ABSTRACT
thesis for the degree of Doctor of Philosophy (PhD)
in the educational program 8D07101 – Petrochemistry
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"Dearomatization of a model hydrocarbon mixture over bifunctional catalysts based on mesoporous aluminosilicates"

General description of the work. This dissertation is dedicated to the synthesis of bifunctional catalysts based on mesoporous aluminosilicate and activated bentonite from the Tagan deposit for processes such as hydrodearomatization and hydrodesulfurization of model hydrocarbons. It includes comprehensive analysis and testing of these catalysts.

Relevance of the study. In recent years, the requirements for diesel fuel quality have become stricter worldwide, including in Kazakhstan. The World Fuel Charter recommends limiting the content of polycyclic aromatic hydrocarbons in diesel fuel to less than 2 wt.%. Furthermore, the Euro-7 standard mandates that sulfur compounds should not exceed 10 ppm, while nitrogen oxide emissions should range between 0.01-0.03 g/km.

Combustion of aromatic hydrocarbons releases highly toxic components into the atmosphere, such as carbon monoxide, sulfur dioxide, and soot. This issue can be addressed through hydrogenation and, to some extent, the hydrocracking of cyclohexane rings in the reaction products. The efficiency of such processes largely depends on the composition of the catalysts. The optimal ratio of active phases to the support enables effective control of the hydrodearomatization process for diesel fractions.

The process efficiency can be enhanced by synthesizing new catalysts that are resistant to sulfur, oxygen, and nitrogen heteroatoms and demonstrate high activity in the hydrogenation of aromatic hydrocarbons. Additionally, given the significant presence of polyaromatic sulfur compounds in diesel fuel, the hydrodearomatization process also involves hydrodesulfurization. These processes reduce the environmental impact of fuel production and contribute to achieving Sustainable Development Goal 3 Good Health and Well-being and Goal 13 Climate Action.

Thus, the dissertation dedicated to studying the development of efficient catalysts based on mesoporous aluminosilicates and activated bentonite containing nickel and molybdenum for the hydrodearomatization and hydrodesulfurization of model hydrocarbons is highly relevant.

Purpose of the work: Development of novel efficient catalysts based on mesoporous aluminosilicate and activated bentonite, promoted with nickel and molybdenum salts, for performing the dearomatization and desulfurization processes of model hydrocarbons in a high-pressure autoclave.

To achieve this goal, the following tasks were set:

1. Synthesis of Al-HMS type mesoporous aluminosilicates with various Si/Al ratios, possessing high textural properties.
2. Synthesis of bifunctional catalysts based on Al-HMS and pre-activated bentonite from the Tagan deposit, promoted with nickel and molybdenum salts.

3. Comprehensive study of the physico-chemical properties of the obtained samples.

4. Investigation of the effect of the Si/Al ratio in Al-HMS-type mesoporous aluminosilicate in a bifunctional catalyst, temperature on process conversion and selectivity, as well as the influence of reaction time on changes in the composition of hydrogenation products of a model mixture.

5. Examination of sulfur compounds' effect on the hydrodearomatization process using the catalyst that demonstrated the highest efficiency in the hydrogenation reaction of the model compound.

6. Suggestion of the proposed mechanism and kinetics of hydrogenation reaction of model hydrocarbon over a synthesized bifunctional catalyst.

7. Study of the physico-chemical properties and stability characterization of catalyst based on mesoporous aluminosilicate and activated bentonite after the hydrogenation process.

The object of the study: mesoporous aluminosilicate, activated bentonite, Ni-Mo promoted bifunctional catalysts, model hydrocarbons.

The subject of the study: methods for synthesizing highly efficient catalysts for the model compounds' hydrodearomatization and hydrodesulfurization processes, as well as the study of their physico-chemical properties and catalytic efficiency.

Research methods: The synthesized samples were characterized using the following methods: inductively coupled plasma optical emission spectroscopy (ICP-OES), X-Ray diffraction (XRD), high-resolution solid-state NMR spectroscopy (^{27}Al NMR), Fourier-Transform infrared spectroscopy (FTIR), nitrogen adsorption-desorption isotherms, temperature-programmed desorption of ammonia (TPD-NH_3), Py-FTIR (Pyridine adsorption FTIR), thermogravimetric analysis (TGA), X-Ray photoelectron spectroscopy (XPS), temperature-programmed reduction with hydrogen (TPR-H_2) and Uv-vis spectroscopy. The composition of the model hydrocarbons after catalytic testing was analyzed using gas chromatography-mass spectrometry (GC-MS).

Scientific novelty and main results of the study:

1. Al-HMS type mesoporous aluminosilicates with varying Si/Al ratios (10, 30, 50, and 70) were synthesized using the template method. The obtained materials demonstrated high textural properties: the specific surface area ranged from 818 to 956 m^2/g, the average pore volume from 0.87 to 0.98 cm^3/g, and the average pore size from 3.47 to 3.86 nm.

2. Bifunctional catalysts promoted with Ni-Mo ions were synthesized based on Al-HMS with varying Si/Al ratios and pre-activated bentonite from the Tagan deposit.

3. The study established the influence of aluminum concentration on the physico-chemical properties of the synthesized samples.

4. For the first time, the optimal parameters for the dearomatization of a model mixture in a high-pressure reactor were determined at a temperature range of 220-300°C, hydrogen pressure of 6 MPa, and reaction duration of 1-8 hours using a nickel-molybdenum catalyst based on Al-HMS with various Si/Al ratios and activated bentonite. For the Ni-Mo-Al-HMS-H-bentonite catalyst, the optimal Si/Al ratio was found to be 10, and the optimal reaction temperature was 240°C. A stable composition

of hydrogenation process products was observed under the specified parameters when the reaction duration reached 5 hours.

5. The effect of sulfur-containing compounds on the dearomatization of model hydrocarbons was investigated in the presence of the Ni-Mo-Al-HMS(10)-H-bentonite catalyst at a temperature range of 220-300°C, hydrogen pressure of 6 MPa, and a reaction time of 5 hours. The optimal reaction temperature with the addition of dibenzothiophene was 260°C, where the selectivity to 2-methyldecalin reached 68%. The conversion of the hydrodesulfurization process for the sulfur compound was 76%.

6. The proposed mechanism and kinetics of the hydrodearomatization reaction of a model hydrocarbon over the bifunctional Ni-Mo-Al-HMS-H-bentonite catalyst have been suggested.

7. It was shown that the structure of the catalyst based on mesoporous aluminosilicate, activated bentonite, and promoted with nickel and molybdenum salts is preserved after dearomatization and desulfurization reactions, despite a decrease in textural properties. Additionally, the effectiveness of new and regenerated catalysts in the hydrogenation reaction was evaluated, and their stability was determined: 5 cycles without regeneration in the absence of sulfur-containing hydrocarbons and 4 cycles in their presence.

The main provisions for defense:

1. Increasing the aluminum content during the synthesis of Al-HMS (from Si/Al = 70 to Si/Al = 10) contributes to an increase in the proportion of tetrahedral aluminum compared to octahedral aluminum and an increase in the number of acidic centers.

2. The highest efficiency in the hydrogenation process of 2-methylnaphthalene (97% conversion, 93% selectivity for 2-methyldecaline) and a mixture of 2-methylnaphthalene with dibenzothiophene (92% conversion, 68% selectivity for 2-methyldecaline) is achieved on the Ni-Mo-Al-HMS(10)-H-bentonite catalyst at 240°C and 260°C, respectively.

3. The Ni-Mo-Al-HMS(10)-H-bentonite catalyst maintained hydrogenation efficiency for 2-methylnaphthalene over 5 cycles without regeneration and in the hydrogenation of the 2-methylnaphthalene and dibenzothiophene mixture over 4 cycles.

Theoretical and practical significance of the work: The patterns obtained in the hydrogenation processes of model compounds using structured mesoporous aluminosilicates and bentonite from the Tagan deposit demonstrate the significant potential of these materials. As repeatedly emphasized by the President of the Republic of Kazakhstan, the development of the petrochemical industry, including the creation and production of catalysts that account for the compositional features of Kazakhstani oil, significantly contributes to the country's economic efficiency. The use of inexpensive active centers in catalysts, resistant to poisons, and the selection of mesoporous aluminosilicates and bentonite as their acidic components prevent diffusion limitations in the hydrogenation process. Specifically, nickel and molybdenum are effective alternatives to traditional platinum and palladium-based catalyst systems. Due to their high catalytic efficiency and affordable cost, transition metals provide an opportunity to replace expensive precious metals while maintaining the efficiency of the technological process. The results obtained in this dissertation

contribute to the development of technologies for producing heterogeneous catalysts for refining processes and obtaining high-quality fuels. Furthermore, given the large reserves of bentonite and hydrocarbon raw materials in the country, the creation of new technologies based on Kazakhstan's raw material base is an urgent issue.

Compliance with the directions of development of science or government programs. The dissertation was carried out as part of the ADBIOCAP and FAUPORES projects (M-2735/30VCININ.541A.641.00) of the Madrid Community and the Rey Juan Carlos University. The physico-chemical properties of the synthesized samples were studied at Rey Juan Carlos University (Mostoles, Spain). Additionally, the physico-chemical properties and catalytic efficiency of the obtained samples were determined at Bar-Ilan University (Ramat Gan, Israel) as part of the international “Sandwich” scholarship, supported by the Council for Higher Education in Israel.

Publications. The results of the dissertation research have been published in 10 scientific works, including:

- 1 article in an international journal with a non-zero impact factor (IF = 4.8; Q = 1; percentile 87) indexed in the Web of Science and Scopus databases;
- 3 articles in scientific 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;
- 6 abstracts presented at international scientific conferences.

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

1. A. Abdrassilova, G. Vassilina, K. Abdildina, L. Briones, A. Peral, J. M. Escola. The notable features of mesoporous aluminosilicates as catalytic supports for hydrodearomatization and hydrodesulfurization of fuels // Microporous and Mesoporous Materials. – 2025. – V. 384. – P. 113457. (Writing – original draft, software, resources, investigation, data curation, conceptualization)

2. C. Molina, A. Abdrassilova, M.I. Ávila, M.M. Alonso-Doncel, J. Cueto, G. Gómez-Pozuelo, L. Briones, J.A. Botas, D.P. Serrano, A. Peral, J.M. Escola. Tailoring the preparation of USY zeolite with uniform mesoporosity for improved catalytic activity in phenol/isopropanol alkylation // Microporous and Mesoporous Materials. – 2025. – V. 392. – P. 113629. (Investigation, Data curation)

3. Абдрасилова А.К., Абдильдина К.М., Василина Г.К., Классен И.А., Забара Н.А., Байдулла Д.Р. Мезопористые алюмосиликаты как перспективные носители катализаторов нефтехимических процессов // Нефть и Газ. – 2022. – V. 6. – P.115-125. (Literature review preparation, experimental data collection, result processing and description)

4. Василина Г.К., Абдрасилова А.К. Влияние природы источника алюминияна физико-химические характеристики носителя каталитических систем для нефтехимической промышленности // Нефть и Газ. – 2022. – V. 6. – P. 161-173. (Literature review preparation, experimental data collection, result processing and description)

5. Abdrassilova A., Vassilina G., Abdildina K., Kanapiyeva F. Study of catalysts based on mesoporous aluminosilicate in the dearomatization process of a model

mixture: physicochemical characteristics and catalytic activity // Bulletin of Shakarim University. – 2024. – No. 1 (13). – P. 161-173. (Literature review, experimental data collection, result processing and description)

6. The PhD student's contribution to the preparation of materials for scientific conferences and congresses (Obtaining and describing experimental data, processing and discussing analysis results, writing abstracts)