ni-Mo-containing catalysts, diesel fuel.

The subject of the study: methods for the synthesis of effective catalysts for the process of hydroisodewaxing of diesel fuels and their physico-mechanical and physico-chemical properties, as well as catalytic activity.

Research methods: The synthesized samples were studied by the following methods: low-temperature nitrogen adsorption/desorption, small-angle and wide-angle scattering (XRD), diffuse reflectance Fourier transform infrared spectroscopy of adsorbed pyridine (DRIFT), Fourier transform infrared spectroscopy (FTIR), temperature-programmed ammonia desorption (TPD-NH_3), temperature-programmed hydrogen reduction (TPV-H_2) and scanning electron microscopy (SEM). The composition and physico-chemical characteristics of diesel fractions before and after testing were analyzed by chromato-mass spectrometry and the following characteristics were determined: cloud point and pour point of diesel fractions, density, sulfur content, flash points in a closed cup, cold filter plugging point (CFPP), cetane index and cetane number.

Scientific novelty and main results of the study:

1. Mesoporous materials with a highly developed specific surface of more than 500 m^2/g, pore volumes of more than 0.8 cm^3/g and pore sizes in the mesopore range (2-4 nm) have been synthesized by the co-condensation method of $(C_2H_5O)_4Si$ and $(second\text{-}BuO)_3Al/Al(Oi\text{-}Pr)_3$ and hexadecylamine as a structurant.

2. For the first time, bifunctional catalysts based on mesoporous aluminosilicate and activated bentonite from the Tagan field (Ni/MAS-H-bentonite, Mo/MAS-H-bentonite and Ni-Mo/MAS-H-bentonite) with the necessary balance of strengths of Lewis and Brønsted acid sites of catalysts, allowing them to selectively conduct the process of hydroisodewaxing of diesel fuels.

3. The physicochemical characteristics of the synthesized catalysts (Ni/MAS-H-bentonite, Mo/MAS-H-bentonite and Ni-Mo/MAS-H-bentonite) were studied using the method of low-temperature nitrogen adsorption/desorption, small-angle and wide-

angle scattering, FT-IR spectroscopy of adsorbed pyridine, FT-IR spectroscopy, temperature-programmed ammonia desorption, temperature-programmed reduction with hydrogen.

4. For the first time, the influence of the nature and content of promoting additives on the activity of bifunctional catalysts, the acid components of which are mesoporous aluminosilicates and activated bentonite, was studied in the process of hydrodewaxing of the diesel fraction in a flow-type reactor in the temperature range of 260–340°C, pressure of 1–3 MPa, volume raw material feed rate 0.5-2 h^{-1}.

5. It has been established that the maximum yield of the diesel fraction of 97.4% in the process of hydroisodewaxing on a 5%Ni-1%Mo/MAS-H-bentonite catalyst is achieved at a temperature of 320 °C, a pressure of 2 MPa and a feed space velocity of 1 h^{-1}.

6. It has been established that the use of the synthesized bifunctional catalyst 5% Ni-1% Mo/MAS-H-bentonite (35:65 wt.%) in the process of hydroisodewaxing of diesel fractions, under optimal process conditions, makes it possible to obtain diesel fuel with low-temperature characteristics, meeting the requirements for cold climate fuels: cold filter plugging point - minus 33 ºC, flash point in a closed cup - 39 ºC and pour point - minus 36 ºC.

7. A probable mechanism for the conversion of higher n-paraffins in the process of hydroisodewaxing of diesel fractions in the presence of bifunctional nickel-, molybdenum-, nickel-molybdenum-containing catalysts based on mesoporous aluminosilicates and activated bentonite is proposed.

The main provisions for defense:

1. The use of the method proposed in the work for the synthesis of mesoporous material by co-condensation of $(C_2H_5O)4Si$ and $(sec\text{-}BuO)_3Al/Al(Oi\text{-}Pr)_3$ and using hexadecylamine as a structure-forming agent makes it possible to obtain samples with a specific surface area of more than 500 m^2/g, pore volumes greater than 0.8 cm^3/g and pore sizes in the mesopore range (2-4 nm).

2. Promotion of the support (MAS-H-bentonite) of the bifunctional catalyst by bimetallic systems (Ni-Mo) in comparison with monometallic systems contributes to the achievement of the necessary balance of strengths of the Lewis and Brønsted acid sites of catalysts, which allows them to selectively conduct the process of hydroisodewaxing of diesel fuels.

3. The highest yield of the diesel fraction (97.4%) in the process of hydroisodewaxing is achieved on the 5% Ni - 1% Mo/MAS-H-bentonite (35:65 wt.%) catalyst, which makes it possible to obtain diesel fuel with low-temperature characteristics: cold filter plugging point - minus 33ºC, flash point in a closed cup - 39 ºC and pour point - minus 36 ºC.

Theoretical and practical significance of the work: The study of the activity of promoted catalysts in the process of hydroisodewaxing of diesel fractions meets the technological needs of the country's petrochemical industry. Taking into account the specifics of Kazakhstani oil and the use of domestic raw materials (bentonite of the Tagan field) in the composition of catalysts will contribute to the import substitution of

expensive foreign catalysts based on platinum, which will also give a positive economic effect. In addition, the development of the petrochemical industry and the development / production of catalysts will contribute to the diversification of the country's economy, the importance of which was also noted by the President of the Republic of Kazakhstan on several occasions. The established activity of promoted catalysts based on mesoporous aluminosilicates and natural bentonite in the process of hydroisodewaxing of diesel fuels will make it possible to contribute to the development of catalyst production technology and generate their own trends in the field of improving the performance characteristics of diesel fuels.

Compliance with the directions of development of science or government programs. The work was carried out within the framework of projects funded by the Ministry of Science and Higher Education of the Republic of Kazakhstan: AP08052032 “Development of a technology for obtaining new catalysts based on mesoporous aluminosilicates for the production of diesel fuel with improved low-temperature properties” (state registration number 0120RK00096, 2020-2022); AP15473256 "Investigation of the activity of promoted composites based on mesoporous aluminosilicates in the diesel fractions' dewaxing process" (state registration number 0122RK00919, 2022-2024).

Publications. The research results of the dissertation work were published in 17 scientific papers, including:

– 1 article in the international peer-reviewed journal «Open Chemistry» (Q2, percentile 54%);

– 7 articles included in the list of journals recommended by the Committee for Quality Assurance in the Field of Science and Higher Education of the Ministry of Science and Higher Education of the Republic of Kazakhstan;

– 9 materials and abstracts at international scientific conferences.

Personal contribution of the doctoral student to the preparation of each publication:

1. Article «The mesoporous aluminosilicate application as support for bifunctional catalysts for n-hexadecane hydroconversion» in «Open Chemistry» journal: preparation of a review and analysis of literature data, obtaining experimental data at Gazi University, obtaining and processing results, analysis of literature data.

2. Article «N-hexadecane hydroisomerization in the presence of Al-HMS – based bifunctional catalyst» in «Chemical Journal of Kazakhstan» journal: obtaining experimental data, preparation of a review and data analysis.

3. Article «Hydroisomerization of diesel fractions of Kumkol and Zhetybay oils in the presence of a bifunctional catalyst based on mesoporous aluminosilicate» in «Industry of Kazakhstan» journal: obtaining experimental data, preparation of a review and data analysis.

4. Article «Physico-chemical characteristics and catalytic activity of composites based on mesoporous aluminosilicates» in «Chemical Journal of Kazakhstan» journal: obtaining and discussing experimental data, preparing a review of literature data.

5. Article «Synthesis and physicochemical characteristics of mesoporous aluminosilicates» in «News of National Academy of Sciences of the Republic of Kazakhstan» JSC «Institute of Fuel, Catalysis and Electrochemistry named after. D.V. Sokolsky» journal: preparing a review and analyzing data, obtaining and discussing experimental data, obtaining and processing results.

6. Article «Evolution and role of the dewaxing process in oil refining» in «Oil and Gas» journal: review preparation and data analysis.

7. Article «The role of the binder in the composition of catalysts for the hydroisomerization process» in «Oil and Gas» journal: preparing a review, obtaining and discussing experimental data, obtaining and processing results.

8. Article «Mesoporous aluminosilicates as promising carriers of catalysts for petrochemical processes» in «Oil and Gas» journal: obtaining and discussing experimental data, obtaining and processing results.

9. Materials of theses of scientific conferences and symposiums: obtaining and description of experimental data, discussion and receiving of analysis results, preparation of materials.