

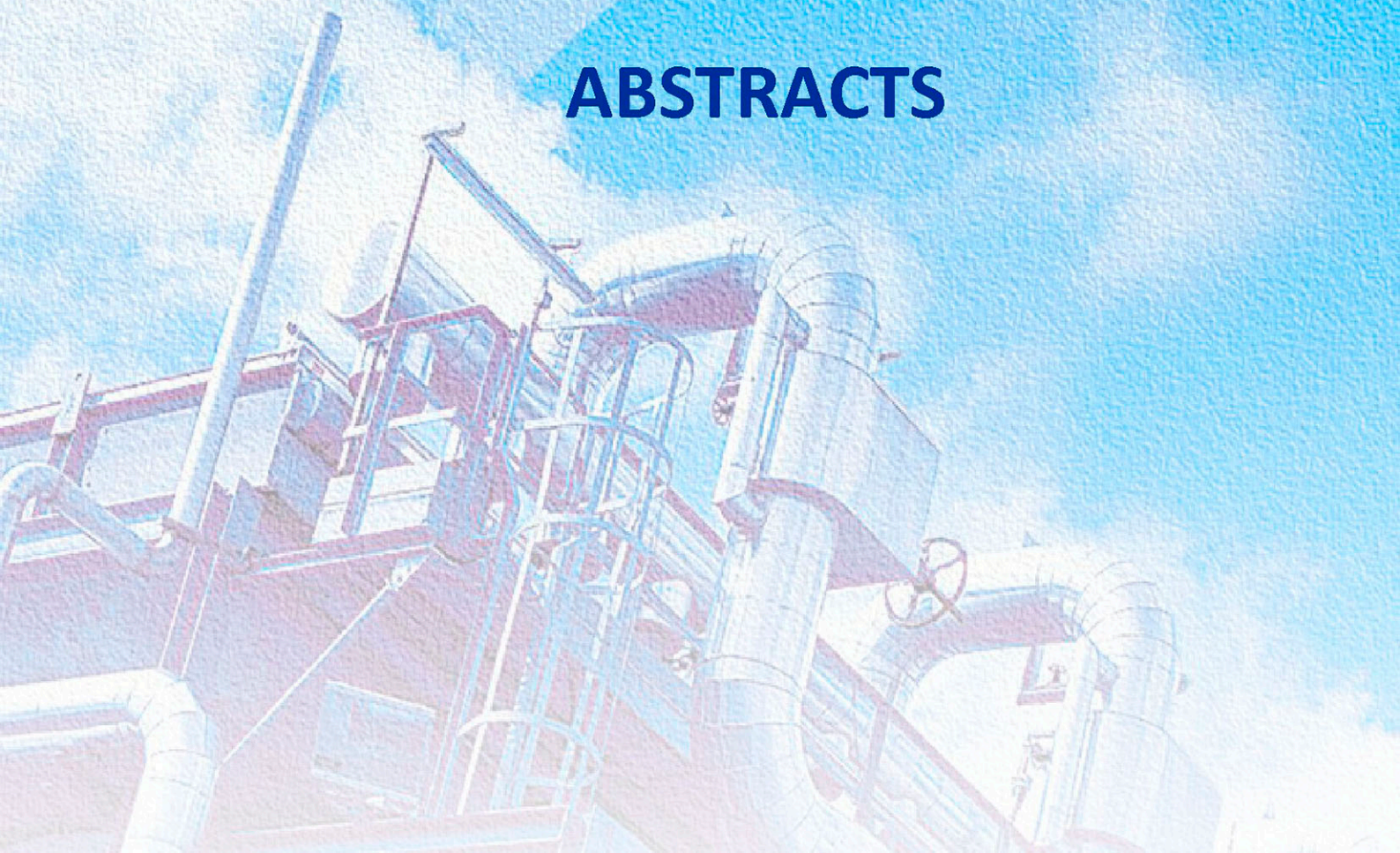


Boreskov Institute of Catalysis SB RAS
Institute of Hydrocarbons Processing SB RAS
PJSC Gazprom Neft

II Scientific-Technological Symposium
CATALYTIC HYDROPROCESSING
IN OIL REFINING

Belgrade, Serbia,
April 17-23, 2016

ABSTRACTS



Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia
Institute of Hydrocarbons Processing SB RAS, Omsk, Russia
PJSC Gazprom Neft, St. Petersburg, Russia



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Сборник включает тезисы пленарных, ключевых лекций, устных, стендовых и заочных докладов секций:

The collection includes abstracts of plenary lectures, key, oral, poster and virtual presentations of the following scientific fields:

- **Section I.** CATALYSTS FOR HYDROGENATIVE PROCESSES: PRACTICAL AND FUNDAMENTAL ASPECTS;
- **Section II.** DEVELOPMENT, ENGINEERING, MODELLING AND PRACTICAL APPLICATION OF HYDROPROCESSING TECHNOLOGIES;
- **Section III.** HYDROGENATIVE PROCESSING OF HEAVY OILS, SHALE OILS, RENEWABLE AND ALTERNATIVE FEEDSTOCKS.

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PLENARY LECTURES

MULTISCALE REACTION ENGINEERING IN HYDROPROCESSING

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Oil refining remains the main source of transportation fuels world-wide. Over the years the industry has adapted to changing sources of starting raw materials and has invented and implemented numerous large scale catalytic processes in producing a variety of fuels to meet the market demands. The success of oil refining to generate desired products is based on a series of hydroprocessing operations, most of which require solid catalysts and reliable methods for generation of hydrogen. Modern refineries, often called “cathedrals of chemical engineering”, are excellent examples of the triumph of the systematic application of the chemical reaction engineering (CRE) methodology over seemingly intractable complexity. It is thus not surprising that refining operations remain among the best in process E factors (i.e. lowest undesired byproducts per unit of desired product produced).

We will first discuss what has contributed to the current success in hydro processing and what can we expect in the future with new catalyst and reactor developments. The need for systematic application of multiscale analysis in transport – kinetic interactions will be illustrated to enable scale – up from micro units to large plants. The benefits of current advances in catalysts are often limited by employing them in existing reactor types (e.g. trickle beds, packed bubble columns, ebullated beds, slurry systems) where their potential cannot be fully realized. We will illustrate how the need to handle new difficult feeds has resulted in ingenious improvements in commercial reactor design, how the advanced flow monitoring technologies applied in the lab can be used to improve moving bed and fluidized bed operations. At the end we summarize what developments are needed to formulate an improved scientific basis for hydroprocessing operations that will enable speedier and more reliable scale up. One should not forget the need to educate new generations in this important field, and pre-competitive research involving research institutes, academia and industry is the best way of doing it.

Acknowledgment

I am indebted to my colleagues and friends R. Gupta of Exxon Mobil, K. Van den Busche of UOP, F. Larachi of University of Laval, and my ex students C. Foote of ExxonMobil, P.L. Mills of Texas A&M at Kingsville for pointing out interesting material that I decided to discuss in this lecture. B. Wook Lee's help in preparing the slides is most gratefully acknowledged.

MODERN TRENDS IN THE DEVELOPMENT OF CATALYSTS AND CATALYTIC TECHNOLOGIES FOR REFINERY

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Catalytic technologies are the key to advanced processing of hydrocarbon raw materials. The refinery complexity index (the so-called Nelson index) shows the perfection of a particular plant *versus* a plant engaged specifically in the processing of crude oil.

A low Nelson index is characteristic of the simplest physical and thermal processes in refinery and oil chemistry, while the catalytic processes can only provide the deep processing and, correspondingly, the high Nelson index.

The key element in advancing catalytic processes is the development of new catalysts for refinery and oil chemistry.

The reported data relate to new developed processes for a number of processes for hydrotreatment of oil fractions:

- Catalysts for selective hydrotreatment of catcracking gasoline that allow deep gasoline hydrotreatment to be achieved without fractioning and provide no more than 0.1-1.0 point decrease in RON;
- Catalyst for advanced hydrotreatment of diesel fractions at flow rate of 1.0-1.2 h⁻¹ and inlet temperature no more than 340 °C to provide the residual sulfur content less than 10 ppm;
- Catalysts for hydrotreatment of vacuum gasoil at 375-380 °C and low gas generation to provide the residual sulfur content less than 150-200 ppm.

New catalysts for hydrocracking of vacuum gasoil (VGO) provide higher yields of middle distillates (kerosene and diesel fuel): more than 90 % of VGO per pass and more than 80 % of diesel fractions.

The developed catalysts for dehydrogenation of light hydrocarbons in vacuum provide deep processing of ethanol to oil chemicals. The catalysts for selective oxidation of ethanol to acetic acid and catalytic processing of ethanol to ultrahighmolecular polyethylene (UHMPE), multilayer carbon nanotubes (MCNT), UHMPE and MCNT based composite materials are discussed as examples.

Some data on industrial employing of the new developed catalysts also are reported.

HYDROPROCESSING, A SUITE OF VERSATILE TECHNOLOGIES TO MEET THE FUEL PRODUCERS' RAPIDLY EVOLVING NEEDS

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The volatility of the fossil fuel markets and the tightening specifications to curb SO_x, soot and CO₂ emissions associated with the consumption of distillate-range transportation fuels are leading to an array of interesting new challenges and opportunities for refiners, which can be addressed with a suitable portfolio of Hydroprocessing (HP) technologies. Refiners' feedstock slates are also continuing to diversify, with the need to process FT waxes, to bring bio-based feeds to specification so they fit into the mainstream fuel distribution network and to convert heavier boiling streams, getting ever closer to the bottom of the barrel.

In this presentation, we will, at first, sketch out a number of macro-market drivers and illustrate how these directly impact the technology selections for Hydroprocessing. We will then provide an overview of the most advanced HP technologies, followed by some of the key advances in the fundamental understanding of catalyst functionalities, feedstock characterization and model representations for this field.

This scientific progress, the enhanced modeling capabilities and the application of molecule management have inspired and are continuing to inspire step-change technology improvements in what some would consider a mature field. The material value impact of these improvements will be illustrated in 3 case studies: conventional middle distillate production from fossil sources, recent advances in the conversion of heavy oil to fuels and the commercialization of the production of fully blendable fuels from bio-based sources.

DEVELOPMENT OF ZEOLITE BASED MICRO-MESOPOROUS CATALYSTS FOR PETROCHEMISTRY AND OIL REFINING

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Hierarchical micro-mesoporous materials have emerged as an important class of catalytic materials, which has significant advantages with respect to both zeolites and ordered mesoporous solids. Nowadays this class of materials involves different structural types: nanosized zeolites with mesopores in between the crystallites; delaminated zeolites; zeolitic nanosheets; mesoporous zeolites; ordered mesoporous materials with fully or partially crystalline zeolitic walls, micro-mesoporous composites and etc. The literature on these materials is growing almost exponentially and a great deal of reviews highlighting various aspects of the recent achievements in this area has appeared recently [1].

This lecture is devoted to micro-mesoporous materials obtained by zeolites recrystallization, which has been demonstrated to be a versatile tool for the tailored synthesis of mesoporous zeolites, micro-mesoporous nanocomposites and ordered mesoporous materials with zeolytic fragments in the walls [2]. The lecture will cover the recent achievements in the field of the development of this type of micro-mesoporous materials. The recrystallized materials will be classified into three distinctly different groups depending on the degree of recrystallization: i) mesoporous zeolites (RZEO-1); ii) micro-mesoporous nanocomposites (RZEO-2); iii) mesoporous materials with zeolytic fragments in the walls (RZEO-3). The first part of the lecture will be focused on the mechanism of zeolite recrystallization, which determines the main synthetic strategies leading to different types of recrystallized materials. In the second part, a comprehensive view on their structure, texture and porosity in connection with acidic and diffusion properties will be given. The third part will be devoted to the engineering of recrystallized materials for the specific catalytic applications in petrochemistry and oil refining.

The specific attention will be focused on the impact of recrystallization on the improvement of the catalytic performance of zeolites and mesoporous materials in various catalytic reactions including cracking and hydrocracking of alkanes,

hydroisomerization of n-alkanes, C₁₀₊ alkylaromatics dealkylation, alkylation and transalkylation of aromatics, dehydration of methanol into DME, skeletal isomerization of 1-butene, disproportionation of toluene and cumene and upgrading of bio-oils. It will be demonstrated that the choice of the optimal recrystallized material is governed by the two main factors: i) the size of reactant/product with respect to the size zeolitic micropores; ii) the acidic strength required for the specific reaction. If the reactants and products are very bulky and cannot diffuse into zeolitic micropores but strong acidity is not required, RZEO-2 and RZEO-3 are the optimal catalysts. Nanocomposite materials RZEO-2 are especially advantageous in the sequential reactions, involving transformation of large reactant in the mesopores and smaller intermediate in the micropores. In the case of the reactions demanding strong acidity, such as FCC, cumene disproportionation or biphenyl transalkylation with diisopropylbenzene, RZEO-1 is the most appropriate.

In the last part of the lecture the advantages and disadvantages of micro-mesoporous materials obtained by zeolites recrystallization with respect to pure micro- and mesoporous molecular sieves and other hierarchical zeolites will be critically analyzed and the future opportunities and perspectives will be discussed.

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Acknowledgements

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CONVERSION OF NATURAL GAS-(COAL- OR BIOMASS-) DERIVED SYNTHESIS GAS TO TRANSPORTATION FUELS AND CHEMICAL FEEDSTOCKS VIA FISCHER-TROPSCH SYNTHESIS

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The renewed interest in conversion of syngas into hydrocarbons using Fischer-Tropsch synthesis (FTS) is principally due to the concerns about rational use of fossil and renewable resources. Both fossil and renewable resources can be converted into liquid fuels and chemical feedstocks using XTL (X-To-Liquid) technologies, where X can be natural, associated or shale Gas, Coal or Biomass. The heart of the GTL, BTL and CTL processes is the FTS reaction in which syngas is converted to hydrocarbons over a cobalt or an iron catalyst. Cobalt is the catalyst of choice for low temperature FTS and high H_2/CO feed ratio (GTL application), due to its high activity and selectivity towards desired products, as well as the absence of water-gas shift reaction. Iron based catalysts are used to process coal derived synthesis gas (low H_2/CO feed ratio), due to their ability to generate H_2 internally via the WGS reaction.

There are two general types of FTS technology that are currently employed on a commercial scale: high and low temperature Fischer-Tropsch (HTFT and LTFT), where the latter is typically used in the industry for synthesis of liquid fuels. LTFT is characterized by three-phase operation and is mainly conducted in two types of commercial reactors: slurry bubble column (SBCR) and multi-tubular fixed-bed reactors (MTFBR). These reactors are depicted in Figure 1.

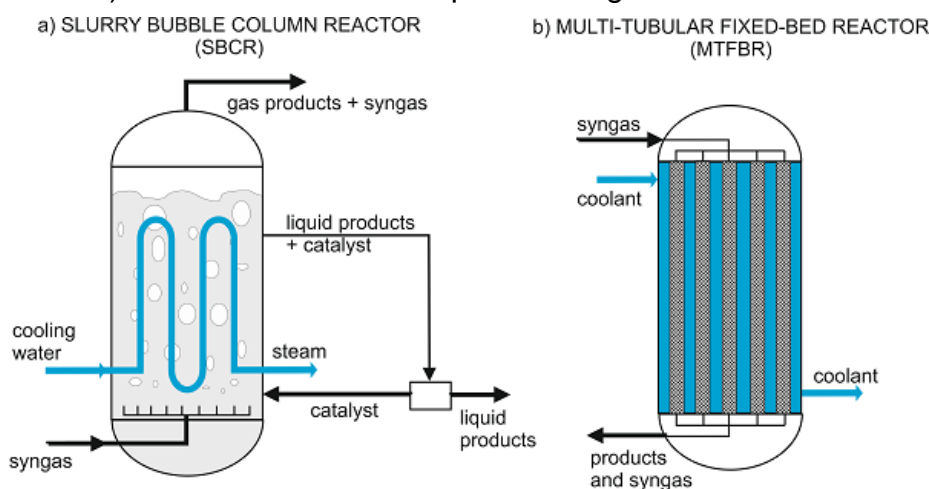


Figure 1. Commercial industrial reactors for LTFT

The reaction is highly exothermic and heat removal presents one of the main challenges when choosing the reactor type. However, other issues that also have to be considered are catalyst effectiveness, catalyst deactivation and regeneration, pressure drop etc. The differences between these reactor types have already been discussed elsewhere. The major downsides of SBCR are difficult scale-up, separation of active catalysts from wax and catalyst deactivation due to attrition, while the drawbacks of MTFBR are high capital cost, poor heat removal, high mass transfer resistances and high pressure drop. Also, several micro-channel based Fischer-Tropsch reactors for small scale applications have been under development (Compact GTL, Velocys) and are ready for commercialization. Process intensification also improves attractiveness of FTS for conversion of ligninocellulosic biomass into synthetic fuels using BTL technology. The efficiency of the BTL process is strongly affected by the cost related to biomass collection and transport. Design of smaller highly efficient BTL units is expected to significantly improve the cost-efficiency.

Recent developments and trends in XTL technology, including a brief review of kinetic modeling approaches for primary and secondary reactions will be discussed in this lecture.

UPGRADING OF HEAVY OILS AND RESIDUA BY MODERATE CATALYTIC HYDROPROCESSING

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HIDRO-IMP® is a catalytic hydroprocessing technology for the upgrading of heavy and extra-heavy crude oils in order to improve their pumpability through pipelines and to provide a better quality feedstock to refineries. The produced upgraded oil exhibits similar properties than those of intermediate crude oils, but with lesser sulfur and other impurities content. The main feature of the HIDRO-IMP® process is an arrangement of fixed-bed reactors in series loaded with a graded bed system consisting of selective catalysts for hydrotreating and hydroconversion, in combination with moderate-pressure operating conditions to minimize sludge and sediments formation.

The basic process scheme of the HIDRO-IMP® technology involves splitting a full boiling range heavy crude oil into a light fraction and a heavy fraction. The heavy fraction is subjected to hydroprocessing conditions in a first fixed-bed reactor, where substantial metals and asphaltenes removal is achieved and at least a portion of sulfur and nitrogen is eliminated. The partially converted products from this stage enter a second fixed-bed reactor to achieve substantial sulfur and nitrogen removal and a moderate level of hydrocracking. The reactor effluent is sent to a high pressure separator where the liquid products are recovered from the gases. The liquid stream from the high pressure separator is provided with additional stripping in order to remove the remaining dissolved hydrogen sulfide. The gas mixture from the high pressure separator is fed to the scrubbing unit in order to remove hydrogen sulfide and ammonia, and the resulting high hydrogen purity stream is recompressed and recycled to the reaction system. Finally, the liquid stream is either mixed with the light fraction to obtain the upgraded oil or both streams (product from the reactors and light fraction from fractionation) can be sent to distillation of crude oil. The first option aims at producing better quality upgraded oil for commercialization purposes (upstream sector) and the objective of the second option is to serve as a pretreating of the crude oil before it enters the atmospheric distillation column. For the production of upgraded oil for transportation, the process scheme is reduced substantially, e.g. only one reactor and one catalyst are needed.

RUSSIA'S OIL DILEMMA: TO GO NORTH-EAST OR TO GO DEEP?

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Russia is one of the biggest oil and gas producers and one of the main exporters of hydrocarbons. Hydrocarbon production plays a crucial role in the Russian economy, financial system and its economic and political negotiations with many countries abroad.

The oil and gas sector in Russia is “responsible” for:

- 20 % of GDP;
- 52 % of the federal budget receivables in 2014 (31.4 % in 2004);
- 67 % of export revenue;
- 25 % of fixed capital investments.

The main topic of this lecture is the economic foundation of liquid hydrocarbon production in Russia. The lecture will show the basic trends in Russian hydrocarbon production and the steps and measures required to develop production and to export the products. Development of mature areas is a natural source of exports westward, while new fields and new areas are located in the north-east of Russia, closer to the Asia-Pacific market. At the same time, northern and central Arctic fields and areas are close to both the European and Asian markets and the exact itinerary depends on transportation facilities and price conditions.

A very important feature of Russian oil development is that the fields and refineries are located quite far from each other. While the main fields are located in Siberia, most of the refineries are in the European part of Russia at distances from the fields exceeding 1.5 thousand km. This means a low level of flexibility of the producing companies in the case of oil delivery to other destinations. Behind this feature there was the logic of the centrally planned economy with one decision-making centre. In the case of market- or price-driven necessities it was not easy to realise producer (seller) intentions to deliver oil to other refineries or to other destinations. Historically, all the pipelines were oriented from east to west. Only two ran in other directions: from West Siberia to the south (to Kazakhstan) and to the east (to the Angarsk refinery located in eastern Siberia). All the volumes of oil and refined products delivered east of Angarsk were transported only by rail.

PL-7

There is no need to talk about oil reserve depletion per se: Russia still has abundant resources. However, questions arise regarding the industry organisation and the resource management which are behind the permanent changes in the resource base which are taking place. Since the mid of 90th the sector structure was drastically transformed. The main features were the following:

- the formation of vertically integrated companies, including for the production, processing and sale of oil products;
- an (initially) partial privatisation of the newly-formed companies;
- leaving the oil trunkline system in state hands;
- opening windows for companies to export oil and oil products.

Among the most urgent and important outcomes of the changes was the opportunity for the newly-formed companies to decide how and where to allocate money. The transformation resulted in a revival of oil production in Russia. Among the main drivers of this were access to capital, the use of modern technology, and the opportunity to allocate resources according to company priorities.

According to estimates from the Ministry of Natural Resources, costly (or expensive to produce) oil could reach a level of 52 Mt a year by the 2016. This will require up to 100 bn USD of additional investments. All the major and giant fields previously discovered and brought into development are now in a declining state of production, while newly-discovered deposits have much smaller reserves per field

On the other hand, not only are the sizes of deposits decreasing, but the conditions of oil production are also changing, with a drastic increase in the numbers of deposits with difficult reservoir characteristics (which makes the use of traditional water-flow technology problematic) and containing oil of high viscosity.

Besides heavy oils and complex fields, Russia has a significant potential for natural liquid gas production (light and ultra light oil and gas condensates). The long-term production of these hydrocarbons is related to the development of gas condensate deposits in the northern part of West Siberia, in the Yamal-Nenets Autonomous Okrug (YaNAO), and in the shelf area of Russia's Arctic seas. Nowadays, increases in the production of this type of liquid hydrocarbons is one of the factors sustaining the total liquid (oil and condensates) production in Russia (natural liquid gas production currently surpasses 21 Mt). Nonetheless, this source should not be viewed as a leading one, despite its important role (3 to 4 % of gross liquid hydrocarbon production). Condensates are a by-product of gas production and

this source's main limiting factor is the low level of gas production, which is limited not only by market size but also by both pipeline system capacity and investment levels. The level of growth in condensate production is very low, mainly due to emphasis on the development of projects approved and started earlier with certain specific characteristics: deeper and smaller pools with higher reservoir pressures. These need more advanced technology and more experienced personnel.

Russia has a significant resource potential of liquid hydrocarbons which can allow production to be both maintained and increased in the foreseeable future (until 2030-2040). However, potential itself does not mean high and efficient production levels. The abundant resources require not only investments but also a different industry structure (oriented towards economic efficiency) and a more appropriate competition-oriented resource regime and more advanced technological basis: a growing portion of the oil resources in Russia are now classified as hard to extract. As the conditions of the reserves and hydrocarbon production have become much more complicated – the composition of the hydrocarbon mix has drastically changed towards heavy and highly-viscous hydrocarbons – different technologies and, above all, a change in the institutional system are required, ranging from overhauling taxation on hydrocarbon production to encouraging new entrants into the sector. During the period of high prices and intensive redevelopment of existing fields, the structure of the oil industry became much more monopolised than before (large and vertically-integrated companies produce more than 85 % of Russian oil). The combination of the changing resource base and much lower oil prices now requires a 'balanced approach' to developing liquid hydrocarbon production, taking the following steps:

- a) further development of major fields previously brought into development,
- b) exploration of new regions with a potential for "fresh reserves" (Eastern Siberia and the Far East), and finally
- c) increasing the production of heavy and highly-viscous oil (Tatarstan, Bashkortostan, Western Siberia, the Republic of Sakha (Yakutia)).

The dynamics of liquid hydrocarbon production in Russia, as well as of exports to foreign markets, will largely depend on how well Russia can adapt to these challenges. In this respect, access to technology plays a crucial role.

KEYNOTE LECTURES

HIGH THROUGHPUT EXPERIMENTATION AS EFFICIENT TOOL FOR TESTING OF COMMERCIAL HYDROPROCESSING CATALYSTS

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1. Introduction

Increasing global demands for fuels, the tightening of environmental regulations and the optimization of refineries have led to an increasing demand for commercial catalyst testing capacity for refining applications. High throughput catalyst testing is a time- and cost-efficient approach that can meet this demand. In the past, the domain of high throughput testing focused on the evaluation of powder samples (typically below 200 μm). Over the last couple of years, hte has developed standard operating procedures (SOPs) for parallel testing of full-size commercial catalysts at scales of 1 to 100 ml. These SOPs do not only apply model feeds but in most cases real refinery feedstocks such as diesel, vacuum gas oil (VGO), deasphalted oil (DAO), atmospheric residue or wax while maintaining the high level of data quality.

In the present paper we will review the state-of-the-art of high throughput parallel testing of commercial catalysts for Hydroprocessing of oil fractions. We will describe the basic principles and will choose selected case studies to emphasize the benefit of high throughput experimentation.

2. Case Studies

2.1. Hydrocracking of a hydrotreated VGO

Hydrocracking of a hydrotreated VGO was studied for 4 extrudate benchmark catalysts in the 1 ml scale in a 16-fold fixed-bed reactor system. Interpolation of the 350+Conversion vs. reactor temperature led to a clear differentiation of the catalysts with a precision better than 1 °C. The precision of the middle distillate selectivity at constant conversion was better than 0.5 % absolute. The comparison of model feed versus real feedstock showed a clear impact on catalyst performance and ranking.

2.2. Hydrotreating of atmospheric residue

Residue Hydrotreating on stacked beds of extrudate catalysts with different functionalities for demetallation (HDM), desulfurisation (HDS), denitrogenation (HDN) and different bed length were tested at constant conditions in a 16-fold reactor system. The study showed that the HDS activity follows the experimental catalyst

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design (see Figure 1), and the effect of the independent variables can be used to build a kinetic model based on a single experiment.

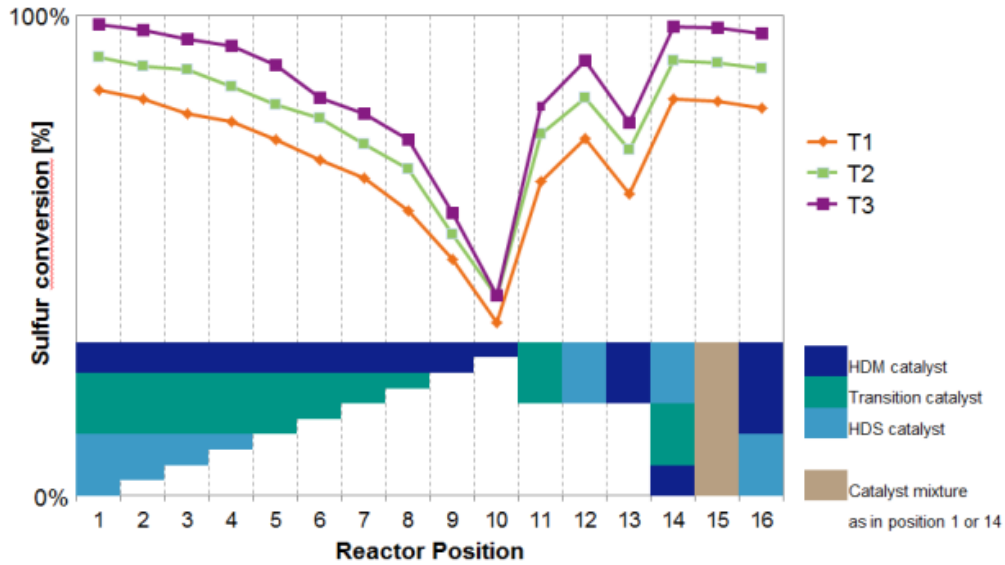


Fig. 1. HDS activity as function of plate design [1]

2.3. Downscaling testing of commercial catalysts

In this case study, the progress in experimental procedures and workflows developed at the company for ranking of commercial catalysts at different scales in parallel fixed-bed trickle-flow reactor systems will be discussed. The testing of the same two commercial HDS catalysts at 1.5 ml catalyst volume is compared to tests in the 35 ml scale. The aim of the company workflows is not only to rank catalysts at a certain scale under given fluid dynamic conditions, but even more important to get the same quantitative ranking at different scales by tuning the fluid dynamic environment in the reactor systems. The data obtained confirms that these workflows allow up- or downscaling of commercial catalyst testing in bench-scale reactor systems depending on the focus of a testing campaign. We will also explain the importance of reproducible reactor packing, controlling the particle size distribution of diluent materials and embedding of extrudates in smaller inert particles.

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CATALYSTS AND TECHNOLOGIES OF FUEL AND OIL FRACTIONS HYDROTREATMENT

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Stricter environmental requirements for commercial oil products, as well as the need to expand the resources for their production stimulate the development of new high-effective hydrotreating catalysts and technics of its reactivation.

The report presents the results of the research and development of new hydrotreating catalysts for hydroprocessing of various hydrocarbon raw feeds (FCC gasoline, diesel cuts, and vacuum gas oil (VGO)).

New approaches for designing of transition metal sulfide catalysts were used:

- The use of carbon coated supports for controlling active phase morphology and catalytic properties in hydrogenating reactions.
- Simultaneous use of heteropolyanions and chelating agents, that allowed to change significantly the promotion ratio and morphology of active phase species and, thereby, catalytic properties in HDS and HYD reactions.
- Detailed investigation of the genesis of CoMo/Al₂O₃ catalysts active phase prepared with the use of Co₂Mo₁₀ heteropolyanion and cobalt citrate.

The used approaches allowed us to develop new catalysts for (i) deep diesel hydrotreating, (ii) selective hydrotreating of FCC gasoline with saving octane number, and (iii) deep VGO hydrotreating. All catalysts have been successfully tested in conditions close to industrial.

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STATUS OF HYDROGENATION PROCESSES IN RUSSIA. CHALLENGES AND PROSPECTS

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At present a wide range of different factors has an impact on oil refining and petrochemical industry in Russia. It includes deterioration of hydrocarbon feed, changes in the economic situation and foreign policy related to the fall in crude oil prices, introduction of a new tax system in Russia, sanctions imposed on equipment and catalysts and, as a consequence, slowdown of the modernization process within the framework of the four-party agreement. Weakening of the national currency, sharp fall in crude oil and petroleum product prices on the foreign markets and the impact of tax manouevre make it difficult to invest in oil refining and lead to lower refining profits.

Basic processes which are to be implemented at refineries according to the General Development Plan for the Russian Oil Sector Until 2020 are presented in Table 1.

Table 1. Implementation of processes increasing depth of oil conversion and improving oil products quality until 2020

Process	Total capacity, MTA	Quantity of units
<i>Deep Conversion Processes</i>		
VGO catalytic cracking	11,5	8
VGO hydrocracking	48,8	16
Oil residues hydrocracking	15,7	6
Coking	12,8	9
Group III lube oils (for Euro-5 engines)	1,6	7
Hydrogen production	1,0	14
<i>Processes improving the oil product quality</i>		
Isomerization	7,4	12
Alkylation	2,6	11
Reforming	8,5	8
Hydrotreating	56,2	31

Of great importance among such processes are modern options of VGO and oil residue hydrocracking, as well as various types of oil distillates hydrotreating and hydrofining.

Major challenges of hydrogenation processes development for Russia are currently related to improving of processes and catalysts for diesel oil production with a sulfur content below 10 ppm and high cetane numbers, which will require introduction of a dearomatization stage into the production process, construction of costly hydrotreating plants operating under high hydrogen pressure or heavy feed hydrocracking plants to produce diesel fuel components.

Russia places great importance on developing processes that allow to improve diesel low-temperature characteristics (maximum filtration temperature, pour point), which can be implemented by means of catalytic dewaxing based on selective hydrocracking of normal paraffins or by means of isodewaxing of normal paraffins forming branched structures.

It is possible to use process solutions for diesel fuel production that combine stages of hydrotreatment, dearomatization and catalytic dewaxing.

Hydrogenation processes to treat thermocatalytic processes products is also of interest. Options based on combinations of hydrogenation, hydrogenolysis and use of high-pressure units have the most promising outlook.

Oil production processes meeting state-of-the-art ecological and operating parameters is a special direction of hydrogenation processes development. Challenges to be addressed as part of this direction is primarily related to implementation of hydrocracking processes.

Due to the increased share of heavy feed involved into processing, capacities of heavy oil residues hydrocracking plants are also on a rise. A strong interest is shown to the processes of heavy feed hydroconversion. A hydrofining process for heavy residues and bituminous oils with the use of leading-edge nanoscale catalysts has been currently developed in Russia.

To ensure implementation of new plant construction projects, a modern base will have to be created for development and putting into operation of catalytic systems with various depth of conversion.

HYDROCRACKING AND HYDRODEAROMATIZATION USING DISPERSED SLURRY CATALYSTS

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Dispersed slurry catalysts, which offer better contact with the reactants than the supported extrudate catalysts, have drawn again much attention in recent years, especially in connection with hydroconversion of heavy petroleum feedstocks. The key to the higher activity of dispersed catalysts is believed to be their nanoeterogeneous nature and high extent of catalytic dispersion and their ability to preserve the state of high dispersion under reaction conditions [1-2]. The latest development of dispersed catalysts present strong indications that such technologies will play a role in the future refinery and petrochemical industry. Due to the high activity of these dispersed iron-based catalysts, they can be used in small concentrations of 0.1-1.0 wt % based on metal relative to weight of feed for the various hydrogenation and hydroconversion reactions, conversion of syngas to alcohols and hydrocarbons, polymerization. The synthetic methods for preparation of dispersed catalysts for the slurry process are divided into water-soluble catalyst and oil-soluble catalyst. In the paper we investigated and evaluated the application of bimetallic water- and oil-soluble precursors of sulfide catalysts (NiW, NiCo, NiMo, NiMoW, NiCoMo) and the combination of bimetallic water- and oil-soluble catalysts and dispersed acid materials (Lewis acids, modified nanosized alumina, titanium oxide, zeolite Y and BEA) in the slurry-phase catalytic hydroconversion of a number model compounds, cyclic oils and vacuum gasoil.

A number of approaches to the synthesis of dispersed catalyst are discussed:

- a) Use of emulsion in feedstock of water or DMSO solutions of thiosalts of W and Mo in combination with emulsion of Ni or Co solutions;
- b) Use of emulsions in feedstock water or DMSO solutions of polymetallic salts with citric acid or heteropolyacids and in situ sulfidation;
- c) Use of dispersion of soluble amphiphilic polymer-based polymetallic complexes (e.g. based on polymaleic acids copolymers) in feedstock combined with in situ sulfidation;

- d) Use of oil-soluble precursors (ethylhexanoate of Ni and Co, carbonyls of W and Mo) in combination with in situ sulfidation;
- e) Use of thiocomplexes of W and Mo dispersed in polypropylene amine dendritic networks in combination with ex situ and in situ sulfidation.

The hydrogenation and hydrocracking of substituted and polysubstituted naphthalenes, polyalkylnaphthalenes and tetralins, cyclic oil and VGO are studied. The effects of nanosized acid components additives on the hydrocracking and hydrogenation of aromatics, hydrodesulfurization and hydrodenitrogenation in slurry system with in situ generation of nanoparticles are discussed

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THE SYNTHESIS OF HIGH-OCTANE COMPONENTS FROM THE PRODUCTS OF CATALYTIC CRACKING

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Environmental protection of megapolices by the use of advanced and economical high-compression engines makes it necessary to raise the production of high-octane components (HOCs). Unfortunately, such components are often produced by harmful technologies. For example, sulfuric acid or hydrogen fluoride alkylation and synthesis of N-monomethylanilin. As a result, environmental enhancement of megapolices is accompanied by deterioration of ecological situation at the sites of HOC production. It should be noted that the widely employed high-octane components are far from being ecologically harmless. For example, methyl tert-butyl ether was barred from use in the USA. Evidently, the diversification of high-octane additives to motor fuels and the development of advanced ecologically clean technologies of their production are important tasks.

The discovery of the nitrous oxide ability to convert olefins into carbonyl compounds with a selectivity above 90% [1] and industrial implementation of the process for cyclopentanone and cyclododecanone synthesis (30 thousand tons per year) by BASF [2] open new prospects for the production of high-octane components of motor fuel from catalytic cracking products. A relatively high demand for HOCs can completely solve the problem of a reasonable use of nitrous oxide, whose wastes are estimated as 700 thousand tons per year. In this work, new ways for obtaining high-octane components from light fractions of catalytic cracking are reported. The fraction of olefins in gaseous products of catalytic cracking reaches 85%. With the use of nitrous oxide these olefins are converted with a high selectivity into carbonyl compounds, mostly ketones. The process runs in the gas phase without a catalyst over a temperature range of 350-450 °C at a pressure of 10-50 atm. Water is not formed in the process, and the resulting oxygenates have high octane numbers. Oxidation of the butane-butylene fraction (BBF) of catalytic cracking yields oxygenates with the blending octane number 118-133 RON units (Table). Note that

the conventional sulfuric acid alkylation yields products with the octane number 94-98 RON units.

Table. Characteristics of AI-92 gasoline compounded with high-octane components obtained from BBF

Sample	Oxygenate content, wt %	Oxygen content (ASTM D5622 method), wt %	Octane number of gasoline with additive		Tars, mg/100 cm ³	Blending octane number of additive	
			RON	MON		RON	MON
Oxygenate obtained by oxidation of BBF with nitrous oxide							
Gasoline	0	0.028	91.0	83.5	0.6	-	-
BBF-N ₂ O	5	1.1	93.1	84.5	0.8	133.0	103.5
BBF-N ₂ O	10	2.3	93.7	85	0.8	118.0	98.5
Product of oxygenate hydrogenation							
Gasoline	0	0,028	92,6	84,0	0,2	-	-
BBF-N ₂ O-H ₂	5	1.2	93.5	84.6	1.2	110.6	96.0
BBF-N ₂ O-H ₂	10	2.4	94.5	85.1	1.0	111.6	95.0

A mixture of carbonyl compounds obtained by the oxidation of BBF with nitrous oxide can be subjected to aldol condensation and methylation with methanol to produce branched ketones. Hydrogenation of carbonyl compounds leads to a complete conversion of aldehydes to alcohols, while ketones are converted incompletely under certain conditions. Blending octane number of the hydrogenated product is at a level of 111-112 RON and 95-96 MON, which is lower as compared to the oxidation product of BBF (118-133 RON and 99-104 MON), but higher in comparison with the alkylate (94-98 RON).

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ORAL PRESENTATIONS

Section I.

**CATALYSTS FOR HYDROGENATIVE
PROCESSES:
PRACTICAL AND FUNDAMENTAL ASPECTS**

ZEOLITE CATALYSTS AND PROCESSES FOR GASOLINE CUTS HYDROPROCESSING

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Starting January 1, 2016, all automobile fuels which produced in Russia have to meet the Class 5 requirements (Euro V analogue) [1]. One of limitations applies to benzene concentration in the commercial gasoline: it should not exceed 1 vol %. Benzene is a strong carcinogen and its reduction in gasoline pool is observed in the world practice for ages. To date a total of 119 countries have regulated benzene, and 62 countries have a maximum benzene limit of 1 vol.% or lower [2]. It is estimated that by 2030 the regulation policy will apply to reduce benzene air emission by 61.000 tonns and cancer risks from benzene by 37 % [3].

The main source of benzene in the gasoline (70-85 %) is a process of catalytic reforming. Benzene content in the reformat is up to 8 wt %. If the share of reformat in the refinery gasoline pool is high (on the Russian plants sometimes it reaches 80 %, with an average Russian values of 54 %) than the only option to achieve the desired environmental performance would be no dilution of reformulated gasoline by the other components but to reduce (remove, convert, etc) benzene content in the reformat.

One of promising solution of the problem is a process of hydroisomerization of benzene-containing cut. The reaction of benzene hydroisomerization includes the stage of hydrogenation benzene to cyclohexane (CH) and isomerization of the latter to methylcyclopentane (MCP), which has a lager octane number. The parallel process is an increasing of depth of paraffin isomerization.

The catalysts that are extensively studied in the hydroisomerization of benzene and its mixtures with alkanes and cycloalkanes are platinum containing bifunctional ones. Platinum supported onto zeolites, sulfated zirconia, tungstated zirconia and borated alumina systems. Zeolite catalysts are preferred for this process because firstly their industrial application already is well established for the C₅–C₆ alkanes isomerization unit, and secondly, the ratio of acidic and hydrogenation functions in the catalyst can be balanced easily. Previously, we had shown a catalyst based on

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mordenite with an optimum zeolite/binder ratio of the support, and an effective amount of platinum [4, 5].

In this work, the activity and selectivity of the catalysts based on zeolites BEA, ZSM-5 and Y in reaction of hydroisomerization of benzene, n-heptane and mixtures thereof in comparison with mordenite catalyst are shown. Supports and catalysts were prepared on described in [4] technique with the use of a zeolites MOR (Si/Al = 20, 90), BEA (Si/Al = 25, 40), ZSM-5 (Si/Al = 30, 80) and Y (Si/Al = 30). γ -Al₂O₃ acted as the binder, received from a pseudoboehmite. Platinum was incorporated into the calcined supports from cation [Pt(NH₃)₄]²⁺ and anion [PtCl₆]²⁻ forms of precursors. The content of platinum in all samples is 0.3 wt %.

The catalytic parameters of target reactions of benzene and n-heptane depending on zeolite type, Si/Al ratio, and catalyst activation parameters are displayed. The parameters of the influence of the benzene content in the feed to the conversion of n-heptane on zeolites with different structures types are considered.

Moreover, we have studied the mechanical strength of the supports and discovered the nonlinear dependence of the strength of the zeolite content. Contributions to the overall strength of the binder component and a zeolite component are assessed on the basis of data on the textural characteristics of the samples.

Furthermore, we show the options of integration processes of hydroprocessing of benzene- and hexane-containing cuts in the scheme of motor gasoline production.

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EFFICIENT HYDRODEOXYGENATION OF NONLINEAR KETONES ON A Ni-ZEOLITE COMPOSITE CATALYST

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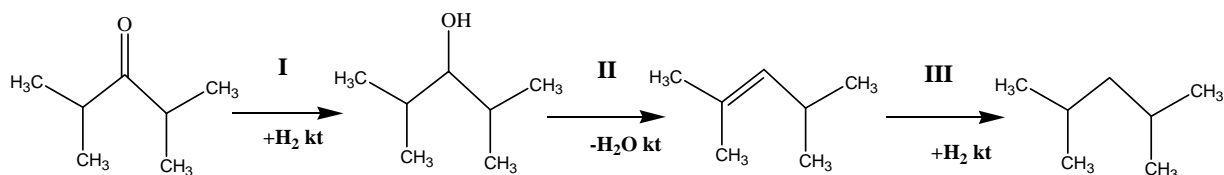
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The reduction of oxygen-containing compounds with hydrogen is used in various industrial processes [1]. Most of them are aimed to convert carbonyl compounds into corresponding alcohols. New fields of modern chemistry, which have emerged due to the need for a higher conversion of hydrocarbon feedstock and the development of biofuel production, imply a processing of oxygenates to hydrocarbons. One of the key steps in such processes is the hydrodeoxygenation of oxygen-containing compounds, which often have a nonlinear structure [2]. The hydrogen reduction of carbonyl compounds to alcohols is a well studied reaction. At the same time, their deeper reduction to alkanes is a challenging problem, especially if the isomeric structure of the product should be preserved [3]. The hydrogenation process may be accompanied by both demethylation and isomerization side reactions.

In this work, diisopropyl ketone (DIK) was used to investigate the features of hydrodeoxygenation of nonlinear ketones into corresponding alkanes, elucidate the reaction regularities, and reveal the efficient catalysts.

The catalytic hydrogenation of DIK proceeds via three consecutive steps. At the first step, the ketone is hydrogenated to the alcohol; at the second step, the alcohol is dehydrated to yield the olefin; and at the third step, the olefin is hydrogenated once again with the formation of a saturated hydrocarbon:



According to offered mechanism, a catalyst for the hydrogenation of DIK should be bifunctional in nature. Its hydrogenating function should be supplemented with the dehydrating action. These reactions are commonly carried out with bifunctional catalysts which represent the metals (Ni, Cu, Pt) deposited on acidic supports (Al_2O_3 or zeolites). The use of such catalysts has two disadvantages: the difficult control

OP-I-2

over the ratio of main reaction products (alcohol and alkane), and a substantial contribution of side reactions.

A possible approach to minimization of detrimental effects may be related to the use of a composite catalyst, which is a mechanical mixture of the catalyst for hydrogenation of carbonyl compounds and the catalyst for dehydration of the alcohol produced at step I. A series of composite catalysts was synthesized for the hydrodeoxygenation of DIK. These catalysts were based on the Ni/Al₂O₃ hydrogenation catalyst in a combination with zeolites of MFI or MTT structure. The reaction was studied in a temperature range of 160-195 °C at a catalyst loading 1 g, contact time 1 s, DIK and H₂ concentrations 9 and 86 mol %, respectively, and pressure 1-20 atm.

The most promising results were obtained with MFI zeolite as the cocatalyst. The main products of the reaction were 2,4- and 2,3-dimethylpentanes, selectivity for these products was 82 and 12 %, respectively, at a 100 % conversion of DIK and total productivity of 1.54 g/g_{cat}. When the reaction was performed at atmospheric pressure, the catalyst was operated for 5.5 hours without a significant loss in activity.

An observed decrease in activity may be related to the formation of unsaturated compounds. Their oligomerization leads to low-volatile products, which remain on the surface of a heterogeneous catalyst and are the main cause of coking. Raising the total pressure of the reaction mixture to 15 atm allowed us to extend the period of stable catalyst operation to several days. It can be supposed that at an elevated pressure the catalyst surface becomes saturated with hydrogen, which increases the hydrogenation rate of the produced olefins and, accordingly, reduces coking.

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PREPARATION AND STUDY OF Pd/SO₄²⁻/ZrO₂/Al₂O₃ CATALYST FOR ISOMERIZATION OF N-HEXANE

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The isomerizate is a valuable component of gasoline, as almost free of sulfur and aromatic hydrocarbons. The catalysts for the isomerization process based on a chlorinated alumina, zeolites, and sulfated zirconium dioxide are used. Catalysts based on sulfated zirconium dioxide are becoming more popular as combine high activity, resistance to poisons and work in the thermodynamic favorable temperature range 140-180 °C. Conventionally, as an active metallic component of the alkane isomerization catalyst is platinum, but palladium catalysts also have highly isomerization ability [1, 2].

In our work catalysts based on sulfated zirconia promoted with palladium Pd/SO₄²⁻/ZrO₂/Al₂O₃ (Pd/SZA) were prepared and investigated. For comparison we used platinum-promoted catalysts Pt/SO₄²⁻/ZrO₂/Al₂O₃ (Pt/SZA). Alumina is added to the catalyst as a binder. The resulting systems were tested in the isomerization reaction of n-hexane. Catalytic tests condition: T = 140-220 °C, P = 1,5 MPa, H₂/n-C₆ = 3 mol/mol, LHSV= 2 h⁻¹.

The obtained results showed that the n-hexane conversion and the yield isomers (Fig. 1a) values for the Pd/SZA and Pt/SZA catalysts are close.

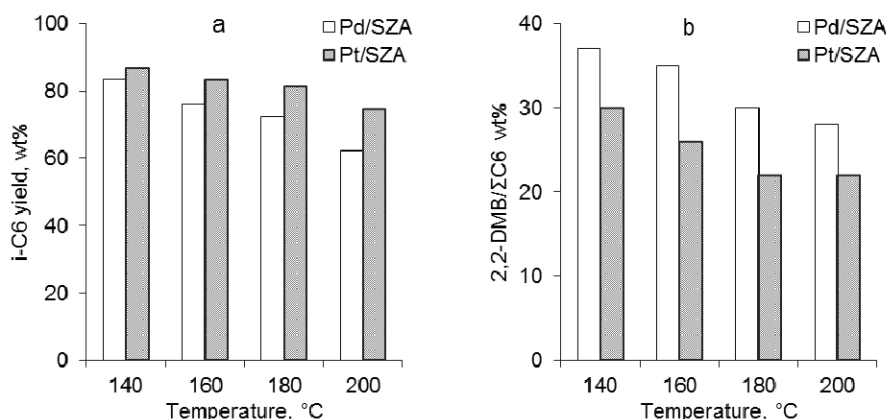


Fig. 1. Hexane isomers yield (a) and rate of 2,2-dimethylbutane in the hexane fraction (b) depending on the temperature.

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However, the depth of isomerization (rate of 2,2-dimethylbutane in the hexane fraction), on Pd/SZA is about 6-8 % more than on Pt/SZA at the entire temperature range (Fig. 1b). The depth of isomerization reflects the share of high-octane component 2,2-dimethylbutane (RON = 92) in the isomerizate and determines its octane characteristics.

We also investigated the state of the metal in the Pd/SZA catalyst using IR diffuse reflectance spectroscopy and XPS methods. In addition, to investigate the role of the palladium state in Pd/SZA, we used an approach based on the study of complex catalytic system by comparison with simple and well characterized catalysts. As such catalysts, Pd/SiO₂, Pd/Al₂O₃ and mechanical mixture with SZA were taken.

Thus, Pd/SZA catalysts are perspective catalysts for C5-C6 alkanes isomerization. In respect that the significantly lower cost of palladium, these catalysts may be considered as alternative to platinum catalysts. Determining the influence of the metal state in the Pd/SZA to catalytic performance will help to establish of effective palladium catalysts based on sulfated zirconia isomerization of pentane-hexane fraction.

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ALUMINA SUPPORTED (Ni)MoWS₂ HYDROTREATING CATALYSTS PREPARED USING MIXED SiW_nMo_{12-n} HETEROPOLYANIONS

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In recent years, it has become necessary to increase significantly the production of clean fuels, with low sulfur and nitrogen content, in order to comply with new environmental legislations worldwide. This objective can be reached by synthesis of more efficient catalysts for hydrotreatment processes. The catalytic removal of sulphur (HDS) is generally performed with molybdenum and tungsten sulphides supported on alumina and promoted by cobalt or/and nickel. These catalysts exhibit high activity in removing sulfur from thiophene, benzothiophene, and some non-refractory dibenzothiophenes compounds. However, their activity is very low in removing sulfur from 4,6-dibenzothiophenes. The new bulk NiMoW catalyst (NEBULA) was developed in 2001 possessed an activity at least three times better than any other hydrotreating catalyst. In this study, ternary transition metal sulfide catalysts supported on alumina were prepared using mixed SiW_nMo_{12-n} heteropolyanions (HPAs). For comparison purposes, catalysts based on separate SiMo₁₂HPA and SiW₁₂HPA were also prepared and studied.

Two heteropolyacids of H₄[SiMo₁W₁₁O₄₀] and H₄[SiMo₃W₉O₄₀] with Keggin structure were prepared and characterized by IR-, Raman and XRD techniques. Elemental composition and structure of prepared HPAs were confirmed. Catalysts supported on Al₂O₃ with equal surface content of metals were synthesized by the incipient wetness technique via impregnation of the supports with aqueous solutions containing the required amounts of SiMo₁₂HPA, SiW₁₂HPA, SiW₁₁Mo₁HPA, SiW₉Mo₃HPA. Chemical composition of the catalysts is shown in Table 1.

Table 1. Chemical composition of prepared catalysts

Catalyst	MoO ₃ , wt %	WO ₃ , wt %	d(Mo) ₁ , at.nm ⁻²	d(W) ₂ , at.nm ⁻²	d(Mo+W) ₁ , at.nm ⁻²
SiMo ₁₂ HPA/Al ₂ O ₃	18.0	–	4.0	–	4.0
SiW ₁₂ HPA/Al ₂ O ₃	–	26.2	–	4.0	4.0
SiW ₁₁ Mo ₁ HPA/Al ₂ O ₃	1.4	24.2	0.3	3.7	4.0
SiW ₉ Mo ₃ HPA/Al ₂ O ₃	4.2	20.1	1.0	3.0	4.0
SiMo ₁₂ HPA+SiW ₁₂ HPA/Al ₂ O ₃ (a)	1.4	24.2	0.3	3.7	4.0
SiMo ₁₂ HPA+SiW ₁₂ HPA/Al ₂ O ₃ (b)	4.2	20.1	1.0	3.0	4.0

^a catalyst was prepared using co-impregnating solution of SiMo₁₂HPA and SiW₁₂HPA with molar W/Mo ratio 11/1,

^b catalyst was prepared using co-impregnating solution of SiMo₁₂HPA and SiW₁₂HPA with molar W/Mo ratio 9/3.

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The hydrotreatment activities were measured on a model feed (1000 ppm of sulfur, 3 wt % of naphthalene and toluene as a solvent) in a bench-scale flow reactor under pressure of hydrogen. Before testing, the catalysts were activated by sulphidation. A mixture of DMDS (2 wt % of S) and decane at 3.5 MPa was used in a stepwise procedure conducted over 10 h at 240 °C and 8 h at 340 °C. The conditions of the tests were the following: temperature 280 °C; pressure 3.0 MPa; feed space velocity 5.5 h⁻¹; a H₂ feedstock ratio 500 NL/L; catalysts mass 0.6 g. Table 2 shows the hydrotreating results for a model feed over the prepared samples.

Table 2. Performances of the catalysts in hydrotreating of DBT and naphthalene

Catalyst	Conversion (%)		Rate constants ($\times 10^{-5} \text{ mol h}^{-1} \text{ g}^{-1}$)		TOF edge values* ($\times 10^{-4} \text{ s}^{-1}$)	
	DBT HDS	Naphthalene HYD	k_{HDS}	k_{HYD}	TOF_{HDS}	TOF_{HYD}
SiMo ₁₂ /Al ₂ O ₃	16.6	13.5	5.6	21.9	1.0	3.9
SiW ₁₂ /Al ₂ O ₃	3.0	3.5	0.9	5.4	0.2	1.4
SiMo ₁ W ₁₁ /Al ₂ O ₃	7.2	7.5	2.3	11.7	0.4	2.1
SiMo ₃ W ₉ /Al ₂ O ₃	18.2	18.6	6.2	31.2	1.1	5.5
SiMo ₁₂ +SiW ₁₂ /Al ₂ O ₃ (a)	5.1	5.3	1.6	8.2	0.4	1.8
SiMo ₁₂ + SiW ₁₂ /Al ₂ O ₃ (b)	6.6	6.1	2.1	9.5	0.5	2.2

* TOF number was calculated using TEM and XPS measurements of sulfided samples

Moreover, Ni-promoted series of the catalysts was also prepared and tested. It was observed that catalysts based on mixed SiMo_nW_{12-n}HPA in both non-promoted and Ni-promoted series were the most active in HDS of DBT and HYD of naphthalene. Comparison of two catalysts prepared from one mixed SiMo_nW_{12-n}HPA and from two HPAs (SiMo₁₂HPA and SiW₁₂HPA) with the same metal content allowed to conclude that close interaction of both metal in one mixed HPA structure is more preferable for catalyst activity.

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B₂O₃-Al₂O₃ – SUPPORT FOR CATALYST OF HYDROCARBONS PROCESSING

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The anions modification of alumina is widely known method for regulation of supports and catalysts acidity. Using BO₃³⁻ anion as a modifier allows to obtain a thermally and chemically stable supports and catalysts with the desired Brönsted acidity and texture by a simple method for a synthesis. In this research, the borated alumina was investigated as a support for bi- and polyfunctional catalysts for hydroisomerization of benzene-containing gasoline fractions, direct synthesis of propylene from ethylene and hydrodeoxygenation of vegetable oils. The borated alumina was prepared by mixing H₃BO₃ and AlOOH with followed by drying and calcining.

Pt/B₂O₃-Al₂O₃ catalysts had higher catalytic activity in hydroisomerization of benzene-containing gasoline fractions over the known catalysts based on Beta and Mordenite zeolite. Upon using Pt/B₂O₃-Al₂O₃ the benzene in reformat gasoline was completely removed at temperature up to 350 °C and the WHSV 3 h⁻¹. The yield of gasoline was at 96 wt % and the octane number was retained.

Ni-Mo-S/B₂O₃-Al₂O₃ catalyst was tested in hydrodeoxygenation of vegetable oils. It was shown that the full hydrodeoxygenation of vegetable oils was achieved at WHSV 1 h⁻¹ and 4 MPa 380 °C and was stable during 400 h. The diesel fraction mainly consisted of C₁₈ hydrocarbons (predominantly isoparaffins) and the yield was at 76 wt %. An iodine number for diesel fraction was not more than 0.2.

PdO-Re₂O₇/B₂O₃-Al₂O₃ catalyst was tested in direct synthesis of propylene from ethylene via the dimerization of ethylene to butene-1 in the first step, isomerization of butene-1 to butene-2 in the second step and then the metathesis of butenes-2 and ethylene to form propylene in the third step. At WHSV 0.5 h⁻¹ and 80 °C the ethylene conversion was about 70 % and propylene yield was at 43 %. This behavior is due to the acidity of the catalyst and to the stabilization of the of palladium and rhenium on the B₂O₃-Al₂O₃ support, i.e. dimerization, isomerization, and metathesis reactions are taking place.

EFFICIENT HYDRODESULFURIZATION CATALYSTS BASED ON KEGGIN POLYOXOMETALATES

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Hydrodesulfurization (HDS) driven by ever stringent environmental legislation is one of the most important processes of the petroleum industry. Present day HDS technology largely employs sulfided Co(Ni)Mo/ γ -Al₂O₃ catalysts [1]. These catalysts, although durable, are not sufficiently active and selective to achieve the required very low sulfur content in transportation fuels. Consequently, research into improvement of HDS catalysts continues all over the world.

In the past decades, heteropoly compounds, also known as polyoxometalates, have attracted much interest as catalysts of various reactions and as such found application in several large-scale industrial processes. Various types of heteropoly compounds have been used for the preparation of HDS pre-catalysts, the common Keggin type heteropoly compounds comprising heteropoly anions of the composition [XM₁₂O₄₀]ⁿ⁻ (M = Mo⁶⁺, W⁶⁺; X = P⁵⁺, Si⁴⁺) most frequently applied. Catalyst preparation methodology through the polyoxometalate route has important advantages such as (i) incorporation of all the elements required for HDS catalyst within heteropoly compound thus allowing the preparation of oxidic precursor in a single impregnation step, (ii) close interaction between the key elements in the pre-catalyst and sulfided catalyst and (iii) extraneous counter ions can be excluded from the impregnation solution to reduce waste [2-4].

Here bulk and supported HDS catalysts based on Mo and W and containing Co or Ni as promoters and phosphorus as a modifier were prepared through the polyoxometalate route using Keggin type phosphomolybdates and phosphotungstates and tested in the HDS of thiophene at 350-400 °C and 1 bar pressure in a fixed-bed continuous flow reactor [2,3]. The corresponding oxidic pre-catalysts retained intact Keggin structure of the parent polyoxometalates and possessed Brønsted and Lewis acidity. In the course of sulfidation, the oxidic pre-catalysts transformed into an active sulfidic phase with the loss of Keggin structure

and catalyst acidity. Catalyst activity increased in the order of supports: $\text{SiO}_2 < \text{TiO}_2 < \gamma\text{-Al}_2\text{O}_3$. $\text{CoMo}/\gamma\text{-Al}_2\text{O}_3$ catalyst prepared through the polyoxometalate route showed higher HDS activity and butene selectivity than industrial catalyst of comparable composition. Similarly, NiMo/SiO_2 catalyst prepared through the polyoxometalate route underwent faster sulfidation and showed higher thiophene conversion and higher butene selectivity than conventional industrial $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst with similar Mo loading.

Previously, a silica-supported monometallic tungstophosphoric heteropoly acid (HPA), $\text{H}_3\text{PW}_{12}\text{O}_{40}$, was found to be an efficient catalyst for the HDS of dibenzothiophene (DBT) [4]. Over a 30 wt % HPA/ SiO_2 catalyst in a trickle bed flow reactor at industrially relevant gas and liquid space velocities (GHSV 600 h^{-1} and LHSV 6 h^{-1}) and an H_2 pressure of 30 bar, the HDS proceeded with a DBT conversion of 58 % at $290 \text{ }^\circ\text{C}$ and 80 % at $350 \text{ }^\circ\text{C}$. These values are comparable to the performance of the industrial $\text{Co-Mo}/\text{Al}_2\text{O}_3$ catalyst. No loss of catalytic activity was observed for a period of 56 h. ^{31}P MAS NMR and TGA data showed that the HPA decomposed upon the interaction with $\text{H}_2\text{S}/\text{H}_2$ to yield the active HDS catalyst.

These results indicate that polyoxometalate catalyst preparation route can be considered a performance enhancement methodology for HDS catalysis. These catalysts have the potential of reducing hydrogen consumption in HDS process and the loss of high octane alkenes in the final gasoline pool.

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INFLUENCE OF Mg ON ACTIVITY AND SELECTIVITY OF ASA CATALYSTS IN HDS OF FCC GASOLINE

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FCC gasoline is one of the most important components of blended gasoline. The main characteristic of FCC gasoline is high research octane number – 92-93 points. However it is also characterised by high sulfur content – 150-3500 ppm. Hydrotreating of full FCC gasoline fraction results in inevitable octane number loss. To avoid octane number loss, it is necessary to use catalysts with high activity in hydrodesulfurisation and high selectivity to conversion of high-octane components. It was shown earlier that catalytic activity and selectivity can be improved by the use of amorphous silica-alumina (ASA) supports [1]. Also, it was defined that simultaneous incorporation of alkaline and alkaline earth metals, like Mg, into catalysts with ASA increases catalyst selectivity [2]. However, it was not clear how metal should be incorporated into ASA catalyst to achieve the best activity and selectivity.

In present work Co-Mo catalysts based on ASA supports were studied. The catalysts differed in the method of Mg incorporation into catalyst structure. Influence of the method of Mg incorporation on catalyst structure, activity and selectivity was studied.

Mg was incorporated by three ways: 1. During preparation of ASA; 2. During preparation of a support; 3. By impregnation of a support with Mg-containing solution before (MgCoMo) or after (CoMoMg) impregnation by Co-Mo solution. Also the ASA catalyst without Mg (CoMoASA) and the catalyst based on alumina (CoMoAl) were prepared. Mg content in all samples was 1 % wt. To introduce Co and Mo into catalyst, the solution containing ammonium heptamolibdate and cobalt nitrate was used to obtain 3.3 ± 0.3 % of Mo and 0.7 ± 0.1 % Co. ASA powders, supports and catalysts were studied by HRTEM, nitrogen adsorption, chemical analysis and XPS. Catalysts were tested in HDS of model fuel at 2,5 MPa, 220-260 °C, LHSV = 10 h^{-1} , $\text{H}_2/\text{feed} = 200$.

According to HRTEM and XPS data all catalysts contain sulfide active component that is similar to Co-Mo-S phase. This phase was shown to have high activity in HDS [3]. Stacking number and length of active component in ASA catalysts were higher than in CoMoAl. It was specified by preferential localization of active component particles on alumina surface, while ASA surface is practically unoccupied. On top of that HRTEM images of the catalyst with Mg in the support, CoMoMg and MgCoMo

samples contain surface fragments with Mg particles. Thus, Mg has high interaction with a support surface in these samples. On the other hand, the catalyst with Mg in ASA doesn't contain separate Mg particles that can indicate a formation of Mg-ASA compounds. Textural characteristics of catalysts strongly depend on catalyst and support composition. However, it is necessary to point out that ASA catalysts have high surface area and pore volume that are necessary for high activity in HDS.

Catalytic tests showed that incorporation of Mg into catalyst structure results in the increase of catalyst HDS activity (Figure). It was noted that ASA catalyst without Mg inferior in activity to alumina catalyst, while incorporation of Mg results in its significant increase. The highest activity was obtained for the catalyst with Mg in the support. Selectivity of catalysts was estimated as octane/(octene-1+isomers) ratio. It is seen that the highest selectivity was obtained for the catalyst with the lowest activity. It was noted that catalyst with Mg in the support and MgCoMo catalyst combine high activity and selectivity. It can be due to the formation of similar acid sites that are suitable for target reaction.

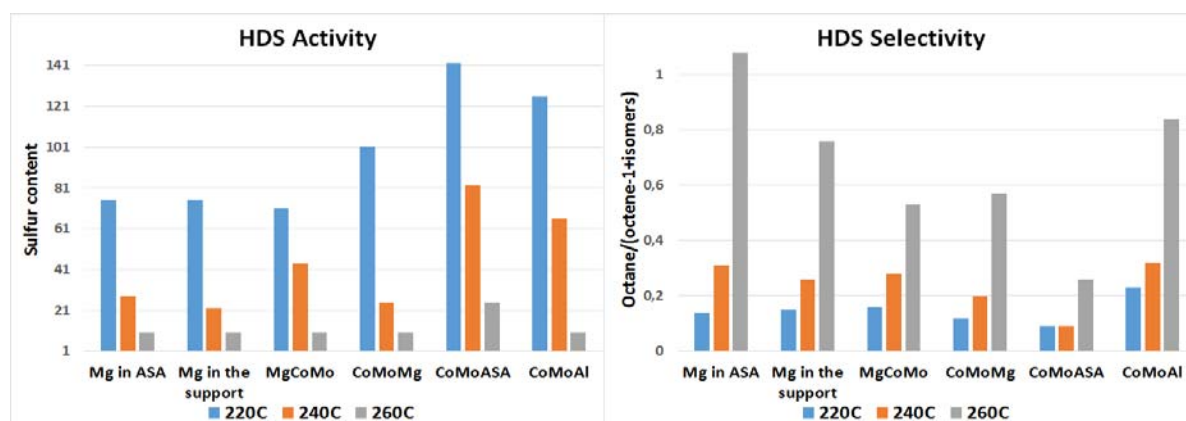


Figure – Activity and selectivity for catalysts

Present work demonstrates that the use of combination of Mg and ASA results the increase of activity and selectivity in catalysts.

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Acknowledgements

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EFFECT OF SUPPORT IN HYDROTREATING CATALYSTS PREPARED USING PW₁₂-HETEROPOLYACID AND Ni CITRATE ON MORPHOLOGICAL AND STRUCTURAL CHANGES IN NiWS SPECIES AND THEIR ACTIVITIES

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The hydrotreating of petroleum fractions is the central refining process in order to produce clean fuels that meets the actual ecological requirements. It is well known that nitrogen-containing compounds and aromatic hydrocarbons present in high content in heavy and secondary oil fractions and residues have inhibiting effects on the HDS. NiW based catalysts having outstanding catalytic actions in hydrogenation (HYD) and hydrodenitrogenation (HDN) reactions especially at severe conditions and, therefore, attract great attention of scientists. The objective of this work was to study the effect of support in the catalysts prepared with the 12-tungstophosphoric HPA and nickel citrate on the morphology and composition of NiWS phase species active phase and hence on the HDS, HYD and HDN activities.

The Ni-PW supported catalysts with different W loading (from 1.4 to 7 at W/nm²) and constant Ni/W ratio ($Ni/(Ni + W) = 0.45$) were prepared by the incipient wetness technique via impregnation of the support (mesostructured Al₂O₃ prepared using Pluronic P123 template (denoted as *m*-Al₂O₃), conventional TH-Al₂O₃, hybrid sample *m/TH*-Al₂O₃ prepared using mesostructured AlOOH and conventional AlOOH, TiO₂, ZrO₂, SiO₂) with aqueous solutions containing the required amounts of H₃PW₁₂O₄₀ and Ni citrate.

The prepared samples were studied by N₂ adsorption, Raman spectroscopy, XRD, H₂-TPR, HRTEM and XPS methods. Catalysts were tested in a hydrotreating of model feed (1000 ppm of sulfur from dibenzothiophene (DBT), 3 wt % of naphthalene, 0.46 wt % of quinoline and toluene as a solvent) in a bench-scale flow reactor under pressure of hydrogen. The conditions of the tests were the following: temperature 280 °C; pressure 3.0 MPa; feed space velocity 40 and 80 h⁻¹; a hydrogen : feedstock ratio 500 NL/L; catalysts volume – 0.3 cm³.

Nature and textural properties of the support significantly affect all the characteristics of the active phase. NiWS catalysts supported on the carriers with large surface area (SiO₂ and *m*-Al₂O₃) had minimum length of the NiWS particles.

Maximum of NiWS concentration was achieved at a high content of metals (6.8 at of W/nm^2 for Al_2O_3 and > 3 at W/nm^2 for ZrO_2 and TiO_2). Conversion of DBT on the synthesized catalysts was measured from 25 to 45 %. For evaluation of the catalytic activity, specific rate constant in DBT HDS referred to the mole of W in the catalysts was calculated. Depending on the nature of the carrier, the catalyst activity at the constant W loading ($\sim 3-4$ W at/ nm^2) decreases in the following order:

$m-Al_2O_3(m/TH-Al_2O_3) \approx SiO_2 > TH-Al_2O_3 \approx TiO_2 > ZrO_2$ (Fig. 1).

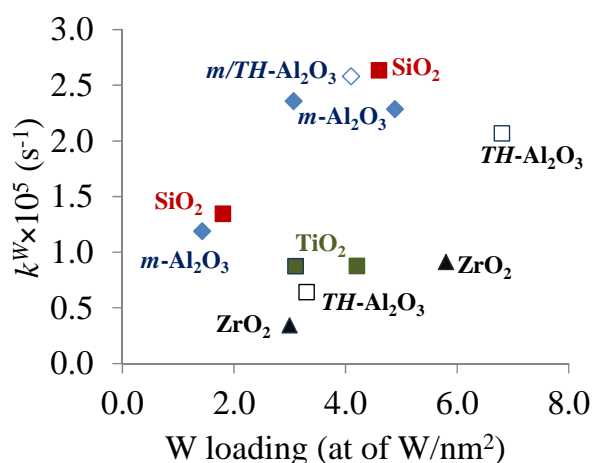


Fig. 1. Dependence of rate constant in DBT HDS on W loading in NiW catalysts supported on different supports

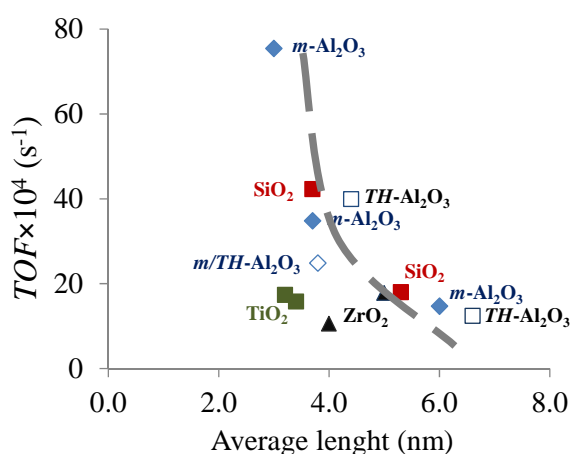


Fig. 2. Dependence of TOF number in DBT HDS on average length of NiWS species supported on different supports with varying W loadings

The content of metal edge sites was calculated using TEM results and amount of W in sulfide species $(Ni)WS_2$ from XPS allowing to access to TOF number normalized on metal edge sites. Using mesostructured alumina $m-Al_2O_3$ allowed to obtain an effective NiW hydrotreating catalyst at a low W content (4 W at/ nm^2) having an average length of 3.8 nm and average stacking number of WS_2 1.8. The Ni-PW/ $m-Al_2O_3$ catalyst indicated the highest TOF number in DBT HDS reaction due to optimal morphological properties of formed NiWS species.

Acknowledgements

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EFFECT OF THERMAL TREATMENT ON THE PROPERTIES OF NiW/Al₂O₃ HDS CATALYSTS PREPARED WITH CITRIC ACID

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Thermal treatment is one of the key factors determining the structure of active phase and activity of supported bimetallic HDS catalysts. The aim of this work is to study the effect of thermal treatment on the properties of NiW/Al₂O₃ catalysts prepared with citric acid (CA). Four NiW/Al₂O₃ catalysts with the same loading of 3.4 wt % NiO and 21.4 wt % WO₃ were prepared by the incipient wetness impregnation method with an aqueous solution prepared with ammonium paratungstate, nickel (II) hydroxide and citric acid (ratio CA/W=1) followed by drying and calcination at different temperatures (120, 220, 300 and 450 °C). The sulfidation of the catalysts was carried in H₂S flow for 4 h at 400 °C and atmospheric pressure.

As shown by FTIR spectroscopy, Raman spectroscopy and TGA the partial decomposition of metal complexes with CA starts at 220 °C and fully completes at 450 °C. HRTEM of the sulfided catalysts showed that stacking number of WS₂ increases with the increase of the calcination temperature while the slab length has minimum at 220 °C. For catalysts calcined above 300 °C tungsten oxide particles were observed on TEM micrographs. The results of XPS indicated that the sulfidation degree of W decreases with the increase of the calcination temperature while a local maximum at 300 °C was observed for nickel sulfidation degree.

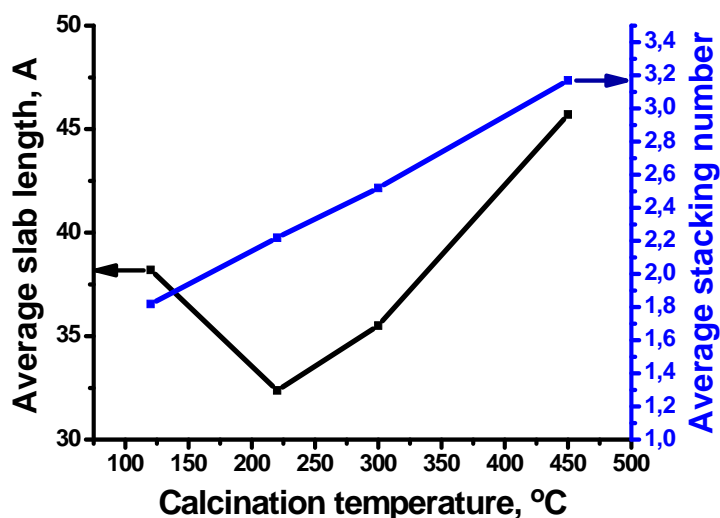


Fig. 1. Average slab length and stacking number of the WS₂ in the sulfided catalysts

The catalysts were tested in simultaneous HDS of DBT, HDN of quinoline and hydrogenation of naphthalene. Testing of the catalysts showed the correlation between activity in DBT HDS, quinoline HDN and naphthalene hydrogenation. The catalyst calcined at 300 °C showed the highest activity in all these reactions. The high activity of this catalyst can be dealt with increasing of the stacking number of WS₂ what can facilitate π -adsorption of compounds containing conjugated aromatic rings. On the other hand the high activity can be result of the formation of so-called Type «0» NiS_x-WO_y phase having high activity in hydrogenation reactions [1] what can be expected according HRTEM and XPS data. The calcination at lower temperatures than 300 °C leads to lower stacking degree of WS₂ and do not facilitate NiS_x-WO_y phase formation while calcination at 450 °C leads to the low dispersion of the WS₂ phase and formation of low-active nickel oxide species what results in low activity. As a result an optimization of thermal treatment conditions of NiW/Al₂O₃ catalysts results in significant increase of their activity.

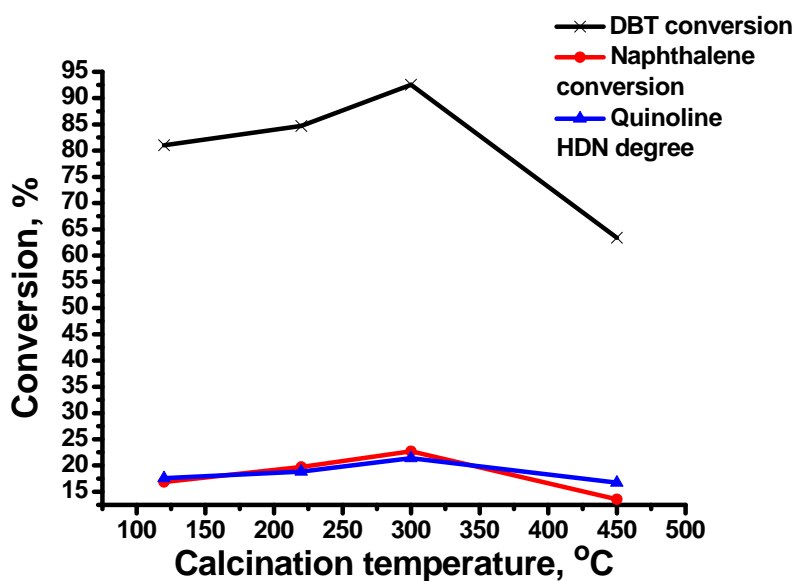


Fig. 2. Results of the testing of the catalysts (conditions: $T = 300$ °C, $p = 3.5$ MPa, $LHSV = 20$ h⁻¹, $H_2/Feed = 500$ m³/m³)

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A NOVEL CATALYSTS FOR THE ISOMERIZATION OF C₅-C₇ HYDROCARBONS

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Production of motor gasoline in Russia in 2014 amounted to 38,4 mln. tons with a research octane number (RON) of averaged gasoline pool equal to 93,2 point. Share of modern motor gasoline with RON 95 and higher in gasoline fund is 25,8 %. Russian refineries have no technical capability to produce all the commercial gasoline with RON 95. For this reason, the requirements of technical regulations to the 4-5 commercial gasoline classes to meet the octane index of 95 points (at least) [1] has been suspended in Russia. Nevertheless, stringent requirements to the quality of motor gasoline by aromatics content and specifically benzene remain valid.

For the majority of Russian refineries, especially medium and small capacity, the challenge is to achieve a qualitative improvement of produced gasoline in the short term. Currently, a major component of gasoline is a product of processing of straight-run $ibp \div 180$ °C fraction in high-octane components. The $ibp \div 70$ °C fraction is processed by isomerisation technology and the $100 \div 180$ °C fraction undergoes catalytic reforming. The $70 \div 100$ °C middle fraction does not undergo the qualified processing. The direction of this fraction in the feedstock for reforming, which is practiced in many refineries, leads to increase of aromatic hydrocarbons (including benzene) in the commercial gasoline and to worsen of its environmental performance.

Ecological properties and octane characteristics of the commercial gasoline is possible to improve with the addition to the standard factory technology, such as isomerization of $ibp \div 70$ °C fraction and catalytic reforming of $100 \div 180$ °C, a new technology – isomerization of straight-run gasoline $70 \div 100$ °C fraction (C₇ hydrocarbons).

New catalysts based on mordenite and WO₃/ZrO₂ for isomerization of 70-100 °C fraction (C₇ hydrocarbons) are developed. Realization of $70 \div 100$ °C fraction isomerization technology is unknown in the world of oil processing. In this paper, the

optimal composition of new catalysts for the production of high-octane components of motor gasoline, the content of mordenite zeolite, WO_3 and ZrO_2 and additions of alumina are examined.

New catalysts based on sulfated zirconia dioxide placed in the pores of the alumina support for isomerization of C_5 - C_6 hydrocarbons (straight-run gasoline ibp÷70 °C fraction) are developed. This catalysts equals to the best industry analogues in the yield of isomerate and the depth of the isomerization. However, the content of expensive sulfated zirconia dioxide as active phase in supported catalyst is 2÷3 times lower.

New catalysts and processes are designed to produce high-octane gasoline components that meet the latest environmental requirements. Industrial implementation of C_7 hydrocarbons isomerization technology give an opportunity to increase the octane number of the gasoline pool significantly and to provide the producing of the commercial gasoline with RON 95 and more.

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INFLUENCE OF B ON PROPERTIES AND CATALYTIC ACTIVITY OF CoMo/Al₂O₃ CATALYSTS FOR HYDROTREATING OF DIESEL FUELS

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It is well known that Boron addition can change acidic properties of CoMo catalysts and decrease interaction between active component and a support. It results in the increase of catalytic activity in hydrotreating of diesel fuels [1,2].

Boron modified CoMo catalysts were synthesized and hereinafter denoted as CoMo/Al₂O₃-x, where x is mass fraction of B in a support. Catalysts and supports were characterized by various physical methods: nitrogen adsorption (NA), XPS, HRTEM and IR. Catalysts were tested in hydrotreating of diesel fuel fraction, which was consisted of 0.5 vol. % gasoil of catalytic cracking (S content - 2750 ppm).

It is found that addition of 1-3 % of Boron does not have a significant influence on textural characteristic of catalysts (table 1) and on CoMoS phase content. Binding energies (BE) in Mo3d and Co2p spectra are typical for Mo⁴⁺ и Co²⁺ in CoMoS phase [3,4]. All catalysts contain > 70 % of CoMoS phase that is typical for highly active CoMo hydrotreating catalysts [3].

Table 1 – NA, XPS, HRTEM and catalytic activity data of CoMo/Al₂O₃-x catalysts

Catalyst	NA		XPS		HRTEM		Catalytic activity at 360 °C
	Surface area, m ² /g	Volume pore, cm ³ /g	BE, eV		Average slab length, nm	Average slab number	Residual sulfur content in diesel, ppm
			Mo3d	Co2p			
CoMo/Al ₂ O ₃ -0	176	0,41	229.0	779.0	–	–	26,6
CoMo/Al ₂ O ₃ -1	169	0,43	229.1	779.1	3,8	1,05	9,8
CoMo/Al ₂ O ₃ -1,5	168	0,39	229.0	779.1	3,5	1,22	6,6
CoMo/Al ₂ O ₃ -2	176	0,41	229.1	779.0	3,5	1,20	5,3
CoMo/Al ₂ O ₃ -3	158	0,39	229.0	779.1	3,4	1,09	8,0

XPS spectra of B contain one peak that corresponds to BE = 192.7 eV (figure 1) and it is less than typical BE of B₂O₃ [5]. It can be accounted for by the interaction between B particles and a support. Difference in intensities of B1s peak (figure 1) is due to various Boron distribution on a support surface. The most uniform distribution is reached when the B concentration is 1.5-2 % by mass. Decrease in intensity for

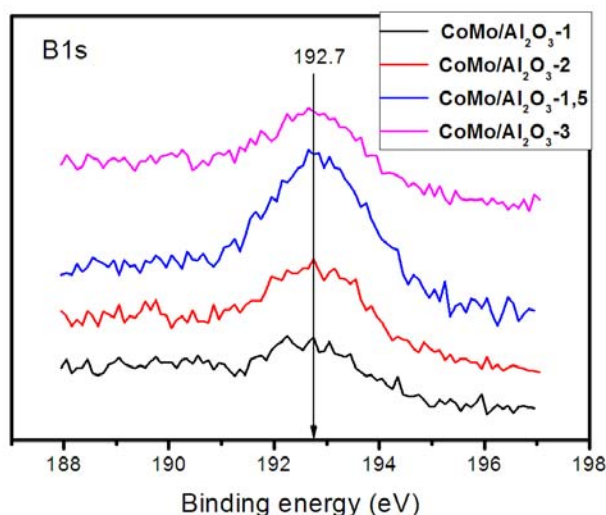


Figure 1 – B 1s XPS spectra

CoMo/Al₂O₃-3 may be caused by Boron incorporation in Al₂O₃ crystal lattice or aggregation of boron particles on the surface. According to IR, spectra of catalysts contain the bands at 1230, 1385-1450 cm⁻¹ and 3695 cm⁻¹ that correspond to BO₃, BO₄ [6, 7] and B-OH [8, 9] groups respectively. Also, changes in active component morphology are observed. Interaction

between active component and a support is decreased which is caused by reducing of average slab length and increase of slab average number (table 1). According to CO adsorption, boron incorporation results in the decrease of Lewis strong and weak acidic sites concentration while Brønsted acidic sites one changes insignificantly when the boron is added. It is noted that catalytic activity in hydrodesulfurization (HDS) reactions of boron catalysts is higher in comparison with alumina one (table 1). The modified catalysts are allow to receive Ultra-Low Sulfur Diesel (S content < 10 ppm).

Thus, it was defined that boron addition resulted in reduction of interaction between active component and a support, changes of acidic properties and increase of catalytic activity in HDS reactions. It was found that the boron optimal concentration in HDS reactions was 1.5-2 % by mass.

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INVESTIGATION OF STEAM CRACKING OF HEAVY OIL IN THE PRESENCE OF Ni- AND Mo-BASED NANODISPersed CATALYSTS

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Heavy hydrocarbon feedstock (heavy oils, natural bitumens, heavy residues) is a future of petroleum industry. The most common approaches for heavy oil upgrading are based on two strategies: carbon rejection by coking, and hydrogen saturation. The hydrogen saturation is usually carried out by hydrogenation and hydrocracking in the presence of Ni- and/or Mo-containing catalysts at high pressures of H₂. In such processes hydrogen is considered as an agent for of hydrocarbon radicals quenching, which are being formed due to thermal cracking. Water can also be a perspective more available alternative to hydrogen for hydrocarbon radicals quenching [1-2].

The aim of the work is investigation of steam cracking of high-sulfuric heavy oil (HO) (Tatarstan, Russia) in the presence of dispersed Ni- and Mo-containing catalysts. The experiments have been carried out in batch mode with the use of batch reactor at 425 °C at catalysts concentration 0.3-2.0 wt %, water to feed ratio (wt) 0.3 : 1 and time of the process – 1 hour.

Investigation of the steam cracking process in the absence of catalysts revealed that in comparison with the thermal cracking of the heavy oil, the presence of water results in a substantial increase of the degree of conversion of high-boiling fractions (bp. > 500 °C) and increasing the yield of light fractions.

Testing of the Ni- and Mo-containing ultradispersed catalysts showed that their use, in whole, improves the properties of the liquid products, increases the yield of light products and products fraction with boiling point up to 500 °C (so-called "synthetic oil"); in liquid products, sulfur content drops from 3.3 to 3.2-2.7 wt % and H : C ratio increases from 1.63-1.64 to 1.66-1.69. In the case of employing of the Ni-containing catalysts, an increase of coke and gaseous products yields with nickel content increasing in the feed was found. However, at the minimal Ni concentration (0.3 wt %) performance of the steam cracking was acceptable, with minimal yields of coke and gaseous products. In the case of molybdenum – on the contrary, at higher

concentrations of Mo, yields of the undesirable products have not been increased, while improving the depth of desulfurization and other parameters of the process. Furthermore, a different mechanism for removing sulfur from liquid products was discovered: in the case of nickel, sulfur was mainly absorbed by the catalyst, while in the case of molybdenum sulfur was not accumulated in the coke and transferred into gaseous products. The experiment on catalytic cracking of the heavy oil in the presence of 2 wt % Mo showed that in the absence of water, sulfur accumulates in the coke when in the presence of water, it promotes desulfurization process with removing sulfur in the form of gaseous products in significant degree.

The solid products of catalytic steam cracking of the heavy oil in the presence of ultradispersed Ni- and Mo-containing catalysts were studied by XRD and HRTEM. Results of the investigation of Ni-containing solid product indicated that the precursor of nickel active component was almost completely converted after the process into nickel sulfide (Ni_9S_8) phase particles which, according to the TEM has dimensions of 15-50 nm and according to XRD – 21-25 nm. Thus, Ni seems to be involved in the process in the form of nanoparticles with a size smaller than 50 nm, which are during the process almost completely sulfided into Ni_9S_8 phase, thus acting, basically, as the active one.

In the case of molybdenum, by XRD investigation it was found that the catalyst particles are only MoO_2 phase with OSR size 36-43 nm. Whereas by HRTEM it was found that the active component is in the form of two well-crystallized phases in a matrix of amorphous carbon: MoO_2 particles and agglomerates (20-100 nm) and MoS_2 chains, the length of which is 10-15 nm and thickness of 1-2 MoS_2 layers. The MoS_2 chains are both in contact with the molybdenum oxide phase and at a distance from the MoO_2 particles. However, to establishing the presence of molybdenum sulfide phase by XRD was failed to detect because this method requires that the MoS_2 phase formed a crystallized structure with thicker layers.

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PECULIARITIES OF CATALYST DEACTIVATION IN FUELS HYDROPROCESSING

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Catalyst deactivation plays an important role in hydrocarbons processing. According to prof. Delmon, about 90 % of total expenditures in catalytic processes relate to deactivation problem [1]. It include costs for development of: 1 – special catalyst with high resistance to poisons; 2 – procedure and equipment for catalyst regeneration (FCC); 3 – technology of feed purification (HDS, HDN, Ads.); 4 – special process condition (P , T , H_2 , H_2O).

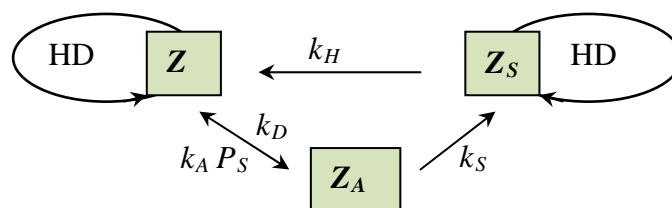
Generally, deactivation of catalysts becomes the key problem in modern catalysis, the main goal of which is no longer “higher activity”, but the “higher stability” and selectivity.

In refinery technology, the processes under an H_2 atmosphere are distinguished (except high pressure of H_2) by mechanisms of catalyst activation and deactivation.

The main peculiarity is a mutual action of different deactivation processes [2]: poisoning (by S, N, and O); coking (condensed and polymeric cokes); metal deposition (Ni, V); and phase transformation of catalyst active components.

Because of excess hydrogen, the catalyst deactivation becomes reversible when the catalyst activity (a) attains some stationary (or residual) value (a_S) [3, 4]. This allows realizing some processes in pseudo-stationary regime, despite the deactivation of the catalyst.

An example is the reversible transformation of different active sites (HDS and HDA) to each other in Ni-Mo/ Al_2O_3 catalyst, and formation of intermediate compounds like non-stoichiometric surface sulfides (Mo_xS_y). To explain observed dependencies the following mechanism is suggested [5], with two catalytic cycles on active centers Z_A and Z_S :

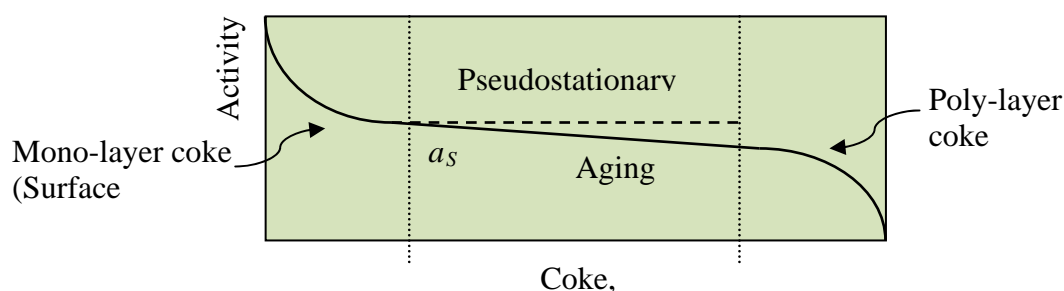


The concentration of intermediate surface compound ($Z_A S$) depends on partial pressure ratio (P_H / P_S) of H_2 and sulfur compounds. The process dynamics is

determined by rapid adsorption ($k_A P_S$) and desorption (k_D) stages, and by slow surface reconstruction stage (k_S).

Another peculiarity is a complex feedstock in these processes, with a wide distribution in boiling temperatures. This leads to a difference in reaction and deactivation kinetics in a catalyst pores filled with gas and with liquid. Even a capillary condensation of some reagent fractions takes place. Then, at reactor inlet and outlet the mixture is gaseous (vapors), but inside the catalyst pellets both gas-phase reactions (in large pores) and liquid-phase reactions (in small pores) occur [6]. Due to an extremely low solubility of H_2 in hydrocarbons, the H_2/HC molar ratio in a gas phase (large pores) equals to 3–5, but only to 10^{-3} in a liquid phase (small pores) [6]. It was found that the rate of poisoning under capillary condensation is 2 ± 6 times slower than in gas phase [7]. The retardation of poisoning is due to a change in the H_2S /hydrocarbons ratio near the active sites when compared with the gas phase [8].

The main cause of deactivation is coke formation. Due to the catalyst self-regeneration by H_2 , even coking becomes partly reversible, and it can be divided to three periods [3]:



All these peculiarities will be presented and discussed in the report.

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INFLUENCE OF METHOD OF ACTIVE COMPONENTS DRAWING ON THE DISTRIBUTION OF HYDRATING METALS IN CATALYSTS OF HYDRO PURIFICATION

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Keywords: hydro process, complex solution, Macro-distribution, Hydro-Desulfurization.

Bearing sulfides of molybdenum promoted by ions of cobalt and nickel are the base components of active phase of catalysts for majority of processes of hydro processing of oil raw material. Besides structure of the active component in these catalysts also distribution of oxide precursors and localization of the sulfide phase of bearer have an important meaning. The aim of this work is an investigation of influence of the nature of bearer and the method of its synthesis on the phase composition; value of surface; distribution of active components by core of bearer; texture- strengthen and catalytically properties of NiO-CoO-MoO₃ (ACNM) catalysts of hydro purification.

For synthesis of bearers the enriched Angren kaolin and two types of Al(OH)₃ differing by crystallite (the dimensions of primary crystals are indicated in brackets), texture and surface properties were used. Small- crystalline aluminum hydroxide (GOA-M) accordance to data of radio phase analysis is a mixture of bemit and psevdobemit (3÷25 nm) containing 1-3 % bierit (~ 100 nm). The surface of GOA-M has possessed by collection of moderate and very weak acid centers with $+3,8 \leq pK_a < +6,8$.

Large - crystalline aluminum hydroxide (GOA-K) consisting from bierit (20÷25 nm); hydrargillit (28÷300 nm) and bemit (20÷100 nm) has a more expressed basic character. On its surface a very weak acid centers with pK_a in narrow interval (+6 ÷ +7) and some quantity of base centers with pK_a = +9.3 were identified.

Objects of this investigation were obtained by different methods: mixing aluminum hydroxide (GOA-M or GOA-K) and kaolin was impregnated by complex solution of salts, containing n-molibdate of ammonium; nitrates of cobalt and nickel, stabilized by phosphoric acid, single and two time impregnation of tempered alumo-kaolin bearers by complex solution of Co, Ni and Mo salts.

Structure of active components was determined by electronic spectrums of diffusion reflection (spectrometer "Hitachi- 330"). Macro- distribution of elements by

corn of bearer was investigated on the scan electronic microscope with diameter of microzond 2,5 mkm.

Spectral investigations have shown a variety and different ratios of structures forming at contact of complex solutions of active components with different types of $\text{Al}(\text{OH})_3$ and kaolin. To ions $\text{CO}_{\text{oh}}^{2+}$ in structure of cobalt molibdates with different degree of hydration can be attributed the wide band of absorption at $19,6 \text{ ksm}^{-1}$ with shoulder about $21,3 \text{ ksm}^{-1}$. To ions $\text{Ni}_{\text{Td}}^{2+}$ in structures near to NiMoO_4 the band about $13,0\text{-}13,2 \text{ ksm}^{-1}$ was corresponded.

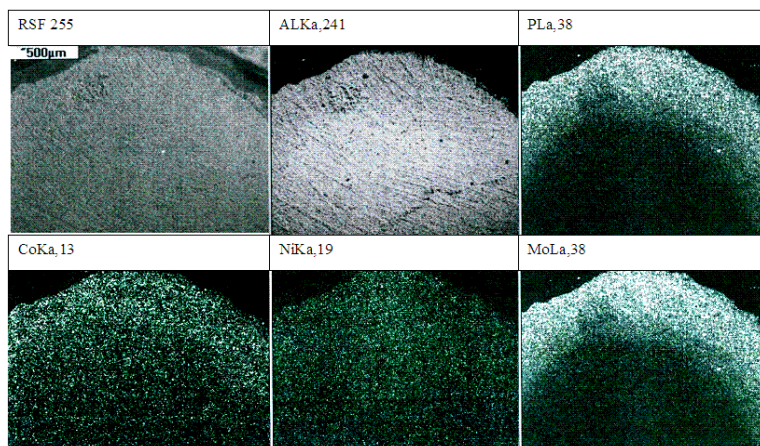


Figure 1. Macro-distribution of elements by granular cut of catalyst AKHM obtained by impregnation of bearer AK-1 by complex solution of active components

Profile investigation of Co, Ni and Mo changing concentration (names of elements are displayed in upper corner corresponding photographs) by corn of bearer has determined an uniform distribution of active metals and phosphorous (Fig. 1). This is caused by good mixing of catalytically mass and

deep interaction of compounds of hydrating elements with GOA-M what has hindered to their migration from granola's surface at drying and tempering.

Drawing of active components on the comparatively narrowly-porous bearer AK-1 has accompanied by increasing of mechanical strength of granules on 10-15 % and decreasing of the effective radius of pores from 3.9 to 3.6 nm. Negligible increasing of part of micropores with radius less 5 nm on the phone of decreasing nearly twice of volume and radius of micropores has witnessed about high-dispersion state of Ni-Co-Mo structures mainly localized in mesopores with radius 40-60 nm. The absorbed bands corresponding to molibdates of cobalt ($27,0\text{-}23,0$ and $14,0\text{-}12,0 \text{ ksm}^{-1}$) and nickel ($13,2 \text{ ksm}^{-1}$) displaid very distinctly but bands of NiAl_2O_4 were absent.

At zounding of cut of catalyst sample on the AK-2 for estimation of macro-distribution of active elements it was determined the presence of surface ring with width 360 mkm with uniform content of molybdenum – 14.8-14.5 %. In following zone with width 270 mkm concentration of molybdenum has decreased to 9 % and inside granular it's content varied from 7,5 to 7.2 %. Profile of phosphorous concentration

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changing at transference from surface (5,05 %) to center of granular (0,4 %) completely has correlated with molybdenum distribution (Figure 2). Molybdenum parallel with phosphorous is more active than cautions of Ni and Co and has penetrated deep into granular an by this reason at transference from surface to center it's concentration monotonously has decreased from 12,8 to 9,5 %. Also it was determined an monotonous disappearance of between-zoned concentration boundaries of molybdenum at increasing of common content of phosphorous in catalyst from 2,0 to 7,0 %.

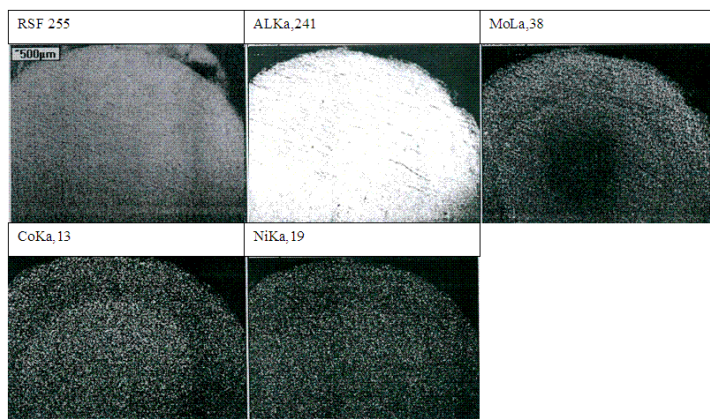


Figure 2. Macro-distribution of elements by granular cut of catalyst ACNM

The following plotting of active metals is accompanied by simultaneous decreasing of the effective radius of pores and the specific surface of catalysts. Difference in electronic spectrums ACNM catalysts is only in lesser width of band of charge transition of Mo^{6+} in comparison with previous

serums owing to lesser degree of polymerization molybdate ions at first impregnation by weak-based solution of aluminum para-molybdate. The samples are characterized by small quantity of weak-bonding structures of molybdenum, nickel and cobalt.

Concentration of Mo in the surface zone with width about 430 μm was about 13.5 mas % and then narrowing has appeared with width 70 μm where content of Mo has decreased to 7.5 %, then concentration again has increased and at 430 μm it has decreased smooth by from 12.2 to 8.0 mas %; in central zone of granular concentration of Mo was equaled approximately to 6.5 %.

Data by catalytically activity have shown the influence of method of catalysts synthesis on their hydrating ability. Catalysts have different catalytically activity with near content of active elements but different type of their distribution. The most depth of remainder (boiling temperature 520 K) at 570 K, pressure of hydrogen 3.0 MPa and volumetric rate 1.0 h^{-1} has been reached on the catalyst with primary micro-distribution of active components in mesopores with radius 7-10 nm and also macro-distribution with width surface ring with higher concentration of molybdenum and phosphorous and also uniform macro-distribution of cobalt and nickel.

EFFECT OF STATE HYDROGENATING COMPONENT ON THE PROPERTIES OF Pt-CONTAINING CATALYSTS OF ONE-STEP VEGETABLE OIL HYDROCRACKING

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Hydrocracking of fat and oil raw materials is highly demanding technology of the production of diesel fuels components with improved environmental and operational properties. The catalysts of hydrotreating with the active phase Ni-Mo(W)-S supported on SAPO-11 allow to produce diesel fuel with cold flow properties, which meet current requirements. However, the stability of hydrotreating catalysts is maintained by a special introduction of non environmental friendly sulfur compounds into the reaction medium. Therefore, the development of non-sulfide hydrocracking catalysts providing one-step production of components of diesel fuels with improved low temperature properties is actual. The main objective of this research was studying the effect of the nature oxide supports and platinum precursors on the properties of bifunctional Pt-containing catalysts for hydrocracking of vegetable oil.

The supports (γ -Al₂O₃ (A) and ZrO₂ (Z)) were prepared by calcination of pseudoboehmite and zirconia hydrate, respectively. The ZrO₂-Al₂O₃ (ZA) (2.5 wt % Al₂O₃) support was synthesized by calcination a mixed hydroxide obtained by precipitation from a solution of zirconium and aluminum nitrate salts. Sample supports B₂O₃-Al₂O₃ (BA) and B₂O₃-ZrO₂ (BZ) (20 wt % B₂O₃) was synthesized by mixing zirconium hydroxide or pseudoboehmite with a solution of boric acid, followed by calcination. In all cases, the calcination is performed in air at a final temperature of 550 (A, BA) or 600 °C (Z, ZA, BZ). Then, the platinum (0.5 wt %) was introduced by wet impregnation of the supports with an aqueous solutions of H₂PtCl₆ (^a) and [Pt(NH₃)₄]Cl₂ (^b). The obtained materials were calcined in air at 500 °C and underwent to reduction treatment in hydrogen flow at 500 °C. The catalysts were characterized by N₂ adsorption, XRD, TPR-H₂, chemisorption of H₂, TPD-NH₃, FT-IR adsorbed CO and HRTEM techniques. The catalytic tests were carried out in a continuous flow fixed bed reactor at temperature of 380 °C, pressure of 4.0 MPa, WHSV of 1.0 h⁻¹, H₂/feed ratio of 1400 (v/v), TOS of 20 h. The purified sunflower oil was used as the feedstock. Contents of gasoline (IBP-150 °C), diesel (150-350 °C)

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and heavy gas oil (350 °C-FBP) in liquid product were determined by simulation distillation.

As can be seen from Table 1, borate-containing catalysts Pt/BA, Pt/BZ are X-ray amorphous and characterized by high levels of acid sites. All the catalysts which produced using anionic precursor $[\text{PtCl}_6]^{2-}$, have greater dispersion of the metal, compared with catalysts obtained by the cationic precursor $[\text{Pt}(\text{NH}_3)_4]^{2+}$. This is due to sorptive fixing of the $[\text{PtCl}_6]^{2-}$ ions on the surface of supports. Platinum dispersion on catalysts with alumina support is higher than dispersion on zirconia based systems due to developed textural characteristics.

Table 1. Catalysts characterization

Sample	Surface area, m ² /g	Pore volume, cm ³ /g	Pore size, nm	Desorption NH ₃ , μmol/g	Phase composition, %	Dispersion of platinum	State of platinum
Pt/A ^a	179	0.48	10.8	326	gamma	1.00	Pt ⁰
Pt/A ^b	182	0.47	10.4	310		0.59	
Pt/BA ^a	203	0.50	9.9	498	amorphous	0.76	Pt ⁰
Pt/BA ^b	226	0.52	9.1	430		0.29	
Pt/Z ^a	59	0.14	9.7	212	T-ZrO ₂ (~15),	0.19	Pt ^{δ+} , Pt ⁰
Pt/Z ^b	60	0.14	9.4	172	M-ZrO ₂ (~85)	0.15	
Pt/ZA ^a	67	0.15	9.1	187	T-ZrO ₂ (~86),	0.15	Pt ^{δ+} , Pt ⁰
Pt/ZA ^b	66	0.15	9.2	159	M-ZrO ₂ (~14)	0.10	
Pt/BZ ^a	150	0.16	4.4	353	am., traces T,	0.07	Pt ⁰
Pt/BZ ^b	153	0.17	4.4	339	M-ZrO ₂	0.02	

According to the catalytic tests all systems provide complete hydrodeoxygenation vegetable oil. On the catalysts Pt/BA^a and Pt/BZ^a the yield of the diesel fraction (80.7 and 72.7 wt %) is higher than on systems Pt/BA^b and Pt/BZ^b (77.4 and 69.1 wt %, respectively). Diesel fractions obtained on the catalysts Pt/BA^a and Pt/BZ^a, also contain large amounts of iso- and cycloalkanes (28.3 and 60.7 wt %) compared with diesel fractions formed on systems Pt/BA^b and Pt/BZ^b (19.2 and 31.3 wt %). This fact is due to the greater acidity of borate-containing systems, synthesized using anion precursor platinum (Table 1). Furthermore, the presence of these hydrocarbons in the diesel fraction formed on Pt/BA and Pt/BZ catalysts may be associated with a predominance of Brønsted acid sites on catalyst surface. Catalysts Pt/A, Pt/ZA and Pt/Z, characterized by the acidity of Lewis type, contribute to the preferably n-alkanes formation (up to 97.5-94.0 wt % in the diesel fraction). It is shown that all platinum-supported systems, regardless of the state their hydrogenated components, are effective catalysts for hydrocracking of vegetable oils. Using the catalysts Pt/BA and Pt/BZ, prepared with H₂PtCl₆ is preferred because of the formation of large amounts of iso- and cycloalkanes, potentially providing good cold flow properties of diesel fuels.

CURRENT STATUS OF RESEARCH AND DEVELOPMENT PROSPECTS OF THE PROCESS AND CATALYSTS OF GASOLINE FRACTIONS REFORMING

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The problems associated with the currently existing trends of the need to increase the efficiency of modern refining naphtha processes (reforming, isomerization) at simultaneous tightening of the requirements for environmental safety of fuel are discussed.

Studies of the structure of the active centers of catalysts of reforming, biforming, isomerization of C₅-C₆ alkanes, hydroisomerization of arenes and hydrocracking of C₇ alkanes that are developing in IHCP SB RAS formed the basis of a systematic approach to their preparation, which allowed to solve the complex issues of increasing the efficiency of their actions for activity, selectivity and resistance to deactivation in work and regeneration cycles for a fairly short time [1]. The experience of solving of the problems in the process of development of new industrial catalysts is analyzed.

The prospects of using integrated naphtha refining processes with a combination of previously known processes (reforming, isomerization) and new processes (biforming, ekoforming) with the inclusion of benzene-methylcyclopentane isomerisation and n-alkanes selective cracking steps in its technological schemes are substantiated.

The usage of such schemes allows to product fuels Class 4 and 5 without using of oxygenates and other expensive fuel additives.

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Current status of research and development prospects of the process and catalysts of gasoline fractions reforming

ORAL PRESENTATIONS

Section II.

**DEVELOPMENT, ENGINEERING, MODELLING
AND PRACTICAL APPLICATION OF
HYDROPROCESSING TECHNOLOGIES**

ADAPTING CRACKED NAPHTHA HYDROTREATING TO FEED CHARACTERISTICS FOR ULTRA-LOW-SULFUR GASOLINE PRODUCTION

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Due to increasing environmental concerns, constraints relative to exhaust fuel compositions are reinforced worldwide and forthcoming China V, Bharat VI and US Tier 3 standards will impose a maximum total sulfur content of 10 wt ppm in gasoline by 2017-2020 [1-3]. Gasoline produced in FCC units represents, on an average basis, 40 % vol of the gasoline pool but accounts for 95 % for the total sulfur amount [4]. Therefore, FCC gasoline hydrodesulfurization (HDS) is a key process to achieve on-road gasoline specifications. However, hydrodesulfurization (HDS) of thiophenes and benzothiophenes contained in FCC gasoline, results in octane loss since a partial hydrogenation of olefins (HYD) is observed. Hence, selective HDS of FCC gasoline with high sulfur removal and limited olefin hydrogenation (HYD) is the preferred solution to achieve tough sulfur reduction while maintaining excellent octane levels.

In most FCC gasoline desulfurization design (see below on fig. 1), after selective diolefins hydrogenation (SHU) of full range cracked naphtha, light gasoline is fractionated away from the heavy gasoline and treated separately. This operation is fulfilled to preclude hydrogenation of the highly concentrated light olefins in the HDS reactor. Mercaptans in light naphtha may be removed by thioetherification prior to splitting within the selective hydrogenation unit or by wet caustic wash afterwards. Heavy gasoline follows selective hydrodesulfurization (HDS and polishing).

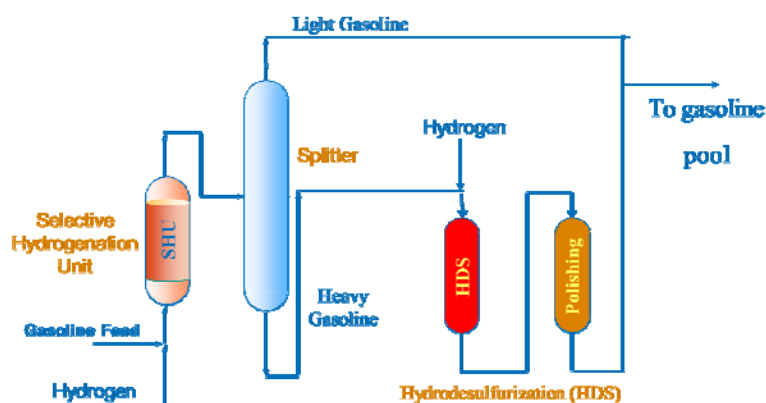


Figure 1. Typical (PrimeG+™) FCC gasoline desulfurization Unit

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As an alternative to a conventional unit design, FCC full range naphtha (FRCN) can be separated into three main fractions through splitting or distillation: light cut naphtha (LCN), medium or intermediate cut naphtha (MCN or ICN) and heavy cut naphtha (HCN).

In this study, different narrow MCN cuts were prepared from a FCC full range naphtha with final boiling of 100 °C, 140 °C and 160 °C. Detailed characterization of (C5-C9) hydrocarbons and speciation of sulfur compounds of all feeds was also carried out. Selective HDS experiments were also performed to evaluate feeds reactivity and selectivity as a function of the final boiling point, operating conditions being adjusted for each feed.

On the basis of experimental results, a comparison of different process schemes is proposed and examined. In particular, parallel processing of MCN and HCN to achieve 10 wt ppm sulfur level and its advantages over conventional HDS process will be discussed. Feed staging solutions, i.e. staged introduction of the feed into the HDS reactor(s) to promote desulfurization of the sulfur-rich, olefin poor back end of the feed while reducing the saturation of the high octane olefins in the olefin-rich, sulfur-poor front end, will also be considered.

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CRACKING CATALYSTS DEVELOPED IN THE INSTITUTE OF HYDROCARBONS PROCESSING OF SB RAS

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Cracking catalysts developed in the IHP SB RAS based on microcrystalline ultrastable zeolite Y in HRE-form with the following characteristics:

- crystal size – 0.3-0.8 μm ;
- $\text{SiO}_2 / \text{Al}_2\text{O}_3$ ratio – 6.5-7.5;
- rare earth oxide content – 2.5-6.5 % wt;
- sodium oxide content – less than 0.8 % wt.

The use of microcrystalline zeolite significantly reduces diffusion limitations to the hydrocarbons cracking.

The composition of catalyst matrix includes amorphous aluminosilicate, which possesses both Lewis and Bronsted acidity. The matrix also contains aluminum oxide (source is reprecipitation aluminum hydroxide, or thermochemical activation product), which possesses a high Lewis acidity. Furthermore, the matrix includes bentonite clay with a high binding property.

Regulation of the ratio between alumina and amorphous aluminosilicate allows to significantly modify contributions of Lewis and Bronsted acidity to the total acidity. This is a major way to configure cracking catalyst composition for the conversion of feeds with different qualities.

Using of the second zeolite (ZSM-5 type zeolite) allowed to develop new series of cracking catalysts:

- catalysts for produce gasoline with high octane characteristics and cracking gas with high olefin content;
- catalysts for deep catalytic cracking process – these catalysts allow to produce C_3 and C_4 olefins up to 38 % wt.

Currently catalysts developed in the IHP SB RAS applied on 4 industrial catalytic cracking units in the Russian Federation. The total capacity of these units is about 7 million tons hydrocarbons per year.

ALKYLATION OF ISOBUTANE WITH BUTENES ON A SOLID CATALYST USING CATALYTIC DISTILLATION WITH EXTERNAL REACTION SECTIONS

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Alkylation of isobutane with butenes is one of the most important processes making high octane number gasoline. The modern processes for industrial alkylation are based on utilization of sulphuric and hydrofluoric acids, which have a number of drawbacks related to utilization of refrigerating agents, corrosion, pollution and safety.

Due to these clear shortcomings there is an apparent interest to apply solid catalysts. The difficulty of solid catalysts application in alkylation is related to rapid catalyst deactivation. To prevent it an excess of isobutane to olefin is required. Consequently operating costs for solid-catalyzed alkylation are increased. In order to reduce heat consumption the catalytic distillation could be proposed.

The purpose of this research is to analyze the efficiency of catalytic distillation and to adapt the catalytic distillation approach to alkylation of isobutane with butenes on a solid catalyst. There are several possible structures of catalytic distillation which differ in reaction and separation sections position. It has been established in our previous research [1] that the reaction section should be located above the butane separation zone (top of the column) and alkylate stabilization (n-butane separation) should be performed in a separate conventional distillation column (Figure 1, case «A»).

Simulations of the described processes were performed using with a chemical optimization software. Distillation modeling was based on MESH (material balance, phase-equilibrium, mole balance and energy balance) equations approach. A set of seven alkylation reactions was simulated using conversion type equations. The calculations of selectivity were based on experimental data obtained in laboratory scale experiments for a zeolitic catalyst.

Process simulations were performed for the paraffin to olefin ratio 10, pressure – 10 bar, feed reactor temperature 65 °C and isobutane concentration in the recycle stream – 90 mass. %. The feedstock was C₄ fraction from FCC and butane – isobutane mixture.

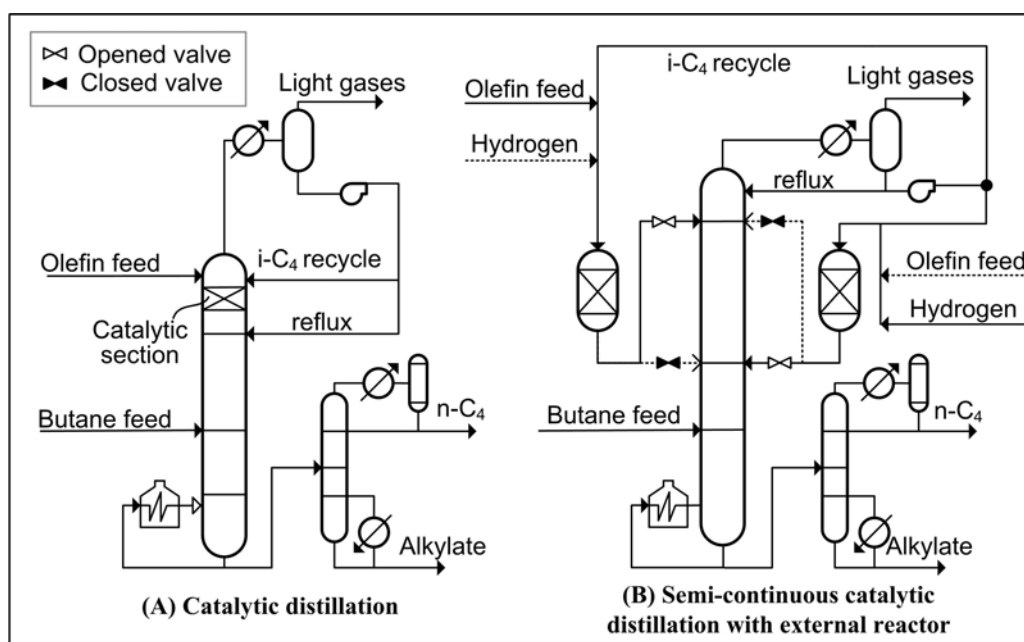


Figure 1. Simulated process arrangements.

The overall energy consumption of a catalytic distillation unit (case «A») was 2.44 GJ per ton of alkylate. Octane number (RON) of alkylate was equal to 91.5 and the vapour pressure – 45 kPa.

Such case of alkylation has a significant drawback since it is possible to arrange continuous catalyst regeneration requiring elevated temperature and presence of dissolved hydrogen in isobutane stream. High activity of solid alkylation catalysts can be maintained only up to 20-40 h, which leads to frequent changes of reaction/regeneration process steps in the reactor section.

The unit with external reaction sections (Figure 1, case «B») can be utilized to perform efficient semi-continuous regeneration. The overall heat consumption in both cases is the same. Another advantage is a possibility to decrease the pressure in the distillation section.

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MICRO-FIBROUS STRUCTURED CATALYSTS VS CONVENTIONAL CATALYTIC SYSTEMS: DIRECT COMPARISON OF THE MASS TRANSFER EFFICIENCY

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The majority of the oil processing and petrochemical processes are performed under the significant influence of the diffusion limitations. Therefore, the development of the new catalysts with improved mass transfer properties is an important task. The possible promising solution in this area is application of structured catalytic systems using the catalyst on the base of microfibrinous supports, produced in the form of cloths, made from glass, mineral, carbon, polymer and other micro-fibers. Such micro-fibrinous catalysts (MFCs) may use noble metals (e.g. Pt or Pd) or transient metal (Cu, V, Fe, Ni, etc.) oxides as active components [1]. The MFCs may be structured in a form of cartridges, characterized with a low pressure drop. There are also characterized with minimized mass transfer limitations both external and internal. As shown [2] by our theoretical estimation, the MFC's cartridges provide the highest unit mass transfer efficiency among all known forms of catalysts, thus highlighting the great engineering potential of structured fiber-glass catalytic systems.

The aim of the given study was to confirm this calculated result by direct experiments. Mass transfer properties of the MFC cartridges were studied in the reaction of deep oxidation of toluene in air flow using the Pt-containing (~0.07 % Pt mass) commercial glass-fiber catalyst IC-12S111 (BIC, Russia). Internal mass transfer limitations were eliminated for this catalyst by application of the very thin (<0.5 mm) catalytic fabric, giving the way to separately study the external mass transfer regularities. Experiments included variation of the reaction temperature, air flow rate and the geometry of catalytic cartridges. Pt-based monolith and granulated catalysts were used as reference catalysts for comparison. The volume of the catalytic cartridge was kept constant in all experiments, though in case of MFC the mass amount of the catalyst in this volume was much lower (less than 150 g per l of the bed) than that for the conventional catalysts.

The observed dependence of the apparent reaction rate upon temperature for different types of the catalyst packing is given in Fig. 1. Comparison was made for temperature region above 200 °C, where the reaction was limited by the external mass transfer.

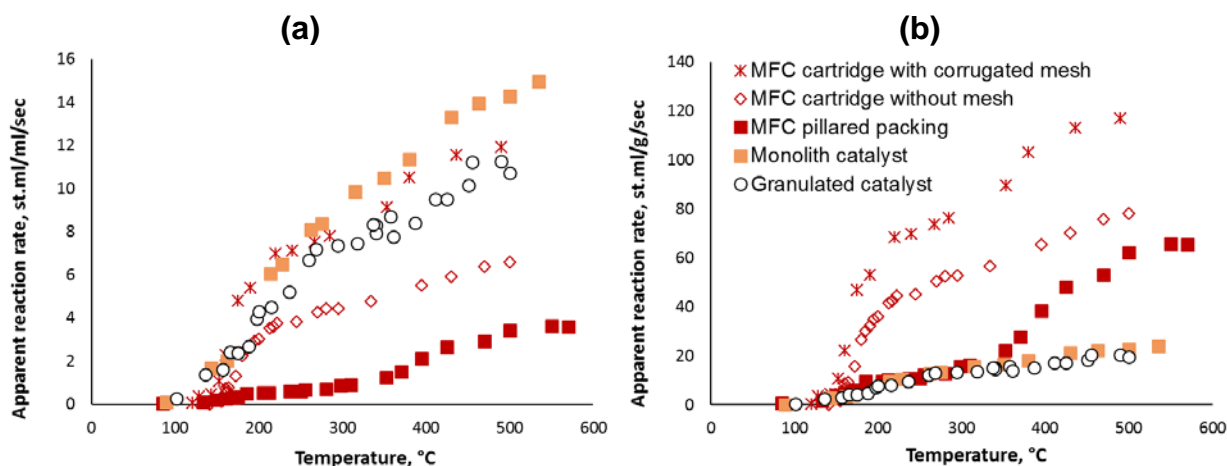


Fig. 1. Dependence of the apparent reaction rate upon temperature in the catalyst beds of different structure: (a) – per unit volume of the catalyst bed, (b) – per unit mass of the catalyst

It is seen that the MFC in the form of cartridges with corrugated structuring wire mesh demonstrates the excellent volume performance competitive to that of the monolith catalyst (Fig. 1a). At the same time, all MFCs look much more efficient than conventional catalysts in terms of apparent reaction rate per unit catalyst mass (Fig. 1b). MFCs may be applied for intensification of many catalytic processes in oil processing and petrochemistry.

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RATIONAL USE OF THE PRODUCTS OF HYDROCRACKING IN THE "ENVIRONMENTALLY FRIENDLY" MOTOR FUELS

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In connection with the deepening of the oil processing and reality of structure of production of motor diesel and marine fuels in their composition they began widely using the products of deeper processing of petroleum feedstocks, which differ from products of straight distillation oil in its hydrocarbonaceous and chemical composition, as well as in its physico-chemical, operational and environmental properties [1-3].

Bunker fuel (BF) developed in accordance with the requirements of Russian standards is necessary for vessels equipped with high-speed diesel plants. In comparison with diesel fuel, intended primarily for ground equipment, to BF not such tough requirements are applied both in cetane number and the sulfur content, which is much tougher due to the recent RF Government Regulation, adopted the Declaration of the Customs Union and the decision of the International maritime organization (IMO) for the prevention of pollution through vessels and for protection of the environment against emissions of sulfur compounds especially in the controlled coastal areas. In addition, BF should have a weighted fractional composition and flow within 180-400 °C.

To improve the environment one of the main requirements for diesel and marine fuels is an extremely low toxicity of combustion products, determined by the content of sulphur oxides and soot. Analysis of the chemical composition of diesel fuels shows that to meet this requirement it is necessary to reduce the content in the fuel aromatic hydrocarbons, especially polycyclic and sulfur, which is achieved by the technological means through hydrogenation processes [1-3].

In this paper we have conducted research on the development of new technology of production of ecologically friendly low-viscosity marine fuel (BF-EF) based on hydrocatalytic processes products. It was studied the quality of the original components of the fuel, selected from existing industrial installations of one of the Russian oil refineries, and obtained on their basis of a test piece of BF-EF with mass

sulfur content less than 0,2 %. The analysis of obtained results showed the possibility of production of BF-EF on domestic enterprises with the appropriate set of processing units [4-5]. The choice of the component composition and obtaining of test pieces of BF-EF was carried out on the basis of the determination of the main physico-chemical properties of different fuel blends obtained by direct compounding the light gas oil of catalytic cracking with diesel oil cut from the hydro cracker unit, by unconverted oil and hydrotreated straight run diesel in various mass ratios.

However, since the obtained test pieces of BF on the pour point did not meet the requirements of the standards, to improve their low temperature properties the studies have been conducted on the selection of domestic and foreign depressor additives type Dodiflow 4300 and Dodiflow 4598 (with disperser), as a result of which was found their optimum content in the fuel.

Thus, the organization of industrial production low-viscosity marine fuel with improved environmental and low temperature properties on oil refinery plants with modern hydrocatalytic processes would increase the oil processing depth, expand the product range and its scope of application, improve its quality and competitiveness in the domestic and foreign markets, as well as solve ecological problems.

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DEMETALLIZATION OF HEAVY OIL AS A COMPLEX PROBLEM

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There is a strong global trend to "weighting" and, consequently, to an increase in metal content of extracted oil. Ordering of literature data and own studies showed the possibility of obtaining in the process of refining the industrial standard concentrates containing both a number of rare metals. Maximum concentrations of the elements are distributed on various refinery fractions as follows: gas oil (350 °C) – Si, P; gas oil (420 °C) – Hf, W, Ru, Pd, Cd, Pb, Ga; oil – Ba, Sr, Ce, Pr, Nd, Yb, U, Hg, Ge, As; tar – Co, Mo, Se, Te, Ga, Ag, Re; bitumen – Rb, Be, B, Mg, Al, Sc, Y, Ti, V, Cr, Mn, Fe, Ni, Zr, Nb, Rh, Cu, Zn, Sb [1]. It is proved that there is a principal possibility of integration into a large-scale technological schemes of oil refining processes associated produce concentrates containing rare and precious metals. Implementation of this should lead to insertion of that margin obtaining metals from a hydrocarbon feedstock will be much higher than in processes for the preparation of conventional rare metal ore materials. Abroad from petroleum feedstocks receive about 8-10 % of the volume of world production of vanadium [2-4]. Nearly all methods of use or refining petroleum fuel oil it is possible to extract a given amount of vanadium and other metals. The main methods are: the burning of fuel oil; gasification of oil or tar; residue hydrocracking and tars, colvoliz heavy oil feedstock; deep thermal processing of heavy oil feedstock (thermal cracking, visbreaking, steam cracking "Eureka", delayed coking, cracking thermometers, thermometers cracking coke gasification, pyrolysis of heavy raw materials) and others.

As part of this work explored alternative processes demetallization of petroleum feedstock using energy input to the system using a variety of physical methods of influence, involving or taking place in conjunction with the adsorption and heterogeneous catalysis processes. The process of cavitation leaching of heavy oil suspensions (THC), the Timan-Pechersk Russian province. Implementation of the proposed method can reduce the density of THC 5-10 degrees API with a simultaneous decrease in viscosity at 80-90 %, the sulfur content – up to 40 % and heavy metals – more than 60 %. The proposed process is designed based on the technology of solvent deasphalting (SDA) using light hydrocarbon solvents, and

comprises an extraction step in an ultrasonic field with the separation of the insoluble fraction of asphaltenes in which a considerable part concentrated source of heavy metals and sulfur. The main feature of this method – and the consistent use of acoustic cavitation effects, can improve the efficiency of mass transfer on the ATS stage, thereby reducing the required extraction time. It is showing the ability to speed up the process (SDA) by the catalytic action of peroxides, formed in Wh and physical impact on THC. Implementation of the proposed method can reduce the density of THC 5-10 degrees API with a simultaneous decrease in viscosity at 80-90 %, the sulfur content – up to 40 % and heavy metals – more than 60 %.

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SIMULATION AND MODELLING OF AN INDUSTRIAL HYDROTREATING PROCESS USING BLENDS OF STRAIGHT-RUN GAS OIL AND LIGHT CYCLE OIL

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Over the years, hydrotreating process has greatly developed in order to accomplish the growing demand of the market and legal requirements. Due to the complexity of hydrotreating it would be beneficial to develop further understanding of the process through mathematical models which are based on the industrial scale data and real feedstock.

In this research work different kinetic models for reaction of hydrodearomatisation and the influence of reaction rate on performance of the industrial trickle bed reactor for hydrotreating of gas oil and light cycle oil have been analyzed. Several models for wetting efficiency in TBR on industrial level are examined and the influence on reaction rate and reactor performance is discussed.

Mathematical model for co-hydrotreating of straight run gas oil blended with fluid catalytic cracking naphtha and light cycle oil was developed [1,2] using axial distribution of phase equilibrium and effective wetting in the catalyst bed. Model assumes that hydrodesulphurization (HDS) and hydrodearomatisation (HDA) reactions occur on the catalyst surface which is in contact with vapour or liquid phase. Hougen-Watson type kinetic equations for different classes of sulphur compounds were applied in separate material balance equations for vapour and liquid phase. Mass transfer effects were taken into account using overall catalyst effectiveness factor for each of the reactions and overall energy balance equation was included in the model [1,3]. Model results were validated using the industrial test run data performed using liquid hourly space velocities between 1.05 and 1.32 h⁻¹, H₂/oil ratios of 908-1135 Nm³ hydrogen/m³ oil, temperatures of 327 to 334 °C and pressure of 40 bar. Industrial test run was performed under in the catalytic reactor with two layers of conventional Co-Mo/ γ -Al₂O₃ catalyst by increasing volume content of FCC naphtha and light cycle oil fraction in the reactor inlet to 20 % vol. Sulphur inlet concentrations of 6500-8200 ppm were reduced to 36-72 ppm in the hydrotreated oil [2].

The results of the simulations are compared to experimental data and the best model for the investigated process was analysed.

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A NOVEL PROCESS FOR PRODUCTION OF HIGH-PURITY H₂: SORPTION-ENHANCED CHEMICAL LOOPING METHANE REFORMING

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Sorption-enhanced methane reforming (SE-SMR) is an advanced environmentally friendly process for pure H₂ production in a single step. In an effort to reduce the energy demands for the sorbent regeneration, the combination of SE-SMR with chemical looping has been proposed [1]. In this process, the reformer contains, in addition to the sorbent, an oxygen transfer material (OTM) that during reforming is reduced by CH₄ into metallic Ni, serving as the reforming catalyst. The reforming proceeds under near autothermal conditions due to the heat released by the carbonation reaction. In a second step, the saturated sorbent is regenerated, with energy supplied by the exothermic OTM re-oxidation. The key for successful commercialization is the development of sorbents and OTMs with high stability under multiple cycles. In this work, we report results from evaluation of NiO-based OTMs combined with CaO-based CO₂ sorbents under sorption enhanced chemical looping methane reforming (SE-CL-SMR) conditions.

The NiO-based OTMs were prepared via wet impregnation using commercial supports (SiO₂, TiO₂, Al₂O₃, ZrO₂) with constant 40 wt % NiO loading. Pre-reduced OTMs were initially tested as conventional reforming catalysts and the most promising materials (NiO/ZrO₂ & NiO/Al₂O₃) were then tested under chemical looping reforming conditions for 20 redox cycles (reduction/reforming in CH₄/steam at 650 °C, reoxidation at 850 °C in air) [2]. The CaO-based sorbents were prepared via a sol-gel auto-combustion route, using citric acid as a combustion agent and MgO, La₂O₃, Al₂O₃ or ZrO₂ as dopant, with 66 wt % concentration of CaO. The sorbents were tested for 100 sorption/desorption cycles in a TGA. Sorption was performed at 650 °C in 15 % CO₂/N₂ while desorption took place at 850 °C in pure N₂.

Based on these preliminary evaluations, NiO/ZrO₂ and CaO/ZrO₂ were selected as the most promising materials to be tested under SE-CL-SMR conditions, primarily

due to their high stability. A mechanical mixture of NiO/ZrO₂ and CaO/ZrO₂ with a mass ratio of 1.1 was loaded in the reactor. The materials were then exposed to CH₄/steam stream (S/C ratio= 3). The reaction was run isothermally at 650 °C until the sorbent was saturated. After saturation of the sorbent, the feed was switched to air for reoxidation of Ni and regeneration of the sorbent. During the pre-breakthrough period, where NiO reduction, reforming and water gas shift reactions are carried out simultaneously with in-situ CO₂ capture, a very high H₂ concentration was observed (~95 %) with very low CO and CO₂ concentrations (less than 2 % and 3 % respectively). In this region a CH₄ conversion of ~98 % and a H₂ yield of 83 % were achieved. The pre-breakthrough period was followed by a transitional period where the sorbent was gradually saturated (breakthrough) leading to an increase of CO, CO₂ and CH₄ and decrease of H₂ concentration. When the sorbent was completely saturated (post-breakthrough period), the produced CO₂ was not captured anymore and the product concentration of the reactor approached that of conventional reforming (Fig. 1). After switching to air flow and for more than 10 minutes no additional external heating was applied to the reactor. The heat generated by Ni reoxidation was enough to sharply increase the temperature of the reactor from 650 °C to ~830 °C while covering about 27 % of the heat needed for the strongly endothermic sorbent's regeneration (Fig. 2), providing proof-of-concept for the proposed methane reforming process.

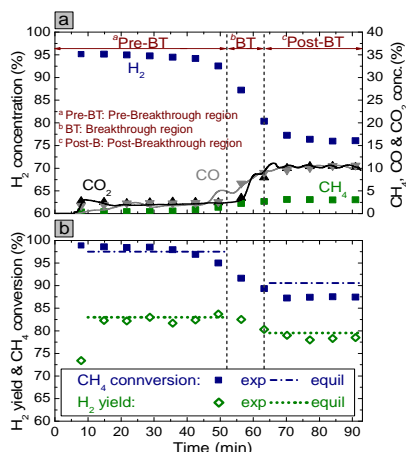


Fig. 1. Reduction-reforming cycle 20

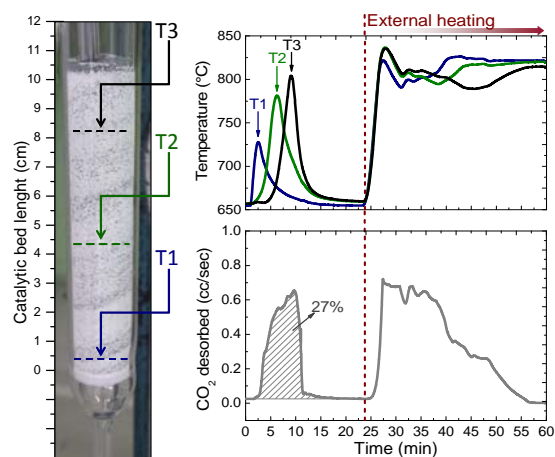


Fig. 2. Reoxidation-calcination cycle 5

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ORAL PRESENTATIONS

Section III.

**HYDROGENATIVE PROCESSING OF HEAVY
OILS, SHALE OILS, RENEWABLE AND
ALTERNATIVE FEEDSTOCKS**

BIOMASS VS. PLASTIC PYROLYSIS OIL UPGRADING VIA HYDROTREATING

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Pyrolysis process can convert solid biomass and wastes such as wood and plastics to higher added-value liquid products (pyrolysis oil). Biomass pyrolysis oil is a dark brown, free-flowing liquid with about 20-30 % water, high acidity and low oxidation stability, rendering it difficult to be directly employed as an alternative fuel. However, biomass pyrolysis oil can be stabilized and converted to a conventional hydrocarbon fuel by converting oxygenates through catalytic hydrotreating. Plastic pyrolysis oil is not including oxygenates, but hydrocarbons (mostly paraffins), which limits its flow properties. Plastic pyrolysis oil can also be upgraded to shorter chain-length paraffins via catalytic hydrotreating.

The aim of this research was to examine pyrolysis oil stabilization and upgrading via catalytic hydrotreating with a commercial hydrotreating catalyst (NiMo/Al₂O₃), utilizing the extensive experience in catalytic hydroprocessing bio-based feedstocks for biofuels production [1-4]. Two types of pyrolysis oils were tested; the first one was produced via catalytic pyrolysis of lignocellulosic biomass (wood from tree beech), which was characterized by 21 wt % oxygen content, high density (1,051 kg/lit) and high acidity, while the second one was produced from pyrolyzed waste plastic bags at high temperature without catalyst, with zero oxygen content and low density (0,768 kg/lit) (see Table 1). It is apparent that the different properties of two pyrolysis oils render different hydrotreating challenges.

Table 1. Properties of Pyrolysis oils before hydrotreatment upgrading

Properties	Units	Wood derived pyrolysis oil	Plastic derived pyrolysis oil
Density	kg/lit	1.051	0.768
Oxygen content	wt %	21	0.3
Viscosity	cSt	14.27	3.5
Pour point	°C	-36	48

A dual stage hydrotreatment was examined for both pyrolysis oils, incorporating a mild hydrotreatment stage that is aimed in stabilization and pre-conditioning, followed by a more severe hydrotreatment stage allowing further upgrading and production

OP-III-1

of fuel-like products. A single stage hydrotreatment of biomass (wood) pyrolysis oil renders a heavy (density:1,056 kg/lit), high sulfur (657 wppm), high O₂ (18 wt %), tar-like product with a boiling point range from 100-670 °C, as a result an additional 2nd stage HDT is required. The product from 2nd stage is characterized by lighter hydrocarbons with density 0.8471 kg/lit, 1 % O₂ content, in the range of 78-580 °C boiling point and calorific value 44.7 Mj/kg.

On the other hand, the product of 1st stage HDT of plastic derived pyrolysis oil renders a lighter product with density 0.766 kg/lit, boiling point ranged from 139-538 °C, zero S and O₂ content and calorific value 46.8 Mj/kg. It is obvious that the product of 1st stage HDT upgrade of plastic derived pyrolysis oil is a better quality product than 2 stage HDT upgrade of wood derived pyrolysis oil. Moreover, a further upgrade with a 2nd stage HDT process of plastic derive pyrolysis oil results in an even lighter liquid product with density 0.655 kg/lit, no S and O₂ content, calorific value 46.9 Mj/kg and boiling point range from 28-195 °C.

The two dual hydroprocessing products of both pyrolysis oil types were also analyzed as potential bio-components for transportation fuels. The waste plastic pyrolysis oil-based product consists of lighter hydrocarbons (figure 1) as compared to the one produced from biomass pyrolysis oil. The biomass pyrolysis oil 2nd stage upgrading renders 44 % diesel, 41 % gasoline/jet and 15 % heavy fuel, while the waste plastic pyrolysis oil 2nd stage hydrotreating offers 87 % gasoline, 5 % kerozene and 8 % lighter components. All the experiments were conducted in CERTH.

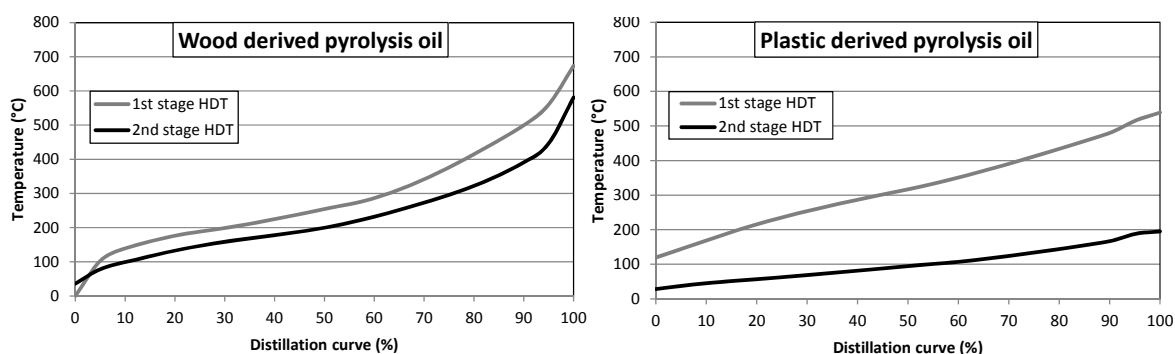


Figure 1. Distillation curve of 1st and 2nd stage HDT upgrade products from wood derive pyrolysis oil and plastic derive pyrolysis oil

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THE STUDY OF INORGANIC ROCK MATRICES FOR DEVELOPMENT OF EFFECTIVE CATALYSTS FOR UPGRADING OF HEAVY OILS IN SITU

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The present paper discusses the results of a study of the catalytic properties of inorganic matrices of oil-bearing rocks with respect to the methane and butane oxidation and hydrocracking of asphaltenes. This research was carried out in an effort to assess the possibility of use of intrinsic catalytic properties for development effective catalysts for upgrading of heavy oils in situ and creation of advanced technologies for enhanced oil recovery (EOR).

Among various chemical processes considered for purpose of EOR one reliable and important approach is the catalytic conversion of heavy oil and non-traditional hydrocarbon compounds achieved directly in the oil field [1-6]. This economically and ecologically attractive approach to enhancing oil recovery imply simultaneous in-field temperature elevation and introduction of nanosize catalysts into the field. We propose, in developing the approach, to employ intrinsic catalytic properties of the inorganic matrix of oil-bearing rocks in order to:

- synthesize in situ active catalytic systems;
- synthesize nanosize clusters of active components on natural inorganic matrices by injecting the precursors into the field;
- catalyze transformations of heavy oil hydrocarbon components

The catalytic and physical-chemical properties of natural inorganic matrices, which contain the heavy hydrocarbon compounds, have been studied in present paper. The mineral matrices (basalts, clays, sandstones) as in the original form and free of heavy hydrocarbons after thermal treatment and calcinations in the atmosphere of corresponding gases (Ar, H₂) have been studied using elementary analysis, X-ray diffraction, transmission electron microscopy of high resolution, IR spectroscopy, methods of adsorption and desorption of nitrogen and ammonia. As a result, the elemental, surface and phase composition and matrix particles morphology, texture and acidic properties have been described.

OP-III-2

The characteristic features of basalt and clay matrices are considerable contents of transition and alkaline earth element oxides (2.75-3.3 wt % Fe; 0.3-0.4 wt % Ti; 7.2-1.4 wt % Mg) and large surface areas (25-15 m²/g) that are sufficient for achieving catalytic reactions on the solid surface. Sandstone matrix samples are characterized by small surface areas, low contents of magnesium and iron, and the absence of manganese and cerium compounds that behave as promoters of catalytic activities to various catalytic systems. The differences in the chemical compositions and textures are the reasons for different catalytic activities of the matrices with respect to transformations of oil hydrocarbon components (oxidation of methane and butane, hydrocracking of heavy oil components - asphaltenes), when the formation of active surface complexes is determining. The use of natural material matrices as catalyst supports (with catalytic systems Fe/basalt, Ni/basalt and Fe/clay as examples) for transformation of oil hydrocarbon components demonstrated that natural inorganic matrices are promising agents for in situ synthesis of active catalytic systems. The obtained experimental data support the hypothesis about feasibility of catalytic reactions in oil beds using natural materials – oil-bearing rocks (sandstones, clays, basalts) – as catalysts and can be use for development of advanced technologies to enhance oil recovery.

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HYDROCONVERSION OF POLIETHYLENE WASTE – A WAY FOR UTILISATION OF THE WASTE PLASTICS

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Currently, plastic materials are now being used in almost every field of human activity. The constantly expanding the production scale and long life time of polymers makes, that it is important to develop new methods for utilization of used polymer products. Reprocessing and use of regranulate is possible only for thermoplastics, however, it is important to notice that reuse of regranulate is only possible for manufacturing products that do not meet of high quality standards. The most popular and widely used plastics are polyethylene and polypropylene, which are characterized by good functional properties and low price. Due to the extremely large scale of application of those materials it becomes essential to develop new high efficiency method of their decomposition. Because of the fact that these materials in chemical structure are the compounds of polyolefins which do not contain heteroatoms in a molecule which could cause deactivation of the catalyst, it can be subjected to catalytic cracking process. Therefore for a number of years there has been great interest of researchers associated with attempts to the effective processing of these materials towards depolymerization and recovery of the monomer, or convert them to the fuel components. However, due to the high volatility of raw material, its pollution and specificity of the cracking process the quality parameters obtained liquid fuels are highly unsatisfactory.

Hydrocracking is a process in which low quality hydrocarbon fractions with a high content of heavy aromatics are both cracked and hydrogenated to valuable gasoline fractions and diesel. Therefore, the catalysts for this process, must simultaneously posses two types of centres namely acid and metallic. The cracking properties are attributed to the acid centres present on the support surface. While the hydrogenating properties are assigned to the metallic centres. The main advantage of the hydrocracking process is the ability to select the reaction conditions in order to obtain products which are directly components of the gasoline, diesel fuel or aviation fuel. Such a composition of the product is not possible to obtain in a conventional

OP-III-3

catalytic cracking process. The most widely used zeolites in hydrocracking reaction are a zeolite Y (synthetic), zeolite X and zeolite ZSM 5. The type of the zeolite determines the selectivity of the catalyst during the reaction.

Hydroconversion of macromolecular polymers were carried out successfully by a number of research centres. It was reported that the zeolite supported platinum catalysts have a high activity and satisfactory stability in plastic waste conversion and the parameters of the obtained liquid fraction are better than the commercial premium gasoline.

In this work the hydroconversion process of the polyethylene was studied. The effect of the polyethylene kind (HDPE and LDPE granulate and plastic waste) on the product composition also was investigated.

Monometallic supported catalyst (Ni and Pt) were prepared using wet impregnation method. The metal loading was 1 and 5 % wt, reactively. As a support material a commercial zeolite (3A, 5A, 13X, MCM41) were used.

In order to achieve the main purpose of this work the catalyst were characterized by various techniques such as: TPR, TPD_{NH_3} , XRD, SEM-EDS, TOF-SIMS methods. The catalytic activity measurements were determined in high pressure autoclave (at 60 bar) after conducting the process for 2 h at 260, 290 and 320 °C, respectively. It was found that catalytic hydroconversion of the polyethylene starts at temperatures higher than 250 °C. Low temperature of the process lead to the formation of an aliphatic products. Increase the process temperature result in increase the amount of aromatic compound in the final product. The catalytic activity performed for monometallic supported catalysts showed that the distribution of the hydrocarbons in the product depends on the catalyst. The activity results in hydroconversion process confirmed also that platinum catalysts exhibited higher activity compared to nickel supported catalyst. It was also found the straight correlation between catalyst acidity and their activity in the studied process.

EFFECT OF THE MINERAL MATRIX ON HYDROCONVERSION OF OIL SHALE

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Due to the decreasing availability of the conventional crude oil resources, combined with the increasing demand for the high-quality motor fuels, special attention is being paid to the alternative oil sources. In this respect, oil shales are one of the most important energy alternatives for the future as the total amount of hydrocarbons in oil shale deposits is several times higher than the conventional crude oil reserves. One of the promising ways for producing high-quality synthetic oil from oil shales is one-stage hydroconversion without preliminary separation of organic and mineral constituents. Conversion of oil shales in the presence of hydrogen requires lower temperatures and provides liquid products of higher quality. It is well known, that the reactions, which are associated with the mineral matter, have a marked influence on the product yield and composition during oil shale pyrolysis and combustion [1-3]. However, the effect of the mineral matter components on the conversion of oil shale in the presence of hydrogen was not studied previously. In this work the influence of oil shale mineral matrix on the yield and properties of shale oil during hydroconversion is studied.

Oil shale samples used in this study were obtained from Kotsebinsk (sample OS-1) and Kashpir (sample OS-2) deposits, located in Volga-Pechora oil shale province, Russia. Conversion was performed in a flow reactor with a fixed bed of the sample at 350-500 °C, 2.0-10.0 MPa in the flow of hydrogen (hydroconversion) or nitrogen (pyrolysis).

Table 1. Characteristics of oil shale samples

Sample	Technical analysis		Elemental analysis, wt %				
	Moisture, wt %	Ash, wt %	C (total)	C (org)	H	N	S
OS-1	6.1	42.6	34.4	33.8	4.6	0.5	6.1
OS-2	7.2	54.9	31.4	28.8	3.1	0.6	5.4

The oil shale samples contain about 40 (OS-1) and 34 wt % (OS-2) of organic matter (Table 1). The mineral matter of the samples is comprised of quartz, calcite,

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kaolinite, illite, montmorillonite and pyrite. The surface area of oil shale mineral matrices obtained by calcination at 600 °C is about 40 m²/g for both samples.

Table 2. Pyrolysis and hydroconversion of Kotsebinsk oil shale

Process conditions	Pyrolysis	Hydroconversion	
	450 °C, 10.0 MPa	400 °C, 10.0 MPa	450 °C, 10.0 MPa
Purge gas	N ₂	H ₂	H ₂
C (org) conversion, %	45.2	91.7	91.0
Shale oil yield, wt %	12.5	30.7	26.6
Gasoline fraction, wt %	11.4	4.4	9.0
Diesel fraction, wt %	16.0	8.1	13.2
Atmospheric residue, wt %	72.6	87.5	77.8
S, wt %	6.2	3.3	3.9
N, wt %	1.4	1.5	1.3
O, wt %	3.4	2.1	2.1

According to obtained results (Table 2) for oil shale conversion in the presence of hydrogen (hydroconversion) and nitrogen (pyrolysis), hydrogen is actively involved in the conversion of kerogen, increasing overall organic carbon conversion and improving the yield and quality of shale oil. The yield of shale oil is more than two times higher for hydroconversion, and obtained oil is characterized by a much lower content of sulfur and oxygen. In order to elucidate the effect of the mineral matrix on the hydroconversion of oil shale the experiments with partially demineralized oil shale or with addition of combusted shale were conducted. During hydroconversion process the decomposition of oil shale kerogen releases reactive hydrocarbon radicals and oxygenates. The role of the hydrogen is to saturate these intermediate species and thereby suppress condensation and polymerization reactions that lead to carbonaceous deposits formation. The mineral matter of oil shale in this case may contribute to these reactions and also may promote secondary reactions, in particular hydrogenation, cracking, hydrodesulfurization and hydrodenitrogenation.

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MONO Ni(Cu) AND BIMETALLIC Pd- Ni(Cu) SUPPORTED CATALYSTS FOR OXY-STEAM REFORMING OF METHANOL REACTION

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The contraction of the petroleum resources and continuous restrictions concerning greenhouse gases emission into the atmosphere resulted in an increase interest in new alternative energy sources. Hydrogen is one of the possible solutions to the existing problem which enables electric energy to be generated in ecologically clean way via fuel cell technology [1-5]. The use of fuel cells to generate energy instead of traditionally used sources such as coal, can reduce emissions of carbon dioxide by 40-60 % and nitrogen oxide by 50-90 %, which negatively impact on the environment. The ideal source of hydrogen is methanol which is characterized by a high ratio of hydrogen to carbon in the molecule. In addition, the absence of a strong C-C bond facilitates the oxy-steam reforming of methanol process. Oxy-steam reforming of methanol is carried out under atmospheric pressure in the temperature range 150-300 °C over Cu, Ni Pd, Au catalysts supported on mono and binary oxide. These catalysts are prepared using various methods which include: impregnation, precipitation, microemulsion, aerogel, co-precipitation, sol-gel and combustion synthesis.

The main purpose of this work was to compare the physicochemical and catalytic properties of copper and nickel based catalysts supported on binary oxide (ZnO-Al₂O₃, CeO₂-Al₂O₃) in oxy-steam reforming of methanol reaction (OSRM). In addition, the influence of the palladium promotion on catalytic reactivity of copper and nickel catalysts in OSRM reaction was also studied. Within this work the physicochemical properties of catalysts have been correlated with their catalytic activity.

The physicochemical properties of monometallic and bimetallic supported catalysts were examined using various techniques such as: BET, SEM-EDS, TOF-SIMS, XRD, TPD-NH₃, FTIR and XPS. The activity tests in oxy-steam reforming of methanol reaction were carried out over prepared catalysts in the temperature range 160 to 300 °C in a flow quartz tubular reactor under atmospheric pressure. The ratio

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of the reactants in the studied reaction was $\text{CH}_3\text{OH} : \text{H}_2\text{O} : \text{O}_2 = 1 : 1 : 0.4$, respectively.

Mono- ZnO, Al_2O_3 , CeO_2 and binary oxides $(\text{ZnO})(\text{Al}_2\text{O}_3)$, $(\text{CeO}_2)(\text{Al}_2\text{O}_3)$ were obtained by precipitation or co-precipitation method, respectively. All obtained supports were dried and then calcined in an air atmosphere at 400 °C for 4 h. Copper and Nickel supported catalysts were prepared by wet impregnation method. While the bimetallic Pd-Ni and Pd-Cu catalysts were obtained by subsequent impregnation method. The prepared monometallic nickel or copper and bimetallic supported catalysts were also dried and finally calcined in an air atmosphere at 400 °C for 4 h. The metal loading for all monometallic catalysts was 5, 20, 40, 60 % wt of Ni or Cu and 1 % wt Pd.

The reactivity results in oxy-steam reforming of methanol showed that copper catalysts are more active than nickel catalysts independently on the support. It was also found that addition of palladium into copper or nickel catalytic system improves the activity and selectivity of monometallic catalyst in OSRM reaction. The selectivity results towards hydrogen formation showed also that monometallic Cu and bimetallic Pd-Cu systems exhibited higher selectivity values compared to the nickel based catalysts. The same tendency was observed in the case of the selectivity results towards carbon dioxide formation. It was also confirmed that activation process performed in a reducing mixture (5 % H_2 -95 % Ar) improves the catalytic activity of both copper and nickel based supported catalysts. The highest methanol conversion and selectivity towards hydrogen formation in OSRM reaction of the reduced Pd-Cu catalyst was explained by Pd-Cu alloy formation.

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BIMETALLIC Pd-Cu/ZnO-Al₂O₃, ZrO₂-Al₂O₃ CATALYSTS FOR METHANOL SYNTHESIS

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Methanol (methyl alcohol, CH₃OH, MeOH) is a key industrial raw material produced via a large-scale synthesis over heterogeneous catalysts. Although the current technological process was developed several decades ago, methanol synthesis still enjoys great popularity. In recent years the global growth of methanol production was observed, which is directly connected with broad potential possibilities of using it as a raw material for the chemical industry or as a source of energy. The main direction of its application is the production of formaldehyde, acetic acid, acetic anhydride, methylamine, methyl chloride and as a solvent. Methanol can also be used directly as a motor fuel. The processing operations of methanol to fuel are also performed (MTG – methanol to gasoline, MOGD – methanol to gasoline and diesel). New technologies are being also developed for producing methanol from ethylene and propylene (MTO – methanol to olefins). In addition, methanol is also the leading source of hydrogen used in a constantly developed fuel cells technology [1].

The escalation of anthropogenic sources of CO₂ emissions affecting on the global warming effect obliges us to adopt efforts, in order to find new and better ways to meet the growing global demand for energy, whilst reducing greenhouse gas emissions. Therefore, in recent years much attention was focused on the possibilities of the methanol synthesis from carbon dioxide and hydrogen [2,3].

The main goal of this study was to investigate the effect of the addition of palladium on the physicochemical properties of copper catalysts and to determine their activity in methanol synthesis reaction carried out from a mixture of carbon dioxide and hydrogen.

A support material has been prepared by co-precipitation of hydroxides of aluminum and zirconium or zinc from aqueous solutions of appropriate nitrates. Next the mixtures of hydroxides were dried and calcined in air atmosphere for 4 h at 400 °C. An active phase (20 % wt of Cu) was introduced by wet impregnation method, then the samples were dried and calcined in air at 400 °C for 4 h. In the case of bimetallic supported catalysts palladium (2 % wt) was deposited on monometallic copper catalyst surface also by impregnation method. In order to

OP-III-6

achieve the purpose of the work the catalytic systems were characterized by various techniques such as: XRD, TPR-H₂, TPD-NH₃, TOF-SIMS, FTIR, SEM-EDS and BET techniques. The catalytic activity tests were carried out in gradientless reactor at 220 °C after 12 h catalyst stabilization. Methanol synthesis was carried out using a mixture of hydrogen and carbon dioxide in a molar ratio CO₂ : H₂ equal 1 : 3. The total flow of the reaction mixture was 80 cm³/min. The analysis of the reaction products was carried out by an on-line gas chromatograph.

The specific surface area measurements performed for all catalysts systems confirmed that introduction of the copper or palladium oxides result in decrease of the specific surface area, what can be explained by blocking of the supports pores by the remaining oxide phase. The acidity measurements carried out for mono- and bimetallic catalysts showed that the introduction of copper oxide into the carrier increases the total acidity of the catalyst system. A similar effect is observed after the introduction of palladium into copper catalyst. The phase composition studies of monometallic copper and bimetallic catalysts reduced at 300 °C in 5 % H₂-95 % Ar mixture showed the presence of metallic copper and the formation of an alloy Pd-Cu phase after activation process, respectively. The formation of the alloy phase was confirmed also by chemisorption of CO FTIR measurements performed for bimetallic catalyst. The catalytic activity measurements performed for the copper catalysts systems supported on ZnO-Al₂O₃ or ZrO₂-Al₂O₃ support showed similar yield in the methanol synthesis reaction carried out from the mixture of carbon dioxide and hydrogen. In addition, the promoting effect of palladium on the catalytic activity and selectivity toward the main reaction product – methanol in the case of copper supported catalyst was confirmed. The improvement of the activity and selectivity of the copper catalyst promoted by palladium should be associated with the formation of Cu-Pd alloy during activation process performed in a reductive mixture of 5 % H₂-95 % Ar at 300 °C.

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POSTER PRESENTATIONS

EFFECTIVENESS OF HDT CATALYSTS DURING CO-PROCESSING OF BIOMASS AND PETROLEUM FRACTIONS

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Hydrotreating of petroleum fractions with lipids feedstocks offers a unique opportunity to produce a sustainable diesel fuel completely compatible with existing fuel infrastructure and engine technology. In this research two commercial catalysts were evaluated ($\text{NiMo/Al}_2\text{O}_3$ and $\text{CoMo/Al}_2\text{O}_3$) regarding their efficiency in hydrodesulfurization (HDS) reactions on co-hydroprocessing of petroleum fraction (gas oil, GO) with a residual lipids feedstock (waste cooking oil, WCO) [1]. Both catalysts were examined in three reaction temperatures (330° , 350° and 370°C) and three GO/WCO blends (100/0, 90/10 and 70/30 v/v) [2].

The results have showed that the presence of WCO in the feed has no obvious effect in the case of the $\text{NiMo/Al}_2\text{O}_3$ catalyst, even in the lowest T (330°C), rendering S removal of 89.1 %, 92 % and 91,89 % for the 100/0, 90/10 and 70/30 blends respectively. In fact, the addition of WCO appears to have positive influence in HDS, as WCO is a sulfur free feedstock, so the HDS efficiency could be theoretically improved, assuming there are no other competitive reactions or catalyst deactivation due to WCO hydroprocessing by-products (CO , CO_2 , H_2O).

The opposite trend was observed with CoMo catalyst. The HDS efficiency of CoMo is significantly affected by the addition of WCO, specifically in the case of the lowest T (330°C), sulfur removal drops from 98 % (100/0 blend) to 87.1 % (90/10 blend) and to 80.9 % (70/30 blend). The HDS effectiveness loss indicates that in the case of CoMo catalyst, the HDS reactions compete with other parallel reactions. Therefore, even though the CoMo catalyst was more effective for pure GO hydrotreatment, the NiMo catalyst is more suitable when WCO co-processing with GO is intended.

As a result an attempt has been made to investigate how the WCO presence influences CoMo activity. The fact that a CoMo catalyst is not as appropriate for co-processing can be attributed to the by-products produced via co-hydroprocessing. Oxygen, as it hinders fuel produced properties, is required to be removed via

PP-1

deoxygenation, decarboxylation and decarbonylation reactions [3]. More specifically, during co-hydroprocessing of petroleum fractions with liquid biomass, carbon monoxide (CO), carbon dioxide (CO₂) and water (H₂O) constitute some of the main by-products which take place due to the oxygen content of biomass. Due to the H₂O, CO₂ and CO formation, it is possible that two competing reversible reactions also take place in the hydrotreating reactor during co-processing, the water gas shift or WGS and methane steam reforming reactions [4]. The influence of the three aforementioned by-products on HDT reactions and on CoMo catalyst activity was examined. In Figure 1, it is depicted how by-products addition affects HDS effectiveness.

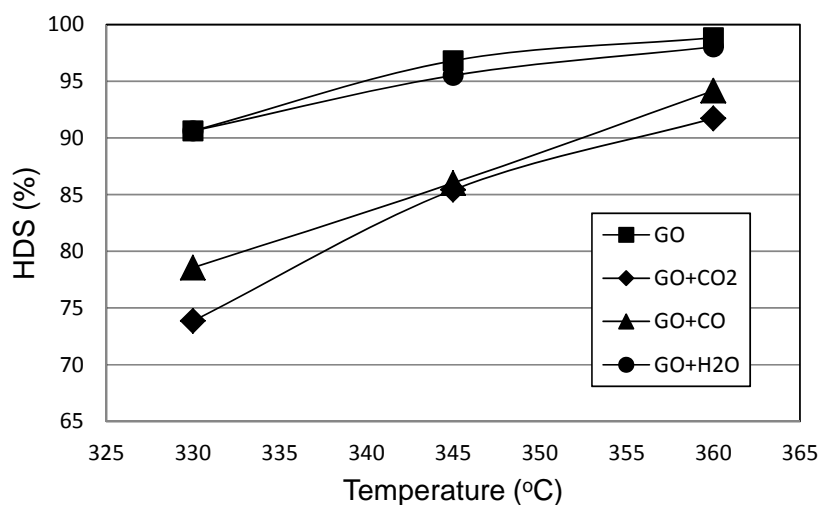


Figure 1. HDS (wt %) of net GO hydrotreatment, GO with CO₂, GO with CO and GO with H₂O at three hydrotreating reaction temperatures

According to Figure 1, H₂O does not influence any key hydrotreating reaction. This can be attributed to the formation of more active dispersed MoS_x species when H₂O is added according to previous studies. An inhibiting effect was, however, observed in the case of CO and CO₂, which is probably attributed to the aforementioned competitive reactions like WGS and methanation, as well as to the absorption of CO or CO₂ on active sites of CoMo catalyst.

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MESOPOROUS AROMATIC FRAMEWORKS AS MATRIX FOR IN SITU PREPARATION OF HYDROGENATION–HYDROCRACKING CATALYSTS

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Porous aromatic frameworks (PAFs) are a new class of porous organic frameworks with regular rigid aromatic structure. Due to their high surface area, thermal and chemical stability, relatively facile functionalization, these materials can be applied in gas storage, gas separation and heterogeneous catalysis [1-3].

Applying PAFs as support for metal nanoparticles is relatively new field of scientific research. Hydrophobic nature of PAF surface improves the transportation of organic substrates, especially arenes, within the pores in comparison with conventional inorganic supports, and rigid ordered structure of PAFs is expected to be a better stabilizer for metal NPs than classical carbon supports.

Recently we have reported the synthesis and effective usage of ruthenium-containing hydrogenation catalysts based on porous aromatic frameworks with diamond-like structure and 3 or 4 benzene ring in the edge [4]. We demonstrated that the structure of the support influences on the catalysts' properties: a size-selective hydrogenation was observed for the catalyst, based on a framework with lesser pore size.

One of the current problems of modern petrochemistry is conversion of heavy hydrocarbons into light products by hydrocracking-hydrogenation reactions. Significant part of these hydrocarbons make up polycyclic aromatic hydrocarbons, such as naphthalene, anthracene, phenanthrene and their derivatives. The traditional hydrocracking conditions include usage of heterogeneous catalysts and high pressures and temperatures. However, the systems "heterogeneity" itself inevitably leads to the enormous role of the diffusion limitations, high probability of polymerization processes resulting in polyaromatic condensed systems and coking, metal deposition on the inner surface under the bulky substrates conversion.

The probable solution of this problem is the transition to slurry processes, in which catalyst's particles have a size of micrometer and less. In this case the diffusion limitations and deactivation probability are decreased due to the carbon depositions,

PP-2

which likely appear as support for the active component. The possible way to do that is to use such catalysts, which can “adapt” themselves in the particles size to the reaction system due to the presence of special carrier-binder for the polymeric nanoparticles. We believe that porous aromatic frameworks will be excellent material for these purposes due to rigid aromatic structure, a wide range of thermal stability and possibility to control the probable initial particle size by changing the material structure.

Starting from PAF-11 framework, we synthesised two different types of catalysts: Ru-PAF-11 (aprox. 5 % Ru), prepared according to a previously reported method [4], and NiWS-PAF-11 (15 % W), obtained through impregnation of $[N(n-Bu)_4]_2[Ni(WS_4)_2]$ with PAF-11 in THF and subsequent evaporation of solvent. Both catalysts were tested in hydrocracking-hydrogenation reactions of naphthalene at 380 °C and 5 MPa H_2 . Notably, the addition of the elemental sulfur to the reaction mixture improved the activity of catalysts.

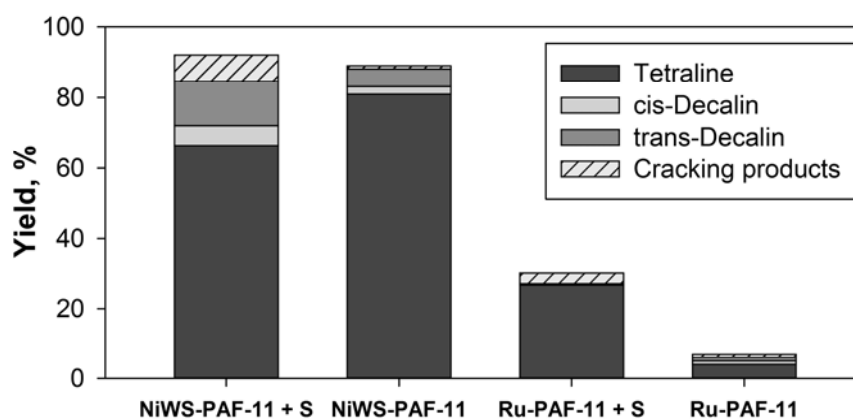


Figure 1. Performances of catalysts in naphthalene hydrocracking reaction

Reaction conditions: 80 mg of naphthalene, 2 ml of benzene, 50 mg of catalyst, 50 mg of sulfur (optional), H_2 (5 MPa), 380 °C, 5 h.

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COLOPHONY HYDROCONVERSION OVER Pt-CONTAINING MESOPOROUS SILICA-ALUMINA CATALYST

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Colophony or rosin is a natural substance obtained by distillation of oil from trees of the pine family. It mainly consists of various monocarboxylic acids typically having the molecular formula $C_{20}H_{30}O_2$ and contains about 70 % of abietic and dehydroabietic acids [1]. Due to the increasing demand for biomass-derived gasoline and diesel fuel additives the idea to use rosin as a feed is very attractive. The chemical route to convert resin acids includes several steps: carboxylic acid functional groups removal to create hydrocarbons, double bonds hydrogenation to form saturated tricyclic ring compounds and ring opening to get branched cycloalkanes [2]. All these reactions can occur over bifunctional catalytic systems combining acidic and hydrogenation functions. It is well known that Ni, Co, Pt, Pd-containing catalysts are usually used for hydrogenation reactions [1-3]. Alumina oxide and zeolites are conventional acidic supports for catalysts preparation but nowadays mesoporous silica-alumina materials, having high surface area and large pore structure, increasingly replace them. Thus the aim of the work was to investigate the behavior of Pt-containing mesoporous silica-alumina catalyst in hydroconversion of rosin.

The composition of colophony, according to analyses by GS-MS was 28 % wt abietic acid, 34,6 % wt dehydroabietic acid, 12,1 % wt tetrahydroabietic acid, 3,6 % wt pimaric acid and 21,7 % wt of an unidentified compound. Mesoporous silica alumina material Al-HMS was prepared according [4] and then was impregnated with H_2PtCl_6 solution, dried and reduced in H_2 flow. Finally synthesized catalyst composed 1 % wt Pt and $SiO_2/Al_2O_3 = 10$ mol. and was characterized by the complex of analytical methods. Hydroconversion was performed using 50 % wt solution of rosin in o-xylene in a batch 20 ml reactor under vigorous stirring. The temperature, H_2 pressure and the time of reaction were varied. Reaction products were analyzed by GC, HPLC and IR spectroscopy methods.

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1%Pt/Al-HMS catalyst had a surface area of 900 m²/g and 4,2 nm pore diameter as measured by nitrogen physisorption. Platinum particles size estimated by TEM was in the range 3-13 nm. NH₃ adsorption data allowed to establish the medium acidic properties of the synthesized catalyst.

The conversion of rosin in a temperature range from 300 to 350 °C was 100%. The identified by GC-MS products were methyl- and i-propyl- substituted tri- and bicyclic hydrocarbons. Reaction products were also analyzed using simulated distillation method to find their fractional composition. It was shown that reaction temperature increasing led to rising the yield of light hydrocarbon fraction boiling below 180 °C and decreasing the high boiling fraction (>360 °C) yield, wherein the yield of diesel fraction almost remains unchanged and reaches 85 wt.% (Fig.1).

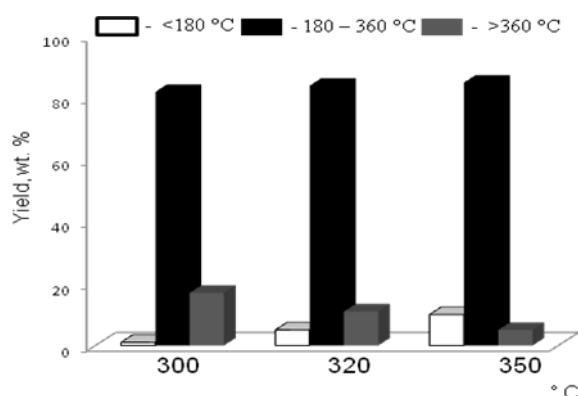


Fig. 1. – Colophony hydroconversion products fractional composition (5 MPa, 5 h, feed/catalyst=20 wt.)

Aromatic hydrocarbon content in the reaction products was estimated using HPLC and it was shown that reaction temperature and H₂ pressure increasing give the possibility to reduce total aromatic content up to 10 wt. %, that

indicates high hydrogenation activity of 1%Pt/Al-HMS catalyst.

Thus catalytic systems based on mesoporous silica-alumina materials can be successfully applied for effective deoxygenation, hydrogenation and cracking of colophony.

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ACTIVITY OF SULFIDE NANOPARTICLES FORMED FROM POLYMETALLIC PRECURSORS IN SLURRY-PHASE HYDROCRACKING

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Slurry phase hydrocracking has proved to be an efficient way to process heavy petroleum feedstock and coal derived liquids. A number of catalyst precursors mainly containing Mo (W) and Co (Ni) compounds have been investigated. Among others, achieving the proper selective interaction between Co (Ni) and Mo (W) and their complete participation in bimetallic sulfide formation is a serious problem for slurry phase hydrogenation processes. Sulfidation of a mixture of individual Co (Ni) and Mo (W) compounds may result in a great amount of monometallic sulfides much less active in hydrogenation/hydrodesulfurization reactions rather than bimetallic sulfides. Utilization of bi- and polymetallic precursors may be a key for solving the problem of poor promotion of Mo (W) sulfide by Co (Ni).

Polycarboxylic acids, for example oxalic, citric, polyacrylic acids seem to be proper ligands to carry several transition metal atoms and also a cracking catalyst metal, such as aluminum, zirconium, if needed. Bimetallic water-soluble complexes have been successfully applied to prepare supported hydrodesulfurization catalysts [1–5]. The current investigation deals with catalytic activity of unsupported sulfides obtained from polycarboxylic acid precursors in hydrocracking of model feedstock.

Citric acid and poly(acrylic acid) as chelating agents were used to synthesize Mo-Co-Ni, Ni-W-Mo and Zr-Mo-Co-Ni aqueous complexes from corresponding inorganic salts. The ratio of (Ni + Co)/(Mo + W + Ni + Co) was varied in order to determine precursor composition that provides the highest degree of promotion of Mo (W) by Co (Ni). Catalytic properties were evaluated in a batch reactor under continuous stirring, initial hydrogen pressure 2 MPa, hydrogen : substrate molar ratio 13:1 and in a temperature range 385-420 °C. Naphthalene and methylnaphthalenes 10 % wt solutions in *n*-hexadecane were used as a model feedstock, and dimethyldisulfide was added to a feedstock as a sulfiding agent. Molar ratio Mo : substrate was 1:59.

Among with determining the optimal precursor composition, different ways for the precursor introduction into the feedstock were analyzed, that is via water-in-feed

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emulsion, dimethyl sulfoxide (DMSO)-in-feed emulsion and in metal oxides suspension obtained by precursor thermal decomposition. Further some of precursors were formed *in situ*, i.e. in feedstock by introducing poly(acrylic acid) and inorganic metal salts.

Catalysts activity in hydrogenation reaction turned out to be sensitive to water concentration in emulsion and generally decreased with water content increase. Addition of a surfactant does not alter the conversion. However, DMSO-in-oil emulsions demonstrated the lowest conversion that is due to intensive formation of metal oxides instead of sulfides. For instance, naphthalene conversion decreased from 44 % to only 20 % when DMSO was used instead of water to introduce Ni_{1,7}WMo₃-citrate in the feedstock.

Activity of the catalyst formed from Ni_{1,7}WMo₃-citrate was compared with that of the catalyst formed from water emulsion of separate inorganic salts under the same naphthalene : Mo ratio and the same metal composition. Under almost the same conversion the first precursor provides higher selectivity towards decaline formation. So polycarboxylic acids as chelating agents enhance formation of polymetallic compounds with close spacing between Co (Ni) and Mo (W) [1] that favors generation of CoMoS (NiWS) phase under sulfidation.

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LIGHT CYCLE OIL HYDROCRACKING AND HYDRODEAROMATIZATION ON UNSUPPORTED Ni-W-S CATALYSTS SYNTHESIZED *IN SITU*

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In recent years the interest in studying of nanoscale particles as catalysts in dispersion systems significantly increased. It is connected to the fact that new promising possibilities of using nanomaterials in many areas of science and technology in particular to obtain of efficient and selective catalysts has been discovered [1-2]. The such dispersed-phase catalytic approach was used for hydroconversion of heavy oil residue, in Fischer-Tropsch process [3]. In this research *in situ* synthesis and catalytic activity in hydrogenation of aromatic hydrocarbons in the presence of nanosized tungsten/nickel sulfides are described.

The preparation method of sulfide catalysts *in situ* in the hydrocarbon solution of substrate for the hydrogenation of polyaromatic hydrocarbons was developed. Oil-soluble salts were used as precursors: tungsten carbonyl $W(CO)_6$ and nickel(II) 2-ethylhexanoate $Ni(C_7H_{15}COO)_2$. Optimal W/Ni ratio was 1/2.

The hydrogenation of aromatic compound has been conducted under hydrogen pressure of 5 MPa and the temperature 350 °C, with the hydrogen/feed about 60. As a substrate the naphthalene, methylnaphthalenes and dimethylnaphthalenes in various solvents, such as hexadecane and benzene, have been selected. For the obtained catalysts the possibility of light cycle oil (LCO) hydrotreating has been investigated.

The catalysts were characterized by high resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS).

Analysis of hydrogenation products of model systems was performed on gas chromatograph. The quantitative content of aromatic hydrocarbons in the LCO hydrogenation products determined by high-performance liquid chromatography (HPLC). Component composition was determined by two-dimensional gas chromatography mass spectrometry (Pegasus® 4D GCxGC-TOFMS).

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It was shown that the catalytic system W/Ni has the high catalytic activity. When the ratio of naphthalene/tungsten was 105/1 and reaction time 10 hours naphthalenes conversion was 100 % and decalins selectivity was more than 50%.

For obtained catalysts the possibility of light cycle oil (LCO) hydrotreating has been investigated. It was shown that this catalyst reduced total sulfur content from 3500 to 58 ppm (HDS = 98.3 %) and total aromatic content from 55.5 to 21 wt % (dearomatisation degree was 62 %) while poly- and diaromatic hydrocarbons were almost absent in the products.

The influence of several zeolites HY (provided by Zeolyst) with different ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ (5.2, 60, 80) has been investigated. It was demonstrated that zeolite Y addition provided a considerable increase part of hydrogenation products as well as cracking products. Thus using unsupported nanosized Ni-W-S catalysts in combination with zeolite made it possible to produce the component of gasoline fraction from low-valuable feedstock like LCO.

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MoNiW SULFIDE CATALYSTS FOR AROMATICS HYDROGENATION SYNTHESIZED BY THERMAL DECOMPOSITION OF POLYMER-METAL COMPLEXES

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The outstanding catalytic actions of nanoscale well-dispersed particles in the processes of hydrogenation (HYD) as well as in performing hydrotreating reactions (HDS, HDN) have attracted great attention of scientists [1]. Many methods have been proposed for preparing unsupported sulfide catalysts, among them: thiosalt decomposition, including decomposition in ionic liquids [2], hydrothermal and solvothermal processes, homogeneous sulfide precipitation. In present work, unsupported bi- NiW, CoMo, NiMo and trimetallic Ni(Co)MoW sulfides with different metal content were obtained by in situ thermal decomposition of polymer–metal complexes prepared using water-soluble and oil-soluble hyperdispersants – maleic anhydride copolymers and various metal precursors such as ammonium heptamolybdate, molybdenum hexacarbonyl, nickel acetate and 12-tungstophosphoric heteropolyacid [3]. It was hypothesized that these polychelates-precursors would provide an effective alternative method of obtaining carbon-containing active Ni(Co)MoW-sulphide phase well dispersed with good HYD catalytic properties.

An activity test for naphthalene (dissolved in n-hexadecane) hydrogenation was performed in a batch stirred reactor at the temperature of 400 °C and a pressure of 2.0 MPa in the presence of sulfur-containing substances. The in situ synthesized particles have been characterized by high resolution transmission electron microscopy (HRTEM),) and X-ray photoelectron spectroscopy (XPS). Thermogravimetric method was used for the evaluation of polychelates's thermal stability.

The research results showed that the hydrogenation activity of carbon-containing NiMoW sulfides obtained by polymer-metal complexes decomposition depends on the water content in precursor, ratio of the metal content in the active phase and decomposition condition. Mo_{1,7}NiWS_x-catalyst prepared from oil-soluble polymer-

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metal complex demonstrated the highest activity in the hydrogenation of naphthalene compared to other samples.

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IMPROVEMENT OF THE ADSORPTION-CATALYTIC SYSTEM FOR ORGANIC IMPURITIES REMOVING

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Removal of volatile organic compounds (VOCs) from industrial waste gases is a very important problem of atmospheric air protection. For diluted gases it is expedient to use thermal and catalytic oxidation of VOCs with oxygen to carbon dioxide and water vapor. The treatment of atmospheric emissions with very low concentrations of impurities (below 0.1 g/m³) is a serious problem, as it requires an additional energy input. Adsorption-catalytic processes based on adsorption of VOCs directly on deep oxidation catalyst's surface at low temperature with periodic regeneration of the catalyst by oxidation of the adsorbed impurities at elevated temperatures are of particular interest in this problem solution [1]. However, their disadvantage is a partial desorption of unoxidized VOCs during heating of the catalyst that leads to the reduction of the purification degree [2].

This study is dedicated to the improvement of the catalyst bed structure, aimed at reduction of the energy consumption and maximal VOCs concentrations in outlet gas during regeneration.

To reduce the energy consumption for initiation of regeneration it's proposed to dispose the heater directly in the catalyst-adsorbent bed inlet part (Fig. 1). During the heating of catalyst bed the adsorbed VOCs start to oxidize with emission of heat, forming a heat wave. The wave expands in all directions due to the heat conductivity, and afterwards the process proceeds in the autothermal regime, not requiring further heating, thus allowing to minimize the process energy consumption. In addition, the process may be realized in a continuous mode using unpurified inlet gas as a regenerating flow.

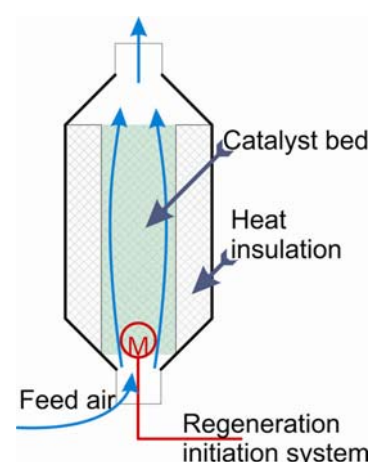


Fig. 1. Heater disposition

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Reduction of the emission of VOCs during the regeneration may be provided by division of catalyst bed into parallel non-interconnected sections in the plane along the gas flow moving (Fig. 2). Each of these sections has an independent heater and the inlet flow is divided between all sections. The regeneration is performed in all sections by turn. The outlet flow of regenerating section mixes with the outlet flows of other sections. Such mixing minimizes the peak concentration of desorbed VOCs in total outlet flow.

The proposed theoretical technological improvements of adsorption-catalytic bed were confirmed by pilot tests in 2-liter catalyst bed with styrene in feed air. The experiments were performed with lean styrene gas (55 ppm styrene in air). The purification degree in these experimental series with styrene was as high as 97–99 %.

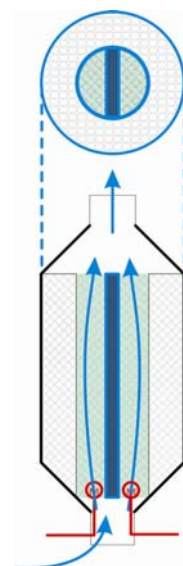


Fig. 2. Reactor with 2 sections

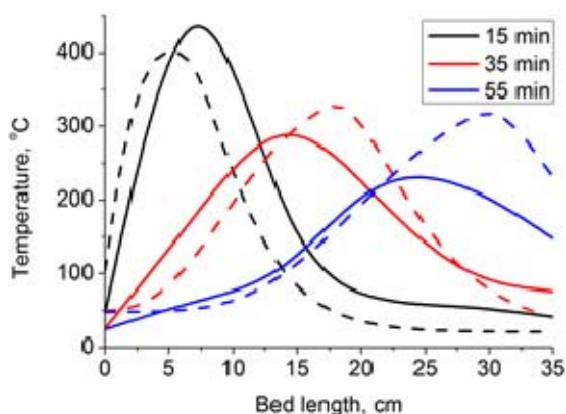


Fig. 3. Experimental (solid) and simulated (dashed) temperature profiles along the reactor axis.

The experiments were also simulated using the mathematical model, proposed earlier [3]. Fig. 3 shows the good accordance between model and experimental profiles.

The described process may be used for efficient and energy-saving purification of waste gases from hydrocarbons and VOCs at oil processing and petrochemical plants.

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PHYSICAL AND CHEMICAL PROPERTIES OF CuCr_2O_4 -BASED GLASS FIBER CATALYST SYNTHESIZED BY SURFACE THERMO-SYNTHESIS METHOD

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Catalytic incineration of volatile organic compounds (VOC) in the waste gases of oil refineries and petrochemical plants is an important environmental protection task worldwide. Catalysts for VOC oxidation are based on transient metals oxides and spinels like CuCr_2O_4 , MnO_x etc. Traditional granulated catalysts are characterized with significant diffusion limitations and high pressure drop. Glass-fiber catalyst (GFC) is a relatively new type of catalytic systems, where the support represents itself the glass microfibers, structured in form of threads in the woven or knitted fabrics. The GFCs may be structured in a form of cartridges, characterized with a low pressure drop and extremely low mass transfer limitations [1].

The samples of CuCr_2O_4 -based GFC for VOC oxidation were prepared by means of the surface thermo-synthesis method [2]. As shown by experiments performed with the model reaction of toluene deep oxidation in air [2] the CuCr_2O_4 -based GFC has the unit activity per volume of the catalyst bed is closed to that of the similar commercial granular catalyst ICT-12-8 ($\text{CuCr}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$). At the same the mass amount of the GFC in the structured cartridge is by an order of magnitude lower than that for ICT-12-8 bed of the same volume. Therefore, the unit activity of CuCr_2O_4 -based GFC per unit mass of the catalyst at 350 °C exceeds the activity of the conventional catalyst by more than an order of magnitude.

A sample of CuCr_2O_4 -based GFC and commercial $\text{CuCr}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalysts was studied by a complex of physical and chemical methods (XRD, SEM, TEM). An analysis of diffractograms GFC obtained by XRD confirmed the presence of phase $\text{Cu}(\text{CrO}_2)_2$ (structure type spinel, $I4_1/amd$) also present are reflexes phases $\alpha\text{-Cr}_2\text{O}_3$ (structural type $\alpha\text{-Al}_2\text{O}_3$, $R3c$) and CuO (structural type NaCl , $C2h$). According to the data obtained by the SEM agglomerate, the size of the active component in the conventional catalyst varies from 1 to 2 μm (figure 1.a). The number of smaller agglomerates with oval shape with sizes 250-500 nm and 400-600 nm is less than 5 %. The sample has a layered structure with an absence of voids. In the GFC sample, the oval form agglomerates with sizes varying from 75 to 150 nm and from

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100 to 200 nm (figure 1.b) were detected. The agglomerates with the dimensions up to 2 μm were observed. According to the image received by the TEM of the reference catalyst, the active component is generally distributed uniformly over the surface of support (figure 2.a). In some areas concentration of active component varies over a wide range (from light to dark). According to obtained TEM data, the $\text{Cu}(\text{CrO}_2)_2$ phase is localized in the GFC in a form of large agglomerates from 500 nm to 2-3 μm on the surface of support and separately from it (figure 2.b). The agglomerates are composed mainly from particles with sizes 15 to 25 nm.

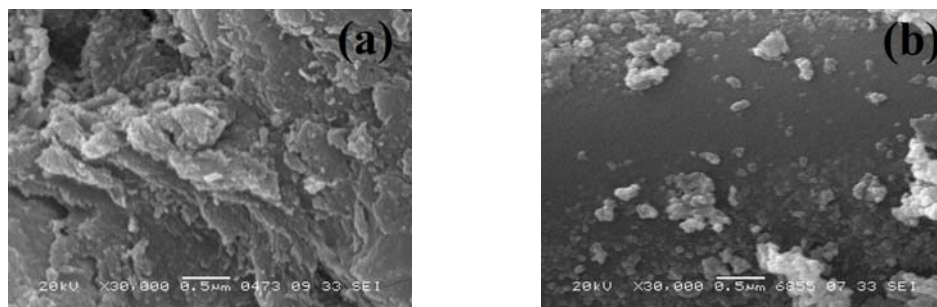


Figure 1. SEM images of commercial $\text{CuCr}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst (a) and GFC (b)

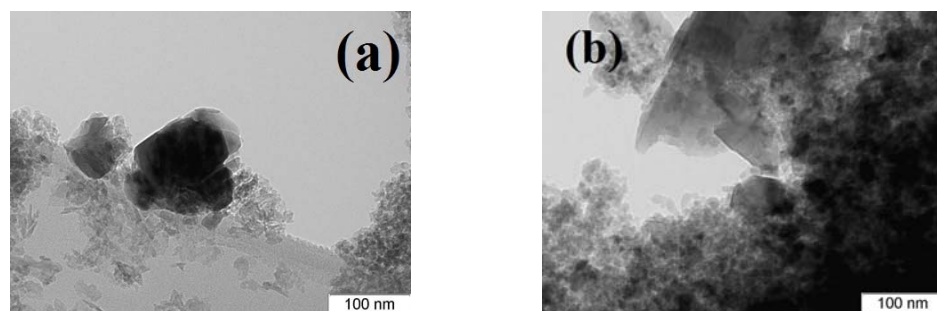


Figure 2. TEM images of commercial $\text{CuCr}_2\text{O}_4/\alpha\text{-Al}_2\text{O}_3$ catalyst (a) and GFC (b)

Characterization of GFC catalyst by SEM, TEM as compared with conventional granular catalyst showed that the morphology of glass-fiber catalyst presented as particles of active component with a sizes 10-25 nm. Used method of preparation promotes deeper penetration of the active component in the subsurface layers (1-4 nm) of the support as compared with traditional catalysts. Summarizing, the much higher apparent activity of the CuCr_2O_4 -based GFC GFC in comparison with the similar conventional catalyst is explained by both the significantly improved mass transfer and the more highly dispersed active state of the iron oxide in the GFC.

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PHYSICAL AND CHEMICAL PROPERTIES OF FeOx-BASED GLASS FIBER CATALYST SYNTHESIZED BY SURFACE THERMO-SYNTHESIS METHOD

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Improvement of the sulfur recovery degree in Claus plants is a traditionally important environmental protection task in the processing of natural gas and oil. The main tool for efficiency increase of sulfur recovery over the last few decades is the application of Claus tail gas clean-up processes including those based on selective catalytic oxidation of hydrogen sulfide into sulfur by oxygen [1]. These processes use the catalysts on the base of iron oxides, which are characterized with high H₂S oxidation selectivity into sulfur. However, these catalysts have rather low activity, especially, at temperatures below 200 °C. Another important challenge in this area is development of the catalyst with enhanced mass transfer properties. Glass-fiber catalyst (GFC) is a relatively new type of catalytic systems, where the support represents itself the glass microfibers, structured in form of threads in the woven or knitted fabrics. The glass-fiber catalysts (GFCs) may be structured in a form of cartridges, characterized with a low pressure drop and extremely low mass transfer limitations [2].

The sample of FeOx-based GFC catalyst for H₂S oxidation was prepared by means of the surface thermo-synthesis method [3]. As shown in experiments, the unit activity of the FeOx-based GFC (calculated per unit mass of the active component) is much higher than that of the conventional catalyst – the difference exceeded an order of magnitude [3].

A samples of GFC and commercial FeOx/Al₂O₃ catalysts were studied by a complex of physical and chemical methods (XRD, SEM, TEM). Crystalline Fe-containing phase in GFC was not observed by XRD. So it was concluded that this phase is either amorphous or particles are very small (< 2 nm). According to the data obtained by the SEM, agglomerate size of the active component granular catalyst IKT 27-42 varies from 250 to 500 nm and of 300 to 700 nm (figure 1.b). They have an oval shape to form agglomerates with sizes varies from 2 to 4 μm. In the GFC sample detected oval form agglomerates with sizes varies from 50 to 60 nm and 70-

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100 nm (figure 1.a). There are two types of agglomerates; small and medium (figure 1.a). Complex formation of irregular shape have an explicit border.

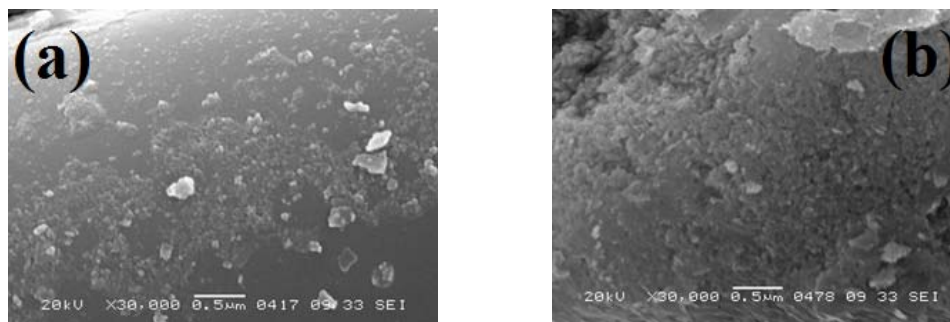


Figure 1. SEM images of glass-fiber (a) and commercial FeOx/Al₂O₃ catalyst (b)

According to TEM, a sample GFC silica is localized in the form of large porous particles on the surface of GF or separately from it (figure 2.a).

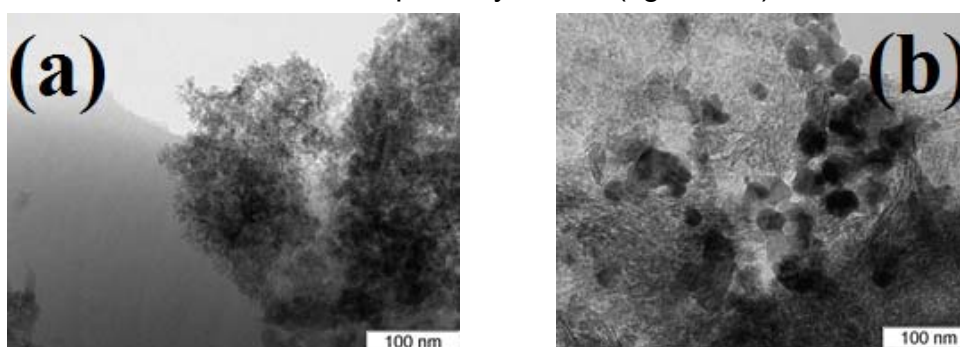


Figure 2. TEM images of glass-fiber (a) and commercial FeOx/Al₂O₃ catalyst (b)

Iron is mainly in the form Fe₂O₃ of islet formations with longitudinal size of 1 to 2 nm and a thickness 0.5-1 nm on the surface and in the subsurface (4-5 nm) layer of silica.

Characterization of GFC catalyst by SEM, TEM as compared with conventional granular catalyst showed that the morphology of glass-fiber catalyst presented as highly dispersed particles of active component with a sizes 1-2 nm (figure 1, 2).

We may summarize that the excellent catalytic performance of Fe-based GFCs in the H₂S selective oxidation reaction is explained by both the significantly improved mass transfer and the more highly dispersed active state of the iron oxide in the GFC.

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MONOMETALLIC Ni SUPPORTED CATALYSTS FOR OXY-STEAM REFORMING OF METHANOL

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A promising method for generation of hydrogen can be oxy-steam reforming of methanol process. Given the relatively mild conditions for conducting this process ($P = 1 \text{ atm}$, $T = 160\text{-}350 \text{ }^\circ\text{C}$), it appears possible to produce hydrogen directly at the place where it is needed. Production of hydrogen by mixed oxygen-steam reforming method of methanol enables running reaction in auto-thermal way, which is economically very advantageous [1]. The main goal of this work was investigation the influence of the kind of support (SnO_2 , Al_2O_3 , CeO_2 , ZnO , $\text{ZnO-Al}_2\text{O}_3$, $\text{CeO}_2\text{-Al}_2\text{O}_3$, $\text{SnO}_2\text{-Al}_2\text{O}_3$) on physicochemical and catalytic properties of monometallic nickel supported catalyst in oxy-steam reforming of methanol (OSRM). The physicochemical properties of the support and supported nickel catalysts were determined by surface area measurements (BET), X-ray diffraction (XRD), temperature – programmed reduction (TPR_{H_2}), scanning electron microscope (SEM – EDS) and temperature – programmed desorption ($\text{NH}_3\text{-TPD}$) techniques. The activity tests in oxy-steam reforming of methanol (OSRM) reaction were carried out over prepared catalysts in the temperature range 200 to 300 °C in a flow quartz tubular reactor under atmospheric pressure. The ratio of the reactants in the studied reaction was $\text{CH}_3\text{OH} : \text{H}_2\text{O} : \text{O}_2 = 1 : 1 : 0.4$, respectively.

The activity results performed for all catalysts showed that nickel systems supported on binary oxides exhibited higher activity compared to the same systems supported on monoxide. The highest methanol conversion in the studied reaction exhibited Ni catalysts supported on $\text{ZnO-Al}_2\text{O}_3$ oxide. The reactivity results performed in the studied reaction showed that activity of the studied systems is associated with the dispersion of active phase. It was also found that reducibility and the acidity of the investigated catalysts has influence on the catalyst activity in OSRM reaction.

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HYDROCONVERSION OF HEAVY RESIDUE ON FINE MoNi CARBIDE CONTAINING CATALYST

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Due to rapid population growth, the consumption of fuels, energy and petrochemical products has increased tremendously. Heavy oils or vacuum residue is considered as an alternate suitable source for transportation fuels, energy and petrochemicals to fulfill the requirements of modern civilization. The goals for upgradation of heavy oils and VR are to decrease viscosity and boiling point, demetallation, desulfurization, level of other impurities and increase H/C ratio with high commercial values. Among all technologies for the conversion of heavy oils and vacuum residues, slurry-phase hydrocracking is the most considerable as it is applicable to upgrade high impurities feeds [1]. A refining process is required for upgrading the heavy oil properties in the presence of catalysts and hydrogen at high pressure. Catalysts must be resistant to deactivation by coke and metals deposits, and also be capable to perform HDS and hydrodenitrogenation (HDN) processes optimally [2].

Transition metal carbides and nitrides have been considered as a possible new generation of catalysts for crude oil hydroprocessing and they have been investigated in processe of HDS [3]. They and have been widely investigated in recent years because of their unique electronic structure and high performance [4]. These catalysts show good catalytic activity and selectivity in hydrogenation, hydrodesulfurization and hydrodenitrogenation in petroleum refining.

Catalysts were prepared using the standard incipient wetness method. Molybdenum and nickel were impregnated at 10 and 3 wt % on carbon black using a aqueous solutions of ammonium heptamolybdate tetrahydrate (Aldrich, 99,98 %) and nickel (II) nitrate hexahydrate, then the sample is dried at 120 °C. Obtained samples were ball milled using a AGO-2 type planetary high energy ball mill with stainless steel vials and balls under air atmosphere for 30 minutes. Prepared samples were tested at 320 °C under a hydrogen atmosphere of 3,5 MPa in hydrodesulfurization model feedstock: solution 4 % dibenzothiophene in heptane. All samples demonstrated high conversion of dibenzothiophene (about 97 %). The reaction

products were cycloalkanes and isoalkanes C6–C7 in an amount 59 % and 38 % respectively. Catalytic tests conducted carbide containing hydroprocessing catalyst during the vacuum residue. Experiment was carried out in a high pressure autoclave without stirring $V = 150 \text{ cm}^3$, $T = 470 \text{ }^\circ\text{C}$, $P_{\text{H}_2} = 7 \text{ MPa}$, the ratio of catalyst : feed = 0.05, the reaction time is 120 minutes. The vacuum residue hydroconversion process with the addition of the catalyst decrease solid products, including coke in 2-3 times in comparison with the process without catalyst.

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EFFECT OF THE COMPONENT COMPOSITION ON PERFORMANCE AND ECOLOGICAL PROPERTIES OF MARINE LOW-VISCOSITY FUELS

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Marine low-viscosity fuel (MLVF) of the highest ecological standard, produced in modern refineries for a country's domestic needs and for export, should comply with the constantly becoming tougher Russian and international standards. Sea basins and SECA areas (SOx Emission Control Areas), where sulphur oxides emission is controlled, and limits are set on its content in marine fuel – no more than 0,1 % wt, are designated in accordance with the "International Convention for the Prevention of Pollution from Ships".

In this regard, the marine low-viscosity fuel's production technique should include hydrogenation processes: hydrofining and, going forward, hydrocracking, producing distillates with a reduced content of sulphur compounds. Involvement of these distillates to MLVF requires a research of their effect on performance and ecological properties of marine low-viscosity fuels along with other used components.

The following results were achieved as a part of the research:

1. The basic physical-chemical and ecological properties of middle distillates of hydrofining, catalytic and thermal cracking processes were measured and analyzed.

2. Hydrocarbon composition is analyzed by the chromatography-mass spectrometry, and the key components of middle distillates of hydrofining, catalytic and thermal cracking processes are found.

3. An interrelation between the basic physical-chemical, ecological and low-temperature properties and hydrocarbon and non-hydrocarbon composition of middle distillates of the oil refining's hydrocatalytic and thermodestructive processes is established.

4. A choice of the optimal manufacture formulation and quality analysis of the marine low-viscosity fuels' test samples with improved ecological and low-temperature properties, which was underlined for development of the industrial technology of producing commercial marine low-viscosity fuels in an oil refinery, were performed on the basis of the dependences, established experimentally.

INTEGRATION OF THE STAGE REFORMING AND HYDROISOMERIZATION OF THE BENZENE-CONTAINING REFORMATE FRACTION AS AN EFFECTIVE WAY FOR IMPROVING THE YIELD AND QUALITY OF HIGH-OCTANE GASOLINE COMPONENTS

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The characteristic tendency of the modern market of motor gasolines in the Russian Federation and foreign developed countries is a toughening of ecological standards on content of aromatic hydrocarbons (incl. benzene) in unleaded gasolines (Euro-5), while maintaining strict requirements to their octane ratings that makes refiners to improve the catalytic production by introducing technologies of receiving high-octane products of non-aromatic type or with a lowered content of aromatic hydrocarbons.

There is a relatively high capacity of catalytic reforming processes in Russia in comparison with the USA and Western Europe: a share of reformates (with a high content of total aromatics and benzene) in the Russian gasoline fund makes about 50 % vol., and a share of catalytic cracked gasoline, isomerates, oxygenates and alkylates, which are high-quality components of modern environmentally friendly motor gasolines, is small, especially when comparing with similar indicators of the USA. Thus, the task of improvement of the reforming process for producing gasoline components (reformates) with improved ecological properties is crucial in Russia. The suggested technology of joint implementation of the stage catalytic reforming and hydroisomerization process allows to produce high-octane gasoline components with a lowered benzene content and marked increase in an yield of a reformat (for 3-6 %) in comparison with the traditional catalytic reforming in a fixed bed.

VIRTUAL PRESENTATIONS

NiW SULFIDE NANOCATALYSTS SUPPORTED ON MESOPOROUS PHENOL-FORMALDEHYDE POLYMERS FOR HYDROGENATION AND HYDROCRACKING

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The use of polymeric carriers with a regular structure to create metal-containing catalysts for various petrochemical processes is one of the fastest growing areas of catalysis [1]. Mesoporous phenol-formaldehyde polymers as carriers for catalysts combine advantages of inorganic regular mesoporous materials like zeolites and SBA-15 type silica and hydrophobic organic polymers [2]. Recently, we have demonstrated the use of these materials as support for noble metal catalysts in hydrogenation of phenylacetylene and naphthalene [3].

In our work NiW sulfide hydrogenation and hydrocracking catalysts prepared *in situ* by decomposition of sulfur-containing precursors supported on mesoporous phenol-formaldehyde polymer were studied. Ammonium thiotungstate and nickel (II) nitrate hexahydrate or tetrabutylammonium nickel thiotungstate complex $[(n-C_4H_9)_4N]_2Ni(WS_4)_2$ were used as the metal source. Catalysts were analyzed after the *in situ* activation by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). The catalytic properties were evaluated in the hydrogenation of naphthalene, 1-methylnaphthalene, 2-methylnaphthalene, 1,3-dimethylnaphthalene and anthracene in a batch reactor at 380 °C and 5.0 MPa. It is found that the resulting catalysts show high activity in the hydrogenation and hydrocracking of aromatic hydrocarbons. Furthermore, additional sulfurization by dimethyl disulfide or elemental sulfur positively influenced catalytic activity.

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HYDROGENATION OF LINEAR AND CYCLIC OLEFINS ON PALLADIUM CATALYST ON CARBON-SILICA SUPPORT

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The choice of the support, that impacts on activity and selectivity of catalyst, is the most important condition in catalytic hydrogenation of unsaturated compounds by molecular hydrogen over heterogeneous catalysts. In spite of a big amount of researches that address the induction of palladium clusters on different supports, there is no information about the catalytic activity of heterogeneous palladium catalysts on carbon-silica supports combining the properties of hydrophobic carbon materials and silica gels.

The results of research of C=C bond hydrogenation reactions with molecular hydrogen in linear (heptene-1, octene-1, nonene-1, decene-1, hexadecene-1, 1,1-diphenylethylene, vinylbenzene, allyl benzene) and cyclic (cyclopentene, cyclohexene, cyclooctene, norbornene, indene, (–)- α - and (–)- β -pinenes) series on 1÷5 % Pd/C-SiO₂ are presented in this work. The 5 % Pd/C catalyst is used for the compare.

Alkenes with phenyl substituents have the highest velocity of hydrogenation on 5 % Pd/C-SiO₂ in explored α -olefins series with linear structure. In case of linear alkenes (heptene-1, octene-1, nonene-1, decene-1, hexadecene-1) hydrogenation, initial velocity of the process for this series is not related to the alkyl fragment length. With the increase of aliphatic alkenes conversion, as distinguished from olefins with phenyl substituent, the gradual decrease of reaction velocity is observed. It is triggered by hydrogenation products build-up in reacting mass. Generated palladium catalysts are more in hydrogenation reactions in comparison with Pd/C.

STYRENE POLYMERIZATION BY DISPERSING BENTONITE

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Perspective direction of creating ion-exchange composite materials based on natural minerals with highoperating characteristics. The simplest way to obtain them is mechanochemical method [1,2].

In case of intensive dispersion of the solid phase in presence of the monomer, on the newly formed surfaces happenedgraft polymerization [3]. These allow to hydrophobize surface of hydrophilic mineral and improve their compatibility with the polymer. Analogously other methods of modifying solid bodies mechanochemical graft polymerization can be regarded as one of the effective ways of directed change of nature of the particle surface. Thus it is possible to obtain organomineral system with a wide range of applications.

We studied bentonite dispersion with styrene. Final product of the following reaction after separation him from solid part of a polymer, is soluble in organic solventspolymer. In the dynamic conditions of mechanical impact causes a break already grafted to the surface of the macromolecular chains, which explains the formation of the soluble fraction of the polymer. Average molecular weight of 12,000. The small value connected with high concentration of active centers A direct estimate by electron paramagnetic resonance method is result the amount of the last vibration grinding of quartz at -196 °C showed that forms an average of $2 \cdot 10^7$ particles per gram [3]. At higher temperatures their concentration is less, but anyway sufficient to process efficiency does not affected oxygen in the air. As a result, the role of factor of recombination and disproportionation is growing macroradicals.

Another reason for obtaining products with a lou molecular weight is a flowing along with the polymerization processes of degradation of the macromolecules. This is indicated by the data on reduction of the molecular weight of polystyrene.

It should be noted that, when bentonite mixed with styrene is able to induce almost instantaneous polymerization at room temperature in the presence of atmospheric oxygen. This is due to the high activity of the montmorillonite clay, subjected to an acid treatment. This results in substitution of metal cations occupying exchange position on the surface of the bentonite mineral acid hydrogen ions. The result is exchange acid centers (H^+ , Al^{3+}) [4].

Results variations in the yield of percentage of polymer in a system monomer composition (dispersion 15 min, the total amount of the components is 5 g) showed that the mixing ratio bentonite: styrene equal to 60:40 by weight. % leads to the

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highest content of the polymer product, due to favorable conditions for grinding in these conditions and low absolute amount of polymerized substance. Decrease output polystyrene connected with increasing of monomer concentration and system viscosity and decreasing process efficiency.

When dispersing increases the number of active centers, and at the same yield of the polymer increases and then becomes independent of the time of grinding. It is connected to the processes of degradation and worsening conditions for the formation of new centers of the polymerization reaction a result changes in system viscosity.

The results of the extraction data show the different contributions of chemisorption bonds during interaction depending on the ratio of components and the duration of modification of bentonite. The amount to grafting polymers 3-4 %.

The XRD patterns of samples showed that the resulting penetration of macromolecules between the layers of montmorillonite interplanar spacing varies from 14.8 to 15.4 Å.

The structure of the montmorillonite is easily exposed to profound changes in the machining process. [5] Mechanochemical activation in the presence of styrene causes changes in the nearest coordination sphere of aluminum atoms. The NMR spectrum of ^{27}Al present only the signal from the aluminum ions in the octahedral oxygen coordination. Mechanochemical modification of bentonite in environment of styrene reduces of the signal characteristic for aluminum carcass, and is accompanied by a change in position of the maximum signal induced by aluminum atoms in the cation positions downfield. This demonstrates the realization of acid sites related to four-coordinated Al^{3+} during the polymerization of styrene during dispersion.

During the intensive mechanical dispersing of natural bentonite the polymerization of styrene carried in ordinary conditions obtained graft polymers with containing inorganic components and organic nature.

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ALKYLATION OF ISOBUTANE ON COPPERCONTAINING ZEOLITE CATALYSTS

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One of the most perspective directions development of the petrochemical industry - production of the reformulated gasoline which is an alternative environmentally pure power source now. One of receiving which most economically expedient ways the catalytic alkylation (**A**) which is carried out on the catalysts promoted by cations of the 8th group, high cost complicates their broad application.

The copper-containing catalysts on the one hand are effective in reactions of aromatization, isomerization, hydrocracking, with another - are less expensive. Thus, obtaining mechanically strong, thermally stable copper-containing zeolite catalysts (**ZC**), effective in the reactions of A is one of the most important tasks.

The specific surface area (Ssa) found by chromatographic method for thermal desorption of N₂, a total pore volume (V_Σ) - wetness of the water sample, crush strength of granules (P_□) was evaluated in MT-2C, an integral function of Hammett (H₀) - pH metric curves by kinetic control ΔpH liquid solutions (Table 1). The number atoms of Al n(Al) - offset ~1000 cm⁻¹ band IR spectra (SHIMADZUFTIR-8400S).

Synthesis Cu-containing **ZC** was performed promotion by Cu⁰ from solution CuCl₂ zeolite bases HM-G, HM-AS (based on NaM) and HY-G, HY-AG (based on NaY) and modified by dealkalization and dealuminizing. The binders used for the synthesis of carriers liquid glass **LG** (G), and combinations **LG** + pseudoboehmite **PB** ratio of 2:1 (AS) in an amount of 30 mass % [1].

It is found that high values Ssa 320 and 210 m²/g were observed in the **ZC** based on NaY introduction as a binder **LG**, and combinations **LG+PB**. During the promotion Cu⁰ carriers V_Σ increased 0.39 → 0.43 cm³/g (HM-S → HM-G-Cu), 0.30 → 0.33 cm³/g (HM-AG-Cu) and 0,30 → 0,45 cm³/g (HY-AG-Cu), indicating that the restructuring of the sample. Sample HY-AG after promotion Cu⁰ (HY-AG-Cu) characterized by a sharp increase of the specific surface 2 → 258 m²/g, with some decrease in P_□ 4,6 → 4,0 MPa, while reducing function of Hammett H₀ → 8,5 to 9,8, related to the rearrangement of porous pore structure and canals after the

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introduction of atoms Cu^0 , contributing a large number of defects in the prior modification of disordered cells sodalite zeolite carrier.

IR-spectra shows the most intense band about 1000 cm^{-1} relating the stretching vibrations of Si-O-Al in the transition from the carrier **ZC** are shifted, that indicating changes in the silicon-oxygen cell is associated with a decrease in the content of Al in the structure and decreasing size of the unit cell caused by removal Al, and characterize degree deformation in sodalite cell by modified and promotion.

Table 1 – lattice-strength properties of the modified bases and copper containing ZC

Sample	ρ , g/cm^3	V_{Σ} , cm^3/g	Ssa, m^2/g	ρ , g/cm^3	P_{\square} , MPa	H_0	~ 1000 cm^{-1}	n(Al)	SiO_2 / Al_2O_3	X, %		Sel, $\text{C}_5\text{-C}_8$
										0.5 h	1 h	
Catalysts on the base NaM												
HM-G	0.89	0,39	11	0,89	3,1	9,5	1070	21	9.0	-	-	-
HM-G-Cu	0.81	0,43	28	0,81	3,4	8,4	1072	19	9.0	49	40	41
HM-AG	0.89	0,30	4	0,89	4,6	11,2	1079	13	9.8	-	-	-
HM-AG-Cu	0.72	0,33	7	0,72	5,1	6,8	1074	16	9.8	51	49	16
Catalysts on the base NaY												
HY-G	0.70	0,54	401	0,70	3,0	10,2	1032	51	2.8	-	-	-
HY-G-Cu	0.71	0,45	320	0,71	3,1	8,7	1035	48	2.9	68	58	52
HY-AG	0.89	0,43	2	0,89	4,6	9,8	1039	46	3.2	-	-	-
HY-AG-Cu	0.96	0,36	258	0,96	4,0	8,5	1040	44	3.2	72	68	49

Catalysts synthesized with the introduction **LG + PB** differ high values of P_{\square} (5,1 and 4,0 MPa) and value of the ratio $\text{SiO}_2/\text{Al}_2\text{O}_3$ (9,8 and 3,2), and catalytic activity of X (51 and 72 %) HM-AG-Cu and HY-AG-Cu, respectively, but the values are smaller selectivity $\text{C}_5\text{-C}_8$, compared the **ZC** with injection **LG**. Thus, the best indicators have CC based on NaY, X ~ 68 and 72 % (HY-G-Cu and HY-AG-Cu), did not change significantly during the **A** with a high selectivity to main component C_8 .

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NANOSTRUCTURED CATALYSTS FOR GASOLINE YIELD INCREASE IN THE PROCESS OF ATMOSPHERIC VACUUM CRUDE OIL DISTILLATION

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Oil is the main raw material used for producing motor fuel of various types today. The problem of oil resources depletion can be solved by means of deep oil refining and waste oil disposal.

Designing technological processes for oil refining requires a profound knowledge of its physico-chemical properties, fractional composition, oil reservoir geology, composition and structure of oil reservoir rocks. These factors affect:

- methods of crude oil transportation and refining;
- mass yield of light oil and oil fractions as well as organic synthesis intermediates;
- the optimum composition and the most appropriate types of catalysts used in the process of oil refining;
- methods for providing oil-catalyst contact or light hydrocarbon vapors-catalyst contact [1].

The use of nanostructured metals as catalysts in catalytic compositions (Ni-Cr-Mn, Fe-Cu) proved to be sensible. The particle size of nanostructured metals is 10...15 nm. The particle size was determined by the two-beam electron-ion microscope Neon 40 (Carl Zeiss, Germany). It was experimentally established that gasoline yield increases by 8-10 % at vapor boiling point of 195 °C in the process of crude oil atmospheric distillation. Gasoline yield can increase by 12-20 % in the process of two-stage vacuum oil refining under the pressure of 0,4-0,44 kgf/cm². The effect is explained by the catalytic cracking process combined with the high reactivity of metal catalysts and an extended contact surface due to the high fineness of the metal. [2]

Some problems can arise when nanostructured catalysts are used:

- the catalyst surface oxidation under the influence of atmospheric oxygen in the process of handling a nanostructured catalyst;

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- the catalyst coking and active catalytic sites plugging in the process of oil distillation;
- the chemical bond between the catalyst and the sulfur contained in oil feedstock that results in the catalyst deactivation;
- the catalyst oxidation and burning at high temperatures (over 600 °C).

It is possible to remove the oxide layer from the catalyst surface calcining a nanostructured metal in a high reactivity carbon mixture. This method allows to increase gasoline yield by 5-8 % in the process of atmospheric vacuum crude oil distillation. Calcining nanostructured metals in the presence of coal increases gasoline yield by 6-10 %. The effect of the catalyst regeneration in this case is explained by the chemical bond between oxygen and the oxide layer surface.

The experimental research of atmospheric vacuum crude oil distillation with the use of catalytic compositions of nanostructured metals showed energy consumption reduction by 3 % in the process of heating the reaction mass due to the intensification of oil distillation by catalysts.

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HYDROCONVERSION OF HEAVY WASTES FROM REFINERY IN THE PRESENCE OF ULTRAFINE CATALYSTS

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The problem of converting and recycling of heavy oil wastes (sludges, heavy residue, etc.), being accumulated during storage, transportation and processing stages of oil processing, is one of the most important ecological problems all over the world. However there is no effective technology for separation and processing of organic components containing in heavy oil wastes. The problem causes an inefficient use of oil resources, which can lead to considerable damage for environment and economy of countries [1-4].

The way being proposed for oil sludge processing in our report provides more than 90 % conversion of heavy organic fraction. Conversion products are represented by commercial petrochemicals. The scheme being proposed includes pretreatment of feed with separation of water, solids and light distillate fractions and recycling heavy organic fraction using hydroconversion process. Hydroconversion is performed in presence of highly efficient ultrafine catalyst formed in the reaction medium [5, 6].

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OPTIMIZATION OF DIESEL FUEL COMPONENTS PRODUCTION USING THE MODEL OF INTERCONNECTED HYDROTREATING AND HYDRODEWAXING PROCESSES

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Currently it is a topical problem of increasing the resource efficiency of processes of wide diesel fraction refining, which consists of paraffinic, naphthenic, aromatic and olefinic hydrocarbons, for diesel fuels components production via hydroconversion processes, such as hydrotreating and hydrodewaxing. This problem can be most effectively solved by method of mathematical modelling, taking into account physical-chemical laws of processes and interconnection of processes and apparatus included in technological scheme [1].

It is necessary to take into account the interconnection of hydrodewaxing and hydrotreating processes when modelling chemical engineering system. This is due to the technological features of the process, namely, arrangement of the catalyst layers in the reactor (three dewaxing catalyst layers and one layer of hydrotreating catalyst) because of the fact that in dewaxing process mercaptans are formed, which must be removed in the hydrotreating catalyst for reducing the rate of catalyst deactivation and receiving components of diesel fuels meeting the requirements for sulfur content.

The aim of this work is to develop a mathematical model of coupled processes of hydrotreating and hydrodewaxing of atmospheric gas oil and straight-run diesel fractions mixture, and its application to determine the optimal process temperature required to obtain the components of diesel fuel with the required low temperature performance (cloud point -26 °C, cold filtering plugging point -28 °C, freezing point -35 °C [2]), depending on the composition and flow rate of feedstock.

In order to develop the mathematical model the thermodynamic analysis of reactions occurring in the process was performed; the scheme for hydrocarbon conversions and kinetic model were developed; using experimental data from the industrial hydrodewaxing plant the kinetic parameters of the model were determined; the mode of hydrodynamic flow movement in the reactor was assessed.

By using the developed mathematical model prediction calculation of the reactor was carried out and the optimal temperature of the process when changing the flow

of raw materials from 295 to 315 m³/h was determined. The calculation was performed for the feedstock with the content of n-paraffins C₁₀-C₂₇ equal to 19 wt. %.

Table 1. Results of the forecast based on the model

Feedstock flow rate, m ³ /h	T, °C	Yield of straight chain paraffins C ₁₀ -C ₂₇	Yield of diesel fraction, %	T _{cp} of diesel fraction, °C	T _{fc} of diesel fraction, °C	T _{fp} of diesel fraction, °C
295	348	9,64	60	-23	-24	-32
	352	8,26	59	-26	-28	-35
	356	6,86	58	-29	-32	-38
305	352	8,67	59	-25	-26	-34
	354	7,98	59	-26	-28	-35
	360	5,91	57	-32	-36	-41
315	352	9,07	59	-24	-25	-33
	355	8,03	59	-26	-28	-35
	360	6,31	57	-31	-34	-40

T – temperature in hydrodewaxing reactor; T_{cp} – cloud point; T_{fp} – filterability point; T_f – freezing point.

By increasing the consumption of feedstock in the dewaxing process the maintaining of optimal temperature in the reactor allows obtaining diesel fuel components with the required low temperature properties (cloud point –26 °C, cold filtering plugging point –28 °C, freezing point –35 °C) while maintaining a high yield of them (59 %). By increasing the productivity of the plant from 295 to 315 m³/h the diesel fuel components production is increased from 174 to 185 m³/h.

Increasing the temperature above the optimum results in decrease in the yield of diesel fractions. Therefore, increasing the temperature higher than the optimal is not feasible.

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COMPARISON OF PERFORMANCE OF Pd/ γ -Al₂O₃ CATALYSTS BASED ON ALUMINA WITH DIFFERENT ACIDITY IN THE HYDROGENATION OF 1,3-BUTADIENE

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In the synthesis of supported palladium catalysts were used γ -alumina, which was obtained by isothermal treatment in flowing air at 550 °C (1 h) of unmodified pseudoboehmite and the modified with acetic acid of pseudoboehmite. Modification of aluminum hydroxide were carried out with an aqueous solution of acetic acid, wherein the weight content of acid was 10 %. For this pseudoboehmite was mixed with aqueous acid and was thermostated at 85 °C with continuous stirring until thick plastic mass. The resulting mass was dried at 120 °C for 12 hours.

Peptization of aluminum hydroxide with acetic acid did not lead to a change in the phase composition. Introduction of acetic acid into pseudoboehmite is accompanied by changes in texture characteristics of the prepared alumina compared with the unmodified alumina. It was observed an increase in surface area and decrease in pore spaces with the redistribution of large and medium sized pores in the fine porosity region. The total acidity of aluminum oxides were determined by temperature programmed desorption of ammonia with the temperature range of analysis 25-700 °C. Thus analysis of the two spectra showed a significant increase in the total number of acid sites for alumina synthesized from modified hydroxide. Subsequent partition of the temperature region spectra on the weak ($T_{\text{desorption}} < 200$ °C), medium ($200 < T_d < 300$ °C) and strong ($T_d > 300$ °C) acid sites was showed growth of concentration of the last two types of centers (215.43 to 283.48 $\mu\text{mol/g}$) due to coordinative unsaturated cations alumina. The synthesis of catalysts was carried out by chemisorbtion of palladium acetylacetonate on unmodified (CT 1) and modified (CT 2Ac) alumina. The loading of palladium was 0,5 wt %. Measurements of dispersion were performed with usage the pulse carbon monoxide chemisorption at room temperature and the catalysts were previously were processed in 5 % O₂ dissolved in Ar at 400 °C duration 2 hours, then 10 minutes held in Ar and in 5 % H₂ in Ar at 400 °C duration 2 hours. Catalytic performance of experimental samples were studied in the hydrogenation of butadiene in a laboratory conditions in the flow

fixed bed reactor with the catalyst an amount of 0.05 gram at the temperature range 15-75 °C, atmospheric pressure and the feed space velocity 1500 h⁻¹. The raw materials consisted of 10 % 1,3-butadiene mixture in argon. The molar ratio of hydrogen to 1,3-butadiene was 1.2 : 1. Before testing the catalysts were oxidized and then reduced at 400 °C 2 hours at hydrogen atmosphere. The feedstock and the reaction products were analyzed by gas chromatography, GC Chromos-1000.

The dispersion of active component of CT 1 was 82 % and of CT 2Ac was 95 %. Changing the properties of palladium particles supported to surface of the modified alumina support is accompanied by a change in the adsorption characteristics of catalysts. The catalytic performance shown on Fig. 1. Thus according to the catalytic test, the catalyst synthesized with the usage an unmodified alumina, the CT 2, is characterized with the conversion of 1,3-butadiene, equal to 96.75 % with a selectivity to 1-butene 14.13 % at 75 °C. Application palladium on modified support which has a higher acidity leads to increase in conversion of 1,3-butadiene after 50 °C and at 70 °C the conversion was 98 % with a simultaneous decrease in the selectivity to butene-1.

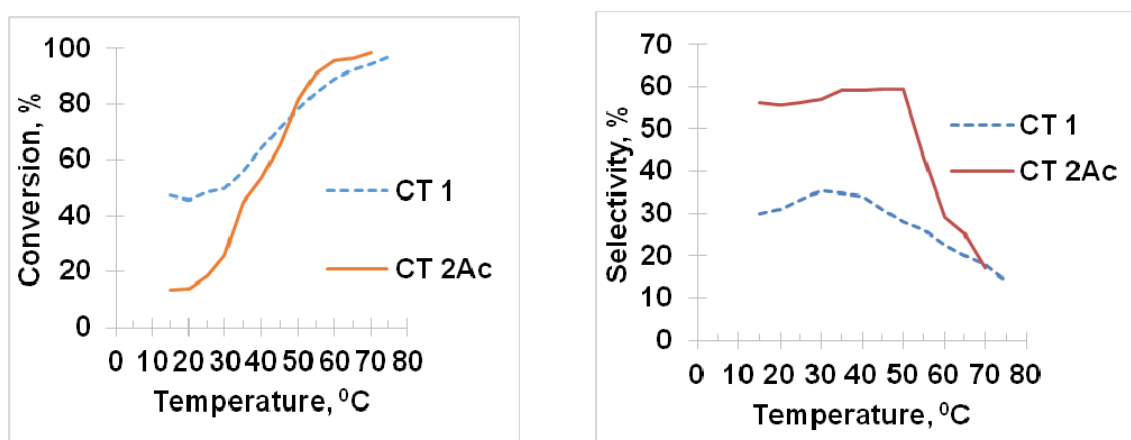


Fig. 1. Curves conversion of temperature

Conclusion

It was shown that the deposition of an organic palladium complex on the surface of alumina, synthesized from modified aluminum hydroxide is accompanied by the formation of highly dispersed state of the active component with a strong interaction metal-support. This leads to increased conversion of 1,3-butadiene with a simultaneous decrease in the selectivity of the latter into butene-1.

THE EFFICIENCY IMPROVEMENT OF THE LIGHT NAPHTHA ISOMERIZATION BY OPTIMAL RAW MATERIALS DISTRIBUTION

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The efficiency improvement of industrial isomerization process is an important technological problem which includes variety of different factors and independent parameters. The long-standing research of catalytic isomerization process in cooperation with industrial engineers from «Kinef» oil refinery provided the foundation of complex mathematical model. It describes both processes on singular stages (feedstock fractionation, reaction process) and interconnections between units of chemical-engineering system at all [1-2].

The purpose of this work is to optimize the feedstock composition of industrial isomerization process in order to provide the efficiency in resources with intensification of stabilization and afterfractionation columns.

The raw material of the isomerization process is a fraction of the IBP-62 °C, coming from the stabilization unit and the after fractionating column block of the straight-run naphtha. A block diagram of the process of material flows preparation of unstable gasoline is shown in Fig. 1.

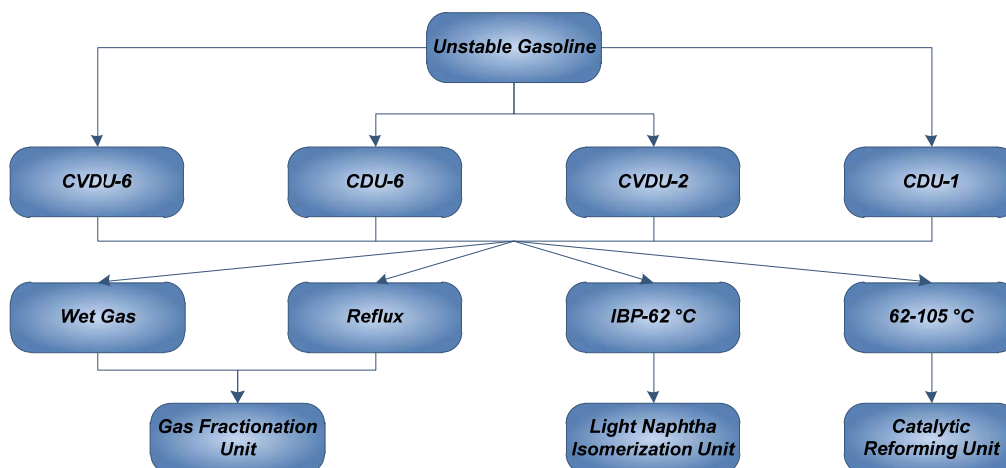


Fig. 1. Block scheme of unstable gasoline material streams

The quality of the raw material supplied to the isomerization unit L-35-11/300 is determined by the operating of the stabilization column block and after fractionating column block of the straight-run naphtha (CVDU-6 CDU-6, CVDU-2, CDU-1). For the

description of complicated chemical-technological system in complex, the method of mathematical modelling of physical and chemical principals of reacting and fractionating processes was used. Calculation of stabilization and after fractionation unit was performed with Aspen HYSYS software. Initial data for calculation are unstable gasoline fraction composition, distillation columns construction, and operating parameters of distillation process.

According to results described in [2], the isomerate RON can range 1 to 1.5 points depending on the feedstock constitution. In such a way in order to meet maximum isomerate RON in constant operating parameters of isomerization reactors it is necessary to match optimal technological parameters of stabilization and after fractionation units in order to provide maximum content of normal C_5-C_6 hydrocarbons and reduction of undesirable components (methylcyclopentane and cyclohexane).

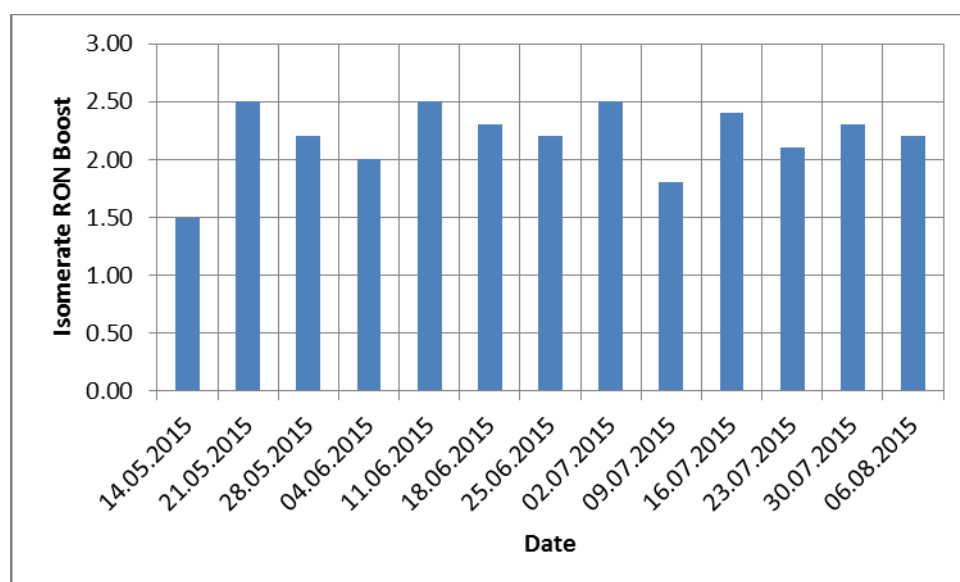


Fig. 2. The boost in isomerate RON provided by stabilization and after fractionation columns operation parameters optimization

Optimization of stabilization and after fractionation columns operating parameters using complex mathematical model of distillation and catalytic conversion of hydrocarbon feedstock allows to increase isomerate RON in 1.5-2.0 points.

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TECHNOLOGY TO SAVE THE RESOURCE OF Pt-CATALYST FOR HIGHER PARAFFINS DEHYDROGENATION

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One of the basic problems, occurring when operating the industrial plants for the hydroconversion processes, which operate at high pressure and temperature conditions, is ensuring the optimal modes from the point of view of energy- and resource efficiency. The engineering of reaction and heat exchanging equipment for hydroconversion processes is performed using consciously high stock of capacity, which negatively influence the resource efficiency of industrial plants. This is also typical of one of the fastest developing production in the world – synthesis of linear alkyl benzene (LAB), which is the basic feedstock for domestic and industrial detergents. Herewith, the throughput of target product is ensured mostly on the stage of higher paraffins dehydrogenation with the obtaining of monoolefins, applicable for LAB production.

On the department of fuel engineering and chemical cybernetics of Tomsk polytechnic university the mathematical model was developed taking into account change in the activity of Pt-catalyst for dehydrogenation process.

The aim of this work is optimization of water flow rate, which compensate the increasing in the rate of Pt-catalyst deactivation by coke under decreasing in pressure and molar ration hydrogen/feedstock.

The conversion to straight chain monoolefins is to be carried out under low pressure, which does not change during the process. However, the decreasing in pressure negatively influences on the time of catalyst operation.

Table 1. Content of olefins and diolefins in the product stream of dehydrogenation reactor depending on the pressure, wt. %

Component	Pressure, MPa						
	0,180	0,185	0,190	0,195	0,200	0,205	0,210
Olefins	10,84	10,23	9,49	8,65	7,74	6,80	5,89
Diolefins	0,69	0,68	0,66	0,64	0,61	0,57	0,52

The calculation, performed using the model, showed that when processing the feedstock, having constant composition, the content of olefins and diolefins in the

product stream of dehydration reactor will increase while decreasing in pressure (Tab. 1).

Diolefins are the basic precursor of coke, which deposits on the surface of dehydrogenation catalyst. Because of this when decrease the pressure, its content will increase at other conditions being equal. At the same time, the pressure in dehydrogenation reactor is ensured by pressure of hydrogen containing gas and molar ratio hydrogen/feedstock.

Decrease in molar ratio hydrogen/feedstock provides increasing in coke deposition on Pt-catalyst surface and decreasing in its service life (fig. 1). Controlling the supply of water into the reactor, estimated using mathematical model of the process, provides compensation of decreasing in catalyst activity (fig. 2).

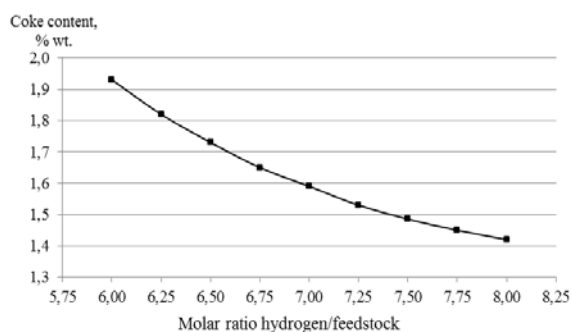


Fig. 1. Dependence of coke content on dehydrogenation catalyst surface on molar ratio hydrogen/feedstock

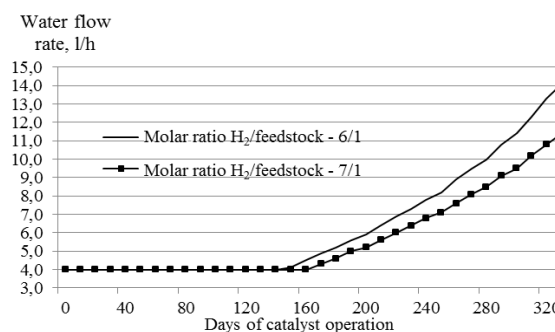


Fig. 2. Dependence of water flow rate into dehydrogenation reactor on molar ratio hydrogen/feedstock and duration of catalyst operation

Therefore, to ensure high selectivity (90 %) of catalyst to formation of olefins and its stability the optimal operating pressure is selected. Herewith, optimal pressure is the “compromise” between high content of straight chain monoolefins and stability of catalyst. To save the service life of the catalyst when operating at lower pressure and lower molar ratio hydrogen/feedstock it is needed to correct water flow rate in dehydrogenation reactor depending on dynamics of coke accumulation, which at this conditions will be more intensive.

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REGENERATION OF CATALYST USING SUPERCRITICAL FLUID CO₂-EXTRACTION PROCESS

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Catalysts are one of the most high-tech and fast enough renewable products. Catalyst efficiency and the duration of their work until it replacement, determine the level of chemical technologies. Often due to the lack of effective methods of catalyst regeneration, many of these products are destroyed after a single use. Therefore, catalyst regeneration is one of the main problems in providing technical and economic efficiency of the vast majority of oil refining and petrochemical processes.

The present work is to dedication to the result of the research new supercritical fluid CO₂-extraction process of regeneration of spent catalyst from the enterprise of "Nizhnekamskneftekhim" (nickel-on-kieselguhr, palladium catalyst LD-265, active aluminum oxide, KU-2FPP). Thermodynamic base of process are researched in each specific case, the choice of optimal property of the polar co-solvent are realized, the results of the process kinetic and the activation of regenerated catalysts are presented.

The extraction kinetics of catalyst regeneration at T = 423 K using modified with various additives SC-CO₂ with an optimal concentration of co-solvents is presented in Fig. 1.

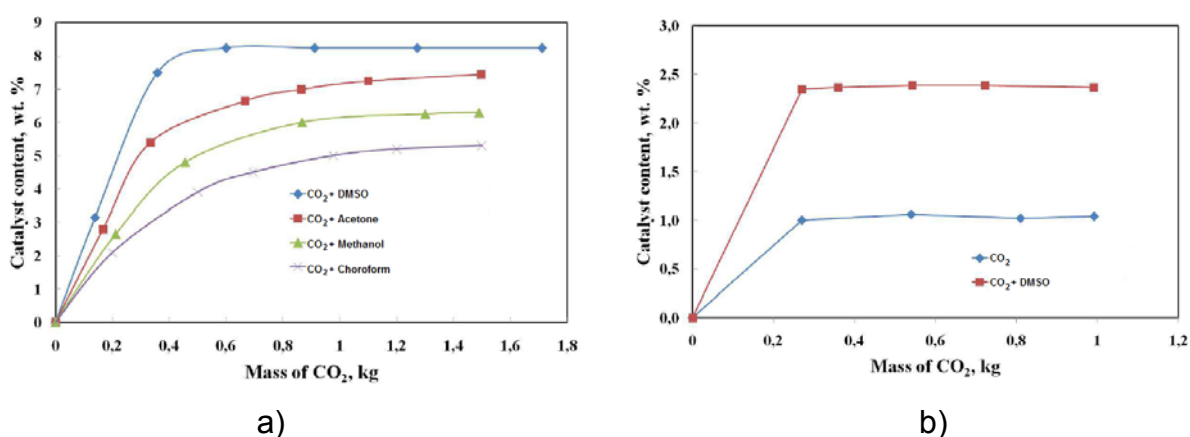


Fig. 1. Change of catalyst's mass in the course of its regeneration
a – nickel-on-kieselguhr P = 30 MPa, b – active aluminum oxide P = 20 MPa

The greatest degree of extraction decontamination compounds is provided when used as co-solvent DMSO, which has a high polarity, and allows the most complete extraction of polar compounds.

The activity of the nickel-on-kieselguhr catalyst was estimated from the extent of hydrogenation of ethylene to ethane (Table 1). Evaluation of the activity of samples of the aluminum-palladium catalyst was carried out on the residual value of diene and bromine numbers in the hydrogenation product (Table. 2).

Table 1. Activity of the samples of nickel-on-kieselguhr catalyst subjected to various treatments in the hydrogenation of ethylene

Product	Sample			
	initial	workedout	Regenerated (SC CO ₂ + 3 % wt methanol)	Regenerated (SC CO ₂)
Ethane, vol %	91.5	87.7	92.9	92.3
Ethylene, vol %	8.5	12.3	7.7	7.1

Table 2. Comparative analysis of hydrogenation results of the benzene-toluene-xylene-fractions, obtained on samples of the palladium catalyst LD-265

Activity index	Sample			
	steam- airtreatme nt	regenerated (SC CO ₂)	Regenerated (SC CO ₂ + 6 % wt DMSO)	Regenerated (SC CO ₂ + 6 % wt ethanol)
Diene number, gJ ₂ /100g	2.85	2.4	1.5	2.0
Bromine number, gBr ₂ /100g	20.5	19.0	16.2	17.0

Thus, the obtained values of the catalytic activity of the hydrogenation catalyst samples demonstrate the effectiveness of the extraction process, at the level of requirements imposed on the catalysts.

USING SULFUR REDUCTION ADDITIVES ON MESOPOROUS MCM-41 IN FLUID CATALYTIC CRACKING OF VACUUM GAS OIL

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In recent years there has been a trend towards stricter environmental requirements for motor fuels in their content of sulfur compounds. Most refiners are faced with the growing demand for fuel containing low levels of sulfur [1, 2]. The fluid catalytic cracking is a large-capacity secondary processing of oil. Its products occupy a key role in the production of trade fuels. In some countries its share in the final product is up to 90 % sulfur, so FCC gasoline undergoes hydroforming. One disadvantage of hydrorefining gasoline fraction is decrease in the octane number due to hydrogenation of olefins and aromatics, so the reduction of sulfur in the catalytic cracking process is an important task for production of high quality motor fuels. Reducing the concentration of sulfur compounds in liquid products makes possible the subsequent hydrotreating gasoline under milder conditions [3, 4].

New materials - structured mesoporous oxides having a pore size of 20 to 500 Å were synthesized in the middle of the 90s [5]. Depending on the synthesis conditions it is possible to control pore size, specific surface area, pore volume, acidity and a number of other indicators [6, 7]. The purpose of this paper is to test a structured mesoporous silica such as MCM-41 as part of a sulfur reduction additive for commercial cracking catalyst.

1. A carrier containing an ordered mesoporous silica MCM-41 type and $\gamma\text{-Al}_2\text{O}_3$ in its composition was synthesized. The sample was characterized by TEM, the low-temperature nitrogen adsorption/desorption, TPD of ammonia and IR.
2. Materials La/MCM-41/ $\gamma\text{-Al}_2\text{O}_3$, W/MCM-41/ $\gamma\text{-Al}_2\text{O}_3$, Ni/MCM-41/ $\gamma\text{-Al}_2\text{O}_3$ were prepared on the basis of MCM-41/ $\gamma\text{-Al}_2\text{O}_3$. These materials are used as additives for commercial microspherical zeolite-containing cracking catalyst.
3. It was shown that the additive La/MCM-41/ $\gamma\text{-Al}_2\text{O}_3$, W/MCM-41/ $\gamma\text{-Al}_2\text{O}_3$ is active in desulfurization liquid cracking products of heavy oil feedstocks, including VGO and oil sludge in fixed-bed MAT unit at 500 °C.

4. It is shown that the addition of La/MCM-41/ γ -Al₂O₃ to industrial catalyst in an amount of 10 % by weight reduces sulfur content up to 40 % in liquid cracking products of VGO.
5. It is found that the results of steaming MCM-41 at 600 °C show the possibility to use it as a component of sulfur reduction additives to the cracking catalyst.

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CATALYTIC ACTION OF MINERALS OF RESERVOIR ROCKS ON THE TRANSFORMATION OF THE HYDROCARBON COMPOSITION OF HEAVY CRUDE OIL IN CONDITION OF STEAM METHOD

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For efficient use of expensive thermal methods of development of heavy hydrocarbon resources necessary to develop fundamental knowledge because they are less studied than conventional resources.

The research aims was to identify the distinctive characteristics of the conversion of hydrocarbon compounds of viscous oil and changes its rheological properties in a steam-extraction techniques, due to the different content of the rock-forming minerals and trace collectors. As the porous media was investigated carbonate species consisting of calcite and dolomite, kaolin. Also well known the important role of clay minerals in the origin, transformation and migration of hydrocarbons [1]. In the literature highlights the initiation of the reaction in the low-temperature oil oxidation with the formation of homogeneous or heterogeneous catalysts [3]. By injection into the formation of vapor comprising nanoscale catalyst and an organic acid, a synergistic effect can be expected by the combination of thermal, gas and hydrodynamic effects. To this end, in an aqueous solution of Al_2O_3 and NiO to particle sizes up to 50-10 nm, nickel and copper sulfates, mono- and polybasic carboxylic acids. Experiments were carried out with extra-viscous oil from carbonate deposits with a density of 0.9857 kg/cm³, a viscosity at reservoir conditions of more than 10,000 mPa·s, with a high content of sulfur and resin-asphaltene substances. A series of experiments was carried out in a heated batch reactor volume of 200 ml, the ratio of air to feed of 1:1. Water is separated from the final product by the standard procedure demulsification Bottle-test. Suspended from a converted oil supplements are not separated.

The presence of the carbonate additives in oil and Al_2O_3 activated the radical chain decomposition reactions and the reactions of cracking. When introduced into the reaction mixture of Ni and Al_2O_3 oxide in the final product noticed the reduction of

the asphaltene concentration increases the yield of light fractions. In the composition of the gasoline fraction as initial oil, and the transformation products dominate cyclopentane and isoprenoid hydrocarbons. During heat treatment of kaolin in the presence of oil and sulfates of Ni and Cu in the composition of the final product reduces the amount of resinous-asphaltene compounds and increases oil content.

The chromatograms of the final products of experiments differ from the initial oil, more uniform distribution of n-alkanes with an increased yield of low molecular weight homologues composition C14-C18, with a small display of bimodality, pronounced in the initial sample. The most interesting structural changes in the structural-group composition observed in four experiments. A more significant increase of aromatic fraction is observed only in the presence of carbonate additive. An analysis of patterns of change in the structural-group composition and component composition of obtained oils indicates the low catalytic activity of the carbonate additive in thermal destructive reactions of aquathermolysis.

As a result of steam stimulation of heavy crude oil in the porous carbonate medium with the presence of Al_2O_3 occurs destruction of resinous-asphaltene compounds, which leads to the formation of new organic compounds and promotes the mobility of the organic substance to increase the percentage of oil recovery from carbonate species and improve the quality of heavy oil which have important practical value. However, a further increase of temperature and pressure, significantly increases the rate of polycondensation reaction of oil hydrocarbon to form a carbonaceous substance bridging the pore space. The established laws of the transformation of heavy high-viscosity oil with the presence of natural mineral supplements included in the petroliferous species lead to greater efficiency of oilfield development at a later stage.

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CATALYSIS IN DISPERSED PHASE: SYNTHESIS AND STUDY OF NANOSCALE CATALYSTS IN ADVANCED REFINING OF PETROLEUM

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Development of new high-efficient methods for deep processing of heavy oil feedstock to produce commercial products is the most important task of modern petrochemical industry. Traditionally catalytic thermal conversion of heavy oil feedstock has limited possibilities on degree of conversion, so in recent years many researchers paid attention on hydroconversion process, which uses ultrafine and nanoscale catalysts. Interaction of small catalyst particles and high molecular weight components of feed during hydroconversion proceeds in the dispersed phase, which provides an effective contact between the reaction phases, and reduces effects of coke on catalyst active sites. One of the most important issues in this research area is the development of methods for preparation of highly stable catalyst systems.

In this paper we propose original approaches to solving this problem. Sulfides of molybdenum, nickel, cobalt and iron, and alumina, being active components of hydroconversion catalysts, are generated *in situ* and *ex situ* in reverse emulsion and microemulsion with precursors in the aqueous phase or by hydrocarbon-mediated fast decomposition of precursor solution at high temperatures [1]. The study found effects of nature of precursor, dispersion media and surfactants on the particle size, also catalyst synthesis conditions were optimized [2-4]. It is found that in presence of native oil stabilizers (bi- and polycyclic aromatics, resins and asphaltenes) catalyst particle size reduces to 25-50 nm [4, 5].

Ultrafine and nanoscale catalyst systems that were prepared in our work performed high activity in hydroconversion of heavy petroleum fractions, being exceeding the activity of conventional catalysts significantly [1,6]. Conversion of 538 °C+ fraction of the feed was higher than 93 %, selectivity on distillate fractions 80 % at catalyst consumption not more than 2000 ppm (based on molybdenum).

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STUDY OF THE REASONS OF DEACTIVATION OF PLATINUM PROMOTED WO_x - ZrO_2 IN THE ISOMERIZATION OF n-HEPTANE-BENZENE MIXTURE

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Catalytic systems based on zirconia modified by tungstate anions are of considerable interest for the development of the hydroisomerization of gasoline fractions with enhanced amount of aromatics.

However catalysts deactivation is an important problem in catalytic conversions of this hydrocarbon mixture resulting in significant loss of efficiency. Research of the reasons of deactivation and elaboration of the methods to eliminate it are important aspects in the governing the catalyst preparation and its use.

The objective of this paper was to study the change of physicochemical properties of platinum-promoted catalysts based on the tungstated zirconia after the test in the isomerization of n-heptane-benzene mixture (23.5 mol %).

The isomerization reaction was carried on an automated catalytic unit with a tubular flow reactor operated at atmospheric pressure in a hydrogen atmosphere and at the temperature range of 200-280 °C. The textural characteristics, phase composition of the catalysts and the amount of carbon deposited on the catalyst surface were investigated after the isomerization reaction.

It was found that the catalyst phase composition and textural properties a not changed during the reaction. Differential scanning calorimetry showed that the amount of carbonaceous deposits on the catalyst surface and the temperature of the their burnout increased as the hydroisomerization temperature increased. Complete removal of residual carbonaceous deposits occurred below 410-420 °C, that is favorable for preserving fine dispersion of platinum component. Different kind of coke burning were related to both its composition and localization on the surface of bifunctional catalysts.

SUPERACID CATALYSTS BASED ON MONTMORILLONITE DURING OLIGOMERIZATION PROCESS OF THE BUTANE-BUTYLENE FRACTION

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In recent decades the solid superacids (anion-modified metal oxides, supported heteropolyacids) has been developed and have been used in processes for the production of motor fuels components: isomerization, alkylation, oligomerization. As an alternative to the above catalysts the variants of super acid catalysts based on anion-modified metal oxide, mixed heteropolyacids (HPA) for the industrial oligomerization process of butane-butene and propane-propenoic fractions that exhibited greater selectivity in the formation of C₅₊ isoolefins can be used.

The authors synthesized the catalyst samples by the known procedure [1]. From acid-activated montmorillonite – MM_{KA} by successive operations involving the synthesis of mixed HPA of 12-series structure of Keggin: Ni_{6-x/2}H_x[SiW₁₁NiO₃₉]·23H₂O, impregnating MM_{KA} granules obtained with aqueous HPA for 2 hours at 90 °C, followed by drying at 110 °C and 300 °C calcination. The nickel content in the synthesized samples of the catalyst K-2/1, K-2/2 and K-2/3 made 0.7, 2.5 and 4.0 % by weight, respectively.

With the purpose of selecting the optimal parameters for the oligomerization process of butane-butylene fraction (BBF) there were examined the catalytic properties of the synthesized samples within a wide temperature range. The feed space velocity was 1 ч⁻¹, pressure was maintained at 2.0 MPa to carry out the reaction in the liquid phase.

Results of testing samples of K-2/1 ÷ K-2/3 in the BBF oligomerization reaction in temperature range of 130-210 °C are shown in Figures 1-2.

Figure 1 shows that conversion reaches its maximum at higher temperatures - about 170 °C. However, a further increase in temperature also adversely affects the degree of conversion. The degree of conversion is reduced from 69.7 to 25.7 % at 170 °C and 210 °C respectively.

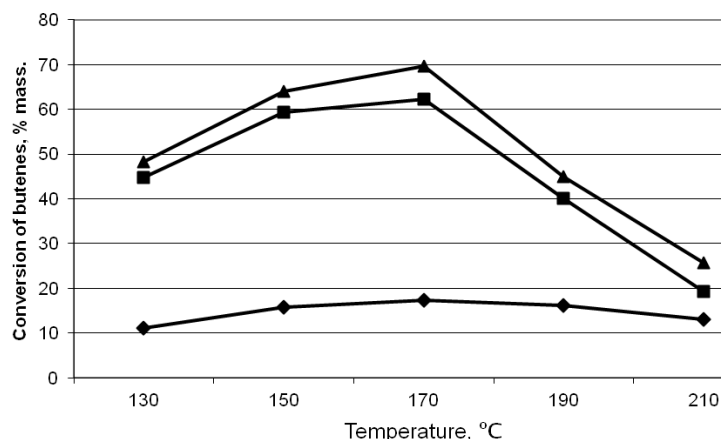


Figure 1. Dependence of butenes conversion to isoolefins on the process temperature for catalyst samples K-2/1÷K-2/3: ♦ – K-2/1; ■ – K-2/2; ▲ – K-2/3

Increasing the concentration of active ingredient in the series of samples has directly proportional affect on the degree of conversion of the butenes, so with increasing nickel content from 0.7 to 4.0 % by weight the conversion is increased from 17.4 to 69.7 %, respectively.

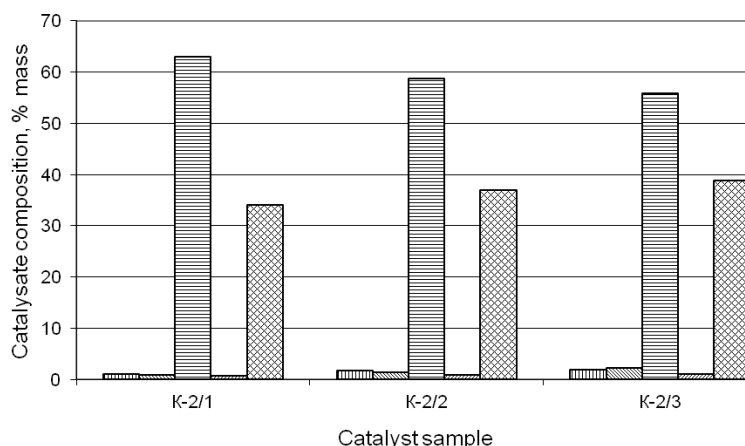


Figure 2. Dependence of the hydrocarbon composition of the catalyzate from the chemical composition of the samples of catalyst (temperature 170 °C):

▤ – isoolefins C₆; ▨ – isoolefins C₇; ▧ – isoolefins C₈;
 ▩ – isoolefins C₉; ▩ – isoolefins C₁₀₊.

With formation selectivity of C₈ isoolefins (Figure 2) there is a different picture, with increased content of active ingredient there is their decline, and the selectivity of isoolefin C₆, C₇, C₉ and C₁₀₊ increases presumably due to increased acid functions: disproportionation and cracking reactions.

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INHIBITION OF Al-Zr-CATALYSTS FOR ISOBUTANE ALKYLATION

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Introduction

A promising direction in the development of alkylation processes is the transition from a liquid-phase catalysts such as HF and H₂SO₄ to a heterogeneous catalysis thus avoiding problems related to chemical corrosion of equipment, toxicity of waste acids and their disposal. For this purpose catalysts based on sulfated oxides of Zr, Al, Si, Ti, Sn can be used, particularly sulfated zirconia (SZr) and alumina-zirconia (AlSZr) compositions featuring high activity in alkylation.

However, the main problem of a wide application of SZr and AlSZr-catalysts is their relatively fast deactivation in the course of alkylation, which is most often associated with side reactions: formation of high molecular hydrocarbons and coke, which block the pore structure and the surface active sites. Therefore, a search for an advanced technology and optimal structures of Zr-containing catalysts with reduced coking capacity is essential.

Experimental/methods

For research the following samples were prepared: AIS-400 (1); AIS-Zr-400 (2); AIS-Zr-500 (3); Al6S-Zr-400 (4); Al6S-Zra-S-400 (5); Al8S-Zr-S-400 (6).

Sulfated alumina (AIS) was prepared by impregnation of γ -Al₂O₃ granules (denoted further as Al, type A-64 of the size 2.0-3.0 mm by solution of H₂SO₄ (10 wt % SO₄²⁻) followed by drying at 110 °C and calcination in air flow at 400 °C for 3 hours. AIS-Zr-400 and AIS-Zr-500 samples were prepared by impregnation of AIS granules with ZrO(NO₃)₂ solution corresponding to 10 wt % ZrO₂, followed by drying at 110 °C and calcination in air flow at 300 (3), 400 (4), 500 (5) 600 °C (6) for 3 h. For other samples were introduced additional processing steps: calcination of carrier at 600 °C (4, 5) or 800 °C (6); second sulfation (5, 6); additional impregnation with ammonium hydroxide (5).

Investigation of activity of the resulting catalysts in the process of isobutane alkylation with isobutylene performed on flow unit under the following conditions: t = 80 °C; p = 6 atm; feed rate of isobutene 0,15 h⁻¹. Chromatographic analysis was carried out using the software and hardware systems «Crystal Lux 4000» and

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“Chromatec-Crystal 5000”. IR-spectroscopy analysis of films of the extracted products was made on IrTracer-100 spectrophotometer by FTIR-method.

Results and discussion

Results on research of activity of the received catalysts within 0.5 h both 1.0 h tests and the hydrocarbonic analysis of the alkylate received for an hour are shown in the table.

Table – Activity and Results hydrocarbon analysis of alkylate

Catalysts	Conversion i-C ₄ (X), %		Selectivity (φ_i), % mass			Paraffin	i-Paraffin	Aromatics	Naphthens	Olefins	i-C ₈
	0.5 h	1,0 h	φ_{C5-C7}	φ_{C8}	φ_{C9+}						
1	99.5	99.4	78.2	2.0	18.3	37.5	27.2	6.1	1.1	26.6	1.3
2	99.5	99.5	71.4	6.3	22.3	43.7	15.5	0	0	40.7	0
3	98.8	99.0	92.8	1.8	3.6	59.2	25.2	0	0	13.7	1.8
4	99.5	99.5	5.9	2.2	61.4	10.1	11.5	38.0	4.0	5.9	0.2
5	99.5	95.6	12.6	2.8	76,0	4.5	24.3	46.5	6.5	9.5	1
6	99.5	99.5	66.1	15.1	16.2	19.4	21.5	4.1	18.0	34.4	8.3

Tests showed that there is a formation of potential products of deactivation irrespective of the used catalyst (tab). So, C₇ olefins are the predominant deactivation components for (1), (2), (3) and (6) samples and aromatic compounds – for (4) and (5) samples. These compounds could block the active sites of the catalyst and reduce X at their sorption by surfaces. However, X of catalysts doesn't decrease except for the sample (5).

IR-spectroscopy for alkylation products extracted in CCl₄ showed that catalysts preferably n- and i-paraffins are adsorbed on the surface. However, presence of absorption bands in the field of 1750-1640 cm⁻¹ indicates the presence of unsaturated and cycling structures and also the possible presence of O-containing compounds – aldehydes and ketones. The last can be formed due to oxidation of unsaturated hydrocarbons on a surface of catalysts at their contact with atmosphere oxygen. On it also points a discoloration of catalysts to the violet after unloading from the reactor. Moreover, the bands corresponding to aromatic compounds on spectra of the films of extracts are not found.

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CONVERTING BITUMINOUS OIL IN SUPERCRITICAL WATER WITH SUSPENDED PARTICLES AND HEMATITE CAUSTOBIOLITES

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The development of heavy hydrocarbon resources is a priority task for the Russian Federation. According to the major oil operators – British Petroleum (BP) and OJSC, the volume of Russian stocks of commercially available oil is 1.8 billion tons of heavy high-viscosity oil and 4.5 billion tonnes of oil in the tar sands. Despite of this fact, the commercial development of these reserves comes slowly. One of the main reasons is the low profitability. Natural bitumen differ greatly from conventional oil in their composition and physico-chemical properties, in high content of resin-asphaltene substances, petroleum acids, sulfur compounds and metals, in high density and viscosity, in low paraffin content. Most of the oilfields of tar and high-viscosity oils requires the use of innovative production methods and energy-saving technologies to process them. Their development is difficult to implement without the development of fundamental knowledge about the transformation of this composition and structure in a variety of natural and man-made conditions [1, 2].

The work is devoted to research the conversion process of bituminous oil in an aqueous medium in the supercritical state in the presence of natural supplements - hematite and caustobiolites. Water in the supercritical state has a low viscosity and high diffusion ability to supramolecular structures and asphaltene oil disperse systems [3]. Conversion experiments were performed in a high temperature oil batch reactor (which was made of stainless steel), in the temperature interval 375-425 °C, at pressures of 21 to 23 MPa.

The object of the study was high viscosity heavy oil from carbonate deposits with a density of 0.9857 kg/cm and a viscosity at reservoir conditions over 9000 MPa·s, with the content of resin-asphaltene substances more than 40 % and sulfur content of more than 6 %. According to GOST R 51858-2002 this oil belongs to the bituminous type. Caustobioliths were selected as an additives (up to $2.94 \cdot 10^{-7}$ M), which were capable of initiating formation of hydrogen protons in these conditions. Hematite Fe_2O_3 (up to $2.06 \cdot 10^{-7}$ M) exhibits catalytic activity in the degradation of

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high-molecular components of the oil, aluminum oxide Al_2O_3 (up to $7.18 \cdot 10^{-7}$ M) is a catalyst for cracking hydrocarbon molecules, nickel sulphate and copper NiSO_4 , CuSO_4 are capable of performing the hydrogenation and dehydrating function. Dispersing additives in an aqueous medium was carried out on the installation of the ultrasonic waves with a frequency of 22 kHz and the energy density of 5 W/cm². Furthermore, water is an effective medium for the uniform distribution of heat over the entire volume of the reactor, preventing local overheating and reduces the partial pressure of the products, preventing the formation of carbonized materials.

Studies have shown that under the influence of water in the supercritical state there is observed a significant change in the component composition of the feed oil. In all the experiments, regardless of the presence of additives, increasing the yield of light hydrocarbon fractions and paraffin-naftenic by reducing the number of pitches. There were changes in the composition and properties of oil converted during the control experiment (425 °C, 23 MPa) so that increased yield of the gasoline fraction to 20 % and a paraffin-naphthenic hydrocarbons to 68.2 %, decreased viscosity of the final product (see Figure). Adding caustobiolites to the original oil in the product, there is a natural increase in the concentration of asphaltenes. Softening temperature and pressure conditions in the introduction, the reaction mixture was further additives; metal oxide does not lead to the expected conversion of resinous-asphaltene compounds, indicating that the dominant effect of process temperature on the product. The element composition of the final products, individual hydrocarbon composition of gasoline fractions, structural-group composition paraffin-naftenic, aromatic resins and asphaltenes, their X-ray analysis showed the direction of the reactions of high molecular components of bituminous oil in supercritical water. The results of the research can be applied in the development of innovative technologies for processing heavy hydrocarbon resources.

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AUTOCATALYTIC PROCESSES IN CONVERSION OF HEAVY OIL IN THE PRESENCE OF NANOSIZED METAL OXIDE PARTICLES OF VARIABLE VALENCE Fe^{+2} , Ni^{+2}

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Over the next 50-100 years hydrocarbon feedstock will remain the main source of energy for transport and energetics, the basis of most synthetic materials and chemical products. Nowadays there is a growing interest in the development of alternative types of reserves of hydrocarbon resources: gas hydrates, shale oil and gas, heavy oil and natural bitumen all around the world. Therefore, possession of technology of its development will ensure a high level of economic development in the country and increase its economic safety [1].

Currently, foreign companies with heavy oil is widely use steam-extraction methods to increase oil productive reservoirs [2]. Catalytic systems based on nanoparticles demonstrate impressive results by conversion of macromolecular components of the oil row under comparatively mild temperature and pressure conditions of aqua thermolysis [3]. The magnetite Fe_3O_4 with particle size of $250 \cdot 10^{-9}$ m, water solutions of Al_2O_3 и ZnO with particle size of $40 \cdot 10^{-9}$ m which are stabilized with methyl isobutyl ketone, nickel carbonate NiCO_3 are used for this purpose. A sample of heavy oil which produced by technology of steam-gravity impact on Ashalchinskoye occurrence of Tatarstan Republic was selected as the object of investigation. Oil density is $0,9857 \text{ kg/sm}^3$, viscosity at reservoir conditions is more than $9000 \text{ mPa}\cdot\text{s}$, the content of resin-asphaltene substances is more than 40 %, of sulphur is more than 6 %. A series of experiments was carried out in a heated batch reactor (autoclave) with 200 ml volume in air.

After the experiment, the reactor was cooled, the final product was removed, water, which separated after sludge, was removed, bound water was separated by the de-emulsification by the standard Bottle-test method, following thermal analysis indicated absence of water in the samples, A suspensional additives are not separated from converted oil.

The impact of temperature and pressure conditions to the initial oil leads to a decrease of its density that is primarily due to decrease in the content of resin, and

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increase in distillate fractions. There is observed significant decrease in concentration of asphaltenes, increase in content of low-boiling fractions, increase in saturated hydrocarbons in the component composition as the result of injection of Fe_2O_3 additive. However, addition of nickel carbonate to Fe_2O_3 during the experiment 4, has not led to the expected results, but has lowered the initial boiling point of the obtained sample. In this regard experiments 2 and 3 can be compared, their temperatures and pressures are similar as the yields of the fuel fractions in the final products, but in the case of ZnO additive the yield of aromatic hydrocarbons, the amount of resin compared to the original oil decreased in the presence of Al_2O_3 .

There is observed the decrease of effective viscosity at a shear rate in the Newtonian flow during the entire range of temperatures for the samples of converted oil. Different values of anomalies index of viscosity of the obtained samples indicate differences in the structure of their three-dimensional structures such as coagulation-crystallization types, where the dominant role is played by high-paraffinic hydrocarbons. Nano-sized metal particles can serve as the embryonic phase in the formation of asphaltene associates and reduce the stability of the oil dispersed phase of the thermal-catalytic refining processes. The distinguishing feature of transformed oils is small anomalies viscosity index from baseline oil samples showing reduced resistance to shear deformations. The results of the research can be applied in the development of innovative technologies of development of occurrences of heavy oils and natural bitumen.

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BIFUNCTIONAL CATALYSTS FOR HALIDE-FREE CARBONYLATION OF DIMETHYL ETHER TO METHYL ACETATE

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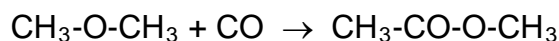
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Acetic acid is an important industrial chemical which is manufactured on a large scale. The main route to acetic acid is through the carbonylation of methanol in the Monsanto process which uses a homogeneous rhodium catalyst and halide promoter [1]. Main disadvantages of this process are: a) halides are highly corrosive and are poisons for many types of catalysts, b) it is difficult to separate the products and catalyst. These problems may be overcome by developing heterogeneous catalyst that can operate effectively without halide promoter.

The production of methyl acetate directly from dimethyl ether was performed by halide-free carbonylation on bifunctional Rh/Cs_xH_{3-x}PW₁₂O₄₀ catalysts [2-3]. DME is more favorable for carbonylation than methanol because it can be produced from syn-gas more effectively [4].



The solid superacid catalysts with high density of Brønsted acid sites Rh/Cs_xH_{3-x}PW₁₂O₄₀ were compared to Rh/SO₄/ZrO₂ and Rh/WO_x/ZrO₂.

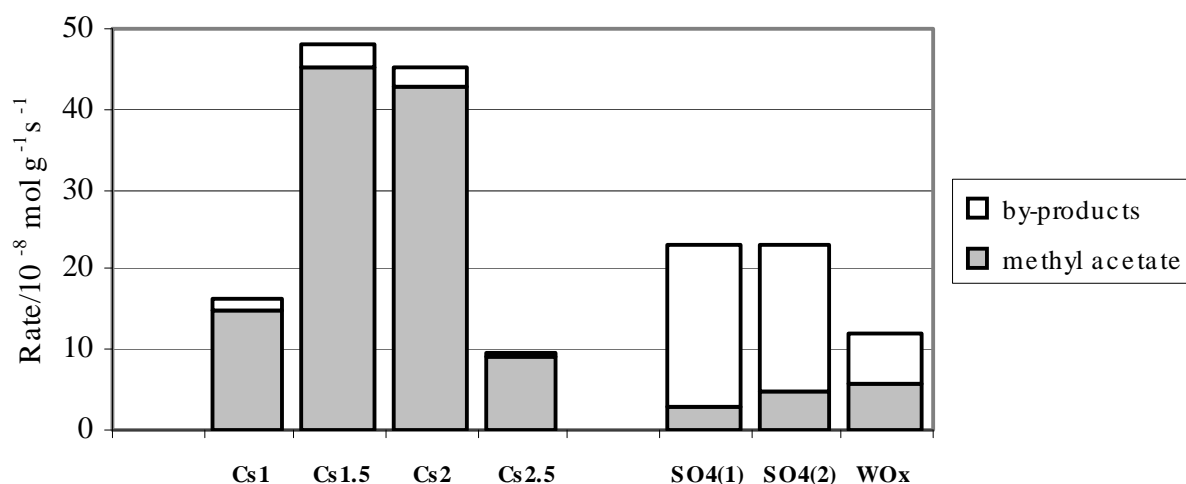


Figure 1. The performance of Rh/Cs_xH_{3-x}PW₁₂O₄₀, Rh/SO₄/ZrO₂ and Rh/WO_x/ZrO₂ catalysts in halide-free DME carbonylation

The correlation between the nature of acid sites and activity and selectivity of the catalysts was found. The strong Brønsted acid sites are effective for activation of C-O

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bond in DME that result in high (96 %) selectivity to methyl acetate. Lewis acid sites induced the cracking of DME molecule that led to the by-products formation and poor (10 %) selectivity.

The behavior of bifunctional $\text{Rh/Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ catalysts can be rationalized qualitatively by assuming that 1) activation of C-O bond in DME molecule and formation of metal-alkyl bond occurs in the presence of the strong Bronsted acid sites, and 2) these acid sites act in conjunction with Rh carbonyl complexes, which are responsible for CO insertion and acetates formation [5,6].

The best catalyst 1 % Rh/Cs_{1.5}H_{1.5}PW₁₂O₄₀ revealed activity to methyl acetate $180 \text{ g l}^{-1}\text{h}^{-1}$, that is one order of magnitude higher than the activity of the rhodium salts of the same acid supported on silica in the iodide-free carbonylation of the DME to methyl acetate [7].

It was shown that effective catalysts for halide-free carbonylation of DME to methyl acetate should have at least two parameters: high specific surface area and high density of Bronsted acid sites. The formation of two crystalline phases was observed for Rh/Cs_xPW catalysts: acidic Cs salt and pure acid. The superacidity and unique catalytic properties of the Rh/Cs_xH_{3-x}PW₁₂O₄₀ systems are determined by the amount of the acid on the surface of Cs phase:

Samples	Real phase composition of acidic Cs salt	Rate of methyl acetate formation, $10^{-8} \text{ mol m}^{-2} \text{ s}^{-1}$
1 % Rh/Cs1.5	0.8HPW/Cs _{2.2} H _{0.8} PW	0.78
1 % Rh/Cs.2.0	0.5HPW/Cs _{2.5} H _{0.5} PW	0.42

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BIMETALLIC SULFIDED CATALYSTS BASED ON NANOSTRUCTURED MESOPOROUS Al-HMS AND Al-MCM-41 IN HYDROCRACKING OF SHALE OIL

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Due to the growth of demand for petroleum products, great attention is given to the refining processes involving alternative sources of hydrocarbons such as shale oil [1]. Hydrocracking is one of the most attractive and promising process in oil refining. Owing to its high flexibility the process increases oil refining efficiency and provides the conversion of hydrocarbon feedstock (vacuum gas oil, light cycle oil) into high quality low-sulfur gasoline and middle distillates [2, 3].

In hydrocracking a high flexibility in product slate can be obtained, depending on catalyst choice and unit configuration. Hydrocracking catalysts are bifunctional systems, where acidic component (alumina, zeolites, aluminosilicates) performs cracking properties and hydro-dehydrogenating component (sulfided Ni, Co, Mo, W) performs hydrogenating and hydrodesulfurisation properties.

Zeolite-containing catalysts are quite active, but the size of the molecules of heavy oil feedstock (polynaphthenes, polycondensed aromatic compounds) exceed the pore size of such catalysts. It makes bulky molecules transformation more difficult because of diffusion limitations [4]. Moreover, catalysts based on zeolites are very sensitive to the presence of heteroatomic compounds and undergo rapid deactivation [5, 6].

Mesoporous aluminosilicates such as Al-HMS and Al-MCM-41 are large pore analogues of the zeolites. The pore size of the materials allows excluding steric hindrances. They are characterized by narrow pore size distribution, high surface area (about 1200 m²/g) and a "soft" acidic sites in comparison with zeolites. Depending on the synthesis conditions it is possible to control structural characteristics (pore size, surface area, pore volume) and the acidity of aluminosilicates [7, 8].

Present investigation is devoted to testing structured mesoporous aluminosilicates such as Al-HMS and Al-MCM-41 as a component of catalyst in hydrocracking of shale oil.

Carriers containing an ordered mesoporous silica Al-HMS and Al-MCM-41 with ratio Si/Al = 5-20 were synthesized. The samples were characterized by TEM, the low-temperature nitrogen adsorption/desorption, TPD of ammonia and IR.

Sulfided catalysts NiS-MoS₂-Al-HMS and NiS-MoS₂-MCM-41 based on mesoporous Al-HMS and Al-MCM-41 were used in hydrocracking of shale oil.

NiS-MoS₂-Al-HMS and NiS-MoS₂-MCM-41 are active in hydrocracking of shale oil at 400-450 °C and hydrogen pressure 5-8 MPa.

NiS-MoS₂-Al-HMS and NiS-MoS₂-MCM-41 showed high selectivity for middle distillates. The use of these catalysts provides sulfur content reduction in liquid hydrocracking products of shale oil.

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CATALYSTS FOR PROCESSING HEAVY OIL DISTILLATES INTO FUEL OIL

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Introduction

Diesel fuel desulphurization is one of the most important problems related to modern technologies of oil processing [1]. The oil refining industry uses chemical and physico-chemical methods for diesel fuel desulphurization. The chemical methods include acid- and hydrotreating; the physical and chemical methods deal with adsorption/absorption [2]. The most widely used technology is hydrotreating. Technological limitations of this technique are high temperature and pressure, complicated implementation [3].

The proposed technology

We propose using a laboratory setup illustrated in Fig. 1 and simultaneous low temperature cracking to clean heavy oil and oil fractions:

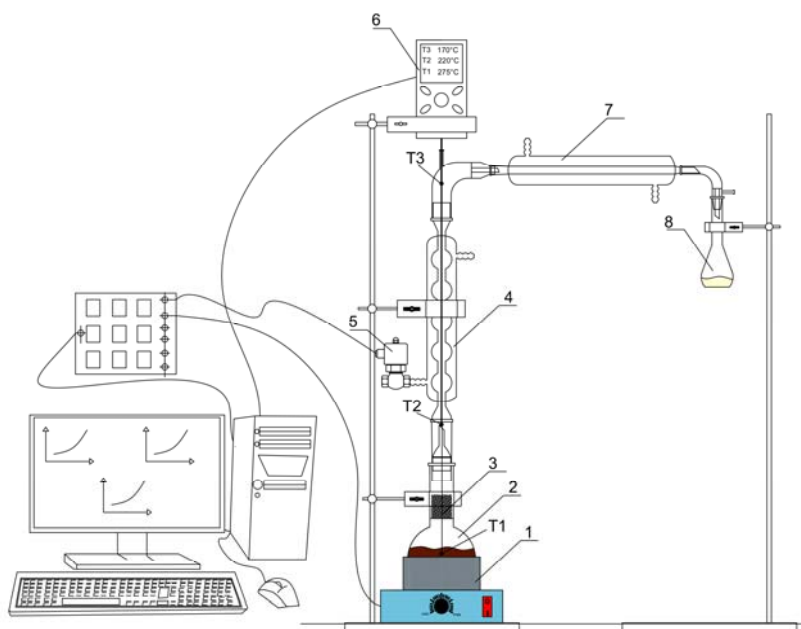


Figure 1. Design of the experimental setup for furnace oil desulphurization with simultaneous cracking
1 - heating mantle, 2 - round-bottom flask, 3 - nozzle with a catalyst 4 - backflow condenser,
5 - electronic gate, 6 - electronic thermometer 7 - condenser, 8 - receiving flask

The technology is simple distillation in the process of which an absorber catalyst is added into the container with some feedstock (2), vapors pass through the nozzle

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(3) with an adsorber catalyst. Distillation temperature is monitored at points T1, T2, T3. The setup has a circuit that regulates the supply of coolant into the backflow condenser.

Mechanism

The catalyst and the adsorbent are one and the same substance which represents the oxides of d-elements enclosed in the carrier that is resin from polynuclear hydrocarbons. Figure 2 illustrates the supposed structure of the catalyst.

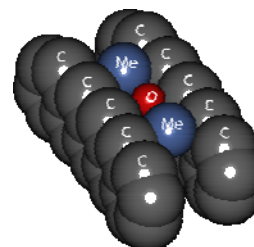


Figure 2. Supposed structure of the active catalytic sites

The catalysis and adsorption processes should be studied in detail. It is assumed that the carbon surface is an adsorbent for sulfur compounds and a substrate for the metal oxide catalyst. Cracking occurs on the active sites, i.e. metal oxide inclusions.

Test Results

The laboratory setup (Fig. 1) was used to test the absorber catalyst. The feedstock for distillation was furnace oil, the distilled product was diesel fuel. Experimental variables were diesel fraction yield (% of feedstock) and the concentration of sulfur compounds (ppm). The results are shown in Table 1.

Table 1. Effect of the absorber catalyst on diesel fraction yield and the concentration of sulfur compounds

Experiment	Diesel fractions yield % wt.	The concentration of sulfur compounds (ppm)
Simple distillation	62.8	1470
Catalytic distillation (an adsorber catalyst is used)	91.8	103

Conclusion

The use of catalysts allows to increase low-boiling fractions yield and reduce the concentration of sulfur compounds. Catalysts have a low production cost.

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THE REACTOR PRESSURE EFFECT ON THE REFORMING CATALYST LIFETIME

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Catalytic naphtha reforming is one of the key processes in petroleum refining, which is used extensively for conversion of low-octane hydrocarbons of naphtha to more valuable high-octane gasoline components. The effectiveness of this industrial process is provided by technological conditions. Major reforming reactions are thermodynamically favored at high temperature and low pressure. Depending on technology used pressure in reactors with catalyst is 0,35-2,0 MPa [1].

Catalytic reforming unit L-35-11/450K «Komsomolsk refinery» JSC is operated in pressure 16,7-17,0 atm. Previous foreign catalyst charge PR-9 has been using at this industrial unit since 2001. It has proven to be appropriate in operation and ensure high specified quality yield [2]. In the spring of 2016 replacement of spent catalyst for new one is planning. With the use of mathematical modelling [3], calculations were carried out and recommendations were issued: the reactor pressure effect on the main process parameters was studied. The results of chromatographic analysis of the hydrocarbon feedstock composition and technological modes of production unit operation were used as initial data.

The studies have shown that reduction of pressure significantly influences some parameters, such as coke formation rate, yield, octane number and etc. (Table 1).

Table 1. The pressure effect on yield and quality of the product

Pressure, MPa	P = 1,4	P = 1,5	P = 1,6	P = 1,7
Activity	0,79			
Inlet temperature, °C	482			
Feedstock flow rate, m ³ /h	68			
Paraffins/(Naphthenes+Aromatics) in feedstock	0,86			
n-Paraffins/i-Paraffins in feedstock	0,69			
Circulation multiplicity, m ³ /m ³	1193,4			
Aromatics, mass %	61,21	61,25	61,31	61,37
Coke deposition, mass %	4,05	4,04	4,04	4,05
Octane number (RON)	93,1	93,1	93,0	93,0
Yield, % mass.	90,27	89,94	89,62	89,21

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The operating pressure reduction of reforming process enhances its selectivity increasing, favors the major reactions dehydrogenation of naphthenes and dehydrocyclization of paraffins, and also hydrocracking inhibiting side reactions and hydrogenolysis. Herewith the specified quality yield increases. Thus, it is recommended to reduce the initial pressure to 2-3 MPa for the desired product yield increasing on average of 1-1,06 mass %. Along with this the coke formation decreasing will be provided by additional supply of promoters in the reaction zone for acid and metal catalyst activity balance.

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MODEL OF SULFUR COMPOUND KINETICS IN THE HYDROTREATING PROCESS BASED ON INDUSTRIAL DATA OF LG-24/7

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Hydrotreating is the process of catalytic refinement applied to diesel fuel. Raw diesel fuel undergoes different hydrogenation reactions under high pressure and temperature. The main aim is to reduce amount of nitrogen, oxygen and sulfur in the fuel. As a side effect the saturation of hydrocarbons can be noted. Hydrotreating is one of the most widely used processes in the industry of secondary oil refinement.

The main aim of this study is to simulate the kinetics and calculate the mass balance of diesel fuel hydrotreating with a focus on the dynamics of sulfur-containing compounds (SCC), such as sulfides, benzothiophene and dibenzothiophene.

The bunch of 300-400 reactions should be shortened to meet the requirements of hardware [1]. Developed kinetic model is presented on the Fig. 1.

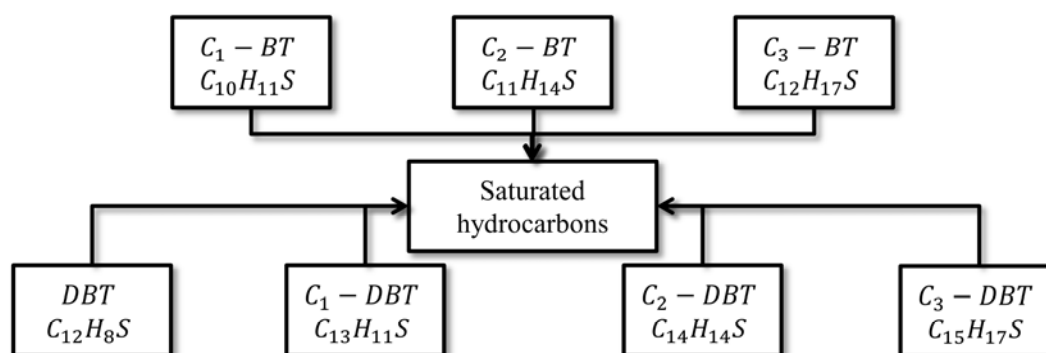


Fig. 1. Shortened kinetic scheme

Full Gibbs energies of reactions presented in the scheme are calculated by using such software packages as GaussView and Gaussian 09. Gibbs energies of the reactions are in strong correlation with rate constants of the hydrodesulfurization reactions which have been determined in previous works by conducting an experiments with the use of laboratory equipment [2]. Obtained rate constants and activation energies are used in the mathematical model.

The developed mathematical model is based on the law of mass action and is represented by the system of differential equations which reflect the change in the concentration of the reactants. Experimental data is taken from the industrial

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hydrotreating set “LG-24/7” with French HR-538 catalyst. Data reflects the state of technological parameters and different sulfur containment in the raw diesel fuel and products.

The data from different days of LG-24/7 monitoring should be selected to calculate the activation energy for each route. This data must have a predetermined tolerance between technical parameters except for temperature. This ensures the purity of the experiment without affection by extraneous factors. Such days have been selected from observations of the entire cycle operation which have diversion of raw diesel fuel temperature fractionation (IBP, 50 %, 90 %, 96 %) not more than 5 %. It provides a compromise between the size of the bunch of experimental data from the monitoring and the accuracy of the activation energy calculation.

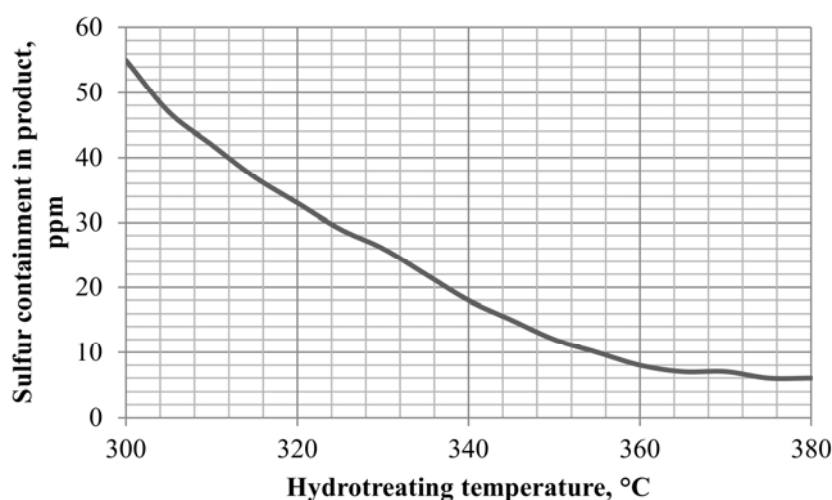


Fig. 2. Change of sulfur containment in hydrotreated product with the temperature rise

According to the latest Euro-5 standard which regulates the quality of diesel fuel, the maximum sulfur content should not exceed 10 ppm. According to the results of calculations residual sulfur content reaches a threshold value of 10 ppm even at 356 °C. Consequently, a further increase of temperature is not recommended because of the additional cost of heating the feed and of catalyst coking acceleration.

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OPTIMIZATION OF REACTOR OF HYDROCARBON REFINING ON ZEOLITE CATALYSTS

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Optimization of design and process parameters of a reactor using the mathematical model reduces the time required for a scaling, start-up operations and entrance of the design mode [1]. The purpose of the work was the selection of the optimal design and operational parameters of the reactor of refining of hydrocarbons on zeolites.

At first, a scheme of hydrocarbons conversion on zeolite catalysts has been proposed. Secondly, thermodynamics of these reactions has been considered. The model of reactor of straight-run gasoline fractions refining in software HYSYS Aspen Plus™ has been developed and its adequacy to experimental data has been shown sufficient for the purpose of designing and scaling [2].

The next step was the choice of parameters that allowed to develop an optimization criterion. The optimization criterion was octane and the relative gasoline yield. Process temperature and volume of the reaction zone have been chosen as variable parameters. Possible intervals of the parameter variations have been reasonably selected. Calculations were performed using the mathematical model for the process temperature T in the range of $335 \leq T \leq 415$ °C and reaction zone V_r in the range of $0.6 \leq V_r \leq 3.4$ m³.

The optimization criterion was developed in dimensionless form. The optimization function was illustrated in the space of optimized parameters that was shown in Figure 1.

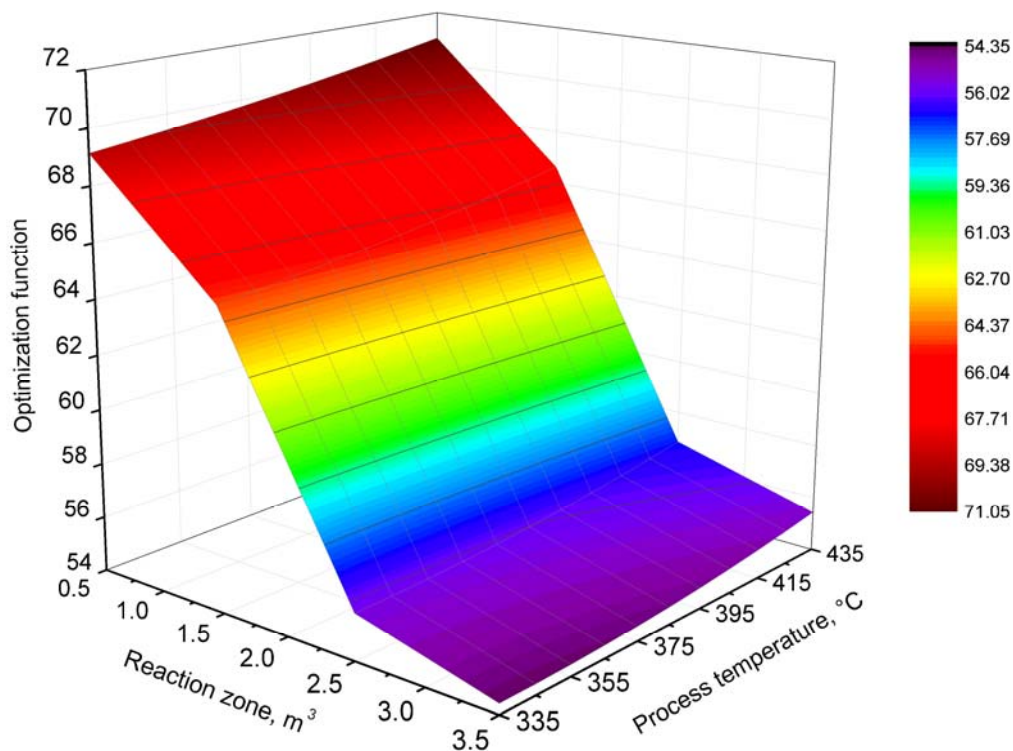


Fig. 1. The optimization function

The results were used to determine the optimal volume of the reaction zone and the optimal process temperature mode.

The developed model can be successfully used to optimize unit performance under different modes: to maximize the gasoline yield or maximize octane of the product gasoline.

The dimensionless form of the optimization criterion makes it a convenient tool for performing of economic optimization and evaluation of energy efficiency.

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APPLICATION OF THE NEW NANOMATERIALS IN THE CRACKING OF PROPANE

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The gaseous hydrocarbon raw materials are a significant part in the fuel balance of the country. In Russia annually up to 15 milliards m³ of accompanying oil gases, which contains C₃-C₄ (liquid petroleum gases LPG): propane and butane are combusted. The producing the ethylene from propane is of particular interest due to its great importance for the polyethylene processing. The catalytic conversion of propane to ethylene was investigated using pure porous monolithic alumina, Fe- and Pt-containing supported catalysts. Nanoporous materials - carbon and alumina - have potentially of great interest as catalyst in such industrial process as conversion of propane to ethylene. Porous monolithic alumina (PMOA) and Fe supported by active carbons (Fe/C) and commercial catalyst - platinum on active γ -alumina (Pt/Al₂O₃) were used as catalysts in this process. The catalytic activities of these catalysts were compared with thermal conversion in similar conditions. PMOA was obtained by oxidizing of plate of aluminum by steam at 30 °C and 60 % humidity [1]. The BET surface of obtained alumina samples were 400 m²/g. It was shown previously [1] that a foam monolithic alumina (or aerogel) is a nanofibrous aluminum oxyhydroxide Al₂O₃·4H₂O contained 40-43 % of water and has an amorphous structure. The parameters of the porous structure were determined from the nitrogen vapors adsorption isotherms at 77 K using the high-vacuum volumetric equipment ASAP-2020 MP (Micromeritics, USA) in the range of relative pressures from 10⁻⁶ to 0.99 (Table 1). The support from microporous carbon, obtained by template synthesis was impregnated by Fe nanoparticles (10 %), and SBET surface is more 860 m²/g.

Table 1. Parameters of the porous structure

Sample	S _{БЭТ} , m ² /g	W _O , cm ³ /g S _{mic} , m ² /g	W _{БЖ} , cm ³ /g des/ads	2 _{xo} , nm BET	2 _{xo} , HMBJH des/ads	S _{ME} , M ² /г t-plot	S _{MP} , M ² /г
PMOA	400	0.011/29.5	0.58/0.56	6.7	9.7/10.0	223	196
Fe/C	860	0.19/345.4	0.38/0.33	1.7	3.2/3.4	20	570

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Of adsorption of water vapor at a temperature of 293 K it was found that catalysts of this type contain about 0.3 mmol/g of acidic centers. Set of methods show that this material is an amorphous aerogel with interwoven fiber thickness of 6 nm.

For comparison it was used Pt/Al₂O₃ commercial catalyst.

The catalytic studies of the conversion propane into ethylene was examined at steady-state conditions in the temperature range 673-1073 K (50 K ramping) and are carried out in a flow system in atmospheric pressure after the reduction in the presence of hydrogen at 900 K for 2 h. Concentrations of products were determined on-line by GH analyses, using GC "Cristal 200M" with Porapac column (2 m) with 3 mm diameter.

At temperatures above 973 K the quantity of gaseous products was diminished, but the hydrogen contents increased up to 6 %, but the carbon residue increased above 20 %. The methane, ethane, ethylene, propylene are the products of propane conversion. The results showed a high conversion into ethylene, typically above 55 % for alumina PMOA. The conversion curves for thermal cracking and Fe/C catalyst are similar, but the selectivity is increased for the Fe/C and has maximum 63 % at 900 K. The activity of Pt/Al₂O₃ commercial catalyst lies near 20 % and selectivity is low 30 %. The maximum selectivity of ethylene in temperature range 750-900 K is 62 % at 830 K for PMOA and 63 % at 890 K for Fe/C catalysts and are much more than for Pt/Al₂O₃ commercial catalyst (30 %) and thermal cracking (45 %).

First studied the reaction of propane cracking catalysts nanofibrous aerogels, alumina, carbon nanotubkok results were compared with data for promyshynnyh platinum catalysts cracking propane.

Results shows that Fe/C and alumina PMOA are more active and selective catalysts as commercial Pt/Al₂O₃. Catalytic conversion propane into ethylene is more selective and effective process as thermal cracking.

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INFLUENCE OF THE PRECURSORS NATURE IN THE PREPARATION OF CHROMIA/ALUMINA CATALYSTS FOR DEHYDROGENATION

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Dehydrogenation processes occupy an important place in the petrochemical industry to obtain unsaturated compounds, which are valuable as monomers for production of synthetic rubber and plastics and are used in the synthesis of high-octane components of gasoline (MTBE, alkylate). The Cr₂O₃/Al₂O₃ systems currently account for over one-half of the global market for industrial C₃–C₅ paraffin dehydrogenation catalysts [1-3]. Numerous studies, presented in reviews [1,2], have shown that chromium is in multiple states: Cr³⁺ (associates Cr³⁺ and α-Cr₂O₃) and Cr⁶⁺ in a small amount. It is asserted that the amount of Cr⁶⁺ on the surface of the catalyst directly influences its catalytic activity. Generally, chromia/alumina catalysts are prepared by applying CrO₃ on a carrier, and further calcining during which most of CrO₃ becomes Cr³⁺. At the same time the impact of the issue of valency of chromium in the precursor compound of the state of the active component in the finished catalyst is poorly represented in literature.

In this paper in order to study the influence of the nature of the precursor of the active component on the formation chromia/alumina catalysts on microspheroidal alumina [3] by impregnation compound in different oxidation states Cr(VI) and Cr(III): CrO₃, Cr(NO₃)₃, Cr(CH₃COO)₃ were deposited. After applying the catalyst samples were dried and heat treated in an oxidizing atmosphere (air) or inert gas (helium). Phase changes and the state of chromium in the catalysts were examined by XRD, TPR, FTIR spectroscopy, DTA and chemical analysis. Genesis compounds deposited during the heat treatment were compared with the transformation of compounds of chromium bulk calcined under similar conditions. The catalytic activity of the samples was tested in the dehydrogenation of isobutane in a fluidized bed catalyst.

It has been found that the determining factors in the formation of the supported oxide particles in the form of a Cr⁶⁺ are atmosphere drying and thermally decomposing the applied compounds. In the catalyst calcined in air the formation of Cr⁶⁺ regardless of the nature of the starting precursor is observed. Formation of ions

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Cr^{6+} from the Cr (III) takes place by partial oxidation of Cr^{3+} ions at the time of decomposition of the starting compounds. With increasing the calcination temperature the amount of Cr^{6+} decreases. However, the specific amount of Cr^{6+} ions (per unit surface area) in the samples calcined at 750 °C differs slightly. This means that the alumina carrier stabilizes its surface only a certain portion of the chromium in the state of Cr^{6+} .

During the heat treatment the sample in a stream of helium of chromium nitrate (III) the formation of Cr^{6+} occurs, which is associated with oxidative action of emitted nitrogen oxides. This sample according to their catalytic performance (table 1) is not inferior to the sample and calcined in air containing twice as much amount of Cr^{6+} ions.

Table 1 – Influence of the precursors nature and the heat treatment atmosphere (750 °C) on the catalytic characteristics of 12 % $\text{Cr}_2\text{O}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst*

Precursor of the active sites	Heat atmosphere	Cr^{6+} (TPR), wt. %	Y, wt. %	S, wt. %	X, %	C, wt. %
$\text{Cr}(\text{NO}_3)_3$	helium	0.6	50.9	85.3	59.7	3.0
$\text{Cr}(\text{CH}_3\text{COO})_3$	helium	0.0	39.2	81.0	48.5	3.3
$\text{Cr}(\text{NO}_3)_3$	air	1.3	52.6	82.9	63.5	3.1
$\text{Cr}(\text{CH}_3\text{COO})_3$	air	1.3	46.5	78.1	59.5	4.0
CrO_3	air	1.8	48.8	83.4	58.5	4.3

*without promoters, T reaction – 580 °C, Y – yield $i\text{-C}_4\text{H}_8$, S – selectivity, X – conversion, C – coke

During the heat treatment in a stream of helium of chromium acetate catalyst formation Cr^{6+} is not detected. However, despite the complete absence of Cr^{6+} ions, the sample has appreciable activity and selectivity, although inferior to the sample calcined in air.

Thus, regardless of the nature of the starting compound chromium (III) and (VI) can highly active and selective catalysts dehydrogenation of isobutane be synthesized. It has been found out that oxide particles are responsible for the catalytic activity in conversion of isobutane both in the rate of Cr^{3+} oxidation, formed on the stage of thermal treatment of the catalyst and Cr^{6+} , which are also reduced to Cr^{3+} ions under the reaction conditions. An approach to regulating the condition of the various active chromium oxide particles in order to achieve optimum performance in activity and selectivity is proposed in the paper.

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HYDRODEAROMATIZATION OF MIDDLE DISTILLATES ON SULFIDED NiW CATALYSTS CONTAINING MICRO/MESOPOROUS NANOCRYSTALS

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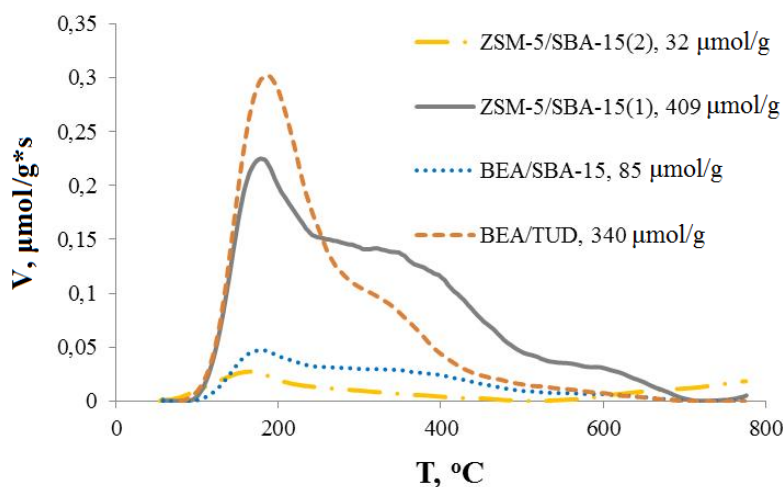
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In recent years, mesoporous materials such as MCM-41, TUD and SBA-15 have attracted considerable attention because of their potential applications in catalysis involving large molecules [1]. But as a rule the acidity of these materials are much lower than conventional microporous materials such as ZSM-5, BEA, Y. However, the use of zeolites in catalysis brings diffusion limitations and a lot of gaseous products. The advantages of both mesoporous materials and microporous zeolites can offer attractive features and circumvent the problems mentioned above.

In our work we synthesized four type of micro/mesoporous aluminosilica by different ways, then we obtained sulfided NiW catalysts using these materials and tested them in hydrodearomatization of methylnaphthalene fraction. Thus, ZSM-5/SBA-15(2) [2] and BEA/SBA-15 [3] were synthesized by zeolitization of a mesoporous SBA-15, the «double templating» method was used to prepare ZSM-5/SBA 15(1) [4] and the last one – BEA/TUD was synthesized by TUD-type mesostructuring of a BEA-zeolite [5]. The materials were characterized by various techniques including XRD, nitrogen adsorption, TEM, ²⁷Al MAS NMR and TPD of NH₃. All samples exhibit type IV isotherms that are typical for mesoporous materials except BEA/SBA-15 type because of mesopore volume was filled by BEA-particles during zeolite crystallization. Combining the results of the N₂ adsorption–desorption experiments and XRD we can conclude that BEA/SBA-15 has no zeolite phase and drastic diminution of the mesoporous structure. The other materials (ZSM-5/SBA-15-types) have pretty wide peaks in high region (5-15° and 20-25°), but it can be explained by small crystals formation. According to data from ²⁷Al NMR the acidity of ZSM-5/SBA-15(1) (the most acidic material) was 409 μmol/g. Solid-state NMR

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method shows that Al atoms have been incorporated into the framework of ZSM-5/SBA-15(1).



Temperature-programmed desorption (TPD) of ammonia spectra
The other materials have more than 40 % of octahedral state-Al in composition.
Hydrodearomatization of methylnaphthalene fraction on NiW/zeolite/MM
(300 °C, 50 atm. H₂, 200 mg of catalyst, 3 ml of substrate)

Content, mass. %	Methylnaph. fraction	I	II	III	IV
Diaromatic hydrocarbons	99.9	53.4	96.5	81.7	83.0
Monoaromatic hydrocarbons	~0	41.6	3.0	15.3	15.0
Saturated hydrocarbons	0.1	5.0	0.5	3.0	2.0
Sulfur, ppm	3660	250	3500	400	520

*I – NiW/ZSM-5/SBA-15(1), II – NiW/BEA/SBA-15, III – NiW/BEA/TUD, IV – NiW/ZSM-5/SBA-15(2)

The catalysts NiW/ZSM 5/SBA-15(1) and NiW/BEA/TUD were pretty active in hydrogenation (HYD) and especially in hydrodesulfurization (HDS). In this way the sulfur content has decreased in 15 times by NiW/ZSM 5/SBA-15(1) catalyst. Comparison of the results of the catalytic studies and phys.-chemical methods of analysis we can conclude the «double templating» method is very promising and application of ZSM-5/SBA-15(1) obtained by this method is not limited only to the process of hydrodearomatization.

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PROSPECTS OF APPLICATION OF OXIDATIVE DESULFURIZATION COMBINED WITH HDS FOR PRODUCTION OF LOW-SULFUR DIESEL FUEL

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One of common methods for removing sulfur-containing compounds from diesel fuel is hydrodesulfurization (HDS) over supported sulfide catalysts CoMo/Al₂O₃. Production of low-sulfur fuel by this method is industrially possible; however, for small refineries it is not economically viable and technically difficult. This requires a change in the main parameters of the process, such as an increase of hydrogen partial pressure and operating temperatures. Therefore, much attention is given to the research for alternative methods of removing sulfur from motor fuels after its prior HDS treatment. One of perspective methods for diesel fuels desulfurization is selective oxidation of their sulfur-containing compounds with oxygen over catalysts (ODS) [1, 2]. This method was poorly explored [3]; however, our results [4-6] showed that the process would be effective in the removal of sulfur compounds, especially dibenzothiophene (DBT) and its family, from diesel fuel in the form of SO₂.

The aim of this work is to study a prospect of ODS for the removal of refractory sulfur compounds (such as DBT and alkyl substituted DBT) from HDS treated diesel fuel by oxygen on the modified CuZnAlO catalyst. Changes of the physico-chemical properties of the catalysts during ODS will be discussed to reveal a catalyst lifetime.

The catalyst CuZnAlO was prepared by a precipitation method with subsequent calcination at 500 °C [7]. After that the catalyst was modified by B and MoO₃. The catalyst was tested at 250-450 °C in ODS of thiophene, DBT and 4,6-dimethyl DBT (DMDBT) dissolved in toluene or hydrodesulfurized diesel fuel (with sulfur content 500 ppm), with oxygen as an oxidant. The ODS tests for model diesel fuels were conducted at a ratio of O₂/S = 30-120, GHSV = 3000 h⁻¹ and WHSV = 6 h⁻¹. Physico-chemical properties of the modified CuZnAlO catalyst before and after the ODS reaction were studied by AAS-ICP, CHNS-analysis, XRD, DTA-TG-MS, TPR-H₂, FTIR, UV-Vis, ESR and XPS.

XRD study showed that the fresh modified CuZnAlO contained CuO and ZnO phases as well as highly dispersed spinel phase. According to TPR-H₂ results, the

modified CuZnAlO catalysts are reduced by H₂ in a single step at a temperature of 200-300 °C, and are characterized by the ratio H₂/Cu = 0.85-1.05. Comparison with literature [8] allows us to conclude that the copper is in the Cu(II) state and it is likely located in CuO and (Cu,Zn)Al₂O₄ species. The main ODS products are SO₂, CO₂, water and desulfurized model diesel fuel. The oxidation of sulfur-containing molecules was found to start at temperatures above 330 °C. The thiophene molecule was shown most resistant to oxidation, while DBT and DMDBT were more easily oxidized to SO₂. The maximum degree of sulfur recovery for thiophene, DBT and DMDBT are observed at T = 400 °C, being about 30, 60 and 80 %, respectively. The nature of sulfur molecules has no effect on toluene conversion. The maximum toluene conversion ca. 4.2 % is observed at T = 400 °C. XRD composition of the spent modified CuZnAlO catalysts includes Cu₂O, Cu⁰, and (Cu,Zn)Al₂O₄. According to CHNS, DTA-TG-MS and SEM data, the modified CuZnAlO catalysts after ODS contain sulfur and hydrocarbons molecules. DTA-TG-MS data show that sulfur is adsorbed as metal sulfides, polysulfides and sulfates.

The ODS of refractory sulfur compounds of model diesel fuels with air was shown to be feasible at atmospheric pressure and moderate temperatures: 330-430 °C. As a result, we can conclude that the nature of the sulfur-containing molecules has a significant impact on the efficiency of sulfur removal from hydrodesulfurized diesel fuels. Sulfur is removed from them via adsorption of sulfur-containing molecules on the catalyst surface, followed by their oxidation to SO₂. The oxidation of sulfur-containing molecules over the modified CuZnAlO catalyst was found to increase in a sequence: thiophene<DBT<DMDBT.

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FILTERLESS TECHNOLOGY FOR HYDROPROCESSES

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Hydroprocesses aimed at manufacturing saturated compounds, ketones, alcohols, amino products, and others are widely abundant in industry of basic organic and petrochemical synthesis. They involve gas-to-liquid processes (GTL) based on Fischer-Tropsch (F-T) synthesis that convert a mix of carbon monoxide and hydrogen (syngas) in the presence of suspended catalysts into liquid hydrocarbons such as syncrude and synthetic fuels, which are marketable products. The technology of these processes passed through the use of reactors of various types and configurations, and at last came to a wide use for these processes of suspension apparatus, or slurry reactors, which efficiency is higher, in many cases, than that of reactors with stationary catalyst.

Separating a catalyst/wax mixture from products is an important challenge in developing slurry reactors. Various techniques to separate wax from catalyst slurries have been used, including sedimentation, filtration, supercritical extraction, magnetic separation, etc. Developing an reactor system with continually present catalyst particles, without having them significantly withdrawn from the reaction system, is a major problem to be solved in industrial slurry processes.

We propose a new filterless technology for hydroprocesses based on a simple and efficient method for removing catalyst particles from the liquid products formed in a slurry reactor which minimizes the slurry holdup and catalyst loss. The principle makes it possible to perform these processes in a continuous technological mode without the removal of the solid catalyst with reaction products [1]. It was determined that under sudden expansion of a flowing slurry stream moving with high velocity, a liquid stream free of solid particles may be removed in a direction 90-180° from the jet direction. The key is that inertia causes the solid particles in the zone of expansion to retain their direction of motion, and not enter a clarified product stream flowing in an opposite direction. All the operations, namely chemical process, heat and mass transfer, circulation of suspension, catalyst separation from the reaction products, and heat removal, are provided in an integrated hydrodynamic system by means of rotation of agitator. Such a method of solid and liquid separation fundamentally

differs from the decantation method based on sedimentation of solid particles, and the hydrocyclone separation method as well.

Combining the slurry reactor and proposed separation device based on the inertial separation principle must create integrated hydrodynamic conditions to ensure effective contact of the gas-liquid-solid phase in the reaction volume. Along with the separation function, the designed slurry reactor allows any three-phase processes to be performed continuously without fine solid particles being withdrawn from the reactor system. The hydraulic tests of reactor systems with different volumes, catalyst supports (activated carbon, alumina, silica gel, Ni-Raney, mica), and solvents showed the ranges of valuable technical characteristics.

The developed filterless technology with a reactor system based on inertial separation can be widely used in industrial chemical and petrochemical hydroprocesses which retain suspended solid particles, such as hydrogenation, oxidation, polymerization, etherification, leaching, adsorption sewage treatment without adsorbent loss, fractionation of polydispersed systems, etc. However, the proposed technology cannot be used for hydroprocesses using nano-catalysts, because nanoparticles do not possess sufficient inertia to retain their direction of motion in the circulation loop. We applied similar reactor systems to perform liquid-phase hydrogenation with finely-powdered suspended catalysts previously [1,2]. The reactor systems can also be efficiently used in alternative GTL product manufacturing via catalytic carbonylation [3,4].

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NEW HYBRID PEROVSKITE-TYPE CATALYSTS $(\text{Gd,Sr})_{n+1}\text{Fe}_n\text{O}_{3n+1}$ FOR DRY REFORMING OF METHANE AND SUBSEQUENT LIGHT OLEFINS PRODUCTION

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At present in the oil processing there is a steady increase of interest in alternative methods for synthesis gas producing, which plays an important role for the motor fuels production and in other chemical processes, particularly, to obtain ethylene and propylene is an important raw material for the chemical industry. Dry reforming of methane (DRM) has great potential economic benefits, because it allows to obtain a synthesis gas with a H_2/CO ratio 2:1 and 1:1. However at the present time there are practically no selective catalysts, that do not undergo the deactivation due to coke formation. Perovskite-like structures, with mixed oxygen-ionic and electronic conductivity, high activity and stability are used as catalysts for high temperature processes.

The nanostructured perovskite-type ferrites $(\text{Gd}, \text{Sr}_{n+1}\text{Fe}_n\text{O}_{3n+1}, \text{A}=\text{Gd}, \text{Sr}, n=1,2,\dots,\infty)$ were synthesized by the high temperature solid state reactions and by sol-gel technology and were studied as the catalysts for dry reforming of methane.

The complex physico-chemical methods of investigation showed that the particles of ferrites are anisotropic. Samples obtained by sol-gel technology are in nanocrystalline state and they have a porous structure, oxides prepared by ceramic technology are in submicrocrystalline state. Mössbauer spectroscopy showed that the iron atoms of the samples synthesized by sol-gel technology are found in a heterovalent state (Fe^{3+} coexists with Fe^{4+}), which are stabilized by presence of oxygen vacancies.

The catalytic activity were studied in a flow apparatus at atmospheric pressure in the temperature range of 773-1223 K for in the DRM process and 300-723 K for the CO hydrogenation and flow rates of 0.5-1.0 l/h. Experiments were carried out with feeding a mixture of gases in a ratio of components $[\text{CH}_4:\text{CO}_2] = 1:1$ for the DRM

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reaction and $[\text{CO}:\text{H}_2] = 1:1$ for the CO hydrogenation. Analyses of the products were performed by chromatography (Crystal 2000M).

Investigated the relationship between catalytic activity and method of producing ferrites, the number of perovskite layers (n), the catalysts composition. It was found that the samples obtained by sol-gel method have higher catalytic activity compared with the ceramic samples. There is due to the state of nanocrystalline and a porous structure of the sol-gel sample. The hydrogen selectivity of the DRM reaction was increased in the row: $\text{GdFeO}_3(\text{ceramic}) < \text{GdFeO}_3(\text{sol-gel}) < \text{GdFeO}_3(\text{sol-gel citric})$. It was observed a correlation between the number of perovskite layers and catalytic activity (increase of KA with increasing n): $\text{GdSrFeO}_4 (n=1) \leq \text{Gd}_2\text{SrFe}_2\text{O}_7 (n=2) < \text{GdFeO}_3 (n=\infty)$. At the same time, the maximum values of light olefins selectivity in the CO hydrogenation showed a $\text{Gd}_2\text{SrFe}_2\text{O}_7(\text{sol-gel}, n=2)$ sample. It was shown that non-isovalent substitution of ions Gd^{3+} by ions Sr^{2+} in matrix of complex oxides causes a lowering of symmetry in the perovskite structure and occurrence of heterovalent state of iron atoms. The increase in the Fe^{4+} proportion lead to reduction of catalytic activity of ferrites in the methane reforming, but it is a favorable to activate the unsaturated compounds formation process. For two series of the systems of variable composition $\text{Gd}_{2-x}\text{Sr}_{1+x}\text{Fe}_2\text{O}_7$ maximum amount of produced CO and H_2 was observed at $x=0,3$. It was suggested that the surface carbonates formation is Gd^{3+} and Sr^{2+} ions and Fe^{3+} ions are responsible for the atomic hydrogen and CH_x -radicals formation.

All the tested ferrites showed a high stability. Catalytic characteristics were preserved during the repeated experiments and were not changed after 50 hours of the experiment. The mass change of the catalyst after completion of all tests did not exceed 1 % for all investigated systems. It may indicate a slight carbonization surface of the tested ferrites and the potential use for their further studies.

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HYDROTREATMENT OF GUAIACOL AND BIO-OIL USING BIFUNCTIONAL CATALYSTS OF NOBLE-METALS SUPPORTED ON MESOPOROUS ZIRCONIA AND ALUMINOSILICATES

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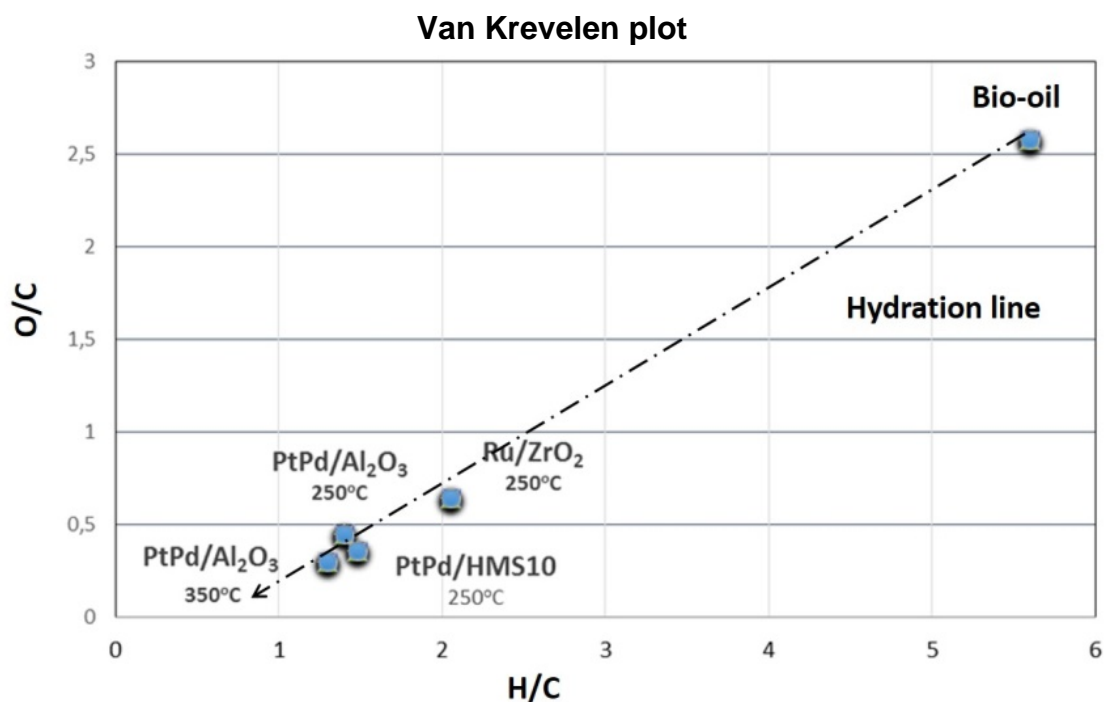
The depletion fossil fuel resources have motivated the worldwide search for new sources of transportation fuels with minimum environmental threats. Biomass is the perspective renewable carbon containing feedstock that can be used for both synthesis of hydrocarbon transportation fuels and chemical production [1]. Biomass is composed of three main biopolymers: cellulose, hemicellulose and lignin, which can be converted using fast pyrolysis technology to obtain a liquid energy carrier known as pyrolysis oil (PO) or bio-oil in high yields (up to 80 wt %) [2]. Hydrocarbons presence in bio-oil in the amounts of less than 20 wt %, the most part of compounds is acids, alcohols, aldehydes and lignins. A mixture containing a such variety of oxygen groups has a limited application potential due to some unfavourable product properties. The bio-oil is polar, not miscible in hydrocarbons, rather acidic due to the presence of organic acids, easily polymerisable substance [3]. As such, the bio-oil is not suitable for co-feeding in existing oil refineries and needs to upgrade. The most advanced and investigated technology of bio-oil upgrading is catalytic hydrotreatment (HDO, hydrodeoxygenation) at elevated temperatures (150-550 °C) and pressures (5-20 MPa) [4].

In this work, we investigated hydrotreatment of bio-oil and its model compound guaiacol over Pt, Pd, Ru, Rh-containing catalysts based on mesoporous zirconium and aluminum silicates. Guaiacol was chosen as major component of bio-oil. It contains hydroxyl and methoxy groups, which are frequently found in various lignin compounds of bio-oil [5]. Two types of mesoporous aluminosilicates (Al-SBA-15, Al-HMS) with different Si/Al ratio and mesoporous zirconium oxide $ZrO_2 \cdot 1.3SiO_2$ were synthesized as described in [6,7]. The supported catalysts were prepared by an incipient-wetness impregnation method. All preparing catalysts were characterized with NH_3 -temperature programmed desorption (NH_3 -TPD), transmission electron microscopy (TEM), N_2 -physisorption and X-ray photoelectron spectroscopy (XPS).

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Experiments with the model feedstock and bio-oil were conducted in an autoclave at 150-400 °C, an initial hydrogen pressure of 5 MPa. Guaiacol dissolved either in undecane or methanol (3 wt % and 50 wt %, respectively) was used as a model feedstock. A large amount of acids and alcohols in bio-oil significantly affects the HDO reaction pathways and can reduce activity of traditional catalysts [8]. Accordingly, methanol (~20 wt % in bio-oil) was chosen to study its influence on HDO process. The liquid phase products were analyzed using a GC and GC-MS. Hydrotreatment of guaiacol dissolved in undecane led to products including benzene, cyclohexane and methylcyclohexane. In the case with methanol obtained liquid phase also contained a complex mixture of several compounds such as methylated and methoxylated phenols and catechols.

The upgrading of bio-oil supplied by the pyrolysis of hardwood sawdust at 500 °C was studied over a supported bimetallic Pt-Pd and Ru catalysts showed the highest activity for HDO of model compound. Characterization of the liquid products was performed using ^1H and ^{13}C NMR spectroscopy, elemental analysis and GC-MS. Elemental analysis (O/C and H/C molar ratio) demonstrated the increase H/C molar ratio which characterized quality of the upgraded oil. O/C molar ratio decreases according to hydrogenation and removing oxygen from bio-oil compounds.



Elemental analysis

Elemental composition (wt.%)	Bio-oil	Water phase HDO products	Organic phase HDO products
H	9,5	10,6	8,4
C	20,3	8,7	49,4
O	70,0	81,0	42,2
N	0,2	~0	~0

¹H-NMR integration data for bio-oil and HDO product

Chemical shift region (ppm)	Type of carbon	%	
		Bio-oil	HDO product
10 - 8,0	-CHO, -COOH	1	~0
8,5 - 6,0	ArH, -HC=C<	10	8
6,0 - 4,4	CH ₃ O-, carbohydrates	22	~0
4,2 - 3,0	CH ₃ O-, -CH ₂ O-,	35	33
3,0 - 1,6	H ₃ C(=O)-, CH ₃ -Ar, CH ₂ Ar-	30	8,5
1,6 - 0,0	-CH ₃ , -CH ₂ -	0,7	49

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IMPROVING THE EFFICIENCY OF PRODUCTION OF DIESEL FUEL FOR COLD CLIMATIC ZONE BY THE CATALYSTS COMPOSITION REGULATION

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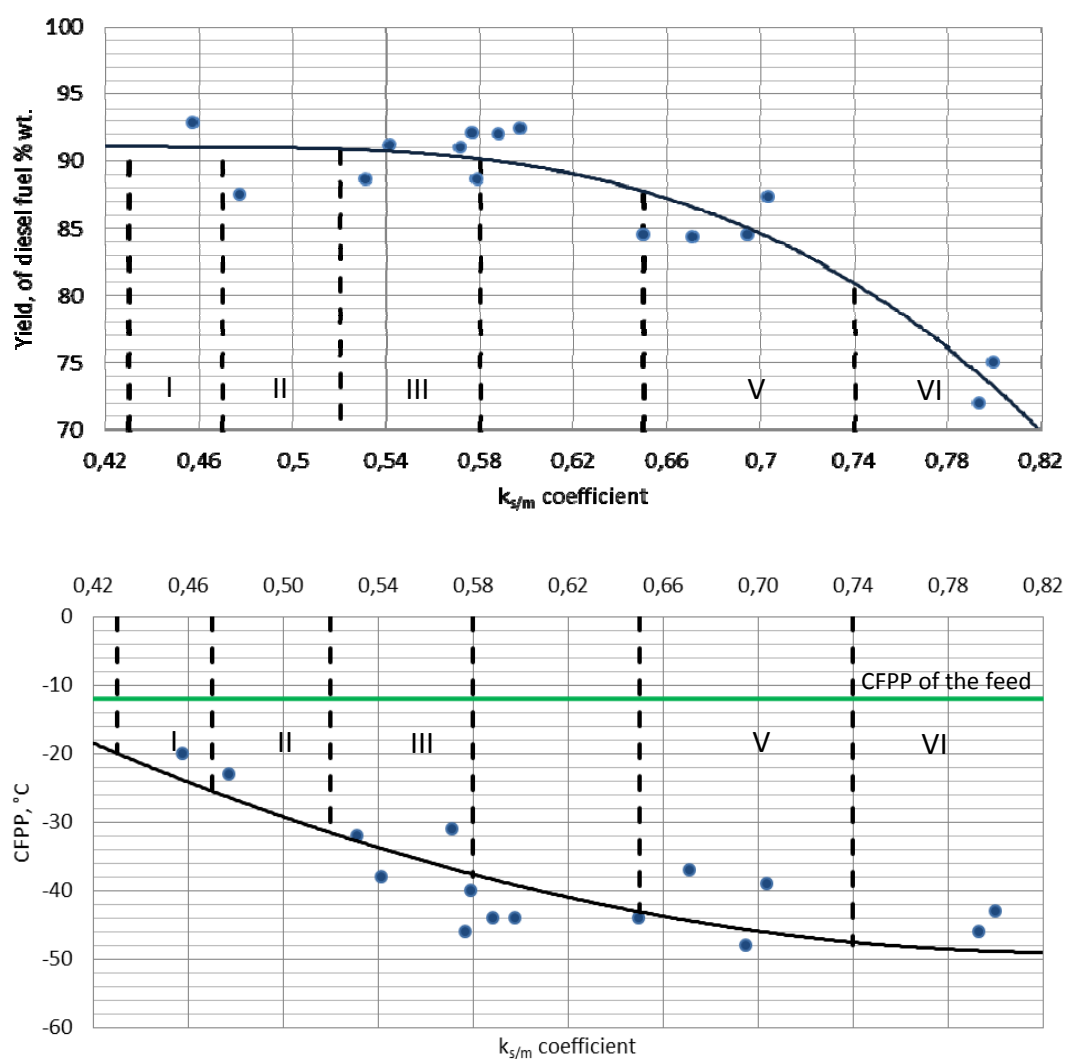
At the present stage oil industry development is focused on the increasing of the production and volume sales of petroleum products with high added value. In the Russian Federation specific petroleum products demand is largely determined by the peculiarities of climate and country's regions geographical position, therefore development of technologies and catalysts for producing of diesel fuels for cold climatic zones is a relevance problem.

In this project we developed the catalytic compositions to improve cold flow properties of hydrotreated diesel fraction. Samples of the first series were synthesized based on the molecular sieves of different structural types (MFI, MEL, MTW, FAU, Beta (BEA), AEL); the second series samples was prepared with zeolites of MFI, MTW, FAU types and zirconia modified with tungstate anions ($\text{WO}_4^{2-}/\text{ZrO}_2$). As components that provide the hydrogenation-dehydrogenation function were chosen mainly metals Ni, Mo, W, Co, Cr, also were used noble metals Pt, Pd, Ir, Ru. All samples were prepared using Al_2O_3 as a binder; some of these samples included the promoters and modifiers.

Acidic characteristics were investigated for the synthesized samples and was determined the ratio of the concentration of strong and middle acid centers designated as the $k_{s/m}$ coefficient. The catalysts were tested in a laboratory unit with flow reactor under the following process parameters: initial temperature 270 °C; pressure 3 MPa; liquid hour space velocity 3 h^{-1} and 1,5-2,0 h^{-1} for samples of the first and second series respectively; H_2/feed ration 1000 nm^3/m^3 . Diesel fractions obtained in the experiments were analyzed according to the main quality indicators, their yield was defined.

On the basis of the obtained results we established dependences of the influence of the $k_{s/m}$ coefficient, determined by the catalyst composition, on the yield and cold flow properties of the resulting diesel fuel. We established that the optimal catalyst for improving of diesel fuel cold flow properties is a sample whose components form a

system with a ratio of concentration of strong and middle acid centers ($k_{s/m}$) in the range of 0,54-0,60. Use of such catalyst allows obtain the diesel fraction with a yield of 90 % wt and CFPP (cold filter plugging point) depression more than 25°. The catalyst with the specified value of coefficient $k_{s/m}$ provides the predominance of hydroisomerization reactions of n-alkanes with a minimum degree of cracking. Based on the determined dependences it is possible to adjust catalyst composition to obtain diesel fuel with desired cold flow properties. Graphs of the received dependences are presented in the figure.



Graphs of the influence of the catalyst acid characteristics on the indicators of process for diesel fuel for cold climatic zone producing

(I, II, III, IV – the range of variation $k_{s/m}$ (between the dotted lines) to obtaining diesel fuel according to class 0, 1, 2, 3, 4 of GOST 32511-2013, VI – to obtaining diesel fuel according to class 4 of GOST R 55475-2013)

ISODEWAXING CATALYST FOR PROCESSING OF VEGETABLE AND PETROLEUM ORIGIN MIDDLE DISTILLATE FRACTIONS

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The development of the catalyst and process technology for hydroisodewaxing of hydroformed vegetable and petroleum origin middle distillate fraction were conducted at VNII NP in order to expand a feedstock base for production of motor fuels for arctic conditions.

The catalyst samples of the brand "ISO" were synthesized by method of wet mixing of the components (10 samples).

As an acid component we used a bicomponent mixture of high-silica zeolites (with $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio from 20.8 to 150): with the big and medium pore size – USY + ZSM-22, CVN + MOR, CVN + Beta, with the big pore size – ZSM-12 + MOR, and also a three-component mixture – CVN + ZSM-12 + Beta. Application of these components will improve the catalytic activity, reduce diffusion braking and reduce the degree of catalyst carbonization. The content of the zeolite component in the samples varied from 40 to 60 % wt.

Transition metals Ni, Mo, W As in form of oxides in an amount of 6.5-21 % wt. were chosen as components that provide the hydrogenation-dehydrogenation function. The use of these metals will ensure stable catalyst operation.

The binder component of synthesized samples is aluminum hydroxide and amorphous silica-alumina with mesoporous structure. To improve the catalyst textural characteristics we included in composition promoters such as oxides of boron and lanthanum in an amount of 2-4 % wt.

The synthesized samples had the following texture characteristics: specific surface area calculated by the BET method is in the range from 155 to 289 m^2/g , pore volume is 0.199-0.339 cm^3/g and an average pore diameter is 9.4-14.2 nm.

The total content of the strong and middle acid sites defined by ammonia TPD method ranges from 629 to 1218 mkmol/g .

Catalysts testing were conducted on a laboratory hydrogenation unit with flow reactor under the following process parameters: pressure 3 MPa, H_2 /feed ration $600 \text{ nm}^3/\text{m}^3$, temperature 265-340 °C, liquid hour space velocity (LHSV) 3 h^{-1} .

As a feedstock we used the middle distillate fraction 140-350 °C after hydroforming process of synthetic oil and straight-run diesel fuel mixture (30 % vol. / 70 % vol.). The feedstock characterized by a density at 15 °C equal $819 \text{ kg}/\text{m}^3$, a cloud point equal minus 4 °C and the cold filter plugging point (CFPP) equal minus 6 °C.

Testing results showed that the most effective catalyst in hydroisodewaxing of petroleum and vegetable origin middle distillate feedstock is a catalyst based on zeolites mixture CVN and MOR. It provides a yield of motor fuels components with good cold flow properties about 92 % wt. Quality of the end products meets the requirements of regulatory documents: quality of jet fuel meets GOST 10227-2013, quality of arctic diesel fuel meets GOST R 55475-2013.

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DETERMINATION OF PARTICLE SIZE OF ASPHALTENE FROM CRUDE OILS AND THEM BLENDS

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Because of the huge world reserves of heavy oils various techniques have been implemented to transport these oils [1], one of the major application techniques is mixed with a lighter diluent such as light oil, diesel or gasoline. But often incompatible crude oils and diluents can lead to precipitation of asphaltenes present in these and cause problems during transport [2,3]. That is why in this work the results on the effect of the average particle size of asphaltenes from different crudes mixing them by different methods are described.

The 7 crude oils used for mixing are very different in their properties as they go from heavy oil to extra light. Also we used different types of mixing to observe the effect of them on average particle size of asphaltenes, which they were: by composition (based on the crude C12 and mixing with the others crudes in 20, 40, 60 and 80 % vol.), conventional (mixing all the crudes in the same proportions by first mixing crudes with similar API gravities) and by extremes (mixing all the crudes in the same proportions in order to mix the crudes first with more difference in API gravities).

The content of sediments affected the average particle size of asphaltenes, since the equipment does not differentiate of asphaltenes and sediments. As the temperature was increasing, the particle size of asphaltenes increased, this effect is more evident in larger asphaltenes. The average particle size of asphaltenes decreased as increased the content of middle distillates in the oil due to their higher content of aromatics, except crude C51 asphaltenes.

Mixtures by composition with average particle size of asphaltenes greater were obtained with the C12 and C17 crudes. This is due the low solubility of the of asphaltenes of the crude C17 in crude C12 maltenes and the contribution of average particle size of asphaltenes of both, which is relatively large.

The best method of mixing is the conventional compared with by extremes. It was observed that in conventional mixing the average particle size of asphaltenes is 60.98 microns, while in method by extremes is 79.11 microns. In both cases, the resulting API gravity is the same.

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ANALYSIS OF COMPATIBILITY AND STABILITY OF ASPHALTENES FROM BLENDS OF CRUDE OILS

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In the oil industry, it is common practice to mix heavy crude oil with light crude oil or other hydrocarbons for reducing its viscosity and for making possible the transport through the production and refining facilities. If the crudes blended are not compatible, blending can cause precipitation of asphaltenes, which cause problems of fouling and plugging in the pipelines and problems in production and refining facilities. With the aim of finding a compatible oil mix to avoid such drawbacks, in this work was performed a study of stability and compatibility of blends from virgin crudes [1, 2].

To complete this goal were prepared seven virgin crudes mixtures in different proportions taking into account different types of blended. After chemistry and physical characterization of crudes and mixtures, it proceed to analyze the stability of the latter by ROFA FRANCE equipment, which is based on the methodology established in the ASTM D7157-12 method.

From the mixtures made it was found that it is convenient to mix crudes oil with similar properties. Further, it showed that the value of stability is independent of some properties from the crude oil, such as asphaltenes content and API gravity. Preliminary results show that it is feasible to promote the transport of crude oil in the oil industry from the dilution of heavy oil with light oil.

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