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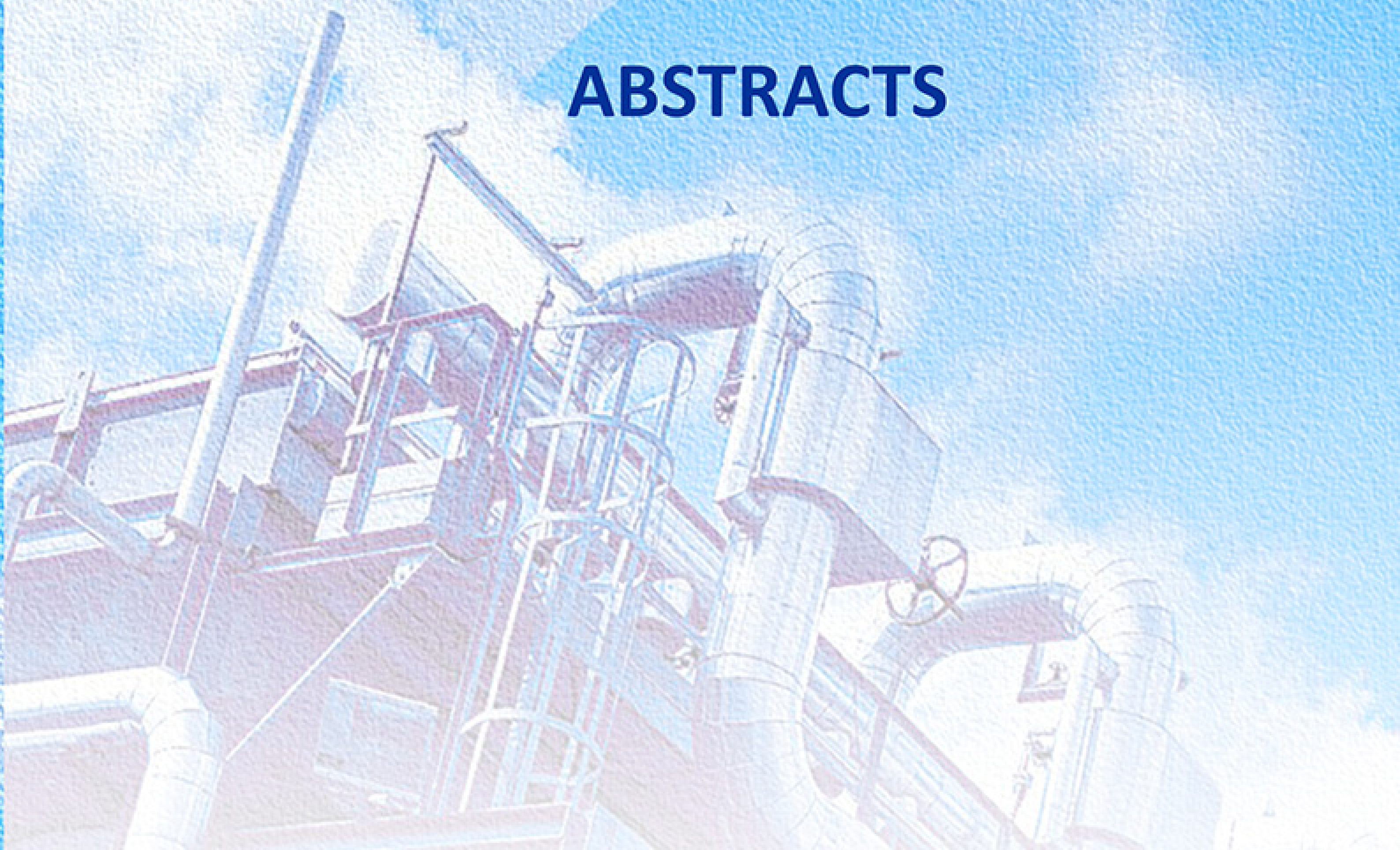
III Scientific-Technological Symposium

CATALYTIC HYDROPROCESSING IN OIL REFINING

Lyon, France,
April 16-20, 2018

ABSTRACTS



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Novosibirsk, 2018

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Сборник включает тезисы пленарных, ключевых лекций, устных и стендовых докладов.
Основные темы научной программы симпозиума:
The collection includes abstracts of plenary and keynote lectures, oral and poster presentations.
The main topics of the Symposium scientific program are:

- Perspective catalysts and hydroprocessing technologies of hydrocarbon fuels
- Promising catalysts and hydrocracking technologies
- Catalysts and hydroprocesses for the alternative and renewable raw materials hydroprocessing
- Catalysts and technologies for fuel and oil fractions hydrotreating
- Heavy oils hydroprocessing
- Catalysts and hydroprocesses for the light hydrocarbon feedstock hydroprocessing
- Industrial experience of production and use of catalytic cracking, reforming, hydrotreatment and hydrocracking catalysts
- Modelling of oil refining and petrochemical catalytic processes
- Catalysis in the production of oil and hydrocarbon feedstocks
- Economic aspects of the catalysts use in oil refining

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PLENARY LECTURES

DESIGNER ZEOLITES FOR HYDROPROCESSING: BETTER, SMALLER, MORE ACCESSIBLE & AFFORDABLE

Jean-Pierre Gilson

Laboratoire Catalyse & Spectrochimie, ENSICAEN - Université de Caen Normadie - CNRS 6 boulevard du Maréchal Juin, 14050 Caen, France

A brief overview of the impact of zeolites in oil refining will be given with a particular emphasis on their applications in Hydroprocessing. Then, building on the "Zeolite Crystal Engineering" strategy practiced in the LCS, the talk will discuss its potential in the three important facets of catalyst performance: activity, selectivity and stability. Recent examples of top-down and bottom-up strategies will highlight improvements in activity and selectivity of Na,H-Y, ZSM-22, ZSM-5 catalysts in cracking, hydroisomerization and aromatics processing. The often-overlooked advantage of hierarchical zeolites in the coking resistance and regenerability of ZSM-5 catalysts will be discussed and serve as a case study to compare bottom-up and top-down procedures. The role of defects, i.e. silanols on the catalytic performances of zeolites will be highlighted and show that more stable zeolite catalysts can be designed on that basis. What could be the ultimate frontier in zeolite particle size reduction will be presented: the so-called "Embryonic Zeolites", located at the interface between (X-Ray) amorphous materials and nanosized molecular sieves. Finally, the possibility to produce defect-free zeolites by incorporating transition metal ions in framework positions will be discussed. Perspectives will be drawn for future research in this very lively area of zeolite chemistry and catalysis.

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PL-2

KINETIC MODELING OF HYDROCRACKING PROCESSES

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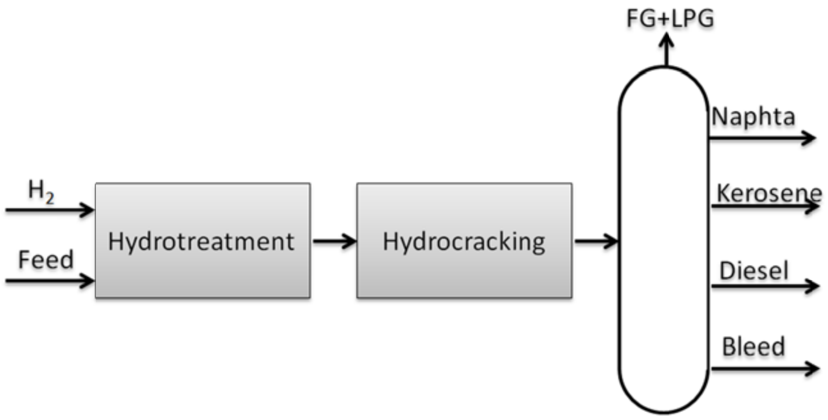
Keywords

Hydrocracking, Vacuum Gas Oil, Single Events, Microkinetic Modeling, Bi-functional Catalyst, continuous lumping, Experimental Design, Kriging

INTRODUCTION

Transformation of heavy crude oil into more valuable light (naphtha) and middle distillates (kerosene and diesel) is becoming increasingly important for the refining industry. A recent study (Mohr et al. 2015) states that the production of conventional crude oil has been constant, while there has been a strong increase in unconventional (i.e. heavier) sources. These unconventional crudes are characterized by a very high residue (>370 °C cut) content, high aromatic content, and high concentration of impurities (e.g. nitrogen, sulfur and metals). The increasing demand of middle distillates as well as the increasingly stringent quality requirements drives the need for increasingly sophisticated refining technology. Catalytic hydrocracking (HCK) is a widely used process capable of a high rate of conversion of residue to high quality middle distillates.

Hydroconversion of vacuum gas oil (VGO) is performed by hydrotreatment (HDT) and hydrocracking (HCK) in two reactors in series. The HDT step is mainly concerned with the removal of impurities; notably the elimination of sulfur and nitrogen from the organic components via hydrodearomatization (HDA), hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) reactions. The majority of the cracking and thus production of lighter and more valuable fractions occurs in the subsequent HCK reactor. A simplified schema of a hydrocracker unit is presented in Figure 1.



The capability of accurately modeling the HCK process is essential to take full advantage of the versatility of the process in terms of feed characteristics, desired yield and operating cost. Chemical engineers will typically use kinetic models to determine the optimal design and operating conditions of a HCK unit for a given task. However, the main difficulty of modeling HCK processes is the very complex nature of the feeds and effluents, compared to more pure systems encountered elsewhere in the chemical industry.

MODELING

In order to simulate the global process, a global methodology has been applied. It is defined in several steps.

Regarding the first reactor, several models are used. For HDS, HDN, HDCa: Simple ODE systems are used because the main difficulty is the definition of the adequate feed descriptor (resins, density…); For conversion and yields : Continuous lumping models are used (Becker et al. 2015) with five continuous families (paraffins, naphtenes, sulfur-containing aromatics, nitrogen-containing aromatics, and sulfur- and nitrogen-free aromatics). A reaction network, including hydrogenation, desulfurization, denitrogenization and cracking is established and used to derive the kinetic rate expressions for each family. A total of 46 model parameters are adjusted, using data from 44 experimental runs acquired on a pilot plant (with several different feedstocks). The same set of parameters was used to simulate hydrotreatment of every feedstock, which extends the range of applicability of the model beyond the one which are typically proposed in literature, which rely on feedstock-specific parameters. The results show that this modeling approach is capable of accurately predicting the total hydrocarbon conversion and yield regardless of feed composition. Furthermore, insights into the underlying reaction mechanisms can be inferred from the kinetic parameters.

Regarding the second reactor, for conversion and yields: two kinds of models can be used: continuous lumping or micro-kinetic models. The two modeling approaches are fundamentally different (P.J. Becker et al. 2016). The traditional lumping models take their starting point in the macroscopic level (i.e. measurable product properties) and derive a set of kinetic equations from there. Microkinetic models (in our case Single Event model) work their way up from the molecular level, by deriving the kinetic equations from the chemical reactions between individual molecules. The single events model should not be considered as an improvement meant to supersede the continuous lumping models currently in use, but rather a distinct modeling approach with a unique field of application. In summary, the following recommendations can be made: 1. The continuous lumping model should be used for practical application, such as commercial simulators for the design and operation of industrial HCK units. It is a relatively simple structure and low computational cost allows for effective implementation of this type of model within existing frameworks. The required input data (SIMDIS & PNA distribution of the feed) are readily available (Per Julian Becker et al. 2016). 2. The Single Events model should essentially be considered as a research and development tool. The complex structure, high computational cost, and requirement for advanced analytical techniques effectively prevents usage of this model in an industrial context. However, the quantity of information and physicochemical nature of the model can be very powerful.

Regarding the product properties (density, RON, Mon, cetane…). Two kind of models can be used: Regressive or interpolated models. For regressive models, polynoms (linear or quadratic) are used. For interpolation models, several techniques can be used: Splines, Kriging …. In our case, we suggest to use Kriging methods because they are more accurate than polynoms and can determine uncertainties (Da Costa et al. 2017).

In order to fit parameters model and to decrease the number of required experiments, experimental design theory is used. In our case, the D-Optimality criteria is used (Celse, Da Costa et Costa 2016). We showed that this technique can be used to reduce drastically the number of experimental points needed to estimate the model parameters. In the present case, if one-step method is applied, 22 points are enough to estimate parameters for HDN model when compared to the original database of 48 points.

The talk will show the main results obtained for each kind of model.

It will also show the new trends regarding this topic by merging Big Data techniques with kinetic models techniques. It can be shown that the association of these two techniques can improve the obtained results.

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PL-3

IN THE PATH FOR [CATALYTIC] FIELD UPGRADING: WHAT WORKS AND WHAT DOESN'T

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Since 1996, when the first field test of a vacuum residue steam processing technology (Aquaconversion) using ultra-dispersed catalysts was performed at the ISLA refinery in Curazao, the value of catalytic field upgrading technologies for heavy oils have been known and documented. The economics of field upgrading, as alternative to the use of dilution, comes out in every study looking efficient for integrated oil companies. That path seem exceedingly justified by the low investments, low environmental impact, low risk modular oil production growth, full effective use of deep conversion refineries and by the strategic relevance of minimizing the dependence on availability of diluents, pipelines capacity, along with minimization of solid by-products in remote areas. A brief historic of these developments will be introduced in this lecture.

Intriguingly, the incorporation of field upgrading as an essential component in the development plans for production fields of non-transportable heavy oils has been inexistent in the last two decades. That slow pace of assimilation is perhaps due to unfamiliarity with processes in general, and with catalytic processes in particular, by the reservoir and field production engineers and by decision makers of integrated oil companies. This lecture attempts to make progresses at reducing these resistances, by exposing the technical essentials that a field upgrading process must fulfill to be practicable and economic, which allows discarding the wide collective of thermal processes.

A brief of catalytic field upgrading processes developed and under development by the author in the last two decades for these purposes, ranging from steam/hydro/processing of vacuum residue to in reservoir hydro-upgrading and steam-upgrading of non-fractionated extra heavy oils will be introduced and economically compared with the traditional solutions previous to 2014, year when the oil prices slumped to a rather new stable level, perhaps placing these complex schemes in the never-more cabinets.

The approaches used by this developer to new ultra-dispersed catalysts, nano-catalysts and fixed bed catalysts, dealing with non-fractionated extra-heavy oils and better adapted to field upgrading processes will also be introduced with several examples.

THE STABILITY AND EVOLUTION OF HEAVY OIL SYSTEMS STUDIED VIA ADVANCED METHODS IN SITU

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In recent years, the petroleum industry has faced considerable challenges associated with the development of efficient technologies for production and processing of heavy crude oils and their components. The difficulties of using this type of crude hydrocarbons are caused by the high cost of recovery and transportation and by fundamental problems that arise in the processing of heavy crude oils using conventional catalytic processes. A highly intractable problem is the formation of deposits in the process equipment during heavy oil transportation and processing, oils [1,2,3,4] resulting in inefficient heat exchange and considerable loss of energy and feed during the industrial process, which can be as high as several percent of the crude oil equivalent. Thus, a fundamental condition for the development of effective processes for heavy oil production and processing is understanding of the key factors that determine the aggregative behaviour and stability of oil disperse systems, behaviour and chemical transformations of their components under various external conditions including elevated temperature and pressure and the presence of aromatic or aliphatic compounds, surfactants, alkenes or polymers specially added to suppress precipitation or compounds used to dissolve asphaltene deposits (alcohols, esters, amines, etc.) including chlorine and sulfur compounds [5,6].

Asphaltenes are known to be among the major components of heavy oils, playing the key role in the formation of precipitates [7,8]. Asphaltenes are prone to self-association to form aggregates, which may induce, under certain conditions, their irreversible flocculation and sedimentation [9]. However, despite the great number of publications devoted to determination of the molecular mass, size and shape ofasphaltene molecules and the structure and physicochemical properties of asphaltenes, their aggregation mechanism in real crude oils still remains an unsolved issue [10].

A significant factor influencing the asphaltene aggregation and precipitation is their local environment, which determines the nature of intermolecular interactions of asphaltenes with other crude oil components. Apart from the pressure and temperature, the chemical composition of the local environment also plays an important role in asphaltene stabilization [8,11]. It is evident that prediction of crude oil stability and solubility of asphaltenes under specified conditions requires the fundamental knowledge of the character of intermolecular interactions between asphaltenes and other heavy oil components present in the local environment; this knowledge can be gained only by means of in situ studies of local rheological properties of crude oils and molecular dynamics of asphaltenes under various conditions.

Currently, the structures and properties of heavy crude oils and oil residues are studied by highly informative physicochemical methods. The description and analysis of the results obtained via each method can cover hundreds of pages; however, one has to admit that the investigations are often encountered with restrictions that preclude unambiguous interpretation of the experimental data and gaining reliable information on the properties and phase composition of crude oils and their behaviour under different external conditions. Actually, the data obtained by even the most advanced physicochemical methods in the *ex situ* mode do not reflect processes that take place in crude oils under real conditions and, hence, they are unable to predict the behaviour of various crude oils and to determine the conditions for their stability and/or formation of oil deposits. As a rule, the methods are used to characterize crude oils and their heavy components, for example, to identify the atomic composition of asphaltene molecular fragments from their exact mass, and to gain information about their structure and physicochemical properties. However, it has to be stated that there is still no clear understanding of the causes for the loss of stability and aggregative stability of various heavy oils under particular conditions [12].

The application of physical methods *in situ* is a milestone on the way to identification of the factors determining the stability of oil disperse systems and elucidation of the mechanisms of aggregation and disaggregation of high-molecular-mass components of heavy oils. It is important to use a set of complementary methods that would cover various spatial and temporal scales for in situ investigations, but not a single, even a unique, method [13]. This would help not only to gain data on the molecular dynamics of asphaltenes and resins and local characteristics of oil disperse systems (viscosity, diffusion and aggregation rate of heavy components), but also to identify the factors determining the stability of oil dispersions and to propose energy-efficient approaches that would ensure higher aggregative stability of heavy oils [14].

Here the potential of physical methods for *in situ* studies of the phase stability and physicochemical evolution of heavy oils is analyzed. The basic principles of *in situ* application of the methods are outlined; the scope and limitations of each approach are discussed. Particular attention is paid to the visualization of the asphaltene aggregation process using attenuated total reflection Fourier transform IR spectroscopy and magnetic resonance imaging, as well as small-angle X-ray and neutron scattering, electron spin resonance and electron and optical microscopy. These methods provide complementary information on the properties and behaviour of oil disperse systems on various spatial and temporal scales ranging from the rotational mobility of asphaltene molecules and the dynamics of their local environment with a characteristic time of $\sim 10^{-10}$ s and evolution of the size characteristics and shape of asphaltene aggregates to visualization of asphaltene aggregation and formation of precipitates in crude oils and their blends with spatial resolution from a few to thousands of micrometres with a characteristic time from seconds to hundreds of hours. The approaches described can be efficiently applied in a wide range of temperatures and pressures, as well as in the presence of chemicals that affect the stability of heavy oils.

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PL-5

A MOLECULAR VIEW OF THE KEY COMPONENTS AND FUNCTIONS OF HYDROPROCESSING CATALYSTS

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Hydrotreatment and hydrocracking processes are playing a key role to produce cleaner fuels from petroleum feedstocks becoming ever more difficult to convert. These processes involve a wide range of reaction mechanisms activated by various catalytic materials: transition metal sulfides, aluminosilicates... Promoting hydrogenolysis, hydrogenation or cracking functions requires to activate C-S, C-N, C-H or C-C bonds by means of a broad spectrum of active sites. Hence, the molecular scale understanding of these active sites and corresponding mechanisms represents a challenging step to improve the rational design of these catalysts.

This lecture will illustrate how modern quantum simulation based on density functional theory (DFT) may be a powerful approach to address the diversity of hydroprocessing catalysts and their multicomponent character. On the one hand, it will be shown how the hydrogenation/hydrogenolysis functions of transition metal sulfides active sites can be described by DFT simulations.[1] The atomic scale features of the active phase and the interaction of the sulfided active sites with relevant molecules found in hydroprocessing will be highlighted.[2]

Regarding the cracking and isomerization functions, theoretical investigations on Brønsted acid sites in interaction with hydrocarbons will be reported on aluminosilicate materials relevant for hydroprocessing such as bulk zeolites, dealuminated zeolites,[3] zeolite surfaces,[4] and amorphous silica-aluminas.

In any cases, it will be underlined how DFT calculations help for the interpretation of experimental observations on those complex catalysts.

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HIERARCHICAL ZEOLITES FOR HYDROCARBON CONVERSION

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Zeolites are crystalline, porous silicates of great importance to catalysis, adsorption and separation. Their appeal can be attributed to distinct pore dimensions, high surface areas, outstanding chemical and thermal stabilities, and the availability of more than 220 topologies that can be targeted by appropriate synthesis. Zeolite synthesis usually involves the judicious choice of a structure-directing agent (SDA) that induces specific molecular interaction with the condensating silica scaffold. As zeolite crystal dimensions are typically much larger than the micropores themselves, a large fraction of the internal acid sites remains unused during chemical reactions, resulting in lower rates and undesired side-reactions such as coking. Thus, one of the grand synthetic challenges in materials chemistry is to fabricate zeolites that do not suffer from mass transport limitations, whilst retaining confinement. In this work I will discuss multi-scale spectroscopic, microscopic and computational approaches used to make significant steps not only in the understanding zeolite formation but also in the design of cheap templated synthesis of hierarchical zeolites. The work starts from the elegant work of the Ryoo group who synthesized 2 nm-thick ZSM-5 nanosheets. Mechanistic understanding about the formation of such materials using diquaternary ammonium surfactants paves the way to identifying conditions under which simpler SDAs can be employed to obtain materials with nearly similar catalytic properties.

Regarding nanosheet ZSM-5 synthesis, in-situ small-angle X-ray scattering, coupled to paracrystalline theory, and backed by electron microscopy, shows that the precursor phase to silicalite-1 nanosheets establishes its meso-scale order within the first five hours of hydrothermal synthesis.[1] Quasi in-situ vibrational and solid-state NMR spectroscopy reveal that this meso-shaped architecture already contains some elementary zeolitic features. The key to this coupled organisation at both micro- and meso-scale, is a structure–directing agent that is ambifunctional in shaping silica at the meso-scale whilst involved in molecular recognition at the micro-scale.[2] The latter feature is particularly important and requires the structure-directing agent to reside within the silica matrix already at early stages of the synthesis. From here, molecular recognition directs stabilization of precursor species and their specific embedding into a lattice, as shown by force-field molecular dynamics calculations.

Based on these insights we were able to explore and identify conditions under which a monoquaternary surfactant like CTAOH, a common surfactant that usually converts silica into MCM-41, can also induce the formation of hierarchical ZSM-5 zeolite with strong improved properties in the methanol-to-hydrocarbons reaction.[3] As a next step, we show how certain non-charged structure-directing agents commonly used for ZSM-5 syntesis can be combined with CTAOH to obtain in a cheap and scalable manner hierarchical ZSM-5 with similar perfomance as ZSM-5 nanosheets.[4]

We will also discuss the impact of nanostructuring of ZSM-5 on the catalytic performance in the hydroconversion of n-alkanes, which relates to industrially important hydroisomerization, hydrocracking and dewaxing reactions. An important finding is that the shape selectivity is hardly influenced by the nanostructuring, that is to say most of the catalytic conversion takes mostly place in the narrow micropores of ZSM-5. Typical zeolites used for this purpose are faujasite and mordenite. As the micropores inside these materials still prevent optimum operation, it is desirable to design solid acids with larger pores. Here we will present for the first time a synthesis method to obtain an X-ray amorphous aluminosilicate with well-defined mesopores and sufficiently strong acidity to render a nearly optimal bifunctional catalyst for the hydrocracking of hexadecane.

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OPERANDO SPECTROSCOPY OF ZEOLITE-BASED CATALYSIS: FROM REACTOR TO ACTIVE SITE

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Zeolites play a central stage in current and future catalytic processes as they combine high activity and stability with shape selectivity. Often in industrial operations zeolite crystals are compounded within mm-sized extrudates or micron-sized spheric particles. These extrudates and particles also contain binder materials, such as alumina, silica and clay minerals, which improve the thermal, structural as well as catalytic properties of the resulting catalyst bodies. Insights in the evolution and distribution of active sites within these industrially sized catalyst bodies at different length scales is crucial for their optimal performance.

This talk aims to provide an overview of the different modern characterization techniques available to uncover heterogeneities within zeolite-based catalysts, either in powder form or in the form of catalyst bodies. We will focus on space- and time-dependent phenomena occurring at different length scales; that is, at the level of catalytic reactors (mm to cm), catalyst bodies (μm to mm), catalyst grains (nm to μm), and active sites (Å to nm). The talk discusses recent advances in the development of space- and time-resolved spectroscopic methods for imaging spatial heterogeneities within catalytic processes at these four length scales. Particular emphasis will be on the use of optical and synchrotron-based methods, their capabilities in providing spatial resolution (1-D and 2-D chemical imaging) and depth profiling (3-D chemical imaging) as well as on their time-resolved application, potential for single-molecule and single-atom detection and use under real reaction conditions.

KEYNOTE LECTURES

NMR SPECTROSCOPY AND IMAGING OF HYDROCARBON CONVERSION PROCESSES

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Further progress in hydroporcessing requires its deeper fundamental understanding in terms of both catalytic and process aspects. The chemical transformations involved in hydroprocessing (hydrogenation, hydrocracking and hydrotreating) all consume hydrogen. This provides an opportunity to develop novel highly sensitive NMR-based approaches for studying both the reaction mechanisms and the physicochemical processes in operating model reactors.

Molecular hydrogen (H_2) is known to exist in two modifications which have different values of the total nuclear spin, namely orthohydrogen (I=1) and parahydrogen (I=0). Normal hydrogen is a 3:1 ortho:para mixture, but samples largely enriched in para-H_2 are easy to produce. Spontaneous para-ortho conversion is slow, but can be induced by, e.g., chemical activation of H_2. This was used since 1930s to probe H_2 activation by heterogeneous hydrogenation catalysts, well before NMR was discovered in 1945.

In 1987, the seminal work of Bowers and Weitekamp has revealed that NMR signals of reaction products and intermediates can be dramatically enhanced by using parahydrogen instead of normal hydrogen in homogeneous hydrogenations. The key condition for this is related to the reaction mechanism and requires that both hydrogen atoms of a single H_2 molecule are added to an unsaturated substrate such that they end up in the same product molecule (pairwise addition). This has been explored in the context of H_2 activation by transition metal complexes and clusters in solution since many such homogeneous catalysts activate H_2 via the formation of metal dihydrides and thus can implement the required pairwise mechanism of H_2 addition. We were able to demonstrate for the first time that similar NMR signal enhancements can be observed in heterogeneous hydrogenations as well [1,2]. The initial work based on the use of molecular Rh complexes immobilized on porous solid supports was later extended to the hydrogenation of alkynes, olefins and dienes on catalysts comprising supported metal nanoparticles such as Pt, Pd, Rh, Ni, Co on γ-Al_2O_3, TiO_2, etc. Our recent efforts showed the feasibility of pairwise H_2 addition over metal sulfides, carbides and oxides, including olefin and diene hydrogenation with parahydrogen over MoS_2. This made it possible, in particular, to apply this technique to study heterogeneous catalytic hydrodesulfurization of thiophene and to draw useful mechanistic conclusions based on the results obtained. Olefin and alkyne oligomerization processes performed in the presence of H_2 were also shown to provide NMR signal enhancement effects, extending this approach to other types of relevant chemical transformations. The most recent trend in this research is the use of single-atom or single-site heterogeneous catalysts as an attempt to maximize the contribution of pairwise H_2 addition to the overall reaction mechanism. An example utilizing the supported Pd-In intermetallic catalyst is illustrated in Figure 1, which in addition also demonstrates the possibility to combine parahydrogen-derived signal enhancement with magnetic resonance imaging to perform chemical characterization of the system under study with spatial resolution [3]. Such possibility is useful for the non-invasive visualization of heat-mass transfer processes and chemical transformations in operating model reactors. Further extension of this approach to other important reactants and catalytic reactions is feasible and will be discussed.

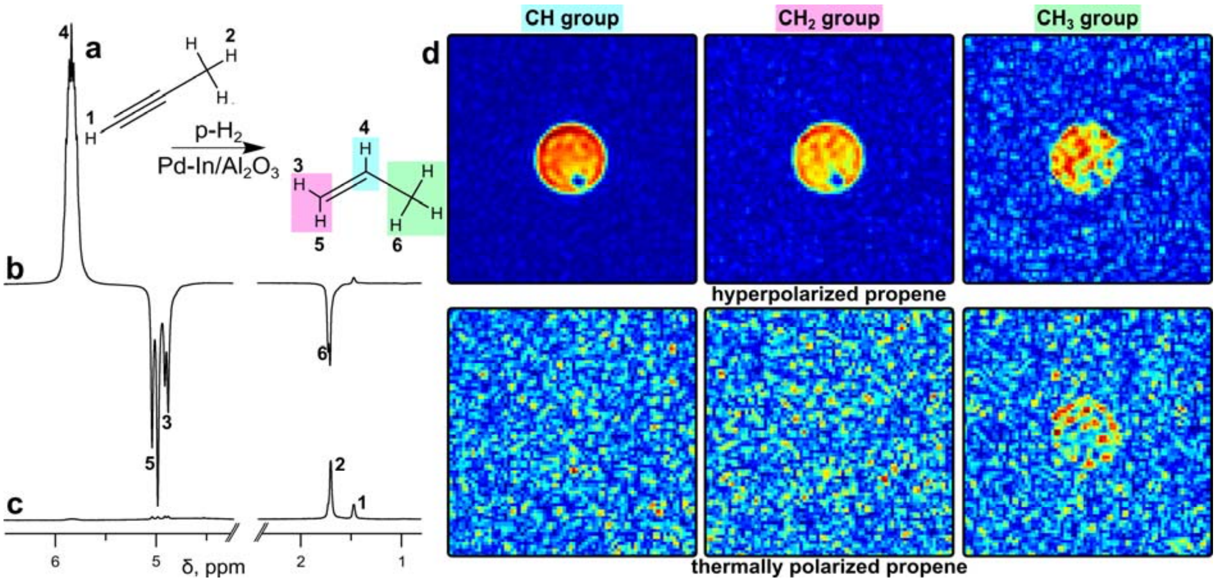

Figure 1. (a) Reaction scheme of propyne hydrogenation; (b) conventional and (c) enhanced ^{1}H NMR spectrum acquired during propyne hydrogenation with para-H_2 over Pd-In/Al_2O_3 (d) The corresponding MR images of a 10-mm NMR tube filled with reaction product propene [3]

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ZEOLITES WITH HIERARCHICAL PORE STRUCTURE FOR HYDROCARBON FEEDSTOCK PRODUCTION

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The ability to generate nanoscale zeolites or direct their assembly into hierarchical structures offers a promising way to enhance their molecular transport properties and coking resistance in catalytic reactions. To this end, synthetic protocols to control the morphology, as well as the underlying controlling mechanisms, have progressed greatly over the past few years. In particular, crystallization by particle attachment (CPA) has been found to be a ubiquitous crystal nucleation and growth pathway in natural and synthetic systems. As crystallization history can significantly influence the particle size, morphology of the final crystal, it is reasonable to intentionally design synthesis strategies by using this non-classical growth pathway.

Here, in this seminar, we will present several process controlled crystallization pathway to fabricate nano or hierarchical zeolites. One example is an orientated assembly strategy to construct hierarchical architectures of silicoaluminophosphates SAPO-11 by using prefabricated nanocrystallites as precursor. Such a synthesis is enabled by interrupting the dry gel conversion process to prepare nanocrystallites, as crystal growth is shown to proceed predominantly by particle attachment. The orientation of assembly can be controlled to form either a three-dimensional, sponge-like morphology or a two-dimensional ‘house-of-cards’ structure, by modifying the additives. Structures with a high degree of control over crystal size, shape, architecture, pore-network and acidic properties are achieved. The catalytic performance for the hydroisomerization of *n*-heptane was evaluated for a series of Pt-supported catalysts, and a record isomer yield (79 %) was attained for a catalyst with sponge-like architecture. The hierarchical architecture influences isomer selectivity for two reasons: expanding the intrinsic reaction controlled regime to be able to work at higher temperatures or conversion levels, and enhancing mass transport to reduce cracking of di-branched isomers. Such an acidity-diffusivity interplay indicates that strong acidity favors isomerization operating at temperatures away from the diffusion limited regime, while crystal size and pore connectivity are key factors for enhancing diffusion.

Another example is the use of organosialne, phenyltrimethoxysilane (PTMS), as novel solely Si source in SAPO-34 synthesis. PTMS as a Si source can significantly influence the crystallization pathway for SAPO-34 synthesis, leading to the formation of nanocrystals (< 100 nm). The protocol can be tailored to generate nanoszied SAPO-34 with enhanced catalytic stability in methanol-to-olefin conversion. The crystallization process was monitored by XRD, SEM, TEM and N_2 physisorption (for calcined samples) measurements of samples quenched at varied time intervals to shed light on structure evolution. It is disclosed that the Si release by decomposition of PTMS governs the crystallization process, leading to the formation of ultra-small, uniform crystallites. The as-prepared nanosized SAPO-34 exhibits a significantly enhanced catalytic stability without scarify light olefin selectivity in MTO reaction. Other examples, such as hierarchical zeolites ZSM-5, ZSM-11 and beta will also be demonstrated.

The results highlight an important role of crystallization process in controlling morphological features of these materials. Hierarchical porosity is not only important to the enhancement of catalyst efficiency, but could also change product distribution as a result of reaction-diffusion interplay.

KL-3

STEM-EDX CHARACTERIZATION OF SULFIDIC HYDROPROCESSING CATALYSTS

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Transmission Electron Microscopy (TEM) has been used for over 30 years for the characterization of Co/Ni-Mo/W sulfidic hydrotreating catalysts. This is mainly due to the good visibility of MoS_2 and WS_2 structures as well as Co_9S_8 and Ni_3S_2 crystals in the TEM micrographs. Initial studies were mainly focused on the MoS_2 dispersion, stacking and the position of the MoS_2 structures on the support. Also the changes of the MoS_2 dispersion on catalyst deactivation [1] were studied and early dispersion models have been presented [2]. Owing to the development of microscopic techniques, it has become possible to characterize the active phase in Co/Ni-Mo/W sulfidic catalysts in more detail. High resolution (HREM) was used to visualize details of the layered MoS_2 structures such as for example the curvature of the MoS_2 layers or the presence of small carbide particles [3]. The progress in the field of Energy-dispersive X-ray spectroscopy (EDX) allows to study the distribution of the active phase throughout the support material as well as the segregation of the Co/Ni promoter on catalyst deativation [4]. Details such as the MoS_2/WS_2 decoration of the Co_9S_8/Ni_3S_2 crystals have been visualized by Scanning TEM-EDX (STEM-EDX) [4].

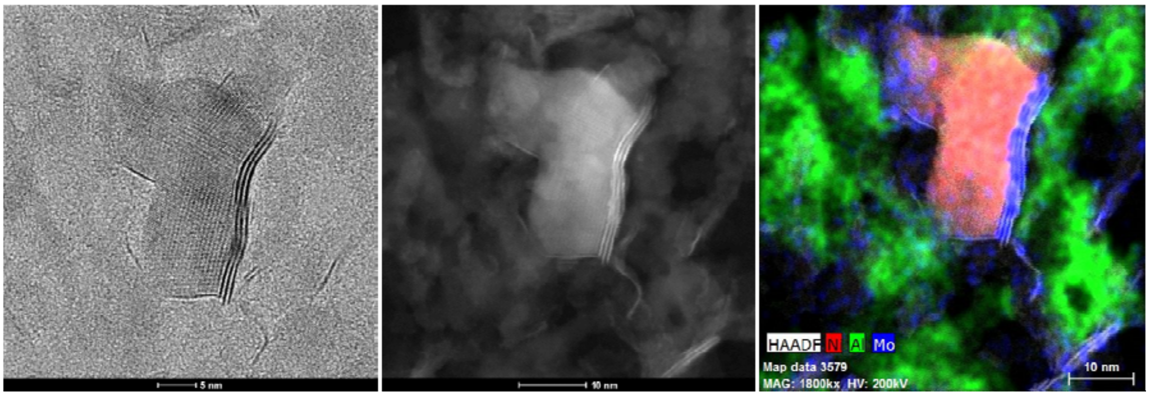

Figure 1. NiMo HPC catalyst: **a.** TEM image, **b.** STEM-HAADF image and **c.** overlay of Ni, Mo and Al elemental maps, showing that NiS_x crystals are decorated with MoS_2 slabs/stacks

Further insights have been obtained from 3D TEM and STEM-High-Angle Annular Dark Field (HAADF) studies. 3D TEM has shown that MoS_2 is present as interconnected complex structures, rather than simple hexagons or triangles, aligned with the support [5]. The 3D STEM-HAADF results show that multiple small irregularly shaped MoS_2 single slabs are lying flat on the surface of a single alumina platelets while a considerable part of the surface and pore volume is still empty. Neighboring structures seem connected. MoS_2 structures are often bent as they follow the surface of the alumina platelets. The 3D reconstruction also shows that the pores of the support are fully accessible for large reactant molecules [6].

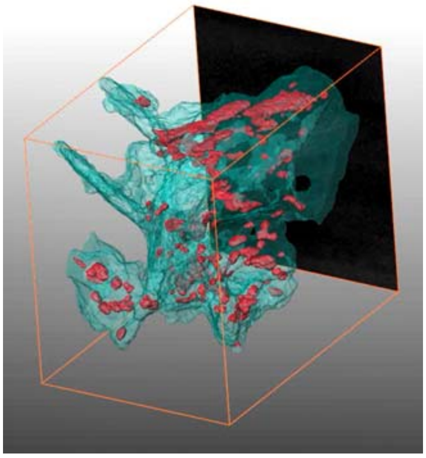

Figure 2. Alumina platelets decorated with several small ribbon-like MoS_2 structures as determined by 3D STEM-HAADF tomography.

The information on the exact shape and size of the MoS_2 structures is important when calculating MoS_2 dispersion. Early models based on 2D-imaging and assuming perfect MoS_2 hexagons projections may result in an erroneous estimation of the number of active sites. 3D STEM-HAADF makes it possible now to investigate the 3D structure of a used HPC catalyst in more detail, despite the high complexity of the material.

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UPGRADING AND REFINING OF CANADIAN OIL SANDS BITUMEN – RESEARCH AT CanmetENERGY, NATURAL RESOURCES CANADA

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Canada's oil sands and heavy oil reserves represent a major North American energy source. However, many technological, economic and environmental challenges must be overcome in order to improve the effectiveness and efficiency for converting these unconventional oils into clean, high quality transportation fuels that meet the ever-increasing environmental responsibility associated with developing these energy resources. Currently Canadian bitumen production is 2.5 MBBL/day, of which 40 % is fully upgraded into synthetic crude oil (SCO), and the other 60 % is diluted and transported to domestic and international refineries. While there are drawbacks associated with exporting diluted bitumen as-is, such as needing over 30 % extra pipeline capacity, the lower quality and hence market value of diluted bitumen relative to conventional crudes, and limited access to world markets, full upgrading of bitumen into SCO requires large capital and operating costs, intensive energy consumption and thus greenhouse gas (GHG) emissions. A third option, partial upgrading, is being developed to convert bitumen to the extent that it requires reduced amounts of, if any, diluent for pipeline transportation. Partial upgrading is expected to result in significant improvement in pipeline capacity, reduced/eliminated requirement for diluents, improved bitumen quality and market value, and reduced capital and operating costs, energy intensity and GHG emissions.

Both full and partial upgrading of bitumen use the following processes, either stand-alone or in combination: atmospheric and/or vacuum distillation; coking; thermal cracking/visbreaking; hydroconversion/hydrocracking; hydrotreating/hydrogenation; or solvent deasphalting/extraction including supercritical water- or solvent-based. Some unconventional technologies are also being developed, for example, cavitation; microwave and electromagnetic radiation heating; or sound/acoustic electrolysis. The objectives of bitumen upgrading may include (but are not limited to): 1) reducing viscosity and density (increasing API gravity); 2) reducing sulphur, nitrogen and other heteroatom contents; 3) removing or partially removing asphaltenes; and 4) reducing total acid number. In order to achieve these objectives, both chemical conversion processes (such as coking and hydroconversion) and physical separation processes (such as distillation and solvent deasphalting) must be utilized as an integrated operation in a bitumen upgrader.

During the past 30 years, CanmetENERGY in Devon, as one of Natural Resources Canada's energy research centers, has conducted R&D to support the sustainable development and use of the oil sands. Through collaboration with other federal and provincial government organizations, industry and academia, CanmetENERGY's R&D in bitumen and heavy oil full and partial upgrading, and petroleum refining, span a wide range of subjects and scales, from catalyst development, and reaction kinetics, to reactor modelling and process simulation; from fundamental molecular simulation to life cycle GHG assessment; and from proof-of-concept studies to bench-scale validation and pilot plant scale demonstrations.

In this lecture, a brief introduction to oil sands bitumen and heavy oil upgrading (including full and partial upgrading) will be given in terms of commercial technologies and industrial practice, and the technologies that are being developed at different technology readiness levels. Following this introduction, discussion will focus on some R&D achievements and activities at the CanmetENERGY-Devon research centre in upgrading technology development and demonstration, advanced characterization of bitumen and heavy oil chemistry, hydroprocessing catalyst development, hydrodesulphurization (HDS) kinetics, hydroprocessing reactor modelling and simulation, process modelling simulation and GHG life cycle assessment of bitumen upgrading and petroleum refining [1]. Co-processing of biocrudes with petroleum and research activities in other CanmetENERGY labs will also be briefly discussed.

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ASSESSING THE CATALYTIC PERFORMANCE DURING HEAVY-OIL HYDROPROCESSING BY FT-ICR

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The kinetic understanding of hydroprocessing is hampered by the multiplicity of phases, active sites, reactions and multiscale phenomena involved [1]. In addition, the complex composition of the feedstock, particularly the heavy ones, increase even further the difficulty to get a faithful kinetic picture. This picture is required for a rational process design and catalyst selection. Typically, the hydroprocessing catalyst possess a combination of sulfurized Mo, Co, Ni or W supported on an alumina based porous material [2]. With these catalysts, the reactions involve hydrodesulphurization, hydrodenitrification, hydrodearomatization and hydrodeoxygenation, while if process conditions are severe enough hydrocracking reactions may occur [3]. Within this framework, we have studied in this work the hydroprocessing of heavy fractions with industrial relevance in the waste-refinery scheme, testing different catalyst and analyzing the results on the basis of a detailed analytical workflow.

The heavy-oil used as feed is a blend of (1) light cycle oil (LCO) produced as byproduct in the fluid catalytic cracking unit of Petronor refinery (Muzkiz, Spain), and (2) scrap tire oil (STO) produced by pyrolyzing tires in a conical spouted bed reactor at 500 °C. The blend of LCO/STO consisted in 4:1 vol. The catalyst tested are commercial ones, characterized by different techniques, such as TPR, TPD and XRD, among many others. The hydroprocessing runs were undertaken at 320 and 400 °C; 80 bar; WHSV = 5 h^{-1}; H_2:oil ratio, 1000 cm^3_N cm^{-3}_{oil}; and time on stream up to 8 h. The analytical workflow applied to the feed and products consists on FID/MS GC×GC, PFPD GC and APPI/ESI FT-ICR.

The composition of the reactant feed (LCO+STO) and the products of selected combinations of catalyst and conditions are displayed in Figure 1, in terms of the aliphatic and aromatic class (radicals), excluding oxygen-, sulfur- and nitrogen-containing molecules and using APPI. These representations are in terms of double bound equivalents (DBEs) *vs*. the number of carbons (Cs) of each species or fraction. Thus, the displacement of the contours of Figure 1 should be interpreted as hydrogenation-hydrodearomatizaton in the DBE-axis and hydrocracking in the C-axis. Interestingly, the number of species detected by the FT-ICR are expanded almost one or two orders of magnitude as compared with the GC×GC.

The results presented in Figure 1 point to certain observations that are well-known in hydroprocessing: (i) highly condensed aromatics, such as phenanthrene or anthracene (DBE = 10) are removed efficiently with all catalysts at 320 °C, but as the temperature is raised (up to 400 °C) the extent of this removal is lowered due to the thermodynamic control of hydrogenation reactions; (ii) using NiW/HY catalyst or high temperatures (400 °C) efficiently removes the heavier fractions (C > 35) so that the yields of gasoline and diesel fractions are amplified.

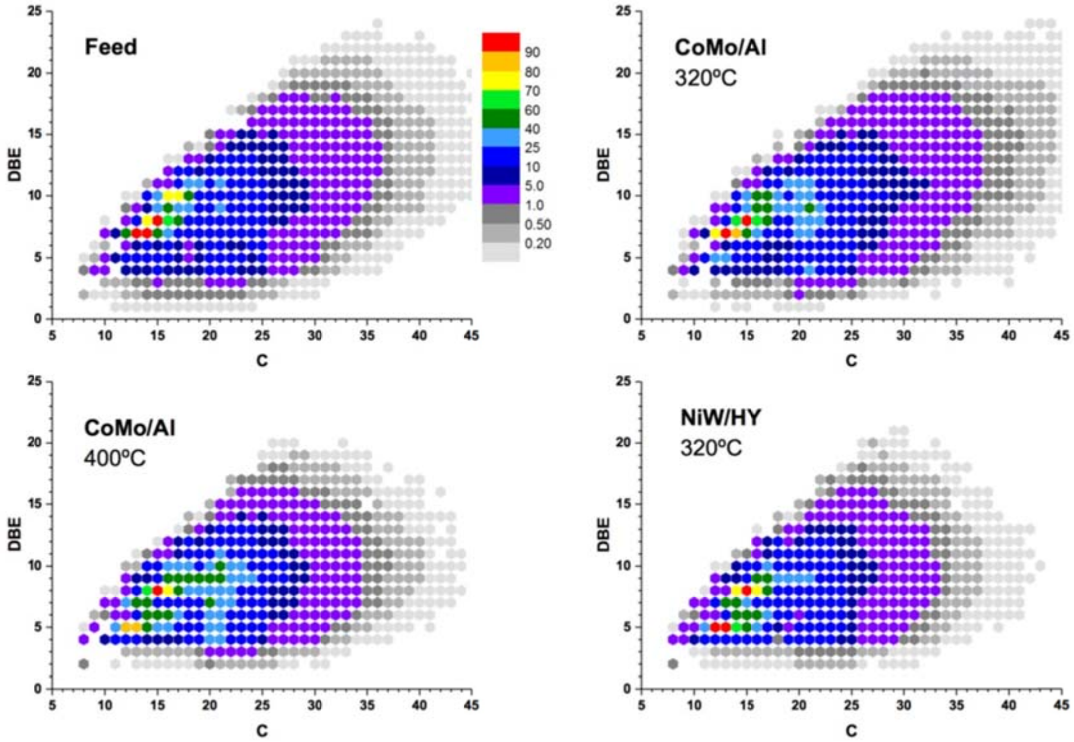

Figure 1. Composition of the feed and products of hydroprocessing using different conditions and catalyst, as obtained by APPI FT-ICR (CH class, radicals)

The breakthrough of this work is correlating the overloaded compositional databases extracted from FT-ICR with key aspects of the feed, catalysts or conditions, to rationally select the best set of parameters for hydroprocessing heavy-oils.

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SELECTIVE POLYAROMATICS SATURATION AND RING OPENING DURING HYDROPROCESSING OF LIGHT CYCLE OIL OVER SULFIDED Ni-Mo/SiO_2-Al_2O_3 CATALYST

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FCC (Fluidized Catalytic Cracking) unit makes 10-20wt% light cycle oil and is considered as low-quality fuel due to the higher concentration of sulfur, nitrogen and polynucleararomatic hydrocarbons content. Hydroprocessing of LCO is still a challenge and there are many available technologies to process LCO in multiple steps. In this paper, light cycle oil hydroprocessing was carried over sulfided Ni-Mo/SiO_2-Al_2O_3 catalyst in a fixed bed reactor. NiMo catalyst, prepared by successive impregnation using commercial SiO_2-Al_2O_3 support was evaluated in LCO hydrotreating reactions at different temperatures, pressures, and H_2/feed ratios. BET, NH_3-TPD SEM, and TEM techniques show that material is an amorphous mesoporous structure with moderate acidity and homogeneous dispersion of metallic sites on the surface. Poly-aromatic hydrocarbons were reduced to 5 wt % from 54 wt % in the hydroprocessed products at 380 °C and 60 bar while mono-aromatics were increased to 50 wt % from 25 wt %. Most of the polyaromatic hydrocarbons were converted to mono-aromatic compounds, and GC-MS analysis shows the conversion of 3 ring poly-aromatic compounds to alkyl substituted tetralin compounds. The minimum sulfur concentration obtained was 170 ppm at 380 °C and 60 bar. The octane number was improved due to higher aromatics content in the hydroprocessed products and makes it suitable as gasoline blending component. The catalyst shows very stable activity with time, for the production of diesel. Hydroprocessed LCO products properties like viscosity, cetane index, °API, and density meets the diesel fuel specification as well.

GCxGC and GC-MS analysis were used to identify the hydrocarbons in the products at different conditions. The molecular changes found in the products indicate that hydrogenation, skeletal isomerization, and hydrocracking reactions are favoured over this catalyst. Best poly-aromatics removal (90 %) and highest percent of paraffins (40-50 wt %) were obtained at moderately high temperature (380 °C), pressure (50-70 bar) and H_2/Feed ratio (1000 nL/L). Process with the best conditions to remove poly-aromatics compounds favours the production of aromatics which could be mixed to gasoline pool due to high octane number and aromatics.

ORAL PRESENTATIONS
Session 1

CATALYSTS FOR HYDROPROCESSING SYNTHESIZED USING SULFONIUM SALTS

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Unsupported metal sulfide catalysts have been prepared in different ways, including the sulfidation of coprecipitated oxides, homogeneous sulfide precipitation, impregnated thiosalt decomposition, hydrothermal and solvothermal processes based on emulsions etc. The ex suti and in situ decomposition of thiosalts of Mo or W is a simple and reproducible method, which has proven useful in the preparation of bi- and trimetallic sulfides with varied stoichiometry. The ammonium or amine containing salts of thiocomplexes are used for synthesis of carbon-containing sulfide catalyst with high surface areas and high catalytic activities. The use of nitrogen precursors has a negative effect on the catalytic properties of the resulting materials, especially for in-situ synthesized WS_2 based catalysts for hydrogenation. The addition activation by sulfur containing compounds are used to synthesize catalyst with high hydrogenation activity.

Here, we developed a new method to prepare active and selective unsupported sulfide catalyst with different Mo and W slab morphology (slab length, stacking number and curvature) by the decomposition in situ of the synthesized sulfonium salts with Ni-W and Co-Mo thiocations in the hydrocarbon feedstock. The resulting catalysts exhibits high activity and stability in the hydrogenation of bicyclic hydrocarbons and in the DBT conversion. The procedure of catalysts synthesis do not include additional sulfidation. It was demonstrated, that the catalytic activity and selectivity of sulfides in hydrogenation and sulfur containing compounds dependent on the nature of sulfonium cation (trialkyl, triaryl) and nature of metals in thio-complexes.

OP-2

MOLECULAR LEVEL INSIGHTS IN HEAVY GAS OIL HYDRODENITROGENATION BY FOURIER TRANSFORM ION CYCLOTRON RESONANCE MASS SPECTROMETRY

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1. Introduction

In spite of extensive studies on model molecules like quinoleine and carbazole [1,2], our knowledge of the dominating reaction pathways in the HDN reaction network of a real gasoil feed is still limited. The main reason is the complexity of the system and the difficulty to achieve a detailed analysis of intermediates and products at a molecular level. We have tackled this problem by applying FT-ICR/MS to hydrotreating effluents.

2. Experimental and methodology

A mixture of SRGO and coker gas oil (50/50 wt %), with a nitrogen content of 700 ppm (40 % basic nitrogen species) was used as feedstock. The gas oil was hydrotreated at 50 bar and 360 °C with a $NiMo/Al_2O_3$ catalyst [1]. Hydrotreated effluents obtained at different space velocities were analyzed for total and basic nitrogen content. The detailed speciation of nitrogen compounds was carried out by FT-ICR/MS in ElectronSprayIonization(+) or ESI(-) mode, for basic and neutral compounds, respectively. Via Kendrick plots, the products were classified into different families, according to their Double Bond Equivalent (number of condensed rings, degree of aromaticity) and carbon number. The concentration of each family was assumed to be proportional to its relative peak intensity in FT-ICR/MS spectra in each fraction.

3. Results & Discussions

At moderate HDN conversion (70 %), the percentage of basic nitrogen molecules had almost doubled compared to the feed. This result highlights that the conversion of neutral nitrogen compounds was initially more rapid than the conversion of basic nitrogen compounds (in line with the findings of model molecules). However, when further increasing HDN conversion, the fraction of basic nitrogen decreased again, meaning that the order of reactivity of basic and neutral nitrogen compounds was reversed in favor of the basic ones at high conversions. The inversion was attributed to inhibition effects (basic compounds are more strongly adsorbed than neutral ones).

The evolution of the DBE-based families as a function of HDN conversion (Figure 1b) gave further insights into the reaction pathways of neutral and basic compounds. For basic compounds, a shift to lower DBEs was observed, which means that partially hydrogenated intermediates, which still contain N, were accumulated at high conversions (in line with the behavior of quinoline). For neutral compounds, such a shift was not observed. Refractory carbazoles and tetrahydrobenzo-carbazoles were present up to very high HDN conversions.

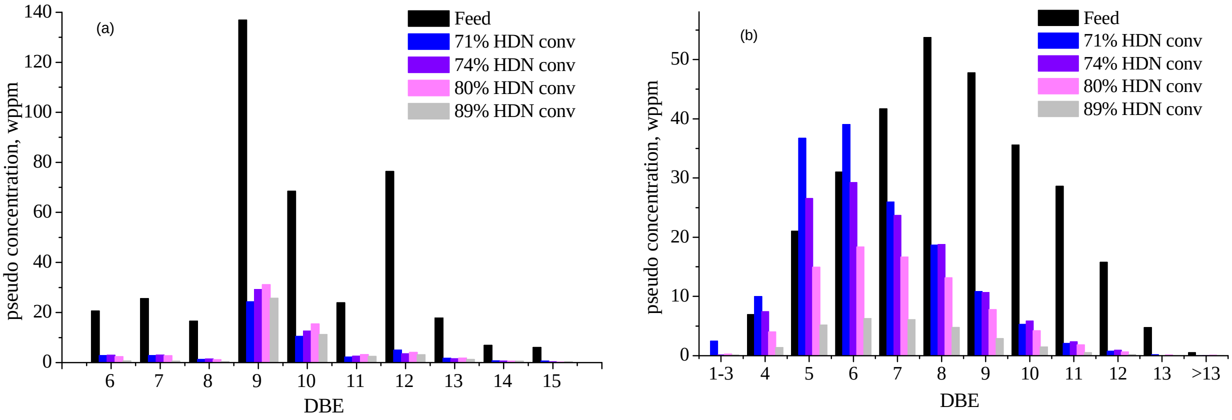

Figure 1. Pseudo concentration of each neutral DBE-based family (a) and basic DBE-based family (b) in the gas oil feed and the hydrotreated effluents

Cracking reactions of N-compounds were not confirmed, but slight changes in the carbon number distribution showed that heavy compounds were more reactive at moderate conversions, but the tendency was inverted at higher HDN levels, presumably because the residual heavy compounds were the most refractory ones.

4. Conclusions

FT-ICR/MS is an excellent tool to gain insights into the reactivity of basic and neutral nitrogen species in gasoil fractions, as a function of their aromaticity and carbon number.

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THE INFLUENCE OF B and P ON THE PROPERTIES OF NiMo/γ-δ-Al_2O_3 VGO HYDROTREATING CATALYSTS

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At present, the development of the processes of vacuum gas oil conversion (VGO) is the most urgent, as it makes the main contribution to the production of target petroleum products. One of such processes of VGO transformation and production of high quality petroleum products is hydrotreatment (HDT).

Ni-Mo/γ-Al_2O_3 [1] catalysts are usually used for VGO HDT. In general, research papers devoted to the increase in the activity of VGO HDT catalysts refers to the modification of the active component of these catalysts by various additives or to the change in the textural characteristics of a support. However, in recent years, several papers have appeared in which HDT catalysts containing δ-Al_2O_3 are used. Thus, it was shown in [2, 3] that such catalysts had higher HDS activity as compared to γ-Al_2O_3. Basically these studies consider catalysts based on pure δ phases and without modifying additives. The main goal of this work is to investigate Ni-Mo/Al_2O_3 containing both γ-Al_2O_3 and δ-Al_2O_3, which are modified by B and P.

To prepare supports, AlOOH powder HQ102B was used. The supports were prepared by peptizing of boehmite with NH_4OH followed by drying at 120 °C and calcination at 900 °C. Modifying agents (B and P) were added at different preparation stages: to the kneading paste of a support or to the impregnating solution. All catalysts contained 12 wt. % of Mo and 3.5 wt. % of Ni. List of catalysts is given in Table 1. Catalysts were tested in hydrotreating of VGO in the following conditions: the feed – straight-run VGO, $P = 16.0$ MPa, $T = 360$-420 °C, $LHSV = 0.75\ h^{-1}$, H_2/feed = 1000.

According to XRD method the prepared samples contained both γ-Al_2O_3 and δ-Al_2O_3 phases. Thus, the selected heat treatment temperature does not allow a complete transfer of $\gamma \rightarrow \delta$. In all cases, the phase ratio was close (with the introduction of B and for pure supports). The introduction of modifiers affects the textural characteristics in different ways. The introduction of P into the solution somewhat reduces the specific surface area of the catalyst, while the introduction of B into the impregnating solution results in a significant reduction in both the specific surface area and the pore volume, with an increase in the average pore diameter. At the same time, the introduction of B into the support, on the contrary, leads to an increase in both the specific surface area and the average pore diameter. Investigation of catalysts by the UV method has shown that only the introduction of B into the support results in a decrease in the size of the particles of the active component, whereas the use of P or the introduction of the modifier into the support does not lead to changes. In addition, HRTEM images showed that active component particles are mainly localized on γ-Al_2O_3 as the multilayer slabs.

Table 1. Characteristics of prepared catalysts

Sample	P	B	Surface area, m^2/g	Pore volume, cm^3/g	D, nm
$NiMo/Al_2O_3$	-	-	120	0.5	166
$NiMoP/Al_2O_3$	IM	-	110	0.5	165
$NiMoB/Al_2O_3$		IM	98	0.4	181
$NiMoPB/Al_2O_3$	IM	IM	86	0.4	151
$NiMoB/Al_2O_3$+B	-	IM+S	111	0.5	172
$NiMoPB/Al_2O_3$+B	IM	IM+S	98	0.4	172

*IM – impregnating solution, S – support

Catalytic activity tests showed (Figure 1) that only introduction of P into impregnating solution ($NiMoP/Al_2O_3$) increases HDS activity. It was noted that in other cases modifying of catalysts resulted in the decrease of HDS activity.

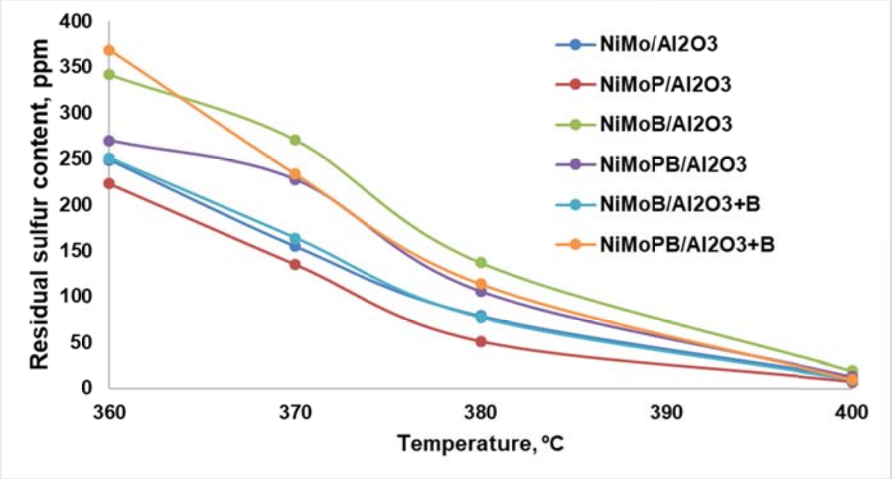

Figure 1. Residual sulfur content of the prepared catalysts

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OP-4

ACTIVE PHASE OF DISPERSED MoS_2 CATALYST IN HYDROCRACKING OF VACUUM RESIDUE

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Recent increase of demand in light oil has spurred research in heavy-oil upgrading technologies [1-4]. Among the heavy oils like petroleum residue and bitumen, vacuum residue (VR) occupying a half of heavier crude oil, has been a target to be upgraded into middle distillates. Slurry phase hydrocracking (HCK) in the presence of unsupported MoS_2 catalysts is one of the most promising processes with high conversion rate of heavy oil to distillates. In particular, the unsupported MoS_2 catalysts shows superior activity and stability over the supported catalyst system for VR HCK [5-7].

The slurry phase hydrocracking (HCK) of vacuum residue (VR) in the presence of dispersed MoS_2 catalyst was investigated under different reaction conditions with varying temperature, pressure, and reaction time. Extended X-ray absorption fine structure (EXAFS) measurements were used to obtain structural information about the dispersed MoS_2 phase in the middle of reaction. At a standard reaction condition of a temperature of 673 K and a pressure of 10.0 MPa in an autoclave batch reactor, kinetic analysis for VR HCK confirmed that the reaction occurs in a parallel manner in the production of liquid oils of 77 % as major products like vacuum gas oil and distillates with the generation of gas and coke of 23 % in the presence of dispersed MoS_2 catalyst (0.113 mmol or 360 ppm Mo). Although lower temperatures below 653 K at 9.5 MPa was found beneficial in coke reduction less than 1.0 wt % in favor of hydrogenation at 33 h of reaction, higher pressures over 15 MPa at 673 K was more influential to accelerate the VR conversion into liquid products reaching 90 % at 4 h of reaction with coke reduction down at 1.2 wt % than the cases under lower pressure conditions below 10 MPa. Analysis of the spent catalysts by EXAFS and TEM demonstrated that the nano-sized MoS_2 phase was well developed from $Mo(CO)_6$ in the early stage of reaction with a lower Mo-S and Mo-Mo coordination verifying the small MoS_2 particles having more exposed and defect sites as active phase.

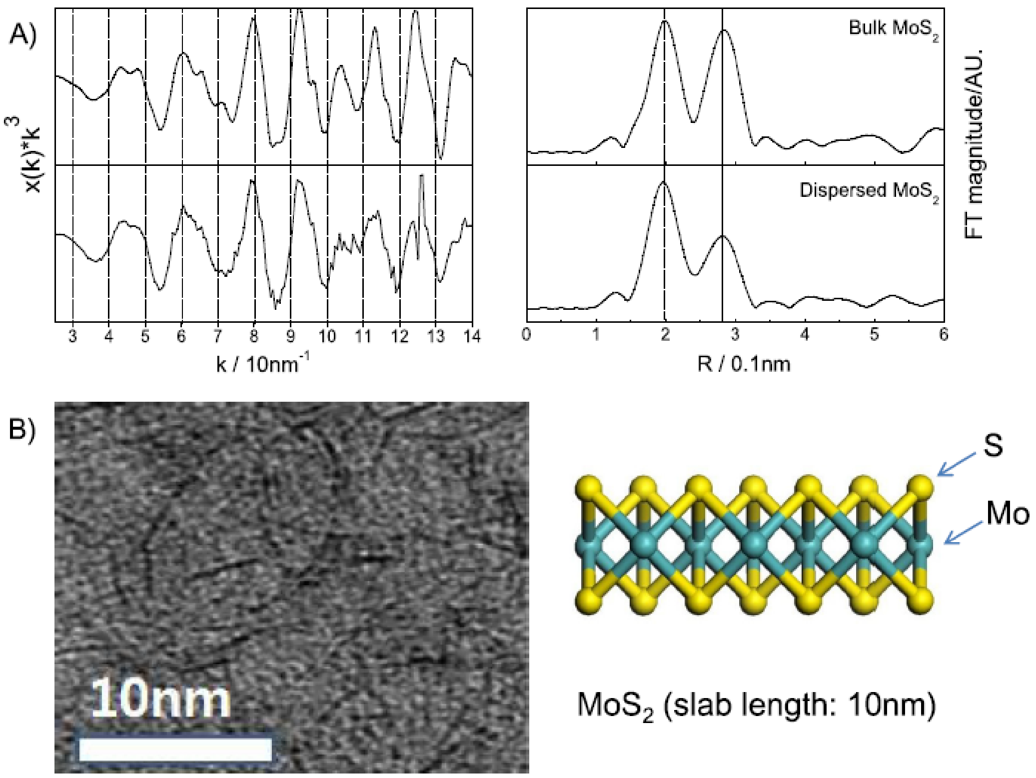

Fig. 1. Formation of dispersed MoS_2 catalyst: A) Mo K-edge EXAFS spectra for dispersed MoS_2 catalyst and bulk MoS_2 reference; B) TEM image of dispersed MoS_2 catalyst

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INVESTIGATION OF Mo_xW_{1-x}/Al_2O_3 CATALYSTS BASED ON $SiMo_xW_{12-x}$ HETEROPOLYACID IN HYDRODESULFURIZATION OF DIBENZOTHIOPHENE AND 4,6-DIMETHYLDIBENZOTHIOPHENE

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Conventional Co(Ni)-Mo(W) alumina supported hydrotreating catalysts exhibit high activity in removing sulfur (HDS) from thiophene and dibenzothiophene (DBT) compounds. However, deep desulfurization and production of ultra-low sulfur fuels are limited by the presence of resistant molecules such as alkyl-substituted dibenzothiophenes. DBTs carrying two alkyl substituents at the 4- and 6-positions are the most resistant to desulfurization due to the steric hindrance around the sulfur atom. Considering the fact that transformation of 4,6-dimethyldibenzothiophene (4,6-DMDBT) is preferable via prehydrogenation pathway the development of a new generation of catalysts with high hydrogenation (HYD) activity is a topical task.

In the present work, Mo_xW_{12-x} catalysts supported on Al_2O_3 were prepared using mixed $H_4SiMo_1W_{11}O_{40}$ and $H_4SiMo_3W_9O_{40}$ Keggin type heteropolyacids (HPAs) and corresponding mixture of monometallic $H_4SiMo_{12}O_{40}$ and $H_4SiW_{12}O_{40}$ HPAs. The chemical compositions of the prepared catalysts are given in Table 1.

Table 1. Composition of precursors and prepared catalysts

Precursor	Catalyst	Mo + W (at·nm^2)	MoO_3 (wt %)	WO_3 (wt %)
$H_4SiMo_{12}O_{40}$	$SiMo_{12}/Al_2O_3$	4	18.0	-
$H_4SiW_{12}O_{40}$	SiW_{12}/Al_2O_3	4	-	26.2
$H_4SiMo_1W_{11}O_{40}$	$SiMo_1W_{11}/Al_2O_3$	4	1.4	24.2
$H_4SiMo_3W_9O_{40}$	$SiMo_3W_9/Al_2O_3$	4	4.2	20.1
$H_4SiMo_{12}O_{40}$ + $H_4SiW_{12}O_{40}$	Ref Mo_1W_{11}	4	1.4	24.2
$H_4SiMo_{12}O_{40}$ + $H_4SiW_{12}O_{40}$	Ref Mo_3W_9	4	4.2	20.1

Synthesized samples were characterized by X-ray Photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), high-resolution transmission electron microscopy (HRTEM) and tested in HDT of the mixture of DBT, 4,6-DMDBT and naphthalene. It was found that using mixed $SiMo_xW_{12-x}$ HPAs as starting precursors had a beneficial effect on the catalytic activity (Fig. 1).

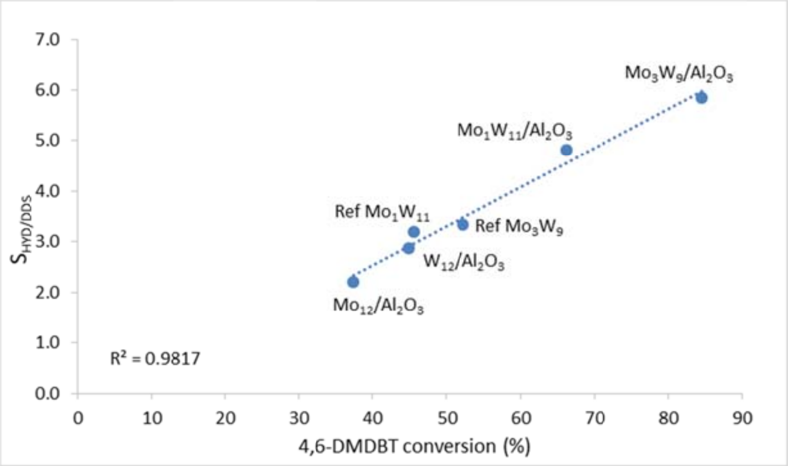

Fig. 1. Relationship between conversion of 4,6-DMDBT and the selectivity ratio $S_{HYD/DDS}$ on SiW_xMo_{12-x}/Al_2O_3 catalysts

Both $SiMo_xW_{12-x}$ HPAs based catalysts had higher rate constants in all studied reactions compared to their corresponding references prepared by mixing of two separate monometallic HPAs. Moreover, mixed HPAs based catalysts had the highest selectivity in respect of HYD pathway of DBT and 4,6-DMDBT HDS. Monometallic reference catalysts demonstrated significantly lower catalytic activity than bimetallic ones.

Furthermore, the formation of mixed $Mo_xW_{1-x}S_2$ phase from mixed molecular precursors was confirmed by EXAFS and HAADF analysis. Therefore, the catalytic synergy of mixed HPAs based catalysts is provided by formation of mixed $Mo_xW_{1-x}S_2$ phase possessing HYD activity, which contributed to increasing HDS of DBT and 4,6-DMDBT.

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OP-6

UV-vis INSIGHT ON THE SUPPORT EFFECTS FOR THE DISPERSION OF SUPPORTED WO_x AS HDS CATALYSTS

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Studies using SiO_2, TiO_2, ZrO_2 and Al_2O_3 [1,2,3] as support exhibited that the term ''support effect'' involves several aspects. We recently published that an appropriate chose of the support can dramatically increase the catalytic performance [4]. In addition, the evidence obtained by HRTEM analysis exhibited an apparent variation of the morphological parameters of the sulfided active phase depending on the support. In this work, we want to get a further insight on the support effects for the dispersion of tungsten oxide (WO_x) based catalysts to be used for HDS. In that sense, the absorption edge energy (E_b) of crystalline WO_x species depends on the number of WO_x neighbors bonded through W–O–W bonds [5]. Thus, a variation on the E_b can be directly related to the size of the nanoparticles of WO_x polytungstates over the surface of a specific substrate. Therefore, we used typical pure oxides such as γ-Al_2O_3 (A), SiO_2 (*S*), TiO_2 (T) and ZrO_2 (Z) as well as AT and ZT mixed oxides to synthesized WO_x base catalysts [4] and analyzed by UV-vis diffuse reflectance spectroscopy (DRS). The WO_x catalysts were prepared by a pore-filling method with a surface density of 2.8 W atoms·nm^{-2}. The DRS spectra obtained were transformed by the Kubelka-Munk function, and the E_b values were obtained according to Webber [6]. The E_b for supports and calcined samples were obtained by plotting $[F(R\infty)\cdot\hbar v]^2$ vs. $\hbar v$, as shown in Fig. 1 and with the intercept of a linear fit to the absorption edge.

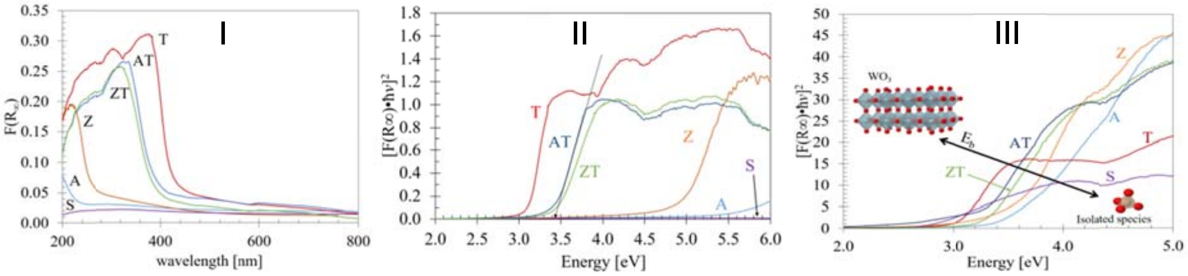

Fig. 1. I) UV-vis diffuse reflectance absorption spectra for supports,
II) Spectral transformation for supports and
III) catalysts samples calcined at 450 °C

The E_b values resulted as follows: 5.62, 4.98, 3.45, 3.41, 3.10 eV for A, Z, ZT, AT and T samples respectively. Any E_b value was observed for *S* sample. The spectral energy transformation yields the following E_b values for the catalysts: 3.62, 3.05, 2.55, 3.58, 3.22 and 3.41 eV for W/A, W/T, W/S, W/Z, W/AT and W/ZT respectively. Once the E_b values for the catalysts were obtained, three tungsten-containing commercial reagents were also analyzed. Sodium tungstate ((Na_2WO_4)-H_2O), tungsten trioxide (WO_3) and ammonium metatungstate ($(NH_4)_6H_2W_{12}O_{40}*6H_2O$) (AMT). The first one presents a W^{6+} coordinated tetrahedral geometry with an average number of nearest W neighbors (N_W) of zero and an E_b of 4.89 eV. The second one (WO_3) exhibited a W^{6+} coordinated octahedral geometry to six oxygen atoms and with six N_W and an E_b of 2.59 eV. Finally, the AMT reagent contains WO_6 octahedral species with four N_W and an E_b of ca. 3.23 eV. With these values, we proposed the following correlation: $N_W = 12.97-2.65*E_b$ to obtain the N_w, which in general terms provide us with an idea of the dispersion. The N_w values obtained for all catalysts were plotted as a function of the slab length reported previously [4]. The results confirmed a linear behavior as seen in Fig. 2 III.

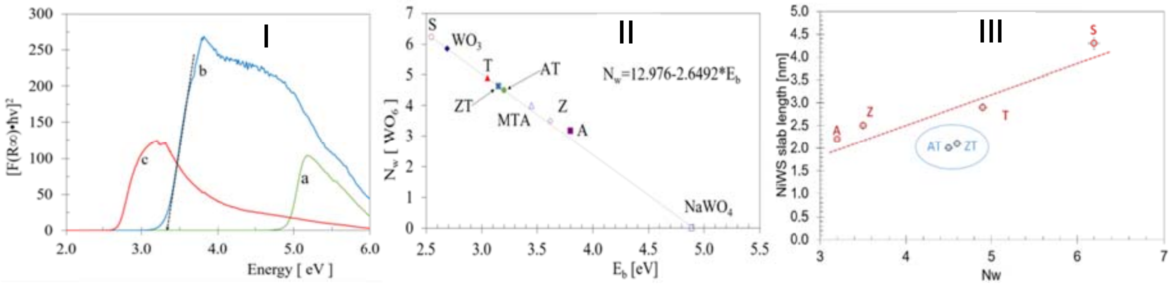

Fig. 2. I) Kubelka-Munk transformation for a) $NaWO_4$, b) AMT, c) WO_3.
II) Correlation between the E_b and the size of the tungsten domain N_w.
III) Correlation between the WS_2 slab length and the N_w for all catalysts

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NiMo/USY-Al_2O_3 HYDROCRACKING CATALYSTS WITH HIERARCHICAL ZEOLITES OBTAINED BY RECRYSTALLIZATION

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Hydrocracking (HC) is one of the main processes in oil refinery for the conversion of a wide range of low-value heavy feedstocks into high-quality products, mainly transportation fuels. HC catalysts are bifunctional catalysts, comprising both hydrogenation and acid functions. For zeolite catalysts mass transfer limitations play an important role during hydrocracking of heavy fractions leading to difficulties of bulky molecules transformation. Much effort was dedicated to the development of the micro-mesoporous zeolite materials, which combine the advantages of both mesoporous molecular sieves and zeolites, namely, improved transport of bulky molecules with high zeolitic acidity. The aim of this study was to investigate the effect of mesoporosity introduced by zeolite Y recrystallization on the acidity and catalytic performance of NiMo/USY-Al_2O_3 hydrocracking catalyst.

Micro-mesoporous zeolites Y (denoted as RFAU) were obtained by hydrothermal treatment of dealuminated zeolite Y denoted as FAU (CBV-720, Zeolyst) in the presence of alkali and CTAB. Supports containing 30 wt % of zeolite were prepared by mixing of RFAU sample with AlOOH, followed by drying and calcination at 550 °C. Deposition of metals was carried out by impregnation with aqueous solutions of nickel carbonate, ammonium heptamolybdate and citric acid. Impregnated catalysts were dried and calcined. NiMo/RFAU-Al_2O_3 catalysts contained 10.0 wt % Mo and 3.0 wt % Ni. The samples were studied by nitrogen adsorption, XRD, HRTEM, TPD-NH_3, XPS, UV-Vis, Raman, IR spectroscopy of adsorbed CO and pyridine. HC tests were carried out using model feed (hexadecane) and VGO.

A series of micro-mesoporous zeolites Y of similar chemical composition with different degree of recrystallization (RFAU1 < RFAU2 < RFAU3) were synthesized from commercially available USY. The increase of recrystallization degree resulted in the increase of mesopore to micropore volume of zeolite Y due to the formation of additional intracrystalline mesoporosity (Table 1). FTIR spectroscopy of adsorbed CO revealed, that the increase of mesopore to micropore volume by recrystallization is accompanied by the decrease of the contribution of strong Brønsted acid sites in faujasite cages and the increase of contribution of Brønsted acid sites at the external surface of microcrystallites or in mesopores, which represent defect silanol OH groups located in the close vicinity of the Lewis acid site (Si-O(H)…Al^{3+}).

Table 1. Textural characteristics of micro-mesoporous Y zeolites and supports

Characteristic	Micro-mesoporous zeolite Y				Support			
	FAU	RFAU1	RFAU2	RFAU3	FAU-Al_2O_3	RFAU1-Al_2O_3	RFAU2-Al_2O_3	RFAU3-Al_2O_3
BET surface area, m^2/g	709	761	772	842	403	409	358	388
Pore volume, cm^3/g	0.45	0.52	0.56	0.63	0.62	0.68	0.55	0.61
Micropore volume, cm^3/g	0.26	0.20	0.17	0.12	0.08	0.04	0.01	0.02

NiMo based HC catalysts were prepared using parent and recrystallized micro-mesoporous zeolites and evaluated in the hydrocracking of hexadecane and VGO. Catalysts obtained with recrystallized zeolites demonstrate superior catalytic performance in hexadecane HC, providing higher activity and liquid products yield.

VGO hydrocracking (16.0 MPa, 410 °C, LHSV of 0.7 h^{-1}, H_2/feed ratio of 1500) was carried out with non-pretreated feedstock and the studied catalysts were loaded in stacked beds containing NiMo/Al_2O_3 as the top layer, NiW/ASA-Al_2O_3 as the interlayer and NiMo/RFAU-Al_2O_3 as the bottom layer. The highest VGO net conversion of 75.5 % and middle distillates yield of 53.0 wt % were achieved over NiMo/RFAU1-Al_2O_3 catalyst obtained with micro-mesoporous material with low degree of recrystallization. This effect is due to the improved accessibility of active sites, easier transport of bulky molecules provided by mesopores, on the one hand, and optimal zeolitic acidity, on the other hand. The highest selectivity to middle distillates was achieved over NiMo/RFAU3-Al_2O_3 catalyst with the highest degree of recrystallization. This observation can be accounted by the decrease of the concentration of strong Brønsted acid sites (bridging Si-O(H)-Al groups) and the increase of the concentration of Brønsted acid sites in mesopores.

Acknowledgements

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OP-8

UNDERSTANDING OF THE RELATIONSHIP BETWEEN THE PHYSIC-CHEMICAL STRUCTURE AND ACTIVITY OF AGED INDUSTRIAL HDS CATALYSTS

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Hydrodesulfurization (HDS) is a major process of petroleum refining for sulphur removal, where CoMoS/Al_2O_3 is the typical catalyst. In the industrial process, these catalysts can perform during an average life cycle of 0,5-2 years, depending on the type of feed used. During the cycle of a HDS process, deactivation of the catalyst is attributed to three main causes: coke deposition (with loss of pore volume), metals deposition and segregation of the active phase.

The aim of this work was to study the effect of coking and the active phase changes on the deactivation of HDS catalysts of CoMoS/Al_2O_3 type, applied to the HDS of a diesel feed. The goal was to find the key operating conditions to obtain a spent catalyst representative of the industrial one. Accelerated aging was achieved using a moderate increase of temperature, decrease of hydrogen flow and increase of coke-forming aromatics content in the feed, for the durations of pilot tests from 7 weeks to 30 days.

Accelerated aging tests have been performed with different feedstocks, hydrogen to oil ratio, and a pre-reduction treatment. After each test, total sulphur has been quantified for liquid samples to calculate activity loss. The catalysts have been characterized in terms of texture (nitrogen adsorption/desorption isotherms), coke properties (Raman, IR, TPO, EPR, ToF-SIMS) and active phase evolution (TEM/EDX, XPS, TPR).

As with the catalysts texture and coke formation, a high amount of aromatics on the feedstock and low hydrogen to oil ratio favor the formation of coke. Up to 5 % wt coke can be formed rapidly, probably on the walls of support pores without any considerable loss of activity. Further increase of coke amount leads to deactivation. Increase of aromatics content and low relative H_2 flow, as applied in the 7-day tests, favored coke formation. However the resulting coke had a graphitic structure that is slightly less organized as compared with the industrial aged catalyst, as attested by

Raman study. We carried out longer (30-day) tests to increase the organization of graphitic coke in order to mimic better the industrial aged catalyst. Even then however, the coke structure failed to represent exactly that of the industrial catalyst. Therefore for the formation of highly organized coke long times at relatively low temperatures are necessary.

In terms of active phase, a long duration, high hydrogen to oil ratio and a pre-reduction treatment favor loss of dispersion of the active phase and formation of cobalt sulfide agglomerates. The observed increase of MoS_2 slabs length is moderate and does not explain the observed loss of activity. The pre-reduction with hydrogen seems to be an effective treatment to simulate the exposure to high temperatures during a long HDS cycle which results in segregation of the active phase, a fingerprint of an industrial spent HDS catalyst.

OP-9

COMPARISON OF Pt-BASED AND TMS CATALYSTS FOR *N*-HEXADECANE HYDROISOMERIZATION

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Hydroisomerization of n-alkane is an important process to improve the octane number of gasoline and to improve the low temperature performance of diesel or lubricants. It is usually carried out on bifunctional catalysts containing metallic sites for hydrogenation/dehydrogenation and acidic sites for skeletal isomerization [1]. In case of the best catalysts, metal components presented by noble metals, such as Pt and Pd. However, the high cost of the noble metal catalysts and its ability to be poisoned with sulfur-containing compounds limits their application. The transition metal sulfides (TMS) catalysts have low cost, sturdy against sulfur-containing compounds and exhibited catalytic activity in hydrogenation/dehydrogenation reaction, that makes them perspective metal component for bifunctional hydroisomerization catalyst.

In this study CoMo and NiW sulfide catalysts supported on composite Al_2O_3-SAPO carrier were investegated in hydroisomerization of *n*-hexadecane. Pt-based catalyst on the same support have been tested as a reference sample.

SAPO-11 was synthesized hydrothermally according to [2]. The Al_2O_3-SAPO carrier was obtaining by co-extrusion technique. Catalysts were synthesized by wetness impregnation with aqueous solutions of required amounts of precoursors. Solids were charecterised with the following methods: powder X-ray diffraction, scanning electron microscopy, low-temperature N_2 adsorption, temperature-programmed desorption of NH_3 and reduction with H_2, transmission electron microscopy and X-ray photoelectron spectroscopy.

Catalytic activty examination in *n*-hexadecane hydroisomerization was performed in bench-scale flow reactor under 1.5 MPa of hydrogen, LHSV = $1 \div 3$ h^{-1}, temperature range from 260 to 340 °C and H_2/feedstock ratio equal 200 nl/l. Reactor was charged with 2.5 cm^3 of catalyst. TMS catalysts were undergo sulfidation procedure, whereas Pt-based sample was activated by reduction in H_2 (10 % vol.) before catalityc tests.

The results of catalytic tests are summarized in table 1.

Table 1. The results of catalytic activity examination

Catalyst	Conversion of n-C_{16}, %				Reaction rate constant*			
	T = 300 °C		T = 320 °C		T = 300 °C		T = 320 °C	
	3 h^{-1}	1 h^{-1}	3 h^{-1}	1 h^{-1}	$k \times 10^5$	$k' \times 10^3$	$k \times 10^5$	$k' \times 10^2$
CoMoS	6	12	8	25	1.6	6.8	3.3	1.4
NiWS	5	12	10	22	2.0	10.6	3.0	1.6
Pt-based	32	71	52	89	24.3	6780.0	42.0	1160.0

* k [mol g^{-1} h^{-1}] is reaction rate constant normalized to catalyst weight (g),
k' [mol mol^{-1} h^{-1}] is reaction rate constant normalized to metal amount in the catalyst (mol)

CoMo and NiW catalyst exhibited very similar catalytic activity in *n*-hexadecane isomerisation, meanwhile Pt-based sample shows much more higher n-C_{16} conversion and isomerization rate constant. However, even at T = 320 °C TMS catalysts allow to convert *n*-hexadecane into *iso*-alkanes for 25 %. At higher temperature value of n-C16 conversion about 60 % can be reached. Taking in account the price for Pt and TMS, it can be concluded, that TMS can be considered as perspective metal component for bifunctional catalyst for *n*-alkanes hydroisomerization, especially for mini oil refinery plants development.

Additionally, kinetic parameters of the *n*-hexadecane hydroisomerisation over TMS-catalysts were investigated.

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ORAL PRESENTATIONS
Session 2

OP-10

HYDROPROCESSING OF HEAVY RESIDUAL OIL: OPPORTUNITIES AND CHALLENGES

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The light crude sources are turning into heavy or extra heavy, which contains large amount of contaminates (S,N, metals, asphaltene etc.) and produce large fraction of bottom of barrel (residue) after distillation. Thus, future crude slate is a key issue facing refiners to invest strategically in order to process larger quantities of sourer crude. Refinery operations have to evolve and include next-generation processes and catalysts to fulfill the demand for high-quality transportation fuels. Since the quality of these products has to be improved to satisfy stringent environmental regulations. Refineries have been traditionally processing light crude oils, face drastic changes in petroleum feed properties, which stubborn great challenges to refining industry to process heavier crude oils. The global trend indicated that the world oil refining industry has to face several challenges for demand as well as supply. At the same time refineries are expected to be under great deal of pressure to accomplish the market demand of high quality fuels (*i.e.*, gasoline and diesel). The world demand for diesel fuels is increasing while fuel oil demand is decreasing.

Hydrotreating technologies are continuously associated with intensive research in development of advanced characterization of heavy crude oil and its residual fraction, catalysts design for oil refining processes [1-3]. Substantial efforts devoted and will continue worldwide to the development of new catalysts and processes for refining, as well as technological development with effective processing residual oil and with better economics to produce high quality of petroleum products. Thus, studies were focused on the quality parameters associated with future feed that is impending due to the presence of high levels of impurities during the hydroprocessing heavy feedstocks, such as:

- Crude oil distillation produce large amount of residue, which have abnormal compositions into both fractions (residue and distillate);
- High levels of contaminates (asphaltene, metals, sulfur, nitrogen) cause many problems during the processing and significantly reduce catalyst life cycle.

In addition, the understanding of such feedstock is limited or difficult to characterize at their molecular level. The heaviest fraction of heavy crude oil is represented by most complex molecule of asphaltenes. Asphaltene are the precursor of the most hetero atoms (S, N *etc*.) and metals (Ni and V). An asphaltene molecule may be 4 to 5 nm in diameter, which is difficult to process in refinery by conventional catalytic system. Metals in the asphaltene aggregates are believed to be associated with the asphaltene sheets, making the asphaltene molecule heavier than its original structure. Hence a design of catalyst formulation required a balance between textural properties, number of active sites and more resistant to deactivation. Therefore, it will be mandatory for researcher to understand the chemistry of complex fossil fuel feedstocks that will be required in order to design suitable catalysts and conditions for processing. New catalyst formulation (technologies) will be required to achieve higher conversion and increased selectivity to distillate range of products. Obviously, the catalyst or/and process should be cost effective, selective high throughput, long life cycle and methodically feasible for commercial application.

In hydroprocessing of heavy oils, different parameters are influencing on its selection and implementation, such as quality of feed, catalyst types and systems, process configuration, reactor type and mode of operation to target desired product slate which directly influenced by the rate of deactivation of the catalyst. It would be of great economic significance if efforts made through intensive research studies in order to better understand the effect of these parameters leading to counter-measures and a prolonged lifetime of the catalyst. In this paper, the impact of major parameters in the heavy oil hydroprocessing will be addressed. The importance of the parameters on the performance through case studies and the potential solution will be also highlighted.

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OP-11

Pt(Pd)/WO_3/ZrO_2 CATALYSTS FOR NOVEL HYDROPROCESS OF C_7-FRACTION ISOMERIZATION

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Nowadays environmental protection regulations are becoming more stringent for automotive fuels. Aromatic hydrocarbons content in 5 class gasolines must not exceed more than 35 vol % (including benzene less than 1 vol %) [1]. It is necessary to reduce the fraction of aromatics in gasolines. One possible way of aromatics content reduction is C_7-fraction isomerization (70–105°C), selected from gasoline fraction with final boiling point 180°C. It will diminish aromatics content in gasoline and keep the high octane number. At present there is no C_7-fraction isomerization in industry, but it is very important process for refining industry.

Catalyst based on tungstated zirconium dioxide for the C_7-fraction isomerization is bifunctional, where WO_3/ZrO_2 is acid component and the platinum group metal (Pt, Pd) is hydrogenation-dehydrogenating component. Previously we studied [2, 3] the effect of WO_3 content and thermal treatment conditions of WO_3/ZrO_2 on the physicochemical and catalytic properties of the n-heptane (model feed) isomerization.

At present work the influence and the role of the metallic component (Pt, Pd) of catalyst based on WO_3/ZrO_2 were investigated. Pt(Pd)/WO_3/ZrO_2 catalysts with platinum and palladium loadings in amount of 0.05, 0.1, 0.3, 0.5, 1.0, 1.5 and 2.0 wt % were synthesized. Fig. 1 shows influence of Pt and Pd content on heptane isomers yieald. For platinum containig catalysts it is seen (fig. 1) maximum yields of isomers are achieved at 1-2 wt % of Pt: sum of C_7-isomers yield is 70-75 wt % and high octane dimethyl and trimethyl substituted isomers (DTMS) yield is 27-29 wt %. In the case of palladium containing catalysts 74 wt % yield of sum of C_7-isomers and 29 wt % yield of DTMS are achieved at 0.1 wt % of Pd.

An equally important role for WO_3/ZrO_2 catalysts with Pt, Pd loadings are the conditions of heat treatment - the temperature of calcination in air flow and the temperature of reduction in hydrogen flow (table 1).

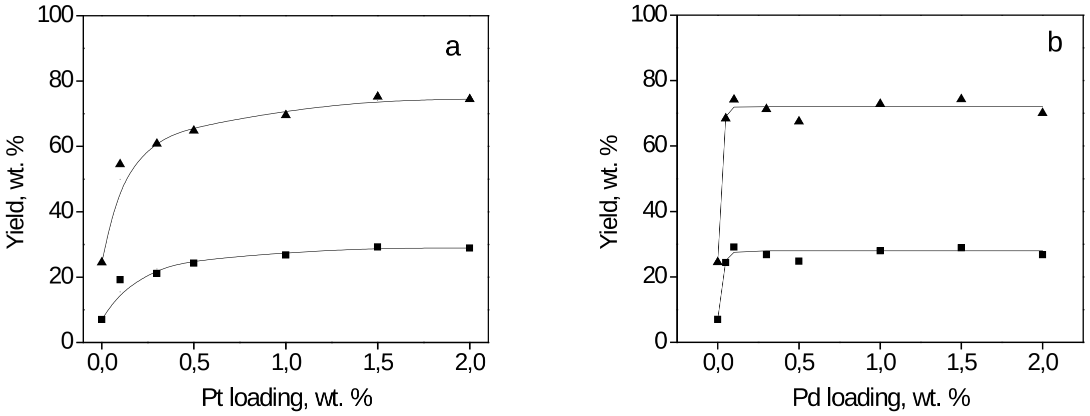

Fig. 1 Effect of Pt (a), Pd (b) loadings on heptane isomers yield: ▲ – sum of isomers; ■ – DTMS

Table 1 Effect of heat treatment conditions of Pt(Pd)/WO_3/ZrO_2 catalysts (Pt, Pd loading – 1.0 wt %) on heptane isomers yield (data with the most high characteristics shown)

Catalyst	Calcination in air flow			Reduction in hydrogen flow		
	T, °C	i-C_7 yield, wt %	DTMS yield, wt %	T, °C	i-C_7 yield, wt %	DTMS yield, wt %
Pt/WO_3/ZrO_2	non calcined	65.4	26.2	200	76.8	31.2
	350	69.7	28.2	300	74.5	29.6
	450	66.6	26.8	400	57.4	21.4
	550	66.6	25.4	500	57.3	20.4
Pd/WO_3/ZrO_2	non calcined	62.8	23.3	200	75.0	27.7
	350	67.1	25.6	300	69.3	26.3
	450	71.7	28.0	400	64.3	21.9
	550	65.8	23.5	500	58.7	20.7

From table 1 it is seen the calcination temperature of Pt(Pd)/WO_3/ZrO_2 catalysts must be in the range of 350-450°C and the reduction temperature must be not high than 300°C at which high heptane isomers yield is achieved.

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OP-12

HYDROTREATING CATALYST SUPPORTED ON ALUMINA COATED WITH BIO-INSPIRED POLYMERS

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Past decades have witnessed the evolution of more stringent environmental regulations, in order to protect the earth atmosphere from pollutants that evolve from the consumption of fossil fuels. This requires the development of highly active and efficient hydrotreating catalysts. The most widely used catalysts for this process contain Mo(W) as the active metal, Ni(Co) as the promoter and Al_2O_3 as the carrier. To improve the catalytic activity, different kinds of additives can be added to control the active phase properties such as dispersion and promotion [1]. Though alumina presents very interesting properties as support, some drawbacks are strongly limiting for the development of the next generation of HDT catalysts such as the upper limit of metal loading keeping high degree of dispersion or the strong interactions with metallic precursors leading to a loss of active phase. In order to avoid such limitations, coating the surface of alumina by polymers is one of the suitable option [2]. The use of bio-molecules and bio-polymers as additives is a newly emerging field, which still leaves room for exciting discoveries. In this work, we explore possible bio-polymers, such as polydopamine [3, 4] and chitosan [2], that are able to coat the alumina surface, and bring their own functional groups (hydroxide, carbonyls, amines) that may help to disperse the metal precursors avoiding detrimental interactions and formation of refractory species inactive in catalysis, as shown on Figure 1.

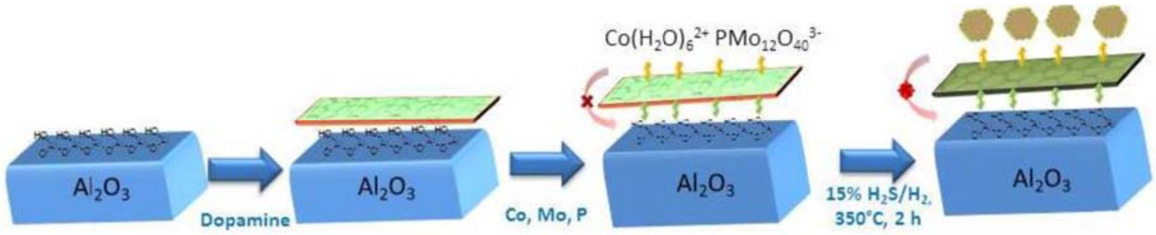

Figure 1. Coating with dopamine in order to tune the metal-support interactions

First, we compared the coating and the co-kneading methods for incorporing the biopolymers. The coating was performed by incipient wetness impregnation on γ-alumina of the desired amount of the polymer, followed by an overnight maturation in a water saturated atmosphere and a drying step at 90 °C. It has to be mentioned here that there was no calcination in order to maintain the functional group of the bio-polymer. In that respect, this method is rather different than the usual coating techniques which use a thermal treatment (pyrolysis or calcination) to transform the organic molecule to a carbon layer at the alumina surface [5]. Performing a chitosan coating by the same method was not possible due to solubility issues. This is why we used also co-kneading. In that case the biopolymer was mixed with alumina powder, methocel, nitric acid and water before kneading, extrusion and drying at 120 °C. Later on, the appropriate amount of cobalt and molybdenum metal precursors, phosphomolybdic acid ($H_3PMo_{12}O_{40}\cdot 30H_2O$) and $Co(NO_3)_2\cdot 6H_2O$, were impregnated with ethanol as a solvent onto the modified alumina to obtain the final CoMoP catalysts with 20 % MoO_3 and a molar ratio Co/(Co+Mo) = 0.3. We also prepared a reference catalyst with the same protocol on non-modified γ-alumina. In order to choose the best alumina modification method, we used a model molecule catalytic test (toluene hydrogenation) to evaluate the catalyst. Previously to the catalytic evaluation, the catalysts were sulfided in gas phase at atmospheric pressure with a 85/15 v/v H_2/H_2S mixture. This hydrogenation test highlighted dopamine as the most efficient alumina modifier compared to other bio-polymers.

The catalysts have been further evaluated on hydrodesulfurization (HDS) of real feestock, using a mixture of straight-run gas oil (SRGO) and light cycle oil (LCO) containing 6815 ppm of S and 488 ppm of N after in-situ sulfidation at 350 °C with a SRGO feed doped with 2 wt % of DMDS (Table 1). Although very small differences were observed in terms of characterization, the CoMoP/Pdop-alumina showed outstanding performances in real diesel HDS. To reach the same conversion, the reactor needs to be operated 7 °C lower, improving the catalytic activity by 25 % (considering a reaction order of 1.3). This activity improvement has been attributed to the decrease of metal support interaction due to the presence of carbonaceous adlayer between the active phase and the support.

Table 1. Performances on HDS of real diesel feedstock

Catalyst	T °C @ 98 % conversion	RVA
20 % CoMoP/γ-Al_2O_3	340 °C	100
20 % CoMoP/Pdop@γ-Al_2O_3	333 °C	125

In conclusion, we developed an easy way to tune the metal-support interactions of hydrotreating catalyst and thus improve the HDS performances by modifying the alumina using a coating with a bio-inspired polymer.

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OP-13

INFLUENCE OF THE WAY OF THE PHOSPHORUS ADDITION ON PROPERTIES OF CoMo-CATALYSTS FOR HYDROTREATING

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The addition of phosphorus as a modifier agent influences positively activity of hydrotreating catalysts in hydrodesufurization (HDS) reactions [1]. It has been found that the maximum catalytic activity in HDS reactions is achieved, when the P content is about 1 wt. % [1]. The widely used methods of P introduction are the following: 1. impregnation of a support by H_3PO_4 solution before or after addition of active metals; 2. impregnation of a support by the joint solution of H_3PO_4 and active metals [1]. The addition of P into catalyst at the stage of a support preparation or preparation of an impregnation solution are more attractive for industrial application, because of the lowest amount of supplemental technological steps. However, the comparative literature data on the influence of P, which was added by the mentioned methods, on the acidic properties of supports and catalysts, the morphology of active component particles and catalytic activity were scarcely discussed. In present study, the influence of the way of P adding on the highly mentioned properties of supports and catalysts was investigated. Catalysts with 1 wt. % of P, which was introduced to catalysts at different stages, were prepared. The support granules were obtained according to methodology described in [2]. The support with P addition was prepared by such method, but the P was added jointly with the peptizer agent solution. The support without addition is denoted as Al. The support with P is denoted as AlP. The catalysts were prepared using a method of the vacuum impregnation as described in [3]. H_3PO_4 was added at the stage of the impregnation solution preparation before (PCoMo/Al) or after (CoMoP/Al) active metals precursors were added. As a reference, the sample without P (CoMo/Al) was prepared. Supports and catalysts were investigated by nitrogen adsorption-desorption method, HRTEM, XPS, IR-spectroscopy, UV–vis DRS, Raman spectroscopy. Catalysts were sulfided in H_2S flow at T = 210 °C, 410 °C. Catalysts were tested in hydrotreating of the model mixture (1500 ppm of DBT in undecan) in the fixed bed reactor in the following conditions: P = 35 atm, LHSV = 40 h^{-1}, a volume ratio of hydrogen/feed – 500, T = 270 °C.

It has been found that the P addition at the support preparation stage results in the decrease of a specific surface area of the support from 296 m^2/g to 236 m^2/g (Table 1). For the P containing support, formation of larger pores with the diameters up to 35 nm in comparison with the support without phosphorus was noted (Figure 1-

a). In addition, for these samples, the mechanical strength reduces from 0.5 MPa to 0.3 MPa, respectively. The P addition to the impregnation solution results in insignificant change of a specific surface area, a pore volume and a pore size distribution for catalysts (Figure 1-b).

Table 1. Characterizations of the samples

Support	S, m^{2}g^{-1}	V, cm^{3}g^{-1}	Catalyst	S, m^{2}g^{-1}	V, cm^{3}g^{-1}	Av. staking number	Av. slab length, nm	Av. number of layers per 1000 nm^2	DBT conversion, %
Al	296	0.77	CoMo/Al	190	0.44	1.25	2.70	80	39
			PCoMo/Al	206	0.45	1.38	2.50	97	85
			CoMoP/Al	214	0.48	1.59	2.46	115	80
AlP	236	0.74	CoMo/AlP	180	0.39	1.40	2.60	125	36

Introduction of P changes the morphology of active component particles. In all cases, there is an increase of the average staking number (Table 1). The maximum growth has been noted for CoMoP/Al sample. It has been found that there is the reduction of the average slab length for P containing samples. At the same time, the average slab lengths for PCoMo/Al (2.5 nm) and for CoMoP/Al (2.46 nm) are less than for CoMo/AlP (2.60). Also, P addition results in the increase of the average number of layers per 1000 nm^2 (Table 1). However, this effect is the greatest for the samples, in which P was added at the support preparation stage (from 80 to 125). In accordance with catalytic tests, it has been found that phosphorus addition results in the increase of DBT conversion with the exception of CoMo/AlP (PCoMo/Al>CoMoP/Al>CoMo/Al>CoMo/AlP). The main positive effect relates to P adsorption on the strong acidic sites (the formation of $AlPO_4$ layers [4]). It prevents the formation of Al-O-Co and Al-O-Mo bonds and results in the increase in sulphidation degree of the active component particles. The ratio of the tetrahedral coordinated Co^{2+} ions decreases at P addition in impregnation solution jointly with citric acid, it leads to the increase in the ratio of CoMoS phase of Type II [5].

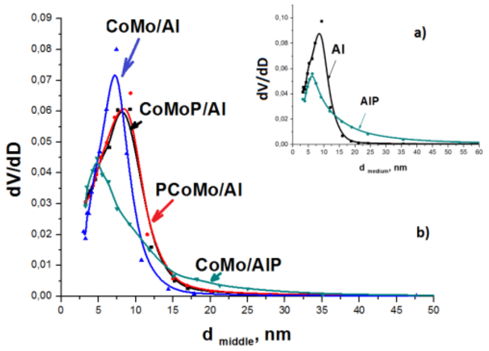

Figure 1. Pore size distribution for supports and catalysts

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OP-14

A CONTROLLED SURFACE CHEMISTRY APPROACH TO THE SYNTHESIS OF HIGHLY ACTIVE Mo HYDROTREATING CATALYSTS

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Hydrotreatment (HDT) is an important catalytic process in petroleum refining which uses sulfided bimetallic phase NiWS or NiMoS (or CoMoS) supported on alumina. Catalysts are prepared via a conventional method using an incipient wetness impregnation of a support with a solution of Mo/W and Ni/Co salts [1]. However, to meet the environmental constraints and increase the energy efficiency of HDT processes, permanent improvements on the performance of these catalytic systems are needed. In this work, we focus on the key activation step of amorphous silica alumina (ASA) supported MoS_2/NiMoS catalysts prepared through conventional (Conv) and controlled surface chemistry (CSC) methods. CSC catalysts were prepared by successively impregnating ASA support with Mo ethoxide and $Ni(acac)_2$ complexe (dissolved in cyclohexane and toluene respectively). The sulfo-reduction step was investigated using time-resolved X-ray absorption spectroscopy (quick-XAS) under a 15% H_2S/H_2 gaseous mixture at 1bar pressure. Pre-sulfided catalysts were also characterized using XPS, EPR, TEM, and STEM-HAADF. The catalysts were finally tested for hydrogenation (HYD) using a toluene model compound.

Figure 1a-1b plots the evolution of the energy position at half normalised absorption of the Ni and Mo K-edges XANES spectra to show their reduction in the catalysts during the sulfidation. For Mo (Figure 1b), the energy is at 20011.5 eV at 50 °C for the CSC NiMo, corresponding well to a Mo oxidation state of +4 [2]. The Conv NiMoP, however, reaches this energy only at ~150 °C. As also observed by TEM for CSC catalysts (Figure 1d), this rapid sulfidation is supported by the formation of MoS_2 nanosheets on the surface after sulfidation at 25 °C for 2h. Simultaneous XAS characterization of the sulfidation at Ni and Mo K-edges reveals that Ni is sulfided at a lower temperature than Mo for Conv NiMoP (Figures 1a, 1c) strongly suggesting that NiS_x are formed in higher proportion for the Conv catalyst than for the CSC ones. The CSC method therefore enables the sulfidation of Mo and Ni at lower T, forming a higher proportion of temperature-stabilised NiMoS phases [3]. Furthermore, through the use of Principal Component Analysis (PCA) and Multivariate Curve Resolution (MCR), we will show through quick-XAS that the sulfidation of CSC catalysts proceeds through a different activation pathway. We believe that the low temperature activation is the origin of the catalytic improvement illustrated in Figure 1e as it induces the formation of different intermediates (compared to Conv NiMoP) and a higher proportion of Ni atoms at edge MoS_2 sites stabilized at lower temperature [3]. This trend will be discussed by considering previous observations reported on NiWS catalysts [4].

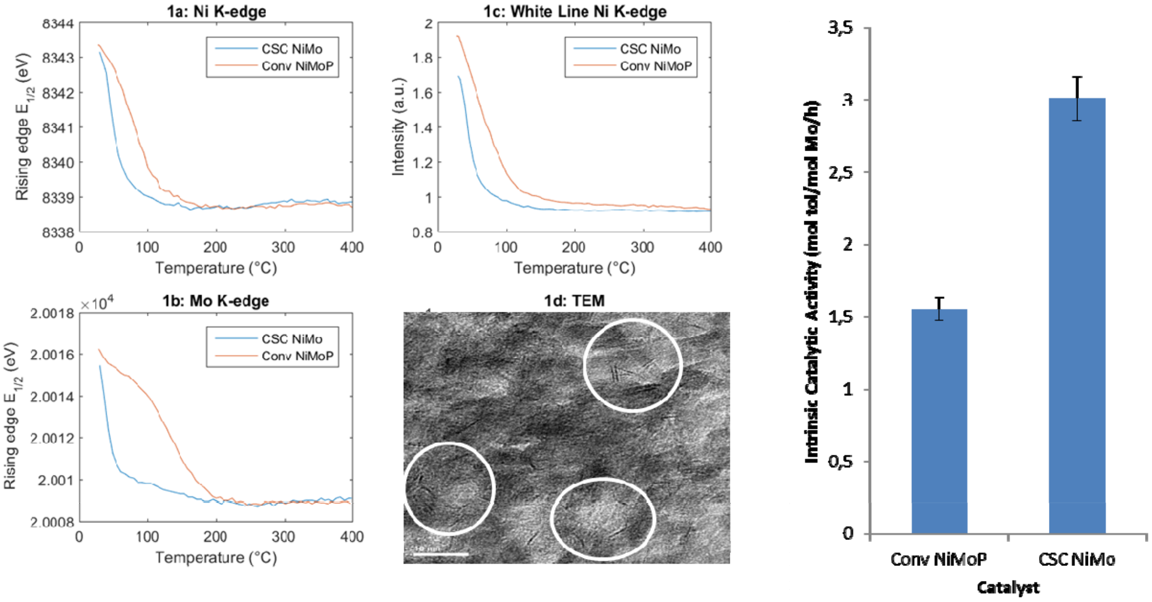

Figure 1. (a, b) Evolution of the edge energy of Ni and Mo at half normalized absorbance of CSC NiMo and Conv NiMoP during the sulfidation; **(c)** Evolution of the white line intensity of Ni; **(d)** TEM micrograph of MoS_2 nanosheets on catalyst surface after activation at 25 °C; **(e)** Intrinsic activities of CSC NiMo and Conv NiMoP catalysts (in mol tol/mol Mo/h)

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OP-15

THE EFFECT OF THERMAL PRETREATMENT ON THE PERFORMANCE OF NiW HYDROCRACKING CATALYSTS

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Hydrocracking catalysts containing amorphous silica-alumina (ASA) as an acid component are known to have a high selectivity to diesel fraction in the hydrocracking of vacuum gasoil (VGO) [1,2]. Chelating agents (EDTA, Citric acid) are widely used to improve the hydrogenation function of HDT catalysts. Generally, HDT catalysts prepared using chelating agents are not undergo to the thermal treatment (except for drying), however, a few of studies have shown that thermal treatment can improve catalytic performance [3,4]. In this paper, the effect of the thermal pretreatment on the performance of NiW/ASA-Al_2O_3 hydrocracking catalysts prepared with the citric acid as chelating agent was studied.

NiW/ASA-Al_2O_3 catalysts were prepared by wetness impregnation method using citrate as an organic modifier. The catalysts were thermally pre-treated at 120 (drying), 300 and 550 °C in static air. The morphology of the surface species in the oxide form of the catalysts was studied by Raman and UV-Vis spectroscopy. The sulfidation of the catalysts was carried out in a liquid-phase regime with DMDS in diesel fraction as sulfiding agent. The catalysts were tested in VGO hydrocracking under the following conditions: temperature 400-420 °C, pressure 16.0 MPa, feed rate 0.71 h^{-1}. Catalysts in the sulfide form after catalytic testing in VGO hydrocracking were studied by HRTEM and NH_3-TPD.

According to the Raman and UV-Vis spectroscopy data thermal pretreatment leads to the destruction of citrate complexes with the formation of nickel and tungsten species with strong interaction with the carrier. NH_3-TPD of the sulfide catalysts showed that the number of strong acidic sites in not changed significantly after supporting of the metals on ASA-Al_2O_3 support, thermal pretreatment in the range of 120-550 °C and sulfidation. On the other hand, the temperature of the thermal pretreatment influences the morphology of the active sulfide component of NiW/AAC-Al_2O_3 catalysts. The maximum dispersion of the sulfide component is achieved at the temperatures of the thermal pretreatment of 120 and 300 °C.

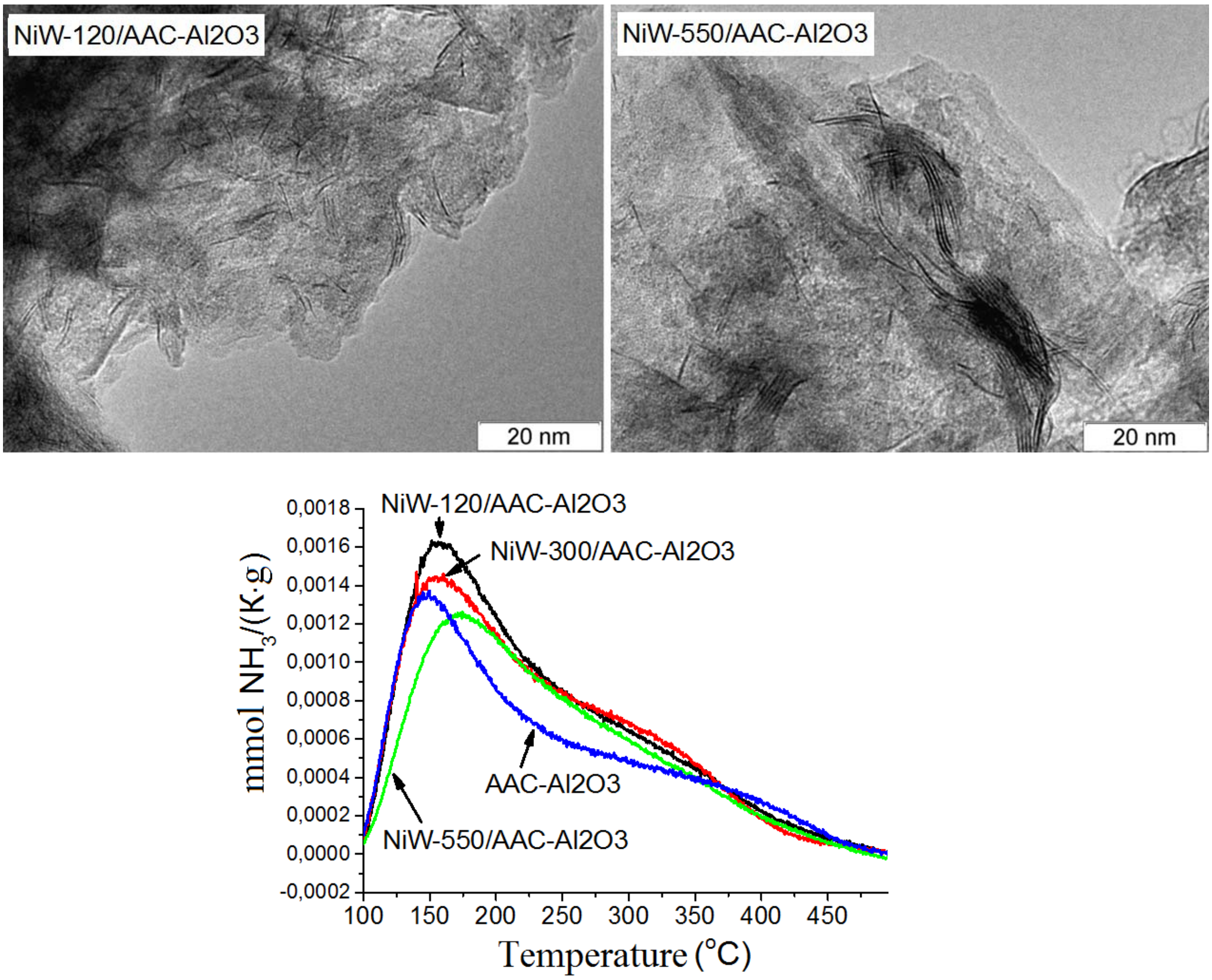

Fig. 1. HRTEM micrographs and NH_3-TPD profiles of sulfide NiW/ASA-Al_2O_3 catalysts with different temperature of thermal pretreatment

The thermal pretreatment temperature of the NiW/AAC-Al_2O_3 catalysts has a significant effect on the properties of VGO hydrocracking products. NiW/AAC-Al_2O_3 catalyst dried at 120 °C showed the highest activity in HDS and HDN, while pre-treatment at 300 °C leads to a slight increase in the hydrogenation of aromatic compounds and the yield of the diesel fraction in the VGO hydrocracking. Calcination at 550 °C leads to a sharp decrease in HDS and HDN activity of the catalysts due to a decrease in the dispersion of the active sulfide component.

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OP-16

EFFECT OF THE HYDROTHERMAL TREATMENT ON THE PROPERTIES OF ALUMINA SUPPORTS AND HYDROPROCESSING CATALYSTS

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In alumina based catalysts, the pore size plays an important role in controlling the effective activity of the catalyst particularly for reactions involving large molecules. Consequently, it is desirable to use catalysts with proper pore structure for better performance. In this study, pore size control in γ-Al_2O_3 hydrotreating catalyst support by hydrothermal treatment was studied. The primary objective of the study was to determine the effectiveness of various reagents in modifying the pore size distribution of alumina support [1]. The mechanism of pore widening in alumina under hydrothermal conditions was also investigated as part of the work. The results showed that reagents such as phenol and acetic acid inhibited pore enlargement while ammonia had an opposite effect and created larger pores in alumina during hydrothermal treatment. Rehydration of γ- Al_2O_3 to well crystallized boehmite during hydrothermal treatment was found to be responsible for pore enlargement [2].

In this study Al_2O_3 samples were hydrothermally treated in the presence of different reagents such as water, phenol, acetic acid, ammonia and n-butylamine. The treated alumina supports were characterized and the changes in the alumina phase and in the key properties such as surface area, pore volume and pore size distribution as a result of hydrothermal treatment were examined.

The following are the important results and conclusions of the study.

- Hydrothermal treatment with water alone led to significant widening of pores in alumina.
- Pore size distribution in alumina support can be controlled with maximum pore volume in any desired pore diameter by controlling the temperature and time used for hydrothermal treatment.
- Reagents such as phenol and acetic acid inhibited pore enlargement in alumina during hydrothermal treatment (Fig. 1).
- Presence of ammonia in water during hydrothermal treatment enhanced pore enlargement and created larger pores in alumina.

- Addition of P or F to alumina suppressed pore enlargement during hydrothermal treatment with water.
- The transformation of γ-Al_2O_3 to large crystallites of boehmite (AlOOH) during hydrothermal treatment was found to be responsible for pore widening in alumina.

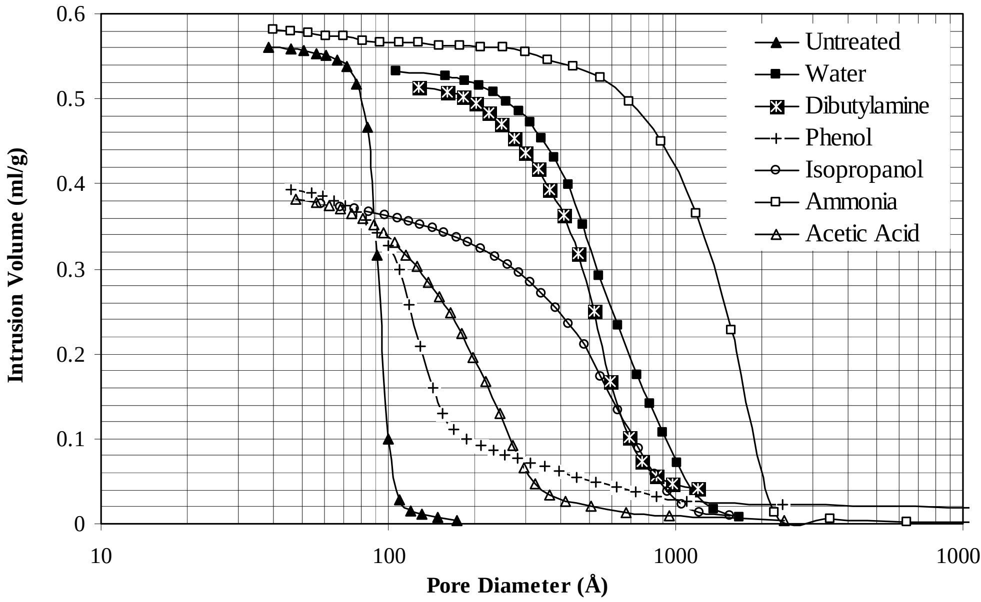

Fig. 1. Pore size distribution in alumina support after hydrothermal treatment with different reagents at 200 °C for 4 hours

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OP-17

MESOPOROUS SILICA ARMED WITH HALLOYSITE NANOTUBES: SYNTHESIS, THERMAL AND MECHANICAL STABILITY, CATALYTIC APPLICATION

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Pure mesoporous silica MCM-41, SBA-15, HMS are perspective materials for different catalytic processes. They are characterised by well-ordered mesoporous structure, high specific surface area and pore size excluding steric hindrances, mass transfer and diffusion limitations [1]. Besides, it is possible to control their chemical and structural properties during the synthesis. Thus, their acidity can be modifide by isomorphous substitution of the framework silica on different heteroelements or chemical modification of the surface with different functional groops and metals. The main disadvantage of amorphous mesoporous materials is thin pore walls. This resultes in poor thermal and mechanical stability compared to zeolites. That is why application of ordered mesoporous silica as a component of catalysts for oil refining processes (hydroprocessing, catalytic racking) is difficult.

In order to improve the thermal and mechanical stability of mentioned silicates, halloysite (natural aluminosilicate multiwall tubes with 50-nm diameter) was proposed in current study. This clay is a cheap, stable and biocompatible material [2].

The purpose of this work is to investigate thermal and mechanical stability of structured mesoporous silica armed with halloysite nanotubes and test these materials as a component of sulfur reduction additives for commercial cracking catalysts.

Structured mesoporous silica MCM-41 type, armed with halloysite nanotubes were synthesized. In order to increase acidity for cracking and sulfur adsorption properties improvement surface modification by La was carried out. The resulting materials containing lanthanium oxide La/MCM-41/Halloysite (1, 3, 5 % wt. by metal content) were characterized by TEM, XRD, low-temperature nitrogen adsorption/desorption, TPD of ammonia and IR spectroscopy. Formation of joint phase of MCM-41 with halloysite nanotubes was proven by TEM and XRD techniques.

Thermal (up to 1200 °C) and mechanical (up to 500 MPa) stability of La/MCM-41/Halloysite (1, 3, 5 % wt. by metal content) were evaluated.

La/MCM-41/Halloysite (1, 3, 5 % wt. by metal content) were tested as a sulfur reduction additives to industrial FCC catalyst in a MAT laboratory system.

It was shown that introduction of 10 % wt. of La/MCM-41/Halloysite additive to industrial catalyst provide more effective reduction (up to 30 %) of sulfur in liquid products of vacuum gas oil cracking compared to FCC catalyst without additive.

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Re-ACTIVATION OF AGED AND REGENERATED HDS CATALYSTS: INFRA-RED CHARACTERIZATIONS OF ACTIVE SITES

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Regeneration and reactivation of used industrial CoMo/Al_2O_3 hydrodesulfurization (HDS) catalysts allows reusing them. Since these catalysts are considered toxic and pollutant, regeneration/reactivation is an interesting procedure from an economical and ecological point of view. The regeneration consists in the oxidation of the spent catalyst that allows removing carbon deposits [1]. Nevertheless, regeneration alone does not restore completely the activity of new generations of HDS catalysts. Consequently, a second stage involving addition of organic compounds and sulfidation procedure has been developed [2-3].

In addition, it is common knowledge that sulfidation is a critical stage that impacts strongly the catalytic performance [4]. Therefore, the impact of different activation procedures has been already studied on CoMo/Al_2O_3 catalysts [5]. Indeed, HDS catalysts investigated in a laboratory scale are typically sulfided under a H_2S/H_2 gas flow at atmospheric pressure. In contrast, in the industrial practice, sulfidation is performed under a so-called "liquid phase sulfidation" at high pressure (HP). This latter procedure is carried out in a pilot plant at HP using organosulfur compounds such as dimethyldisulfide (DMDS) diluted in the charge as sulfidation agent [6].

In this work, two regenerated and re-activated CoMo catalysts (A and B) were tested and compared in thiophene HDS and straight run gasoil (SRGO) HDS. For the first test, sulfidation occurs at atmospheric pressure under H_2S/H_2 flow while for the second the sulfidation is made with DMDS diluted in the charge. Discrepancy between the activity results is then tentatively explained with results obtained by CO adsorption monitored by infrared (IR) spectroscopy.

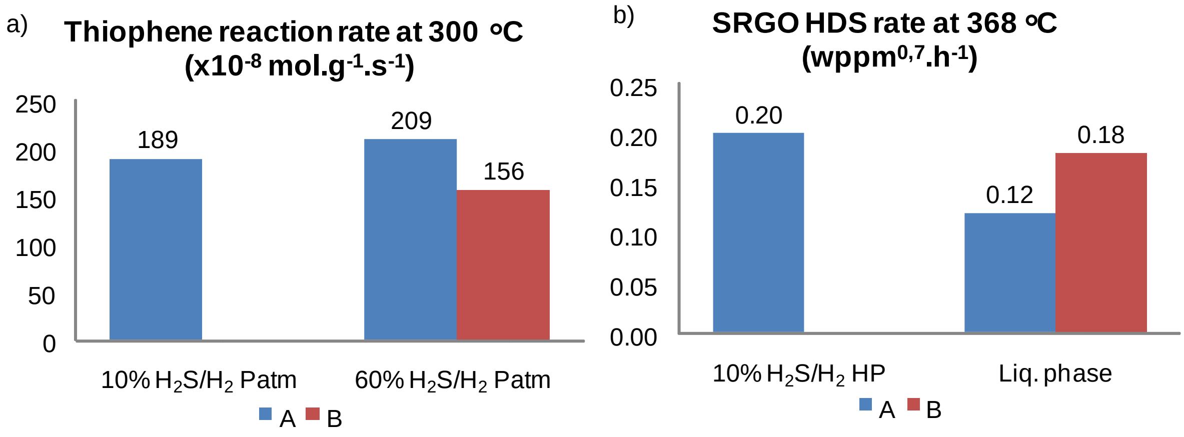

Figure 1. HDS rate a) in thiophene reaction at 300 °C after gas phase sulfidation at atmospheric pressure and b) in straight run gasoil after high pressure gas phase and liquid phase sulfidation

It apperas that the nature of the active sites can be strongly modified by the sulfidation step and thus the active site concentration is not sufficient to account for the observed activity.

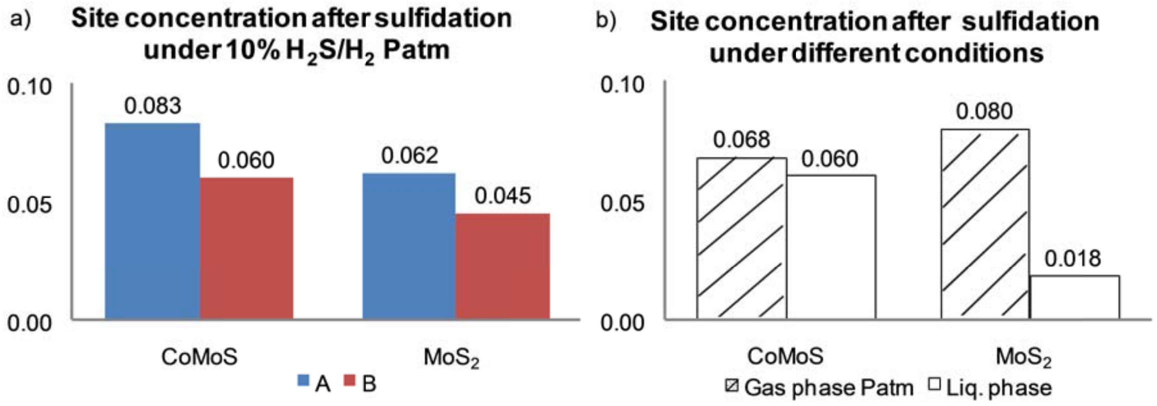

Figure 2. Effect of sulfidation conditions on site concentration after a) gas phase sulfidation under 10 % H_2S/H_2 at atmospheric pressure and b) gas and liquid phase sulfidation [7]

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OP-19

DEVELOPMENT OF GUARD-BED CATALYST FOR SILICON REMOVAL FROM MIDDLE DISTILLATES

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An actual problem in processing petroleum distillates is the presence of silicon compounds, which results in deactivation of hydrotreating catalysts. The origin of silicon compounds are various additives based on polydimethylsiloxane (antifoam, anticorrosive, anti-emulsion, etc.), which are used in oil refineries and during the oil extraction and transportation [1]. To extend service life of hydrotreating catalysts, guard-bed catalysts for silicon removal are loaded layer-by-layer over the main catalyst. The most widely used systems for guarding are NiMo/Al_2O_3 catalysts. The aim of the work is to study the influence of the textural characteristics of NiMo/Al_2O_3 catalysts on the purification of diesel fraction from silicon compounds.

Supports in the form of trilobe granules were obtained by plasticizing of boehmite with aqueous ammonia solution (NH_4OH/Al_2O_3 = 0.09 mol/mol) followed by extrusion, drying at 110 °C and calcination at 550 °C. The boehmite was prepared by hydration of thermoactivated aluminum hydroxide by varying the aging time of the powder in an autoclave (6 to 24 hours). Catalysts (1-2 wt. % Ni + 4-6 wt. % Mo)/Al_2O_3 were synthesized by impregnation of the supports with solutions containing the nickel and molybdenum compounds and citric acid followed by heat treatment. Testing of catalysts was carried out in a fixed bed reactor in the following conditions: $P = 3.8$ MPa, $T = 360$ °C, LHSV = 10.0 h^{-1}, H_2/feed = 550 nm^3/m^3. Diesel fraction with addition of decamethylcyclopentasiloxane was used as a model feed (Si content in the feed = 166 ppm).

It is found that increasing retention time of aluminum hydroxide in the autoclave makes it possible to obtain boehmite powders with particle sizes from 90 to 140 Å. The boehmite powders were used for supports preparation. The supports with the pore diameters from 83 to 216 Å have been obtained.

Table 1 shows characteristics of boehmite powders and corresponding supports.

Table 1. Characteristics of boehmite powders and corresponding supports

Boehmite sample	Aging time, h	Supports	SSA, m^2/g	V, cm^3/g	D, Å
B-1	18	S-1	232	0.48	83
B-2	8	S-2	241	0.61	102
B-3	6	S-3	215	0.69	129
B-4	8	S-4	195	0.75	154
B-5	12	S-5	167	0.85	203
B-6	24	S-6	156	0.84	216

Varying the conditions for the preparation of boehmite powders made it possible to obtain catalysts with different average pore diameter. Different physico-chemical methods show that active component particles uniformly localized in pores and do not plug pores. Table 2 shows the textural characteristics and chemical composition of fresh NiMo/Al_2O_3 catalysts. Testing of catalysts with different textural characteristics in conversion of model feed showed that the higher specific surface area and smaller pore diameter, the higher amount of adsorbed silicon.

Table 2. Chemical composition and textural characteristics of fresh NiMo/Al_2O_3 catalysts

Catalyst	Support	Content, wt. %		SSA, m^2/g	V, cm^3/g	D, Å
		Ni	Mo			
C-1	S-1	1.6	4.9	216	0.42	78
C-2	S-2	1.6	5.0	209	0.55	105
C-3	S-3	1.6	4.7	216	0.65	121
C-4	S-4	1.5	4.7	189	0.68	145
C-5	S-5	1.6	5.0	165	0.73	178
C-6	S-6	1.8	5.7	130	0.68	211

In present work, catalysts for silicon removal from diesel fuel have been studied. It is found that textural characteristics of the catalysts influence significantly on adsorption capacity of silicon compounds. Catalysts with high surface area and lower pore diameter are more effective for silicon removal from diesel.

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OP-20

CoMoP/Al$_2$O$_3$ HYDROTREATING CATALYSTS: EFFECT OF THE METHOD OF PHOSPHORUS ADDITION TO THE IMPREGNATION SOLUTION

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Nowadays, CoMoP/Al$_2$O$_3$ catalysts are widely used for hydrotreating of diesel fuel. Phosphoric acid and different organic ligands (for example citric acid) are added to the impregnation solution, and in this case the formation of many different complexes is occurred [1,2]. This work described the effect of the sequence of phosphorus addition to the impregnation solution on the properties of CoMoP/Al$_2$O$_3$ hydrotreating catalysts.

The series of CoMoP/Al$_2$O$_3$ catalysts with different methods of adding reagents was prepared: the sample with citric acid addition before phosphoric acid was marked as CoMoCitr+P, the sample with simultaneous addition of citric acid and phosphoric acid was marked as CoMoPCitr, and the sample with citric acid addition after phosphoric acid was marked as CoMoP+Citr. Also the catalysts without phosphoric acid (CoMoCitr), without citric acid (CoMoP) and without cobalt and citric acid (MoP) were prepared as comparison samples.

The studying of impregnation solutions and supported catalysts by UV–vis diffuse reflectance spectroscopy, IR-spectroscopy and Raman-spectroscopy was shown that cobalt in the samples was in the identical surrounding, but the differences in the Mo^{6+} surroundings were determined the differences in the coordination of citric acid and phosphoric acid to the molybdenum atoms.

Chemical composition and textural characteristics of the catalysts were obtained. The supported samples were studied by HRTEM after gas-phase sulfidation. Physico-chemical properties of the catalysts are given in this table:

Sample	Chemical analysis data, % mass.			Textural characteristics			HRTEM data for sulfide catalysts		
	Mo	Co	P	S, m^2/g	V, cm^3/g	D, Å	Average number of slabs per 1000 nm^2	Average stacking number	Average slab length, Å
CoMoCitr	15.6	5.30	-	195	0.45	93	33	2.1	27
CoMoP	15.0	5.04	2.48	156	0.39	100	28	2.3	32
MoP	20.3	-	2.75	138	0.38	110	29	1.9	31
CoMoCitr+P	13.5	5.14	2.56	183	0.42	93	39	2.2	32
CoMoCirtP	15.1	4.24	3.06	189	0.46	97	37	2.4	34
CoMoP+Citr	14.6	3.83	2.86	164	0.38	94	37	2.5	34

Catalytic activity in the hydrodesulphurization (HDS) and hydrogenation (HYD) reactions was studied using model fuel 2 % dibenzothiophene (DBT) with undecane. The conditions is P = 35 bar, T = 280 °C, H_2/fuel ratio = 500, LHSV = 80 h^{-1}. The results of testing are presented in this table:

Sample	DBT conversion, %	k(HDS)×10^3, c^{-1}	Content of PhCH in product, %	Content of BPh in product, %
CoMoCitr	57.4	5.26	8.3	67.7
CoMoP	47.2	3.92	9.5	52.6
MoP	10.5	0.68	7.1	5.8
CoMoCitr+P	47.7	4.10	7.5	56.7
CoMoCirtP	10.4	7.49	15.9	76.0
CoMoP+Citr	64.6	6.44	13.9	69.8

It was shown that the sequence of preparation of impregnation solution had influence to the properties of catalysts. Also, the samples prepared with citric and phosphoric acids were more active then samples with only citric acid or with only phosphoric acid. Finally, the sample with simultaneous addition of citric acid and phosphoric acid has the greatest activity in the HDS и HYD of DBT reaction.

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ORAL PRESENTATIONS
Session 3

THREE-STAGE HEAVY OIL HYDROPROCESSING OVER MACROPOROUS CATALYSTS

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Effect of catalyst pore size on heavy oil hydroprocessing has been a matter of discussion for several decades. It is widely known that a developed pore structure is needed for high molecular heavy oil components to access catalytic sites, however, exceedingly high pore volume and size should inevitably lead to the drop in specific surface area and mechanical strength of the catalyst pellet. Therefore, the optimum in the pore size for this particular process is considered to be in the range of 30-50 nm [1]. Nevertheless, more and more decreasing quality of heavy feed encourages researchers to extend the range of the pore size to a macroporous region. A theoretical contribution [2] reports on the superior lifetime and lower deactivation rate of the hierarchically structured catalyst with a meso-macropore network compared with the optimized purely mesoporous structure. The present work is aimed at studying the effect of hierarchical macro-mesoporous structure on the catalyst activity in heavy oil hydroprocessing. A facile "hard" template method using polymeric microbeads has been proposed for the preparation of alumina-supported catalysts with the desired textural parameters. Multistage catalytic experiments have been carried out under conditions close to the industrial ones (350-420 °C, 7 MPa, LHSV 1 h^{-1}, vol. H_2/feed = 1000, 200-800 h on stream), with the I stage providing metal and asphaltene removal, II stage capable of S removal, and III stage designed for hydrocracking of large molecules.

The proposed "hard" template method consists in creation of the additional macropore structure by the removal of polymeric microbeads from the precursor-template composite [3, 4]. Monodispersity and tunable size make these microbeads good templates for the preparation of hierarchical Al_2O_3 with bimodal porosity (10 and ~200 nm) and exceedingly narrow pore size distribution. Therefore, specific surface area (100-150 m^2/g) and mechanical strength (2-5 MPa) values lay in the range typical for purely mesoporous structures, whereas pore volume reaches

0.75-1.20 cm^3/g with 30-75 % of macropore volume fraction.

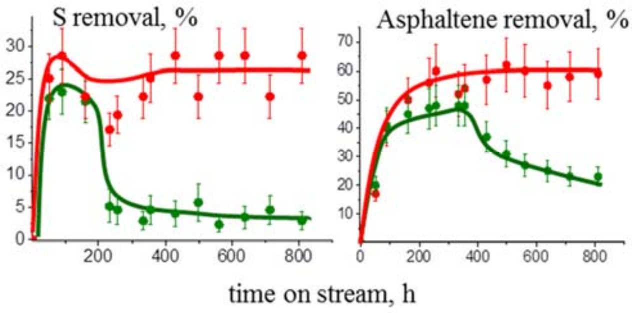

Figure 1. Sulfur and asphaltene removal over hierarchical (red) and mesoporous (green) catalyst

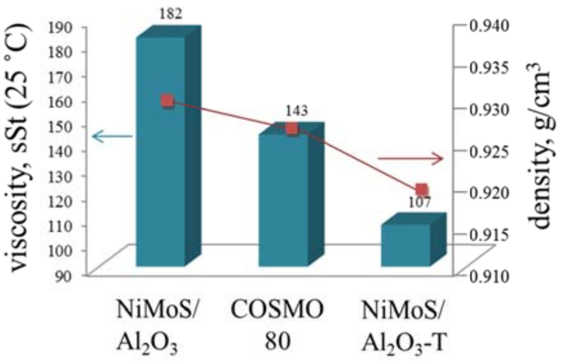

Figure 2. Viscosity and density of the products over the reference (NiMoS/Al_2O_3), commercial (COSMO-80) and hierarchical (NiMoS/Al_2O_3-T) catalyst

The catalysts supported on hierarchical Al_2O_3 were tested in the consecutive three-stage hydroprocessing of heavy Tatar oil in the following order: I stage – metal and asphaltene removal over a “guard-type” catalyst Al_2O_3, II stage – S removal over a hydrotreating NiMoS/Al_2O_3 catalyst, III stage – hydrocracking and isomerization over NiMoS/Al_2O_3-ZSM-5 catalyst modified with zeolite as an acidic additive. The samples based on the reference mesoporous Al_2O_3 and a commercial catalyst COSMO-80 were also investigated for comparison. The experiments over the “guard-type” catalysts clearly revealed a rapid deactivation for the mesoporous sample: it showed a continuous decrease in asphaltene removal and significant drop in S/metal removal after 400 h on stream, while the macro-mesoporous catalyst still had five-fold S removal and three-fold asphaltene conversion, as well as 5-10 times higher demetallization after 800 h on stream. The second stage hydrotreating test demonstrated that the hierarchical NiMoS/Al_2O_3 only had a slightly better S conversion after 200 h on stream when compared to the reference and commercial samples (54 % vs. 47 and 50 %, respectively). Nevertheless, the viscosity of the oil products was substantially lower (by 40-80 %) that indicates the decrease in diffusion restraints in this process. The third stage experiments were carried out with the similar catalysts modified with 15 wt. % of zeolite. In the case of the mesoporous NiMoS/Al_2O_3-ZSM-5, no significant changes were observed in the catalyst activity and stability in comparison with the non-modified sample. The hierarchical structure, otherwise, makes zeolite crystals accessible for high-molecular reagents. So, the templated NiMoS/Al_2O_3-ZSM-5 catalysts showed an extremely high hydrocracking rate leading to the rapid deactivation. A further problem to solve will be a moderation of the catalyst acidity to provide mild hydrocracking reactions. A theoretical modeling of asphaltene diffusion in the hierarchically porous catalyst is also being in progress. The preliminary results do confirm the hypothesis of superior stability of the catalysts with bimodal pore size distribution.

A facile "hard" template method has been applied to the preparation of the hierarchical macro-mesoporous catalyst for heavy oil hydroprocessing. The technique allows one to obtain a narrow bimodal pore size distribution, that imply the specific surface area and mechanical strength values lay in the range typical for purely mesoporous structures, whereas the pore volume reaches 0.75-1.20 cm^3/g with 30-75 vol. % of macropores. The results on the consecutive three-stage hydroprocessing of heavy oil clearly indicate that the developed hierarchical texture improves the catalyst stability against metal and asphaltene deposition by several times, as well as increases hydrocracking activity of $NiMoS/Al_2O_3$ catalysts, especially those modified with zeolite as an acidic additive.

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HYDROCONVERSION OF OIL SHALES: EFFECT OF MINERAL MATRIX ON KEROGEN CONVERSION AND PRODUCT YIELD

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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. Reactions, which are associated with the mineral matrix, have a marked influence on the product yield and composition during oil shale pyrolysis and combustion. However, the effect of the mineral matrix components on the conversion of oil shale in the presence of hydrogen was not studied previously. In this work the influence of mineral matrix on the yield and properties of liquid hydrocarbon products during hydroconversion of oil shale is studied.

Conversion of oil shale was performed in a flow reactor with a fixed bed of the sample at 425 °C, 6.0 MPa in the hydrogen flow. Raw oil shale and additional mineral matrix were loaded in the reactor as separate layers: oil shale as the top layer and mineral matrix as a bottom layer. Hydrogen flowed downwards and products of kerogen conversion proceeded to mineral matrix where the secondary reactions occured. SiC, shale ash (obtained by oil shale calcination at 600 °C), carbonate-free shale ash (obtained by HCl treating of oil shale with subsequent calcination at 600 °C), sandstone, clay and alumina were used as mineral matrices for conversion.

The oil shale was converted in the same conditions irrespectively of the mineral matrix, which was loaded as the bottom layer. Thus, the organic carbon conversion was close to 90 % for all experiments (Table 1). SiC and sandstone are the least active mineral matrices in the conversion of organic matrix providing higher yield of heavy fractions. Shale ash demonstrates higher cracking activity. Carbonates removal by HCl treatment increases cracking activity of shale ash, and slightly decreases desulfurization function. Clay has the highest cracking activity providing low shale oil yield and high yield of coke. This observation can be accounted for the acidic properties of clay mineral. Similar result for products yield is observed for alumina, probably due to high surface area and its acidity. Sulfur content in obtained shale oil correlates well with iron content in mineral matrices: lower sulfur content corresponds to the samples with higher Fe content, excepting sandstone, probably due to its low surface area (3 m^2/g).

Table 1. Hydroconversion of oil shale with addition of mineral matrix

Characteristic	Mineral matrix					
	SiC	**Shale ash**	**Shale ash HCl treated**	**Sandstone**	**Clay**	**Al_2O_3**
C (org) conversion, %	90.6	90.4	90.4	90.5	90.3	90.7
Products yield, wt %						
Shale oil, including:	24.8	21.0	18.8	22.4	15.0	17.2
naphta (<180 °C)	2.7	3.4	3.0	2.8	2.4	2.7
diesel (180-360 °C)	10.6	10.0	9.0	10.3	7.6	8.2
VGO (360-550 °C)	7.6	3.9	4.0	6.0	3.1	3.0
residue (>550 °C)	3.9	3.6	2.8	3.3	2.0	3.2
Spent shale	60.8	60.9	60.7	60.0	60.9	60.5
Coke on mineral matrix	1.1	2.5	2.2	1.0	5.3	4.3
Gas, water, losses	13.3	15.6	18.4	16.5	18.7	18.0
S content in shale oil, wt %	4.7	1.5	1.9	3.8	1.8	4.2
N content in shale oil, wt %	1.1	0.4	0.4	0.8	0.5	0.3

Mineral matrices with different acidity (SiO_2, Al_2O_3, SiO_2-Al_2O_3) as well as matrices with additional amount of Fe were also studied for hydroconversion of oil shale.

According to obtained results, during oil shale hydroconversion clay minerals have pronounced adsorption effect due to the acidic properties, leading to enhanced aromatization and coke formation. Iron species can catalyze hydrogenation, HDS and HDN reactions. Introduction of additional amount of Fe in mineral matrix enhances hydrotreating activity. Mineral matrices, containing Fe and clays, may act as bifunctional catalysts with weak hydrogenation and cracking activity. Carbonates do not affect cracking reactions, acting like a diluent for clay component. However, the presence of carbonates in oil shale mineral matrix may give a positive effect on sulfur removal by calcium sulfate formation. Thus, depending on the composition, mineral matrix of oil shale may have catalytic effect for the kerogen hydroconversion.

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HEAVY OIL UPGRADING VIA CATALYTIC STEAM CRACKING IN THE PRESENCE OF Ni- AND Mo-BASED DISPERSED CATALYSTS

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Due to constantly growing global energy demands, the use of heavy oil feedstocks (HOF), including heavy crude oil, natural bitumen, and residues of petroleum distillation, has been consistently increasing. These feedstocks are characterized by high viscosity, high content of sulphur and metals, large amount of asphalt-resinous components and modest content of light hydrocarbon fractions. At present, the contribution of HOF into overall petroleum refining is low due to the problems with its production, transportation and processing. Hydrogenation is considered as a potential approach to the transformation of HOF into light fractions. In these processes [1], the use of hydrogen is advantageous for the suppression of coke formation and increasing the yield of hydrogen-saturated liquid fractions, resulting in increased commercial value of the products. However, significant investments into hydrogenation technologies makes the use of hydrogen majorly unaffordable. This problem stimulates the search for alternative hydrogen free technological approaches. A number of publications describing thermal and thermocatalytic transformations of HOF in the presence of water has been steadily growing. These transformations lead to reduced viscosity, improved H : C ratio and reduced content of heteroatoms in the resulting products [2].

In this work, the study of the steam cracking process was carried out using an autoclave manufactured by Parker (USA) at the temperatures of 425 and 450 °C, mass ratio of water to feed 0.3 : 1, and mixing rate of 1000 rpm in a 1000 ml batch reactor. The process was catalysed using the dispersed Ni- and Mo-based catalysts. High-sulphuric heavy oil (HO) from Rep. of Tatarstan (Russia) was chosen as the processed substrate in the experiments. Except the catalytic steam cracking (CSC), experiments on thermal cracking (TC), steam cracking (SC), catalytic cracking in the absence of water (CC) and hydrocracking (HC) were considered to establish the effect of water, the catalyst and the other process conditions on the composition and properties of HO conversion products. The evaluation of efficacy was performed using the yields of light fractions (b.t. < 350 °C), synthetic oil (b.t. < 500 °C), semisynthetic oil (total liquid product), coke and gaseous products. In addition, the H : C atomic ratio, sulphur content, density and viscosity were estimated.

The main results shown in Table 1 indicate that as the content of the dispersed Ni-catalyst increases, the yield of liquid products gradually decreases with increasing coke yield. In the case of experiments with Ni content less than 1.0 %, the yield of light products remains constant.

Thus, the use of a dispersed Ni-based catalyst results in an increase of the H : C ratio in liquid products. Moreover, the use of an excess amount of catalyst contributes to an increase in the yield of coke without a significant increase in the H : C ratio.

Table 1. Parameters of treatment processes and products for the high-sulphuric heavy oil

Yield, wt. %	**HO, wt., %**	Treatment processes at 425 °C, 1 h								
		TC	**SC**	**CC**		**CSC**				
				Ni	Mo	Ni			Mo	
				2.0 %	2.0 %	0.3 %	1.0 %	2.0 %	1.0 %	2.0 %
Light fractions	21	47	50	48	48	50	50	46	51	51
Synthetic oil	52	65	64	58	61	63	61	59	64	66
Semisynthetic oil (liquid products in total)	100	83	82	74	82	81	77	76	81	82
Coke	–	8	7	15	8	8	11	13	8	8
Parameters of liquid products:										
H : C ratio	1.74	1.61	1.64	1.64	1.62	1.68	1.67	1.69	1.64	1.70
Sulphur content, wt. %	4.3	3.5	3.3	3.0	2.8	3.2	3.0	2.9	3.1	2.8

Catalytic steam cracking in presence of 2 % Mo-based catalyst at 425 °C results in semi-synthetic oil with a higher H : C ratio and a lower sulphur content compared to the semi-synthetic oil obtained in TC and SC catalyst-free processes and CSC with Ni-based dispersed catalyst.

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OP-24

CATALYTIC CRACKING OF ANTHRACENE AND PHENANTHRENE IN SUPERCRITICAL WATER ENVIRONMENT

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Due to dwindling conventional petroleum resources, the importance of unconventional hydrocarbon feedstocks (heavy oil, bitumen, etc.) is increasing. Recent estimations show that about 80 % of oil reserves are classified as unconventional heavy petroleum feedstocks. Nowadays, heavy oil upgrading by cracking in the presence of water is considered as a potential alternative to traditional approaches to heavy oil feedstocks upgrading based on hydrogen addition and carbon rejection [1]. Upgrading in supercritical water (SCW) medium is known to reduce coke formation and to increase yields to light hydrocarbons [2]. SCW acts as a good solvent for the dissolution and dispersion of coke precursors formed during the cracking process, thus preventing polymerization and hindering coke formation [2]. The addition of active catalysts to these processes can enhance SCW heavy oil upgrading through cracking of hydrocarbons and stabilization of hydrocarbon radicals, including coke precursors, reducing their molecular weight, and hydrotreatment and hydrocracking reactions with H_2 formed in-situ via low-temperature steam reforming and water gas shift reaction. In-situ formed hydrogen is highly reactive and able to hydrogenate coke precursors, stabilizing them to minimize polymerization [2]. For this reason, the research to develop catalysts tailored to these processes is of critical importance. These catalysts should provide good interactions between hydrocarbons and water, and oxidation (to generate CO and more reactive hydrocarbons), cracking (to give rise to lighter fractions) and hydrogenation (to stabilize radicals and avoid coking) functions. Furthermore, they shoud also be stable in SCW medium.

Ni-Mo formulations are the state of the art catalysts for heavy oil hydrocracking due to their good catalytic performance, stability and resistance against deactivation [3]. The aim of this work is to study both the catalytic activity and the stability of a catalysts series of NiMo/SiO_2 composition with different Ni : Mo ratios in the SCW cracking of model polyaromatic hydrocarbons (PAHs) – anthracene and phenanthrene. Their use is common as their structures resemble PAH systems found in asphaltenes.

Results showed that the NiMo/SiO_2 catalysts are active in SCW cracking of polyaromatic compounds, yielding anthracene conversions 17-47 % (Table).

Table. Anthracene conversion, carbon yields (C-mol %) in liquids products, gas and coke together with liquids (C-mol %) and hydrogen production at T = 425 °C, P = 230 bar, t = 1 h

Sample	**Conversion (%)**	**Y_{LP} (%)**	**Y_{coke} (%)**	**Y_{gas} (%)**	**S_{LP} (%)**	**H_2 ($L_{c.n.}$/g ant.)**
Ni40Mo40	46.7	22.7	0.4	23.6	48.6	0.3
Ni30Mo50	33.9	16.4	1.9	15.6	48.5	0.2
Ni20Mo60	34.8	7.4	2.4	25.0	21.3	0.3
Ni10Mo70	17.3	7.1	0.3	9.9	41.1	0.2

Liquid products were mainly oxygen-containing derivatives of anthracene produced through partial oxidation of middle aromatic ring (benzophenone, xanthone, xanthene, fluorenone and anthraquinone). Low coke yields (0.3-2.4 % (C-mol.)) confirm the low coke formation propensity of SCW as reaction medium observed with silica-based catalysts.

More stable phenanthrene, as expected appeared to be less reactive. Its conversions were 12-24 % and the most active catalysts were **Ni40Mo40** and **Ni30Mo50** as well. Non-catalytic run showed almost zero phenanthrene conversion.

A detailed study of the stability of these catalysts under SCW conditions showed significant changes in their structure and composition indicating on the necessity of their further improvement. In any case this study is a successful example on catalytic hydrocarbons upgrading in SCW and provides some insights on the key aspects to develop effective catalysts for this innovative process.

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OP-25

EFFECT OF Co AMOUNT IN CoMo/Al_2O_3-TiO_2 FOR HYDRODEOXYGENATION OF PHENOL

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Introduction

Rewenable pyrolysis oil derived from biomass has been considered as a potential sustitute of fossil fuels. However, pyrolysis bio-oil is composed by 40 wt% of oxygenated compounds which bring undeseable properties. Catalytic hydrodeoxygenation (HDO), is considered an efficient process to remove oxygen from the hydrocarbon feeds [1] . Phenolic compounds has been used as probe molecules since they provide information about catalytic functionalities [2] . Mixed oxide Al_2O_3-TiO_2 support could be used as a potencial catalytic support to hydrodeoxygenation, since it has presented higher activities than alumina supported catalysts due to the decrease of the metal-support interactions which leads to the increase of the Mo in octahedral coordination and subsecuently, during sulphidation, the coordinated unsaturated sites [3] . On this basis, is interestig to study and improve these catalysts aiming to sinergic effect of the cobalt in the catalytic performance.

Experimental methods

Sol-gel Al_2O_3-TiO_2 support (55 wt % Al_2O_3, 45 wt% TiO_2, AT2) was impregnated with Co and Mo (15 wt % Mo, CoMo/AT2) varying the atomic ratio Co/(Co+Mo) = 0.1, 0.2, 0.3, 0.4 and 1. The catalysts were sulphided ex situ with 15 mol% H_2S/H_2 at 400 °C during 2 h. The catalytic performance of the pre sulphided catalysts were tested in a batch reactor at 320 °C, 5.5 MPa, 100 ppm of CS_2 and 2000 ppm fenol. Oxidic catalysts were characterized by temperature programmed reduction (TPR) and diffuse reflectance UV-vis spectroscopy (DRS-UV-vis).

Results and discussion

Figure 1 shows the correlation between Co in octahedral coordination (Co^{Oh}) and the initial reation rate of the HDO of phenol. The catalyst with the highest fraction of Co^{Oh} showed an optimal catalytic activity. This catalyst was the one with the atomic ratio Co/(Co+Mo) = 0.2.

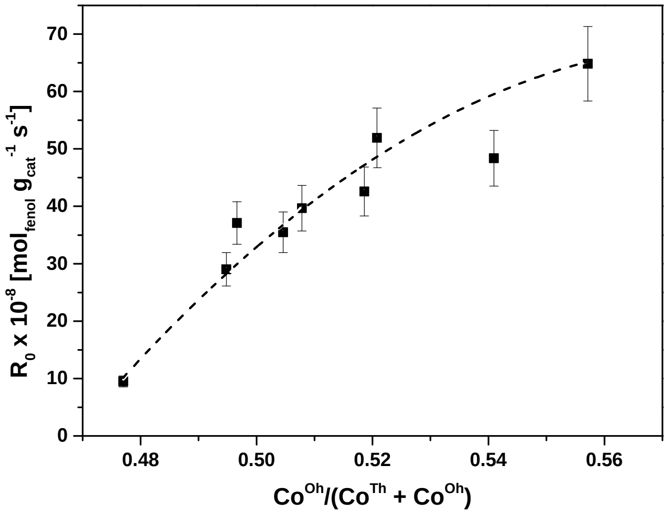

Figure 1. Correlation between initial reaction rate of phenol at 5.5 MPa, 320 °C, 100 ppm CS_2 and Co^{Oh} fraction on the CoMo/AT2 catalysts

At this ratio, Co^{Oh}, is avaible to promote the MoS_2 phase and to form CoMoS II active phase, however at lower ratios than 0.2, the Co^{Oh} is not enough abundant to promote MoS_2 phase. Since Co in tetrahedral coordination (Co^{Th}) is difficult to sulphide, at higher values of Co/(Co+Mo) ratio (0.3 and 0.4), Co^{Th} is more abundant and did not promoted the MoS_2 phase, but it forms Co_9S_8 phase or migrates to the support and promotion is not appropriate. Also, the increase of Co in the surface of the catalyts, increase the hydrogenation route of the HDO of phenol. This indicates that segregated Co, present in atomic ratios higher than 0.1, promotes this route.

Conclusions

The synergic effect are highly dependent of the dispersion and amount of the Co. On this basis, Co in octahedral coordination, has an important roll in the catalytic performance, and selectivity.

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OP-26

PREPARATION OF UNSUPPORTED CARBON-CONTAINING MoS_2 CATALYSTS FOR HYDRODEOXYGENATION OF OLEIC ACID

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Due to disadvantages of biodiesel caused by high oxygen content, resulting in low high viscosity, thermal and oxidation stability, and low heating value, the co-processing of petroleum feedstocks and plant oil has attracted much attention for last decades [1]. The fatty acid undergoes hydrodeoxygenation (HDO) through following reactions: hydrogenation (HYD) removes oxygen in the form of water and yields n-alkane with same carbon number as the corresponding fatty acid, decarbonylation (HDC) and decarboxylation lead to elimination of oxygen in form of CO and water or CO_2, respectively. The formation of CO and CO_2 could affect catalyst deactivation and inhibit the hydrodesulfurization of S-containing compounds from petroleum fractions [2]. The development of unsupported catalytic systems with high HYD/HDC selectivity ($S_{HYD/HDC}$) is a promising direction for improving refining processes of oil and biorenewable feedstocks.

Unsupported Ref-MoS_2 catalysts were synthesized by thermal decomposition of ammonium tetrathiomolybdate (ATTM) in quartz reactor with H_2S/H_2 flow [3]. Et-MoS_2 and Et-MoS_2/C samples were obtained from Mo-catalyst supported on alumina and carbon coated alumina by leaching the support with HF acid. XRD, N_2 adsorption, TPR, TEM techniques were used to characterize prepared materials. Catalytic tests of oleic acid HDO were performed in an R-201 high-pressure batch reactor (300 ml). The catalysts (0.25 g) were activated under H_2S/H_2 (15 % (v/v) H_2S) at 673K for 4 h and transferred at reactor with reactant mixture (5 wt. % of oleic acid in toluen, 1 wt. % i-octane as internal standard, total volume: 150 ml) without contact with air. The autoclave was pressurized with hydrogen to 3.1 MPa and heated up to 573 K at 10 K/min. The stirring speed was kept equal to 300 rpm.

The rate constants in oleic acid HDO for Et-MoS_2 and Et-MoS_2/C were 1.2 times higher than those over the MoS_2/Al_2O_3 and $MoS_2/C/Al_2O_3$ catalysts and close to $CoMoS_2/Al_2O_3$ and $CoMoS_2/C/Al_2O_3$ catalysts [4]. The results of catalyst tests are shown in Fig. 1.

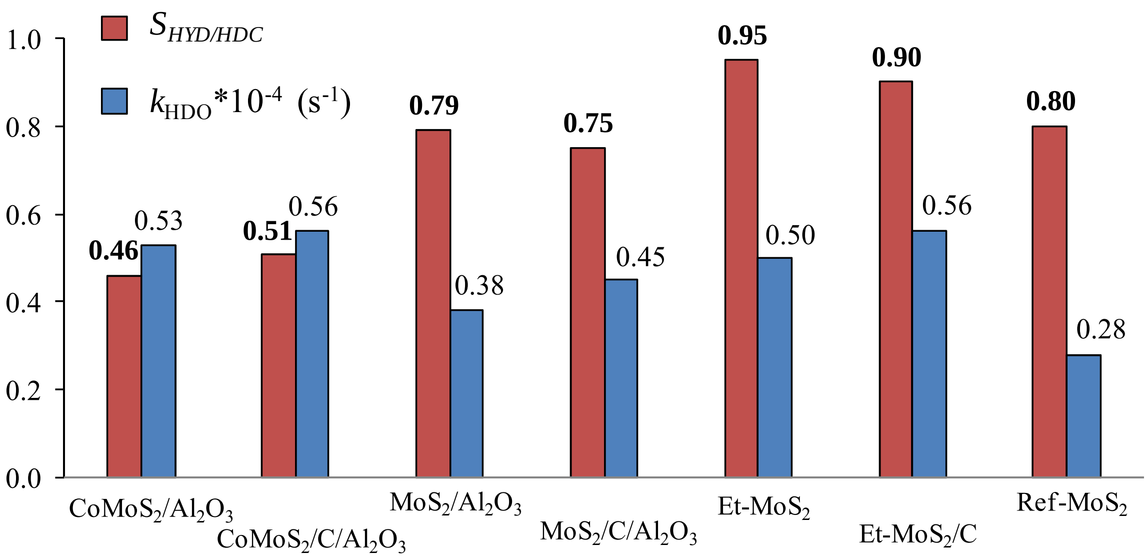

Fig. 1. Rate constants in oleic acid HDO and HYD/HDC selectivity

$S_{HYD/HDC}$ in oleic acid conversion strongly depends on catalyst type. The $CoMoS_2/Al_2O_3$ and $CoMoS_2/C/Al_2O_3$ catalysts show low HYD activity equal to 0.5. Unpromoted MoS_2/Al_2O_3 and $MoS_2/C/Al_2O_3$ catalysts and Ref-MoS_2 had quite similar selectivity close to 0.8. The highest selectivity 0.95 and 0.90 was reached by Et-MoS_2 and Et-MoS_2/C samples indicate that HDO of oleic acid almost for 100 % go through hydrogenation route without any formation of CO and CO_2.

The unsupported molybdenum sulfide catalysts exhibited high hydrogenation activity in oleic acid HDO. The improved catalytic properties of the prepared bulk MoS_2 catalysts might find wide applications in co-hydrotreating of oil fractions and biorenewable feedstocks.

Acknowledgements

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CHARACTERIZATION AND HYDRODEOXYGENATION ACTIVITY FOR Ni-Ru/TiO_2 CATALYSTS

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1. Introduction

The bio-oil of pyrolysis can be upgraded via hydrodeoxygenation (HDO) to remove unfavorable characteristics related to high levels of oxygen (up to 40 wt. %). Hydrocarbon mixtures with similar properties to petrol fuels are obtained as the primary product. Recently, the metallic Ni, Ru and Ru-Ni catalysts supported on Al_2O_3, ZrO_2 and TiO_2 were studied in the HDO reaction with promising results [1]. Ni-Ru/TiO_2 catalysts showed a decrease in activity compared to monometallic Ni and Ru catalyst, suggesting strong metal-support interactions (SMSI) caused during the catalysts calcination step. Therefore, the aim of this work was to investigate the effect of the calcination of the NiRu/TiO_2 catalyst on the metal-support interactions and its impact on phenol HDO catalytic activity.

2. Experimental

NiRu/TiO_2 catalysts were prepared by the wet impregnation of an aqueous solution of (99.999 %; $Ni(NO_3)\cdot 6H_2O$) and (1.5 % Ru/vol; $Ru(NO)(NO_3)_3$). The metal loadings were 10 Ni– and 0.5 Ru–atoms*nm^{-2}. The synthesized materials were dried at 120 °C for 12 h (*uncalcined*-NiRu/TiO_2) and then, calcined at 500 °C for 4 h (*calcined*-NiRu/TiO_2). Catalysts were evaluated in the HDO of phenol in a high-pressure fixed bed catalytic reactor. The catalysts were reduced in-situ at 450 °C for 2 h in H_2. The catalytic bed was heated up 320 °C (3.0 MPa). The liquid feed (2 vol. % of phenol dissolved in dodecane) was mixed with H_2 and introduced into the reaction system using HPLC pump (WHSV = 2.57 h^{-1}). The reactor effluents were condensed and analyzed by a GC Agilent 6890A. Catalytic materials were characterized by TPR, HRTEM, TPD, TGA, and XPS.

3. Results and discussion

Figure 1 shows the TPR profiles for both *uncalcined*- and *calcined*-NiRu/TiO_2 catalysts. For the a) *uncalcined* sample, the sharp reduction peak located at 210 °C was assigned to the reduction of ($Ru^{3+}\rightarrow Ru^0$)[2] and Ni ($Ni^{2+}\rightarrow Ni^0$) [3] complexes occurring simultaniously. The narrow shape of the reduction peak suggested a uniform distribution of metal entities. Furthermore, the peak at 250 °C was associated with the reduction of Ni species with weak interaction with the support. TPR analysis for calcined material indicated a close interaction between metals and the possible formation of bimetallic clusters. It could be assumed that calcination influenced the metal-support interaction and the metal dispersion based on the peak shape. For instance, sharp bands could indicate a more homogeneous particles distribution, while the shifting to higher reduction temperature could be related with stronger metal support interaction. Figure 2 shows the conversion profile for the NiRu catalysts. The uncalcined catalyst was more active and resistant to deactivation than the calcined one. After three hours of reaction time, uncalcined catalysts reached steady state while the calcined material continued deactivating. However, TGA analysis showed a similar amount of superficial coke on each used catalyst after the reaction test. For both catalysts, the selectivity was identical.

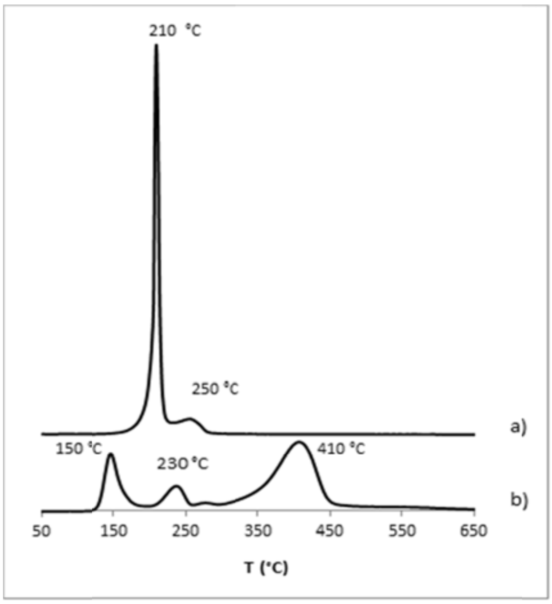

Figure 1. TPR analysis for a) *uncalcined* and b) *calcined*-NiRu/TiO_2

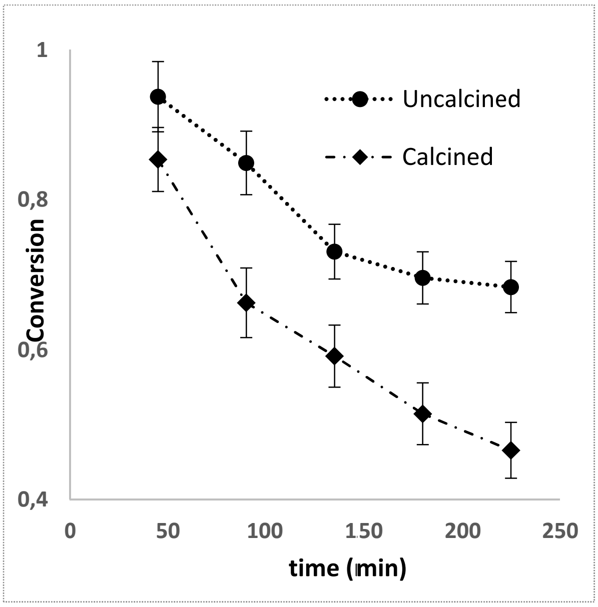

Figure 2. Conversion profile for *calcined*- and *uncalcined*-NiRu/TiO_2

We conclude that thermal treatments influence the metal dispersion and the metal support interaction in NiRu/TiO_2 materials. Hydrogen Chemisorption, TPR, and HRTEM characterization pointed out that dispersion of metal particles was significantly improved when the NiRu/TiO_2 catalyst was only dried and then reduced, while calcination induced SMSI and sintering of metal particles.

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CATALYSTS AND PROCESSES FOR PRODUCTION OF ECOLOGICAL FUELS

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Currently, a production of modern motor gasolines with RON 95 and above in Russia is far behind. Neither Russian refineries has no technical capability to make all commercial gasoline with RON 95. For this reason, the minimum octane index requirement (RON 95) was struck from the Technical Regulations[1]. However, valid stringent requirements for the quality of motor gasoline (content of aromatic hydrocarbons and benzene content separately) are remain [2].

Quality indicators of commercial gasoline can be improved by the implementation of technology, such as the isomerization of straight-run fraction i.b.p.÷70°C and reforming fractions 100÷180°C, new technologies - the isomerization of straight-run fraction of 70÷100°C (heptane fraction).

In this report the catalysts and new processes for the production of high-octane gasoline components, satisfying the requirements of technical regulations are discussed. For isomerization of 70-100 °C fraction (C_7 hydrocarbons) new catalysts based on WO_3/ZrO_2 are developed. As a metallic component, this catalysts contain Pt or Pd. The content of platinum in the optimal catalyst is 0.8-1 wt.%, whereas the amount of palladium can be significantly reduced to 0.05-0.1 wt.% while maintaining high activity. Realization of 70÷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 active components WO_3 and ZrO_2 are discussied.

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. The effect of tin precursor added to the aluminum hydroxide at the peptization stage on the isomerization of n-hexane in the presence of supported Pt/SZ/Al_2O_3(Sn) catalysts was studied. It is shown that in the case of the use of Sn(IV) hydroxide, chloride and sulfate, the particle size of the active tetragonal phase of ZrO_2 supported on the Al_2O_3(Sn) carrier is 3.2 nm, 8.3 nm and 8.4 nm, respectively. The smaller particle size of the active phase of supported zirconia provides a higher specific surface area and, as a result, higher values in the isomerization reaction of n-hexane. 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.

Integration of processes for production of environmental components of gasolines in the total process chain is to lead to raising the octane number gasoline stock and ensure issuance of environmentally friendly commercial gasoline with RON 95.

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ORAL PRESENTATIONS
Session 4

RENEWABLE JET FROM ALGAL OIL

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Algal oils are interesting feedstocks for biofuels production because of the potential for very high yields per acre of land compared to conventional oilseed crops, and the possibility of producing them in regions that do not compete for land resources with food crop production. A novel algal oil was provided to UOP to demonstrate conversion to jet product by UOP's Renewable Jet Fuel Process™. Unlike typical triglycerides and fatty acids that are the usual feeds for diesel/jet biofuel production, this algal oil contained a very low oxygen content (<2 wt %), and a large amount of hydrocarbon molecules in the range of C31-C37 carbon number. To evaluate the potential for this feed, the project proceeded in three phases. In Phase 1, two 1-liter samples of algal oil were provided for laboratory analysis for preliminary determination of the suitability for processing. In Phase 2, a 40-liter sample of algal oil was provided for once-through pilot plant conversion to product, followed by product analysis. In Phase 3, a 160-liter sample of algal oil was provided for conversion in a recycle pilot plant for purposes of yield estimating.

The algal oil was found to possess properties suitable for processing to Renewable Jet fuel. The properties were found to be very consistent from batch to batch. Since both raw and filtered samples were found to be within range for processing it was recommended that the filtration step be eliminated as unnecessary. Jet product from this algal oil is able to meet almost all ASTM D7566 product requirements for renewable jet fuel, with the exception of cycloparaffins concentration. Also, the specific gravity of the product is high and can sometimes be above the specification limit depending on product distillation. Although density and cycloparaffin content in the product was found to be outside of the range specified by ASTM D7566 for "HEFA" type renewable jet fuel, it was within range for ASTM D1655 final blended jet fuel specifications.

Cycloparaffin content of the jet product was found to exceed the 15 wt % limit specified in D7566. Some cyclization of the feed was shown to occur during processing, likely due to the large and highly branched nature of the feed molecules. Cycloparaffins and aromatics are known to have higher densities than their non-cyclic counterparts, leading to the higher specific gravity of the jet product.

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Processing a blend of 80 wt % tallow/20 wt % algal oil is capable of producing a jet product that meets all ASTM D7566 specifications for HEFA-SPK, including cycloparaffin concentration. This work will be instrumental in qualifying algal oil as a feedstock for commercial Renewable Jet production.

OIL-CROP BIOMASS HYDROCONVERSION FOR BIODIESEL PRODUCTION

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Nowadays the biomass conversion is of the great interest. One of the ways to process biomass is the biofuel production. Biogas, bioethanol, and biodiesel are widely used types of biofuel [1]. Biodiesel is the one of the perspective type of biofuel. Typically biodiesel is obtained from oils and fats through methanolysis with use acid or based catalysts. Biodiesel made by this method has such drawback as poor stability due to the oxygen presence. In addition, biodiesel production requires the use of raw with certain quality. For example, waste oil and frying fat are not desirable due to the high concentration of free fatty acids.

The most promising way for biodiesel synthesis is the biomass hydrofining. Hydrofining includes following processes – hydrodeoxygenation, hydrocracking, hydrogenation – to produce 2nd generation biodiesel in form of linear saturated hydrocarbons with carbon number of 15-22 [2].

2nd generation of biodiesel is mixing easily with mineral diesel. Moreover it has higher cetane number, higher energy content, excellent combustion quality, good low-temperature properties, and superior thermal stability, storage stability, and materials compatibility in comparison with both petrol diesel and biodiesel [3].

In this investigation the hydrotreatment of fatty acids was carried out. The stearic acid (99%, KhimMedService, Russia) was used as the model substrate. n-Dodecane (99.9 %, Sigma-Aldrich) was used as a solvent. Palladium supported on hypercrosslinked polystyrene (HPS) of MN270 type (Purolite LTD, UK) was used as **a** catalyst. The metal loading was varied from 1 up to 5 % (wt.). The process was condu**c**ted in stainless steel batch reactor PARR-4307 (USA). The following reaction conditions was varied: hydrogen pressure 0.2 – 2.5 MPa, temperature 100 – 260 °C, concentration of stearic acid 0.05 – 0.2 M. Liquid samples were taken every hour during the process and analyzed using GC-MS.

The catalyst structure was studied using the following physico-chemical methods: low-temperature nitrogen physisorbtion, transmission electron mycroscopy, X-Ray photoelectron spectroscopy, IR-spectroscopy, thermogravimetric analysis.

Figure 1 represents the stearic acid consumption curves for both hydrodeoxygenation and hydrogenation processes in the presence of HPS-based catalysts.

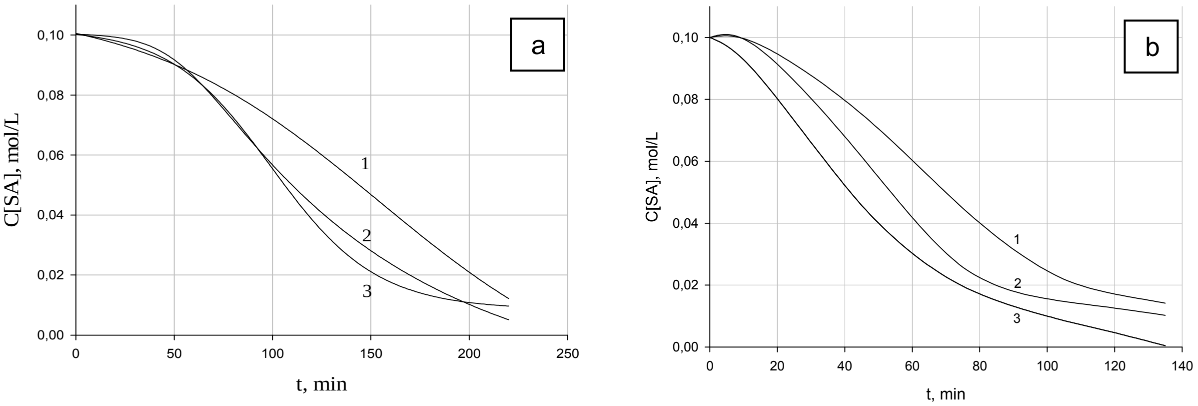

Figure 1. Stearic acid consumption depending on time for catalysts based on HPS MN-270 (1 – 1 %-Pd/MN-270; 2 – 3 %-Pd/MN-270; 3 – 5 %-Pd/MN-270): a – hydrodeoxygenation process; b – hydrogenation process

It was revealed, that the most effective catalytic system in both processes was the catalyst 1%Pd/HPS-MN-270, which has the high surface area (1300 m^2/g) and average pore size 4-6 nm. This catalyst allows achieving the high products yield in hydrodeoxygenation process (selectivity regarding n-heptadecane was 99 % at 100 % substrate conversion) as well as in hydrogenation reaction (selectivity regarding stearyl alcohol was 93 % at 100 % substrate conversion) of stearic acid chosen as model substrate.

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HETEROGENEOUS CATALYSTS FOR BIO-FUEL

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The current global problems are excess emission of greenhouse gasses, increasing demand of energy and increasing industrial wastage [1], [2], [3]. These problems can be controlled and removed by chemical processes such as the conversion of greenhouse gasses and industrial wastages into some useful products, and by producing of renewable energy resources [4]. Herein, various transitions metals (Pt, Pd, Ru, Co, Ni & Cu) loaded carbon nanotubes (MWCNTs) were prepared by a modified wet impregnation method and tested for oxidation of industrial important furfural into furoic-acid, serve as a renewable alternative to terephthalic acid in the production of polymers, open novel possibilities for obtaining value added chemicals from renewable resources [5]. Catalysts and products were characterized by various analytical techniques such as SEM, TEM, XRD, NMR and HPLC.

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LIQUID PHASE CATALYTIC HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL

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Research to develop alternative liquid transport fuels has increased considerably in recent years influenced by the implementation of legislation and directives on alternative energy which sets targets for transposing members. To achieve these targets in an ethical, environmentally sustainable and economical manner the use of lignocellulosic biomass or agri-waste for the production of second generation biofuels is proposed. The production of biofuels from hemicellulose requires acid hydrolysis to open the biomass structure giving large quantities of xylose. The synthesis of furfural as a by-product of this biofuel production process has developed an additional important research area [1].

Selective hydrogenation of furfural has attracted much attention for the production of furfuryl alcohol, methyl furan, tetrahydrofurfuryl alcohol and others [1, 2]. Furfuryl alcohol is widely used in chemical industry, mainly for the production of special resins, polymers and coatings on their basis, which are resistant to acids, alkalies and various solvents. In addition, furfuryl alcohol is employed as diluents for epoxy resins and as a solvent for phenol formaldehyde resins and poorly soluble pigments. In the organic synthesis, furfuryl alcohol is a feedstock for the production of tetrahydrofurfuryl alcohol and 2,3-dihydropyranand an intermediate for the synthesis of lysine, vitamin C, various lubricants and plasticizers .In industry, furfuryl alcohol is obtained by catalytic hydrogenation of furfural in a liquid or vapor phase [3]. The liquid-phase process is carried out with copper chromite systems as the catalysts. The main disadvantage of copper chromite catalysts is their toxicity caused by the presence of chromium oxides, which allows considering such catalysts as environmental pollutants [1-4]. Thus, the development of catalysts that are highly active in hydrogenation of furfural to furfuryl alcohol and contain no chromium is a topical task.

In this work, we studied the catalysts based on noble metals deposited on a variety of supports, including magnetically recoverable in the process of selective hydrogenation of furfural to furfuryl alcohol. Magnetically recoverable catalysts synthesized on the basis of nanoparticles of catalytically active metal (Pd, Pt, Ni), formed on the surface of Fe_3O_4 particles. For the synthesis of the respective catalysts a solution of a stabilizing polymer which was soluble acetates of the corresponding metals was used. After heating to a certain temperature of heat-labile acetates decompose with the formation of magnetically recoverable catalytically active nanoparticles [3]. Testing of the synthesized catalysts in a process for the hydrogenation of furfural was conducted in the reactor PARR 4843 (USA) by varying parameters such as concentration of furfural, the nature and quantity of catalyst, temperature, nature of solvent and the hydrogen pressure. The data on the influence of parameters of the process for conversion of furfural and the selectivity for the target products were obtained.

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RESIDUAL LIPIDS INTEGRATION IN A PETROLEUM REFINERY

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Biofuels are promoted as one of the most significant substitutes of fossil fuels with a considerable share growth in recent years. Hydroprocessing of vegetable oils, waste cooking oils or animal fats is an alternative process to transesterification for producing bio-based diesel fuels [1], [2]. Hydrotreated lipids are referred to Hydrotreated Vegetable Oils (HVOs) or simply renewable diesel [3], [4]. However, the investment cost of a standalone hydroprocessing unit for vegetable or waste oils is very high, which drove research to the alternative pathway of co-hydroprocessing lipids with fossil-based intermediates [5], which further enables an increase of biomass utilization for the production of greener transportation fuels.

This approach allows utilization of existing refinery technology and equipment, rendering it a more economically attractive solution. A technology based on catalytic co-hydroprocessing of Heavy Atmospheric Gas Oil (HAGO) and Waste Cooking Oil (WCO) for hybrid diesel production has been developed in the Centre for Research and Technology Hellas (CERTH). The technology development involved the technical assessment of integrating residual lipids within a conventional refinery and particularly via the catalytic hydrotreatment of HAGO. At the first stage of the technology development a comparison of two commercial hydrotreating catalysts (one $CoMo/Al_2O_3$ and one $NiMo/Al_2O_3$) with respect to hydrotreating reactions (HDS, HDO, HDN) as well as to diesel selectivity, conversion and produc quality was performed, as these two types are the most commonly utilized in commercial hydrotreating applications. Especially in the case of co-hydroprocessing of two different feedstocks, the catalyst selection must accommodate both feedstock characteristics and conversion targets, as well as processing requirements. The second stage was to examine the effect of liquid hourly space velocity (LHSV) and hydrogen-to-oil ratio (H_2/Oil) in co-hydroprocessing of HAGO with WCO, utilizing the optimum catalyst and reaction temperature identified from the first stage. Finally, the third stage targeted to explore the effect of WCO content in co-hydroprocessing with HAGO, utilizing the optimum catalyst and operating parameters identified from the previous stages.

The hybrid diesel product was evaluated as a blending component for market diesel fuel according to a refinery blending strategy and diesel EN 590 specifications. The results have shown that the addition of WCO (5 % to 30 %) in HAGO does not affect negatively the final product quality, but rather improves some of its properties without compensating the diesel yield.

Furthermore the environmental benefits of co-processing residual biomass (WCO) with fossil feedstocks (HAGO) were also evaluated in terms of the corresponding GHG emissions via Life Cycle Assessment (LCA). The LCA results showed that the integration of WCO in the existing diesel production process is exhibiting promising potential, reducing the corresponding GHG emissions.

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CATALYTIC HYDROGENOLYSIS OF DIFFERENT TYPES OF LIGNIN WITH BIO FUELS OBTAINING

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The content of native lignin in the plant biomass reaches 35 wt. %. The chemical composition and structure of the lignin can be considered as a prospective, renewable raw materials for the production of alkylaromatic and saturated hydrocarbons, which may be used as components of motor fuels [1, 2].

Hydrogenolysis of lignin containing material is one of the promising ways of obtaining hydrocarbons. In this work the sawdust softwood was used as a substrate. The sawdust softwood was obtained from sawmill of Sandovsky district of Tver, Russia. We used three types of lignin derived from sawdust softwood: alkaline, sulfate and acetate lignin.

In vitro releasing of the alkali lignin from softwood was carried out after pre-hydrolysis of hemicellulose. Then the sawdust was filtered on a Buchner funnel. Yield of alkali lignin (brown powder) was 6,6 ± 0,3 wt. % [3]. Sulfuric acid lignin was obtained by the Klasson method with Komarov modification. Wood treatment time in the acid was 3 hours. The yield of the sulfuric acid lignin reached 20.8 ± 1.7 wt. % [4]. Acetic acid lignin was obtained using of solution with composition: 24.7 wt % CH_3COOH + 5.3 wt % H_2O_2 + 2 wt % H_2SO_4, for 3 hours. After the treatment liquor was filtered on a Buchner funnel. The yield of the acetic acid lignin was 8-13 wt % [5]. As a catalyst a commercial 5 % Pd / C (Sigma-Aldrich, USA) was used.

The hydrogenolysis process was carried out under the following conditions: 30 mL of lignin was carried out for 4 hours in Parr Series 5000 Multiple Reactor System reactor-cell equipped with magnetic stirrer in the presence of 0.1 g of catalyst at a temperature of 250 °C and hydrogen pressure of 1.0 MPa. The process was conducted at constant stirring (1700 rpm) to eliminate the influence of external diffusion. The following polar solvents are used: 2-propanol, water, and ethanol. Substrate conversion was calculated at the end of the reaction basing on the difference between the initial mass of the substrate and the dry weight of the residue. During both processes liquid phase samples were taken every 30 minutes. The analysis of the samples was performed using GC-2010 chromatograph and GCMS-QP2010S mass spectrometer (SHIMADZU, Japan). The analysis duration was 25 minutes with the following conditions: initial column temperature of 150 °C was maintained for 5 min, and then the temperature was increased up to 250 °C with the heating rate 5°K/min.

The isolating method has significant effects on lignin degree of conversion and liquid yield. The maximum amounts of conversion of 67.5 and 67.0 wt. % were achieved in experiments with the acetic acid lignin using 2-propanol and ethanol, respectively. The highest yields of low-boiling liquid products 38,5 and 38,0 wt. % were obtained in experiments with the alkali lignin. Sulfuric acid lignin, characterized by the most condensed structure has the lowest degree of conversion and liquid yield. 2-propanol demonstrated a high liquid yield and high conversion, probably because it is thermally unstable and decomposes with the release of hydrogen. Recently, this type of hydrogen-donating solvents has found special applications in the hydroprocessing of both biomass and lignin. The main liquid products of the process: phenol, cresol, cyclohexane, benzene, furfuryl alcohol.

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TRANSFORMATION OF REFRACTORY MODEL SULPHUR COMPOUNDS REPRESENTATIVE OF FCC GASOLINE: A THEORETICAL AND EXPERIMENTAL COMBINED APPROACH

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Introduction

Due to increasing environmental concerns, constraints relative to exhaust gas compositions are reinforced worldwide. Thus, China V and US Tier 3 regulations now impose a 10 ppm maximum of sulphur in gasoline [1]. Gasoline produced by the FCC units in refineries represents 40 % of the gasoline composition but accounts for 95 % for the total sulphur amount before hydrodesulfurization (HDS) [2]. Consequently, there is a strong need for developing HDS catalysts with high activity to achieve ultra-deep HDS of FCC gasoline. Meanwhile, these catalysts should also exhibit high selectivity to minimize olefins hydrogenation (HDO) to preserve high octane values. A straightforward solution considered by refiners is to undercut the FCC gasoline range – typically from 220 to 160 °C – to reduce the amount of sulphur in the selective HDS feed. This results in a completely different balance between alkyl thiophenics and alkyl benzothiophenes and, in turn, in a very different feed reactivity. This challenge consequently urges to provide a better understanding of the competitive adsorption between sulphur compounds on the catalyst surface.

In the present work, the transformation of various model sulphur compounds – 2-methylthiophene (2MT), 3-methylthiophene (3MT) and benzothiophene (BT) – as thiophenic compounds representative of a FCC gasoline was compared under HDS operating conditions over a $CoMoS/Al_2O_3$ catalyst. By coupling experimental and theoretical approaches, their reaction scheme and the kinetic parameters – activation energy, reaction rate constant and adsorption constant – of these compounds, were determined using the Langmuir-Hinshelwood formalism. The parameters determined for each compound were then used to model adsorption competitions in mixture.

Materials and Methods

The transformation of sulphur model molecules were studied, separately and in mixtures, in a fixed bed microflow reactor at 250 °C, under 2.0 MPa of total pressure over a conventional CoMoS/Al_2O_3. Sulphur compounds (1000 ppmS) alone or in mixture were diluted in n-heptane. For a better precision in activity measurements, the contact time was chosen such as to keep the overall conversion of sulphur compounds nearly constant around 25 % (24-27 %). Kinetic modeling was carried out using the ReactOp Cascade 3.20 (ChemInform St. Petersburg, Ltd.) software.

Results and Discussion

Benzothiophene was experimentally observed to be more reactive (by a factor of 1.4 and 2.2, respectively) than 3-methylthiophene and 2-methylthiophene (Table 1). Regarding the transformation of BT, ethylbenzene (EB) was the main product of reaction with a selectivity of 88 %. Meanwhile, dihydrobenzothiophene (DHBT) originated from the direct hydrogenation product of BT, with a selectivity of 11 %. Kinetic modeling could confirm that the formation of ethylbenzene directly from BT was a minor pathway. Indeed, the rate constant was much lower ($k = 3.8.10^{8}h^{-1}$) than that via the formation of DHBT ($k = 12\ 10^{12}h^{-1}$). Regarding the transformation of 2MT and 3MT, pentenes and pentane and methylbutenes and methylbutane were respectively the main products. However, strong differences of selectivities towards alkanes and alkenes were noticed as shown by the alkane/alkenes ratio for both molecules, which was higher for the transformation of 2MT than for 3MT.

When these sulfur molecules (BT and 2MT) were hydrodesulfurized in mixture, the reactivity order of the two sulfur compounds (2MT and BT) remained the same, BT being more reactive than 2MT. However, significant differences were observed with respect to their transformation alone. In mixture, a decrease in the conversion of both BT and 2MT was observed suggesting a mutual inhibiting effect. Interestingly, this decrease was significantly higher for 2MT (up to 65 %) than for BT (11 %). These phenomena were also reversible, thus indicating competitive adsorption of the sulfur molecules on the surface of the catalyst. Moreover, dedicated experiments evidenced that inhibition is not due to the formation of H_2S during their transformation but to the non transformed sulfur compounds themselves.

Finally, the stronger inhibiting effect of unconverted BT on the transformation of 2MT could be well described by Langmuir-Hinshelwood kinetics using parameters determined from the single compound experiments. Indeed, the BT adsorption constant was higher than that of 2MT.

Table 1. Transformation of sulphur compounds alone or in mixture. Activity (A.), Adsorption constant determined from kinetic modeling (T = 250 °C, P = 2MPa, $CoMoS/Al_2O_3$)

Sulphur compounds	A. alone ($mmol \cdot h^{-1} \cdot g^{-1}$)	A. in mixture ($mmol \cdot h^{-1} \cdot g^{-1}$)	Adsorption constant (bar^{-1})
2MT	3.8	1.5 (-65 %)	7,1
3MT	5.9	-	10.2
BT	8.3	7.4 (-11 %)	12.1

In conclusion, mutual inhibiting effects between sulphur compounds representative of FCC gasoline were observed under HDS operating conditions. Remarkably, these experimental results in mixture could be described using a Langmuir-Hinshelwood model and kinetic and adsorption parameters determined from single compound experiments.

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EFFECT OF THE INDIUM CONTENT AND PRECURSOR NATURE ON $Pt/Al_2O_3In\text{-}Cl$ REFORMING CATALYSTS

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Catalytic naphtha reforming is a very significant process of oil refinery. In reforming process low octane number hydrocarbons is converted to aromatics with high octane number. Efficiency of the process mostly depends on the properties of the catalyst. The reforming catalysts are based on the $Pt/\gamma\text{-}Al_2O_3$ system. The metallic function is virtually always promoted by the introduction of metals, for example, Sn, Re, Ge, Ir and others. The main positive effects caused by the presence of a promoter include the weakening of platinum particles sintering in the process, a decrease in deactivation by coke, and an increase in selectivity for the reformate. Today the amount of aromatic hydrocarbons in gasoline is limited by ecological demands. It is actually to develop the naphtha reforming catalyst with high isomerization activity. To obtain such characteristics, these catalysts are promoted by Sn, Zr and In. In recent publications, great attention was paid to the Pt-In catalysts [1, 2]. The In_2O_3-containing systems were considered as a new class of catalytic materials.

The goal of our work was to elucidate the effect of the indium content and precursor nature on physicochemical and catalytic properties of bimetallic $Pt/Al_2O_3In\text{-}Cl$ reforming catalysts.

Indium nitrate $In(NO_3)_3{*}5H_2O$, indium hydroxide $In(OH)_3$, and indium acetate $In(CH_3COO)_3$ were chosen as indium precursors. The supports were prepared by mixing aluminum hydroxide with an indium precursor using a peptizing agent. The calculated indium content was 0.1 and 0.3 wt.% In with respect to the weight of calcined alumina.

The catalysts were synthesized by introducing the calculated amounts of Pt and Cl precursors ($H_2PtCl_6{*}5H_2O$ and HCl) by impregnation in excess solution onto alumina promoted with indium in order to obtain 0.2 and 1.2 wt.% Pt and Cl, respectively. Supports and catalysts were characterized by TGA, XRD, the nitrogen adsorption-desorption method, NH_3-TPD, H_2-TPR. Catalysts were tested in a model reaction of n-heptane reforming.

Irrespective of the precursor nature, modification of Al_2O_3 with indium at the peptization step increases S_{BET} and decreases the CSR size.

The introduction of indium into Pt/Al_2O_3-Cl reforming catalysts affects the acidic and metallic functions. Doping of the support with 0.3 wt.% indium results in redistribution of acids sites with different strength: the fraction of weak sites increases, while the fraction of strong ones decreases in comparison with undoped alumina.

The H_2-TPR data testify to a strong Pt-In interaction, which may be accompanied by the formation of Pt-In alloys.

Selectivity in hydrogenolysis, hydrocracking and aromatization reactions decreases with the introduction of indium irrespective of its precursor. The highest gain in isomeric hydrocarbons is observed for the catalyst synthesized using indium hydroxide with 0.3 wt.% In.

The results obtained indicate that it is reasonable to perform further studies for the development of flexible catalytic systems, which make is possible to obtain a reformate with the desired content of both aromatic hydrocarbons and isoalkanes.

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PLATINUM CATALYSTS $Pt/MgAl(M)O_x$ FOR LIGHT AND HIGHER ALKANES DEHYDROGENATION OBTAINED USING THE LAYERED HYDROXIDE

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The use of supports with spatially ordered structure such as layered double hydroxides (LDH) is a promising way to control the characteristics of supported metal and obtain nanoparticles with unusual and uniform properties. LDHs have the composition $(M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2)^{x+}(A^{n-})_{x/n}\ nH_2O$, where M^{2+} and M^{3+} are bi- and trivalent metal cations, and comprise positively charged hydroxide layers and anions A^{n-} located in the interlayer space. With such supports, active metal precursor can be anchored both inner-sphere complex and outer-sphere complex in the interlayer space via anion exchange. In the latter case hydroxide layers create conditions for metal particle synthesis in a two-dimensional nanoreactor. It is important that variation of the nature of interlayer anions, composition and charge of hydroxide layers makes it possible to control not only the amount of anchored Pt precursor, but also the strength of precursor–support interaction and the extent of modifying effect of the support. The interaction of Pt(IV) anionic chloride complexes with the layered hydroxides that comprise Mg^{2+}, Zn^{2+}, Al^{3+}, Ga^{3+} and Sn^{4+} cations and differ in metal ratio was studied. These parameters were found to affect both the support properties and the dispersion, morphology, electronic state and catalytic properties of supported platinum. The novelty of the approach to the synthesis of the catalyst was as follows: 1) modifying cations were introduced into the structure of the support, thus ensuring its uniform distribution on the atomic level and preclude substantial agglomeration during the heat treatment; 2) maximum interaction of platinum with the modifying cation was provided by platinum anchoring via intercalation of Pt anionic complexes into the interlayer space of LDH. Testing the synthesized catalysts in propane dehydrogenation demonstrated that all selected cations are able to influence the properties of platinum. All Ga-containing samples show a higher dehydrogenating activity at high selectivity toward the formation of the target product–propylene. For other systems, there is an optimal amount of modifier (fig. 1). Thus, for the dehydrogenation of propane, the optimal ratio Sn/(Sn+Al) is 0.002. In order to

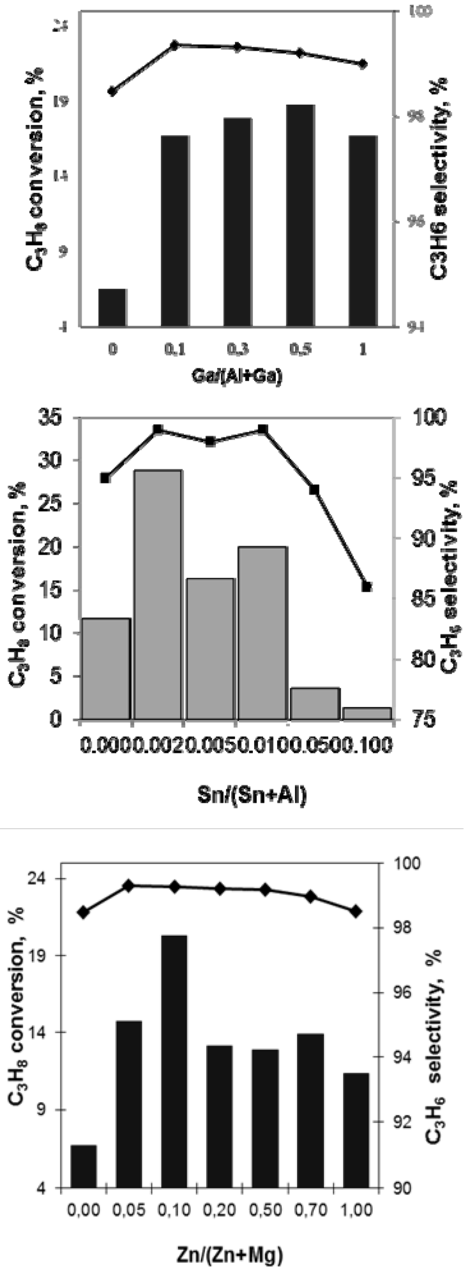

Fig. 1. Propane conversion and selectivity of propylene formation for 0.3%Pt/MgAl(M)Ox samples versus the fraction of M (Ga, Sn, Zn)

achieve maximum activity in the dehydrogenation of n-decane, a higher tin content (Sn/(Sn+Al) = 0.05) is necessary, at which the maximum olefin yield and the minimum yield of cracking and isomerization products are observed. Geometrical and ligand effects are revealed in the modification of the properties of the platinum by Zn^{2+}, Ga^{3+}, Sn^{4+}. Geometric effect is confirmed by the increase in the proportion of M-atoms in the coordination sphere of the platinum and decreasing particle size. As a result, increase the dehydrogenation activity and suppressing C-C bonds hydrogenolysis was observed. Ligand effect appears in the change the electronic state of platinum: the presence of M stabilizes of platinum in the active metal state Pt^o.

It has been shown that the formation of the necessary properties of platinum is also possible with the use of a traditional support (alumina) previously modified by coating the surface thereof LDH selected composition.

The following methods were used: XRD (D8 Advance, Bruker), static volume vacuum system (ASAP-2020M, Micromeritics), TPD CO_2, CO and H_2 pulse chemisorption (AutoChem II 2920, Micromeritics), TEM (JEM-2100, JEOL), XPS (SPECS), EXAFS (ESRF, Grenoble). Catalytic properties of Pt/MgAl(M)Ox were investigated under the following conditions: 550 °C, atm. pressure, WHSV 8 h^{-1} and H_2/C_3H_8 mol ratio of 0.25 (C_3H_8 dehydrogenation); 0.2 MPa, WHSV 17 h^{-1}, $H_2/C_{10}H_{22}$ mol ratio of 7 ($C_{10}H_{22}$ dehydrogenation).

Acknowledgements

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IMPACT OF PROCESSING HEAVY AND LIGHT CYCLE GAS OIL IN MILD HYDROCRACKER UNIT FOR 100 % CONVERSION

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Keywords: Vacuum Gas Oil, ULSD, HDT, H_2 Consumption, Catalyst Deactivation, HDT pilot plant test.

Introduction

This study is focused on processing of Heavy Gas Oil (HGO), Light Cycle Oil (LCO) and various blends of HGO / LCO, in the existing mild hydrocracker unit (MHC) within the limitations of existing equipment & catalyst. The MHC is designed to process straight run HGO, LCO and light light cycle oil (LLCO), with HGO comprising the bulk of the feed. It is a two stage, 100 % conversion unit. Fresh feed was processed in the first stage reactor for hydrotreating while unconverted oil was cycled back from the Fractionator to the second stage reactor for hydrocracking. This pilot scale study provides substantial data for predicting refinery operation in the event of changes in HGO & LCO availability (low or high) due to changes in the operations of other refinery units. Fresh hydrotreatment (HT) & hydrocracking (HC) catalyst were loaded in the pilot plant reactor tube & evaluated at process throughput from 100 % up to 50 % capacity with HGO/LCO feedstock at hydrogen partial pressure 102 bar(g), targeting 100 % conversion per pass basis. Products from the unit include ultra-low sulfur diesel, unstabilized naphtha, and stabilized naphtha. Product qualities were evaluated mainly for sulphur, density, cetane number, aromatics and diesel cut point along with yield. The effects of changes in feedstock, reaction temperature, LHSV & H2/HC ratio are discussed in this paper. Furthermore, impact is envisaged on catalyst life and product quality because of low through put operation. Details of pilot plant design to operate it in recycle mode with vacuum column operation in continuous mode and analysis are discussed, at which operating conditions were tuned in line with commercial unit. The experimental results were primarily compared with commercial operation at test run (PGTR) condition to validate the data on new process conditions studied during six months of extensive pilot plant test at ARRC.

Description of the work

Mild hydrocracking experiments were carried out according to refinery unit test conditions, with reference feed stock HGO, LCO and LLCO, using a fresh catalyst at variable operating conditions, as listed below Table 1. Laboratory analyses were performed on both gas & liquid products using state of art technology analyzers.

Based on analysis results during operation, process conditions were adjusted to meet target yield, conversion and diesel quality parameters. AS shown in fig. 1, several samples points were designed into pilot plant to know the process and reaction chemistry at various stages in the process.

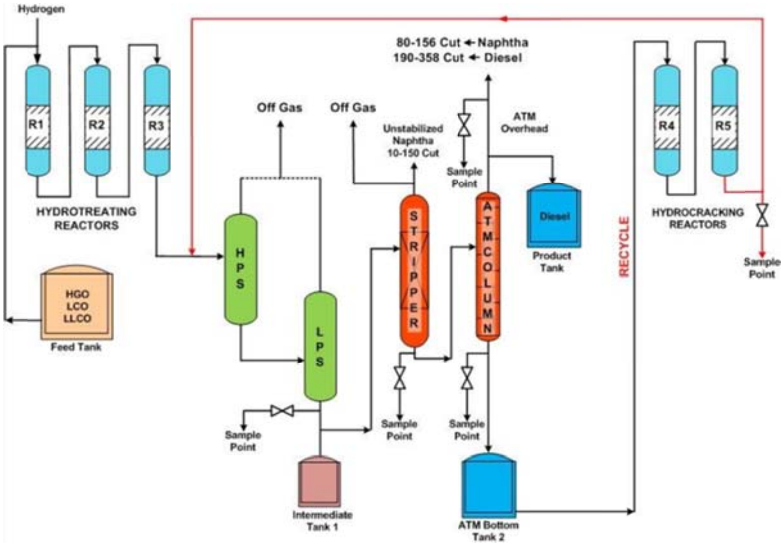

Figure 1. Pilot Plant Configuration Flow Diagram

Table 1. Test operating conditions & results

Test points	Feed composition	Cetane index	HDT Temp (°C)	HCK Temp (°C)	Total aromatics (% mass)	Sulfur (ppm)
1	HGO 50% + LCO 50%	43.6	335	365	30.25	7.3
2	HGO 25% + LCO 75%	35.7	338	360	38.6	5.6
3	HGO 75% + LCO 25%	48.7	338	375	24.57	5.9
4	HGO (80% capacity)	57.7	338	381	14.31	9.5
5	HGO 80%+LCO 20%	50.5	343	378	23.35	7.6
6	HGO (90% capacity)	58.1	341	378	13.45	5.1
7	HGO 50% + LCO 50%	41.1	339	365	36.26	7.3
8	LCO (50% capacity)	27.3	325	150	50.05	6.0
9	LCO (70% capacity)	26.3	329	150	53.11	6.4

Results and discussion

The reference case of HGO 50 %/LCO 50 % was considered, to check the performance of the catalyst & feed blends. The performance has been evaluated at various throughput ratios; HT & HC temperature targeting 100 % conversion while maintaining product quality & quantity for cetane index, total aromatics, sulfur and product yield. As the feed became severe, usually by increasing the LCO percentage in HGO, the cetane index was decreasing & total aromatics were increasing. For example, considering HGO (90 % capacity) at 341 °C, the cetane index was 58.1 & aromatics was 13.45 % whereas at the same temperature and blend feed of 80 % HGO and 20 % LCO; it was 50.5 & 23.35 % respectively. Following observations were made from pilot testing.

1. The PGTR condition in the Pilot Plant is in a close match with the commercial unit conditions which is referred to validate the results from the pilot plant unit.

2. As shown in Table 1; the cases having only HGO as the feed couldn't exceed the capacity of 90 %. In these specific cases, considering different hydro-treating and hydrocracking temperature values; it was observed that the total aromatics content was compromised while the sulfur content was below 10 ppm and cetane index value was within the required criteria.
3. HGO/LCO cases showed that as the LCO content was higher in percentage of the feed, the cetane index quality wasn't good; however, the diesel quality was maintained as the yield was high, ranging from 88.1 % to 110 %.
4. The cases studying only LCO as the feed, it was not possible to operate the hydrocracking process as there was no bottom product. The result in Table 1, showed very low cetane index; but the hydro-treating was well operated as proven in the sulfur values.

Conclusion

In this stud, we tested feed HGO and LCO to study its impact on the product quality & yield. It was very clear that having specific blends of HGO and LCO maintained the required results, as discussed in section 3. This gives a very good view of using it in the gasoline pool in the refinery; to reach the quality needed in the market. Considering some variety in the operating conditions of each way, it was observed that the pilot plant results were in close agreement with commercial unit for PGTR condition. With this reference, all other points tested at pilot plant unit provided valuable input to optimize the feed blend ratio & process conditions. This experiment shows that it has become possible to produce substantial data using pilot plant test to predict commercial unit performance on complex MHC operation. This test also develop high competency for pilot plant operations to operate complex refinery scheme into pilot scale.

Acknowledgement

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OP-39

CATALYTIC PROPERTIES OF IRON-CONTAINING CATALYSTS IN THE REACTION OF DIRECT CO_2 HYDROGENATION AT SUPERCRITICAL CONDITIONS

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At present time the processing of CO_2 is one of the most urgent topic for the investigators of the world due to its ecologic preconditions. Besides carbon dioxide is a promising raw material for the various chemical syntheses in order to obtain valuable products such as CO, hydrocarbons, alcohols, various carbonates and carbamates [1]. The main difficulty on this way is the inertness of the CO_2 molecule.

One of the promising solutions of this problem is the direct catalytic hydrogenation of carbon dioxide on the various heterogeneous catalysts. As a rule, the various transition metals appear in the role of the active phase [2-4]. The difficulty in this case is the short working life of the catalyst due to the deposition of the reaction products on the active sites. A possible solution is to carry out the reaction under the supercritical conditions for CO_2 [5]. The advantages of this mode are not only the increase of the life of the catalyst, but also the increase in the productivity.

In our work, a number of iron-based catalysts have been investigated. The concentration dependence of the catalytic activity on iron catalysts with TiO_2 support (anatase) was constructed, and the influence of the carrier and the method of preparation on the catalytic properties of these catalysts was investigated, as well as the influence of the composition of the reaction mixture and the process of the pressure on the distribution of the final products. It is shown, that iron catalysts demonstrate a satisfactory activity in the reaction of CO_2 direct hydrogenation under the supercritical conditions. The main reaction of products in the gas phase were methane and CO. The formation of C_2+ hydrocarbons was observed, but the selectivity for them throughout the temperature range did not exceed 3-5 %. During the reaction, the liquid products are formed, the main part of which is water. Besides water, these products include alcohols C_1-C_4 and some other oxygenates with a total concentration of up to 5 %.

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LOW-TEMPERATURE SORPTION-ENHANCED DECOMPOSITION OF HYDROGEN SULFIDE: PROCESS CONCEPT

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Active development of hydroprocessing technologies and hydrogen energy require the development of new efficient ways for production of hydrogen, preferably from non-hydrocarbon feedstocks.

Hydrogen sulfide seems to be the very attractive feedstock for this purpose. First, it is the conventional waste from oil and natural gas processing facilities. Second, the bonding energy of hydrogen in H_2S is the lowest among all natural hydrogen-containing compounds.

Unfortunately, the reaction of hydrogen sulfide decomposition

$$H_2S \Leftrightarrow 1/n\ S_n + H_2 \qquad (1)$$

is characterized with severe equilibrium limitations. The complete H_2S decomposition requires the extra-high temperatures (above 1500 °C), leading to high energy consumption, necessity to apply expensive thermostable materials and risk of backward element recombination at cooling stage. In (very typical) case, when the carbonaceous compounds (CO_2, hydrocarbons) are present in the gas feedstock, such temperatures may also cause side reactions with formation of undesired products (coke, CO, COS and CS_2). Due to these reasons, still there is no feasible technology for H_2S decomposition in wide practical application.

The new process approach [1] is based on the chemisorption enhancement of the decomposition reaction (1). The process, involving metal sulfide chemisorbent-catalyst, includes cyclic alteration of two reaction stages technologically separated in time and space:

$$H_2S + MeS_n \Rightarrow H_2 + MeS_{n+1} \qquad (2)$$

$$MeS_{n+1} \Rightarrow MeS_n + 1/n\ S_n \qquad (3)$$

As shown by thermodynamic calculations [2], the reaction (2) is exothermic and the corresponding equilibrium conversion of H_2S may reach 100 % at ambient temperature. Reaction (3) requires moderately increased temperatures (200-400 °C). The whole process may be thus realized at moderate temperatures with achievement of complete H_2S decomposition, the backward recombination of elements is prevented by technological separations of stages (2) and (3) – hydrogen is not persent at stage (3).

Low operation temperatures provide decrease of heat losses to environment, resulting in increased energy efficiency of the process. The process may be based on cheap standard equipment from conventional materials, thus significantly minimizing the capital costs. Besides, the low temperature at H_2S chemisorption stage (2) makes possible to process feedstock gases, containing carbonaceous admixtures, without risk of their involvement to reaction and formation of undesired side products.

The presentation will include overview of the available related experimental data and discussion of the possible process flow-sheets with their comparative analysis.

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OP-41

DYNAMIC MODELING AND SIMULATION OF EXPERIMENTAL CSTR AND SPR FOR HEAVY OIL HYDROCRACKING AND HYDROTREATING

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Abstract

Dynamic modeling and simulation for hydrocracking and hydrotreating of heavy oil in continuous stirred tank and slurry-phase reactors are presented. Mathematical models of perfect mixing and axial dispersion are considered to describe the CSTR and SPR behavior respectively.

Introduction

Slurry-phase hydrocracking consists of mixing the oil feed, hydrogen, and dispersed catalysts together going through the reactor. It has the same processing as thermo-cracking but also reduces coking due to the presence of hydrogen and catalyst that promote hydrogenation reactions [1]. Literature concerning mathematical modeling of hydrocracking in SPR's is scarce, most of the reports are based on computational fluid dynamics models (CFD) formulated in steady-state and focused on the performance of the hydrodynamic variables [2]. The objective of this investigation is to formulate dynamic models for SPR and CSTR as well as to compare the behavior and steady-state predictions of both reactors based on intrinsic kinetic parameters taken from the literature.

Reactors Models

For the CSTR, the well-known consideration of perfect mixing is assumed, as well as for the SPR an axial dispersion model is considered. The gas phase is present in excess, then the reactors can be approximated with homogeneous models. The kinetic expressions used in the model for hydrocracking and hydrotreating reactions were taken from literature [3-4]. Hydrocracking reactions are based on a pseudo-component approach and hydrotreating reactions are based on power law and Langmuir-Hinshelwood approaches.

Results

In Figure 1 it is shown the dynamic behavior of CSTR (dotted line) and SPR (continuous line) reactors for hydrocracking and hydrotreating reactions. As can be seen, the conversion in the SPR is higher than that of CSTR due to there is no catalyst deactivation and the effectiveness factors for catalyst particles equals the unity.

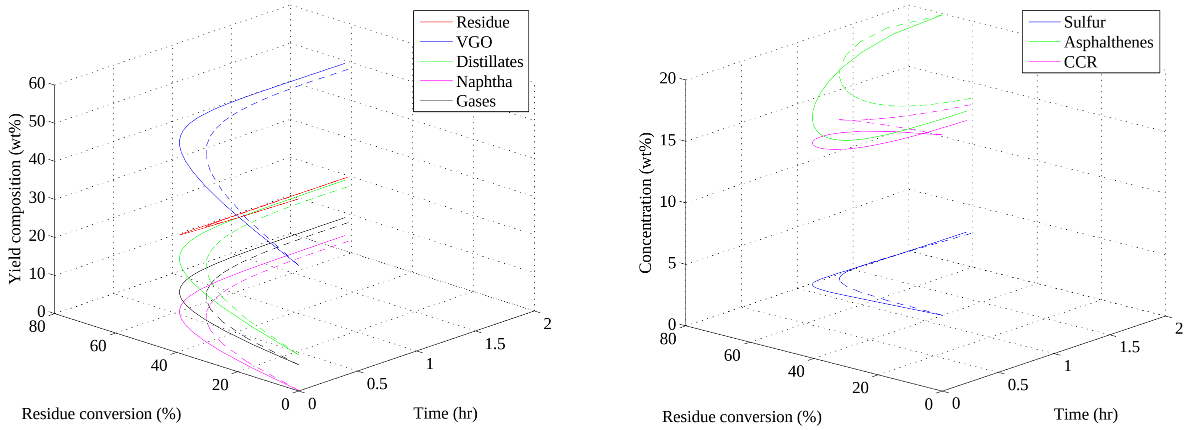

Figure 1.

Conclusions

Hydrocracking as well as catalytic and thermal hydrotreating have been modeled in small-scale isothermal CSTR and SPR based on intrinsic reaction rate coefficients involving catalyst deactivation and catalyst effectiveness factors for each of the reactions. The results have shown that it is possible to approximate a slurry-phase reactor for hydrocracking with an axial dispersion model with appropriate reaction rate coefficients. It was also found that for modeling purposes, the experimental SPR can be conveniently approximated by means of an ADM.

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UNSTEADY-STATE MATHEMATICAL MODEL OF DIESEL FUEL CATALYTIC DEWAXING PROCESS

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Advanced petroleum refining of middle distillates in the process of catalytic dewaxing is the latest way to produce diesel fuels meeting specifications for summer, winter, and arctic grades. Catalytic dewaxing of middle distillates in the hydrogen medium is based on selective hydrocracking and hydroisomerization of straight chain paraffins having high molecular weights. This provides improvement of fuel cold flow properties, such as cloud point, cold filter plugging point, pour point [1].

The object of the current research is the industrial process of catalytic dewaxing over Ni-containing bifunctional catalyst. The feedstock of this process is the mixture of straight run diesel fraction, atmospheric gasoil and naphtha – the product of visbreaking process. The products include hydrocarbon gas; light naphtha; stabilized naphtha; components of diesel fuels: fraction 180-340 °C (gasoil product), fraction >340 °C (fractionator bottom product).

The aim of this work is to develop a mathematical model of diesel fuel catalytic dewaxing process taking into account the factors, which cause unsteady character of the process, such as varying feedstock composition and catalyst deactivation.

The dewaxing catalyst deactivation degree is evaluated. Application of the developed mathematical model for estimating the influence of the technological parameters and feedstock composition on the target product yield and properties is considered. The calculation results are given for the optimal technological modes for various feedstock compositions.

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MODELING OF ONE AND TWO-STAGE REACTORS FOR FISCHER-TROPSCH SYNTHESIS

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Abstract

The modeling of a FBR in 1 and 2 stages for the Fischer-Tropsch synthesis is presented. The reactor was modeled using a non-isothermal pseudohomogeneous approach in which variations of gas density, superficial gas velocity and total pressure in the axial direction are considered.

Introduction

A 2-D pseudohomogeneous PFR model for a FBR FTS reactor with 1 and 2 stages is proposed. Axial density, pressure and gas velocity are considered as variable. A recent correlation was used to estimate the pressure drop, which showed good reliability for complex systems such as FTS [1]. The model is validated using data reported elsewhere [2] for a FBR FTS reactor in 1 and 2 stages. The model predicts more accurately the CO conversion and temperature profiles in the axial direction in comparison with the literature. This work clearly shows the advantages of using a multistage system to improve syngas conversion, reactor temperature control, and the productivity and selectivity of liquid hydrocarbons in the FTS process.

Reactor Model

To predict the syngas conversion and reactor temperature profiles of a FBR FTS reactor, a 2-D pseudo-homogeneous model is proposed. The radial dispersive plug-flow is described by mass and heat balances. The following assumptions were considered: steady-state, PFR regime with no channeling effects, negligible axial and radial dispersion effects of mass and heat, variable density, total pressure and gas velocity, constant temperature of the cooling medium, negligible formation of a wax layer on the catalyst surface of mass and heat external transfer limitations.

Results

Predicted and experimental values of CO conversion are presented in Figure 1. For the first stage, the absolute error between experimental and predicted values is

7,5 % for the proposed model, while for the literature model it is 6.3 %. For the second stage the absolute errors are 1.3 % and 2.0 % respectively. The proposed model better predicts CO conversion at the exit of the second stage compared to the model of Dai et al. [2]. In general to proposed model tends to overestimate the experimental values while the literature model tends to underestimate them. The absolute error between the temperature experimental values and the values predicted by the proposed model were 2.8 K for the first stage and 2.4 K for the second stage, while for the Dai et al. [2] model the errors were 2.0 K and 1.9 K for the first and second stages respectively. In general, the error in the prediction of temperatures is negligible, although the Dai et al. [2] model predicts slightly better the experimental data, which is due to the fact that the temperature curve for the two reactor stages was shifted to an initial temperature of 498 K.

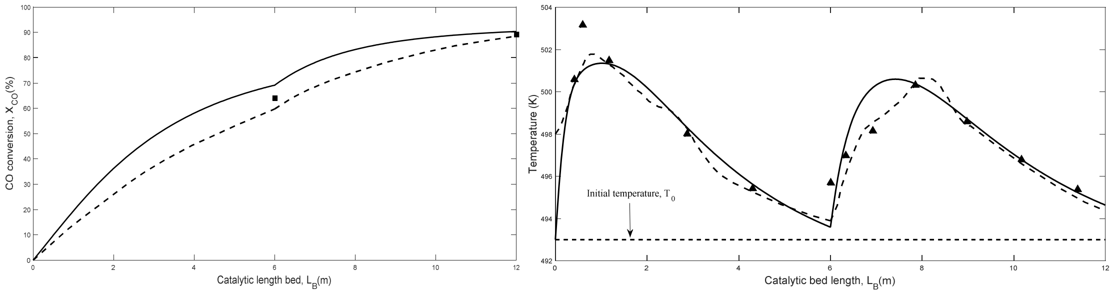

Figure 1. Profiles of CO conversion and temperature

Conclusions

Although 2-D pseudohomogeneous modeling has been reported for describing the behavior of radial temperature profiles in FBR for FTS, a more robust model was developed to improve the prediction of syngas conversion, product selectivity, and temperature profile in the axial and radial directions. More precise correlations for the diffusivity and thermal conductivity, and an equation for the friction factor for better prediction of the gas pressure in the system were considered. The variation of superficial velocity, density and total pressure of gas allows for a better understanding of their effects on reactor performance. It was confirmed that FTS can be further improved by using multistage FBR, since they allow for greatly improving the syngas conversion and better temperature profile.

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INTENSIFICATION OF THE PROCESSES OF DEHYDROGENATION AND DEWAXING OF MIDDLE DISTILLATE FRACTIONS BY REDISTRIBUTION OF HYDROGEN BETWEEN THE UNITS

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The processes of dehydrogenation and dewaxing of hydrocarbons of middle-distillate fractions, which proceed in the hydrogen medium, are of great importance in the petrochemical and oil refining industries, since they increase oil refining depth and allow producing gasoline, kerosene, and diesel fractions used in the production of hydrocarbon fuels, polymer materials, synthetic detergents, rubbers, etc [1]. Herewith, in the process of dehydrogenation of hydrocarbons of middle distillate fractions (C9-C14) hydrogen is formed in the reactions between hydrocarbons, and the excess of hydrogen slows the target reaction of olefin formation and causes the shift of thermodynamic equilibrium to the initial substances. Meanwhile, in the process of hydrodewaxing of hydrocarbons of middle distillate fractions (C5-C27), conversely, hydrogen is a required reagent in the target reaction of hydrocracking of long-chain paraffins, which ensures required feedstock conversion for production of low-freezing diesel fuels [2-3]. Therefore, in this study the authors suggested the way of intensification of the processes of dehydrogenation and dewaxing of middle distillate fractions by means of redistribution of hydrogen between the two units on the base of the influence of hydrogen on the hydrocarbon transformations using mathematical models [4].

In this study it was found that with increasing the temperature from 470 °C to 490 °C and decreasing the hydrogen/feedstock molar ratio in the range of 8.5/1.0 to 6.0/1.0 in the dehydrogenation reactor, the production of olefins is increased by 1.45-1.55 % wt., which makes it possible to reduce hydrogen consumption by 25000 Nm^3/h. Involvement of this additionally available hydrogen in the amount from 10000 to 50000 Nm^3/h in the dewaxing reactor allows increasing the depth of hydrocracking of long-chain paraffins of middle distillate fractions, and, consequently improving low-temperature properties of produced diesel fraction. In such a way cloud temperature and freezing temperature of produced diesel fraction decrease by 1-4 °C and 10-25 °C (at the temperature of 300 °C and 340 °C respectively).

However, when the molar ratio hydrogen/hydrocarbons decreases from 8.5/1.0 to 6.0/1.0 the yield of side products in the dehydrogenation reactor increases: the yield of diolefins increases by 0.1-0.15 % wt., the yield of coke increases by 0.07-0.18 % wt. depending on the feedstock composition, which is due to decrease in the content of hydrogen, which hydrogenates intermediate products of condensation (the coke of amorphous structure). This effect can be compensated by additional water supply in the dehydrogenation reactor, which oxidize the intermediate products of condensation, preventing catalyst deactivation by coke. The calculations with the use of the model showed that at the supply of water by increasing portions simultaneously with temperature rise, the content of coke on the catalyst by the end of the production cycle comprises 1.25-1.56 % wt. depending on the feedstock composition, which is by 0.3-0.6 % wt. lower that in the regime without water supply.

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FEEDBACK AND FEED-FORWARD R&D SYSTEMS FOR THE OPTIMIZATION OF INDUSTRIAL HYDROPROCESSING CATALYTIC SYSTEMS

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The target of this work is describing the way Cepsa faces the continuous optimization of industrial hydroprocessing catalytic systems by maximixing their flexibility and their efficiency versus changes of exogeneous factors. These factors are changes on crude oils basket (pricing, non-stationary demand of certain products) and changes in final product legislation. Such aspects have forced refineries to implement more severe hydrotreatment and conversion pocesses.

Hydroprocessing units at refineries are intended for removing certain compounds (sulphur, nitrogen, metals) of different streams (naphtha, kerosene, diesel, vacuum gas oil…). These refining processes remove substances which are poisons for downstream units as well as fulfill legal limits in terms of sulphur content in products intended for fuels.

In order to do so, catalyst suppliers are continuosly improving their catalytic systems performance. Therefore, selecting and optimizing the best catalytic system for a given refinery configuration is the most relevant industrial challenge. Some aspects such as catalyst price, possibility of regeneration after the industrial cycle and hydrogen consumption have to be considered among others by the refineries with the aim of minimizing the global operating costs (OPEX).

The way in which Cepsa faces these challenges is summarized in the following feedback feed-forward procedure (Figure 1).

OP-45

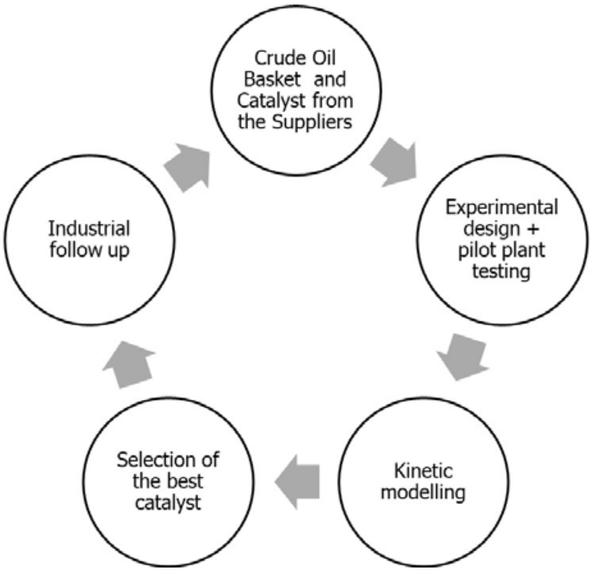

Figure 1. Feedback and feed-forward R&D approach. Source: Cepsa R&D

The first step is determining a representative feedstock from the crude oil basket that refinery expects to process in the following cycle. In the second step, pre-selected catalysts (based on the state of the art alternatives) are tested at pilot plant scale with selected feedstock, being subjected to certain operating conditions corresponding to the industrial reality in order to get a variety of conversion and selectivity data. The raw data are mathematically modelled and validated in order to get a representative kinetic model. Comparing the optimus performance of each model, also valuating economic parameters (hydrogen consumption, pressure, temperature, hydrogen to oil ratio; etc) will determine which catalyst is the most desirable one. Once the catalyst is selected and loaded in the industrial unit, Research and Development (R&D) engineers in combination with the refineries have to follow-up the catalyst performance during the cycle in order to check the deviations versus the kinetic model based predictions and also to optimize their models.

A business case study based on a hydroprocessing unit will be shown in which the feedback feed-forward approach allows the refinery to balance the evolution of crude oil basket and changes on legislation in a most effective way.

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DETERMINATION OF THE POTENTIAL PLATINUM-BEARING CAPACITY OF OILS AND REFINED PRODUCTS

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The patent search performed by us has revealed that data on contents and distribution of the platinum group elements (PGE) in oils in the public national and foreign sources is not available. The more interesting fact is the finding in the petroleum ash and crude oil of some Middle East fields of the higher concentrations of the platinum group metals). Owing to the large volumes of annual production, the oil is the particular conspicuous subject to study the PGE content and distribution with the view of their subsequent extraction. At present the oil industry itself is a major consumer of platinum metals: it is well known the role of these elements in the cracking of oil. It is obvious that data on the platinum metals content in oils can increase the efficiency of complex oil refining processes; it will contribute to the improvement of its refining technology, improve the ecological environment of CHPPs and processing characteristics of liquid fuels. All this determines the extreme importance of the present research issue.

Platinum-group metals in the cracking products of the Kirishi refinery

As far as we know, the behavior of platinum-group metals in the cracking process so far has not been analyzed. And concerning the other accompanying elements in this respect, there is limited data only, the results of which in principle can be reduced to two models:

1. The majority of accompanying elements contained in the crude oil accumulates in the oil residues obtained after distillation (model with vanadium and nickel.
2. The accompanying elements are more or less equally "eroded" by the high-boiling and oil residual fractions (model with Mn, As, I, Br).

The preliminary study for the behavior of platinum-group metals in the cracking process have been carried out on samples of the Kirishi oil refinery for pipeline oil, light and heavy gasoline, vacuum gasoil and straight-run fuel oil (Table 1).

Table 1. The content of platinum-group metals and gold in the products of distillation or petroleum fractions of the Kirishi oil refinery, mg/t

No.	Oil product	Pt	Pd	Ru	Au
1	Pipeline oil	<5	7	<5	<3
2	Light gasoline	<1	<0.5	<1	<1
3	Heavy gasoline	<1	1	<1	<1
4	Gasoil	<5	4	<5	<3
5	Straight-run fuel oil	<5	4	<5	<3

Data analysis of Table 1 shows that the platinum-group metals in the pipeline oil of the Kirishi plant contain in a small quantity, close to the average content of these elements in the oils at all. As a detecting element by which we can consider the behavior of PGE in the cracking process, perhaps, you can use palladium only. Light fractions of oil distillation represented by light and heavy gasoline contain low concentrations of palladium in comparison with the pipeline oil. Platinum, gold and ruthenium seem to show the same trend of behavior. Higher concentrations of palladium are observed in the vacuum gasoil and straight-run fuel oil, and two details draw attention to the following. First, the palladium content in these high-boiling and residual fractions is lower than in the pipeline oil itself. Secondly, in the fuel oil we do not observe the increase in the concentration of this element compared to the vacuum gasoil, while for other accompanying elements this tendency is expressed quite clearly. Other platinum group metals (platinum, ruthenium and gold) behave, apparently, as well as palladium. In general, platinum-group metals in the cracking process are allocated in accordance with the second model as Mn, As, I, Br, but not in accordance with the first one (V, Ni, Na, Al, Ca). Probably this sort of behavior is determined by their overall low number. Also you should draw your attention to the relatively high content of platinum group metals in gasoline, especially in heavy gasoline of the Kirishi oil refinery.

POSTER PRESENTATIONS

RESEARCH OF HEAVY OIL PROCESSING

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At present, light oil deposits are becoming less and, consequently, many oil companies have started to extract and process heavy oil and even natural bitumen. Apart from coal and hydrogen, this oil contains a wide range of different chemical elements, including various metals (vanadium, nickel, titanium, gold, chromium, manganese, iron, etc.). If we consider traditional deposits of metals, it is economically reasonable to consider development of ore deposits containing not less than 0.1 % of metal. And content of some metals in various types of oils and bitumen is close to this value, but unlike rocks, they do not require development of deposits, blasting operations, removal of ore from open-pit mines, crushing and dressing. Previous studies show that some metals accumulate in large numbers in a number of cases compared to their clusters in lithosphere, which enables making a conclusion on economic and technological feasibility of extracting these metals from oil, while improving quality of basic oil products. Thus, heavy oil can be considered as a multipurpose complex mineral, and processing of heavy oils as a “complex problem”, aimed both at increasing the yield of light fractions and “transport” ability of oil, and in extracting metals from heavy asphaltene-resinous fraction.

The recovery of precious metals (such as vanadium, nickel, titanium, iron, etc.) from heavy oil was performed by cavitation extraction technology with the use of light hydrocarbon solvents and chemical extractants, including stage of extraction in ultrasonic field with separation of insoluble fraction of asphaltenes in which a significant part of initial heavy metals and sulfur is concentrated, followed by re-extraction of metals and magnetic separation of metal aggregates. The main feature of this method is consistent use of acoustic and cavitation effects, which enables improving efficiency of mass transfer at the stage of solvent deasphalting (SDA), thereby reducing required extraction time, due to catalytic action of peroxides, including those formed by physical exposure on oil suspension.

Based on theoretical and experimental studies, a diagram of extracting metals from heavy oils was developed and implemented, realizing the principle of “demetallization of heavy oils – a complex problem”, aimed to increase the yield of light fractions and “transport” ability of oil, and extracting metals from heavy asphaltene-resinous fraction. The main feature of this technology is consistent use of acoustic and cavitation effects on oil-water suspensions with additives of polar solvents, which enables improving mass transfer efficiency at SDA stage, thereby reducing required extraction time. Kerosene and tributyl phosphate were used as extractants at different stages of processing crude oil from mixotropic series. Studying specific features of the mechanisms of interaction of extractants with recoverable metals on the grounds of a combination of values of quantum-chemical, physical chemical and structural parameters of metals and extractable “metal-extractant” systems enabled substantiating the use of kerosene and tributyl phosphate at various processing stages for extraction of strategic metals (metal ions) from heavy oils.

Thus, integration of processes of co-production of concentrates containing strategic metals (heavy, rare, rare earths, etc.) into production flows of large-scale oil refining may lead to the fact that profitability of their extraction from hydrocarbon raw materials will be significantly higher than that for technologies for obtaining metals from traditional, though difficult-to-enrich ore raw materials.

STUDYING THE PROCESS OF HYDROCRACKING OF VACUUM GAS OIL

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Under the conditions of decreasing the resource of “light” oil and domination of “heavy” paraffinic oil within oil extraction, hydroconversion processes assume greater and greater importance in oil refining industry [1]. Hydrocracking of vacuum gas oil is now the most important process of deep petroleum refining.

The studies on oil refining processes using the method of mathematical modelling are relevant these days. The models, developed based on the thermodynamic and kinetic regularities of the processes, allows making recommendations for control of the technological parameters of industrial processes, which ensures meeting specifications for product quality and achieving optimal yield of the product in the conditions of constantly changing composition of the feedstock [2].

Hydrocracking is a complex process, which uses hydrogen and converts heavy fraction (vacuum gas oil) into valuable light products, such as naphtha, kerosene and diesel fractions [3]. The material balance of hydrocracking process is presented in Table 1.

Table 1. Material balance of the hydrocracking process

Input		Output	
Vacuum gas oil	100,0	Hydrocarbon gas	4,5
Hydrogen (100 %)	3,0	Naphtha fraction	22,3
		Kerosene fraction	15,0
		Diesel fraction	39,2
		Heavy gas oil	20,0
		Hydrogen sulphide + Ammonia	2,0
Total	103,0	Total	103,0

The first step of the model development is development of a scheme of hydrocarbon conversion at the industrial conditions in the presence of catalyst. To this purpose the composition of feedstock and products should be determined as well as termodynamic analysis of possible reactions should be carried out.

The tasks of this work include studying the composition of feedstock and products of hydrocracking process, thermodynamic analysis of chemical reactions and development of hydrocarbon conversion scheme.

The feedstock composition was determined by the method of liquid adsorption chromatography.

Group compositions of feedstock and product (diesel fraction 200-360 °C) were determined in term of the content of paraffins and naphthenes, aromatics and resins.

The average contents are as follows: paraffins and napthenes – 62.39 wt.%, aromatics – 29.60 wt.%, resins – 8.01 wt.% (feedstock of the first technological line); paraffins and napthenes – 63.08 wt.%, aromatics – 29.00 wt.%, resins – 7.92 wt.% (feedstock of the second technological line); paraffins and napthenes – 86.25 wt.%, aromatics – 13.08 wt.%, resins – 0.66 wt.% (diesel fraction 200-360 °C).

On the basis of obtained results on the feedstock and product composition, the known mechanisms of hydrocracking reactions and thermodynamic analysis of the possible reactions at the industrial technological conditions, the hydrocarbon conversion scheme of vacuum gas oil hydrocracking process was developed.

The developed hydrocarrbon conversion scheme will be used as the base for mathematical model development.

Acknowledgements

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USAGE OF DIALKYL DISULFIDES MIXTURE (DADS) AS A SULFIDING AGENT FOR INDUSTRIAL HYDROTREATING CATALYST

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The technology of refining hydrogenation processes, such as hydrotreating, hydrocracking, and catalytic reforming includes catalyst sulfiding either for activation or to reduce activity of fresh catalyst. Catalysts of hydrotreating and hydrocracking typically are NiMo or CoMo compositions, are transported and loaded in oxide form, while their sulfidation goes already inside of the reactor.

All catalysts are sulfided by H_2S formed in the reactor by a reaction of sulfur source compound with hydrogen. For sulfiding acceleration not only sulfur containing feeds are used, but sulfur-rich reactants. It allows shortening unit ineffective time spent on sulfiding from few days (using only raw feeds) to 12-36 hours (using these reactants).

Among the sulfiding agents, dimethyl disulfide (DMDS) and tertbutyl-polysulfide (TBPS) are the most widely used due to the highest sulfur content, while as the use of other reagents for this purpose is less efficient.

Reactants fitting for sulfiding can be obtained during the processing of sulfur-containing feeds as minor products. For example, modern method of mercaptans removing from hydrocarbon feeds means oxidation in alkaline media by molecular oxygen in catalyst presence. A minor product of this process is the mixture of dialkyl (C_1-C_3) disulfides (DADS) as known as disulfide oil. The issue of utilization of this demercaptanization minor product still is not solved, and disulfide oil has no qualified use while as its storage is ecologically dangerous.

In this work possibility of DADS usage as sulfiding agent for hydrogenation processes catalysts were investigated.

On a continuous-flow reactor with a 10 cm^3 fixed catalyst bed was conducted a study of agent effect (DMDS or DADS mixture) on catalyst sulfidation process and dynamics of change in the content of hydrogen sulfide and hydrocarbons in the gas phase of reactor outlet. Results of the chromatographic analysis show that dynamics of hydrogen sulfide content change have no dependence sulfiding agent type.

A comparative test of industrial hydrotreating catalysts, which were sulfided by DMDS or DADS was conducted on pilot hydrotreating continuous-flow 100 cm^3 fixed bed reactor with hydrogen circulation. Test was conducted at 4.0 MPa, volume H_2 to feedstock ratio 400 nm^3/m^3, LHSV 1.5 h^{-1}. Operation temperature was varied to achieve sulfur content in products lower than 10 ppm.

In hydrotreating of straight-run diesel almost equal hydrodesulfurization activity of DMDS and DADS mixture sulfided catalyst was found out. Quality characteristics of obtained products were equal.

After test catalysts were dumped out from reactors and analyzed. Elemental CHNS-analysis, simultaneous thermal analysis (STA), low-temperature nitrogen adsorption, X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM) were carried out. Carbon and sulfur content in both samples was on the same level. Physical and chemical characteristics of catalysts sulfide by DMDS and DADS mixture have insufficient differences.

Study results allow approving usage of DADS mixture as sulfiding agent for hydrotreating catalysts at industrial process.

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HYDROPROCESSING OF LIGHT CYCLE OIL OVER NiMoS CATALYSTS SUPPORTED ON ORDERED MESOPOROUS POLYMERS

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The conversion of heavy petroleum hydrocarbons (HCs) to lighter products plays an important role in the modern petroleum refining industry. The use of these processes makes it possible to expand the raw material base via increasing the efficiency and degree of conversion of HC feedstocks to motor fuels and intermediates of petrochemical synthesis. Ever tightening requirements for the characteristics of fuels necessitate the development of novel catalyst systems providing the production of motor fuels that meet the modern environmental standards and regulations. For diesel fuels, these requirements primarily concern the content of sulfur and polyaromatic HCs: to meet the Euro-5 environmental standard, the diesel fuel should contain no more than 10 ppm of sulfur compounds and no more than 2% of polycyclic HCs [1]. Light cycle oil (LCO) is one of the recycled oil products used for the production of diesel fuels. LCO is produced by the destructive conversion of final fractions remaining after the straight-run distillation of crude oil [2]. LCO comprises a large amount of aromatic HCs (60–90 wt %) and sulfur compounds (3000–25000 mg/kg), which worsen the quality of this product [3]. To improve the properties of LCO, it is subjected to hydrotreating and hydrodearomatization. Conventional well-proven hydrotreating catalysts are sulfides of molybdenum and tungsten promoted with nickel and cobalt. The efficiency of these catalysts is determined by the structure and size of the active phase nanoparticles, the synthesis method, and the material of the support. In this case, of particular interest are mesoporous organic supports: it is assumed that the use of these supports contributes to the formation of more active sulfide catalysts at lower temperatures owing to the absence of sites for binding the sulfide phase to the support surface.

This study is focused on the activity of in situ synthesized Ni–Mo–S catalysts supported on ordered mesoporous phenol-formaldehyde polymers. Polymeric supports are more hydrophobic than conventional oxide supports; therefore, tetrabutylammonium nickel tetrathiomolybdate is selected as the precursor. The activity of the Ni–Mo–S catalysts is tested in LCO hydroconversion. Catalysts were analyzed after the *in situ* activation by high-resolution transmission electron microscopy (HRTEM) and X-ray photoelectron spectroscopy (XPS). It was found that the resulting catalysts show high activity in the hydrodesulphurization (up to 90%) and hydrodearomatization of polyaromatic hydrocarbons.

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EFFECT OF CITRIC ACID AND TRIETHYLENE GLYCOL ADDITION ON THE REACTIVATION OF HYDROTREATING CATALYSTS

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At present, the production of ultra low sulfur diesel is only possible with the use of modern highly active HDS catalysts. The main feature of these catalysts is the presence of the supported metals primary in the form of CoMoS phase of Type II known as the most active component for hydrotreating reactions [1]. Oxidative regeneration of these catalysts can restore their activity by about 90 %. Currently, on producing ultra low sulfur diesel the HDS degree of the feedstock is not less than 99.5 %. Thereafter, the recovery of catalyst activity only by 90 % results in the need to increase the starting hydrodesulfurization temperature for at least 10-20 °C when using the regenerated catalysts as compared to the fresh ones. This results in the unjustified energy costs and the reduction of the desired product yield.

In this paper, a method of HDS catalysts reactivation is proposed. This method is based on a combination of off-site oxidative regeneration and subsequent reactivation of catalysts by organic complexing agents. In the present investigation the industrial catalyst preparation method was used based on a bimetallic Co-Mo-containing compound application [2].

The HDS activity was assessed on a fixed-bed micro-reactor. Before the test, the catalysts were sulfided in a flow H_2S (500 h^{-1}) at 400 °C for 2 h. Then the HDS activity was tested using a undecane solution containing 1.43 wt.% (2000 ppm S) dibenzothiophene (DBT) as the reactant, under the conditions of 3.5 MPa, LHSV = 80 h^{-1}, H_2/feed = 500 and temperature 280 °C. After calcination the recovery catalyst activity (reactivation) was performed by the impregnation water solution with citric acid and triethylene glycol. The solution was prepared by consecutive dissolving of portions of complexing agents in distilled water. The solution volume was calculated based on the catalyst water capacity.

The catalysts were studied by HRTEM, XPS, FTIR, Raman and UV-VIS spectroscopy. FTIR, Raman and UV-VIS methods revealed the formation of complex compounds of metals in solution in the catalyst pores as well as on the catalyst surface. Investigation of reactivated sulfided samples by XPS showed that the samples contain bimetallic sulfide compounds with the structure of MoS_2 and do not contain oxygenates. HRTEM shows the formation of fine, mainly monolayered particles of CoMoS phase type II.

Reactivated catalysts are showed a significant increase in activity compared to calcined (CoMo-R) in the HDS of DBT. The highest reactivation is observed for the sample reactivated with mixture of citric acid and triethylene glycol (Figure 1). Apparently, this is associated with synergetic effects consisted in positive mutual influence triethylene glycol and citric acid.

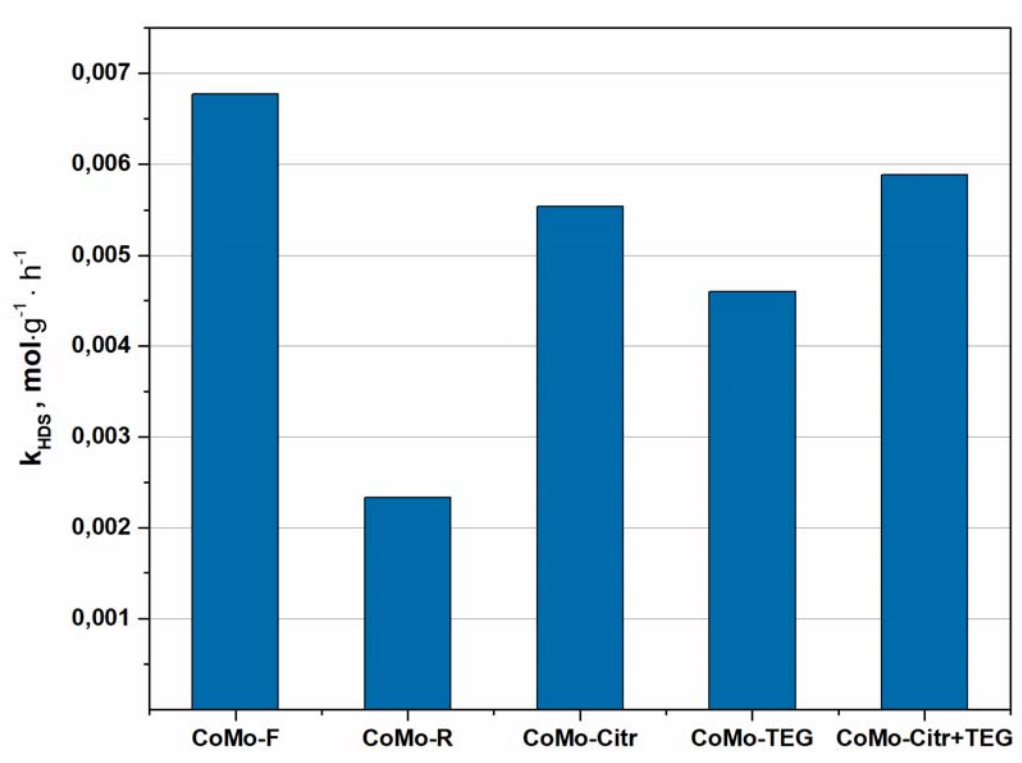

Figure 1. Activities in the HDS DBT for fresh (CoMo-F), calcined (CoMo-R), reactivated by citric acid (CoMo-Citr), reactivated by triethylene glycol (CoMo-TEG) and reactivated by mixture of citric acid and triethylene glycol (CoMo-Citr+TEG) catalysts

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ALTERNATIVE DIESEL FROM WASTE PLASTICS

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The use of plastics has been associated with significant environmental problems due to their continuous accumulation in landfills, as plastic waste does not degrade or degrades at a very low pace. On average, 50 % of the waste plastic generated in Europe is recovered, while the rest is sent to landfills [1]. The increasing availability of such waste material in local communities, coupled with the high energy density, render waste plastics one of the most promising resources for fuel production [2]. The pyrolysis of plastics for fuel production is practiced by several small-size companies worldwide. The pyrolysis of plastics yields on average 45-50 % of oil, 35-40 % of gases, and 10-20 % of tar [1], depending on the pyrolysis technology. The total pyrolysis oil or fractions of it can be further upgraded via suitable conversion processes, such as catalytic hydrotreatment, to meet market fuel standards. Considering all of the above reasons, the aim of this study is the technical evaluation of the potential to convert pyrolysis oil from waste plastics to high-quality diesel fuel by catalytic hydrotreatment upgrade. The pyrolysis was performed in a semi-continuous plant in South East Asia, which is located nearby an old landfill that was supplying the plant with waste plastics. The upgrading of the pyrolysis oil was tested in the hydrotreatment pilot plant of the Centre for Research and Technology Hellas (CERTH) in Greece, rendering the desired diesel fuel. Catalytic hydrotreatment is foreseen as a key upgrading process for the valorization of bio-based feedstocks, such as lipids [3], pyrolysis oils, and bio-oils [4], for the production of high quality renewable fuels. As a result, this process was considered to be the necessary conversion step for the conversion of the mid-distillate fraction of pyrolysis oil to diesel fuel.The proposed methodology renders a promising alternative diesel fuel. In particular, the hydroprocessed mid-distillate fraction of the pyrolysis oil is an excellent ignition-quality mid-distillate fuel that in most cases meets the requirements of the EN

590 standard for automotive diesel (Table 1), and can be considered a promising alternative diesel pool component.

The diesel fuel produced from upgrading the mid-distillate pyrolysis oil fraction was a clear fuel with average sulfur of 12.1 mg/kg. The improvement of both the appearance and sulfur content of the produced fuel was very promising and leads to the further evaluation of the fuel as a potential transportation diesel fuel. The hydroprocessed fuel has an excellent cetane index that approaches 71.5. The density and viscosity have been slightly decreased. The polyaromatic hydrocarbons content has been eliminated, and only a very small amount of monoaromatic hydrocarbons is still present in the fuel. All of these characteristics are an indication of a fuel with high paraffinic hydrocarbons content [5].

Table 1. Analysis of the hydroprocessed mid-distillate fraction of the pyrolysis oil

Property	**Value**	**Unit**	**Limits**		**Test Method**
			Min	**Max**	
Density at 15 °C	790.6	kg/m^3	820	845	EN ISO 12185
Sulfur	12.1	mg/kg	-	10	EN ISO 20846
Cetane Index	71.5	-	46	-	EN ISO 4264
CFPP	2	°C	-	-	EN 116
Viscosity	2.377	mm^2/s	2.000	4.500	EN ISO 3104
Aromatic HC					EN 12916
Mono	1.8	wt %	-	-	-
Di	-	wt %	-	-	-
Tri+	-	wt %	-	-	-

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UNSTEADY MATHEMATICAL MODEL OF H_2SO_4-CATALYZED ISOBUTANE WITH OLEFINES ALKYLATION

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Alkylation of isoparaffins with olefins is one of the most important processes in the Russian oil refining and petrochemical industries.

For the complex study of the influence of the most important parameters on the processes of oil refining and petrochemistry, the most suitable method is mathematical modeling. The purpose of this work is to develop and analyze a mathematical model, its sensitivity to the flow and composition of raw materials, as well as its nonstationarity, which is expressed in the change in the activity of the catalyst when various technological parameters affect it [1, 2].

The thermodynamic analysis of this work made it possible to determine the probability of formation during the sulfuric acid alkylation process of substances such as isooctanes, isoheptanes and other isobaric hydrocarbons.

The network of the hydrocarbon transformation is based on a model that is sufficiently detailed, thereby ensuring the sensitivity of the model to changing the composition of the raw materials, but at the same time, does not complicate the calculations due to a sufficient degree of formalization.

The developed program allows to calculate the composition of the alkylate to be obtained, to determine the yield of the target and by-products, to select the optimal process conditions for the given raw material composition.

In the course of this study it was found that impurities such as n-butane, propane and propylene in the butene fraction negatively affect the yield and quality of alkylbenzene. Thus, an increase in propylene content by 1.5 % lowers the octane number of the product by 1 point. This problem can be solved with propylene by increasing the Isobutene/olefines ratio, however, the thermal effect of the isobutane-propylene interaction is higher than isobutane-butylene, which necessitates a more efficient way of cooling the reactor devices.

An approximate mechanism was established for the formation of high molecular weight hydrocarbons (ASO), which were formed because of the reduced ratio of isobutane: olefins.

Analyzing the effect of high molecular weight hydrocarbons and water formed in the reactor and adversely affecting the octane number of alkylate, the exponential dependence of the decrease in octane number was established. This problem was solved by introducing the deactivation function.

$$K\_\ des = K\_i * e \wedge ((C\_water * \alpha + C\_ASO * \beta)),$$

where α is a coefficient that takes into account the deactivation of the acid by water;

β – coefficient, taking into account the deactivation of acid ASO;

Ki is the formation constant of the substance;

K_dez – the constant of formation of a substance, taking into account the negative influence of impurities in the composition of the catalyst.

The implementation of this deactivation function led to a decrease in the experimental error from 0.66 % to 0.09 % (for research octane number) and from 0.33 % to 0.16 % (for motor octane number).

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STUDYING THE CORRELATION BETWEEN MODES OF TECHNOLOGICAL STAGES OF SYNTHETIC DETERGENTS SYNTHESIS USING THE MATHEMATICAL MODEL

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Alkylbenzenesulfonic acid (ASA) is known to the main ingredient of many commercial formulations for the synthetic detergents. A plant for ASA manufacturing includes a number of consecutive blocks: catalytic dehydrogenation of C9-C14 alkanes over Pt-catalyst yielding a mixture of n-alkenes and n-alkanes; hydrogenation of dienes over nickel-based catalyst; HF-catalyzed alkylation of benzene with alkenes yielding linear alkylbenzenes (LAB); sulfonation of LAB with sulfuric anhydride to produce ASA [1, 2].

The experimental data of the ASA manufacturing unit performance allow concluding that the industrial parameters of the dehydrogenation process influence the efficiency of the LAB and, consequently, the final product manufacturing.

The aim of the current research was to study how the key parameters of the dehydrogenation process influence the alkylation performance and the HF-catalyst activity using the developed computer modeling system. The carried out calculations allowed us to reveal the following results:

- The increase in the hydrogen / feed ratio in the dehydrogenation reactor from 6 to 8 mol/mol leads to decrease in the concentration of diolefins in the dehydrogenation reactor from 0.57 to 0.46 wt. % and to a decrease in the amount of heavy aromatics formed in the alkylation reactor (from 4 to 3 kg/h), as well as a decrease in LAB production by almost 1000 kg/h. It is possible to compensate this negative effect by increasing the activity of the HF catalyst from 0.5 to 0.52 rel. units.
- With an increase in the volume of processed raw materials at the dehydrogenation stage, there is an increase in the content of diolefins in the alkylation feedstock from 56.25 (at the beginning of the catalyst service cycle) to 73.94 kg/h (towards the end of the catalyst service cycle). This leads to an increase in the accumulation of TAP in the alkylation reactor (from 20.27 to 26.64 kg/hour). To maintain the optimal HF activity, witch equals to 0.5. rel.

units, it is necessary to increase the flow rate of HF to the regeneration column from 3.64 to 4.78 m^3/h, as the operating time of the dehydrogenation catalyst increases.

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The research was carried out at Tomsk Polytechnic University within the framework of Tomsk Polytechnic University Competitiveness Enhancement Program grant.

BIMETALLIC SULFUR REMOVAL ADDITIVIES La-Mg-Al-MCM-41/Al_2O_3 FOR FCC CATALYSTS

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Environmental protection is a main problem facing humanity nowadays. Sulfur dioxide is major contributor to air pollution and it has a significant impact upon human health [1]. One of the sources of SO_2 emissions is the combustion of fuels. In this regard, with each year requirements to the sulfur content in motor fuels are toughened. One of components of commercial gasoline is a gasoline fraction of fluid catalytic cracking (FCC), which must be hydrotreated at a high partial pressure of hydrogen, which adversely affects the octane number. The use of additives to cracking catalysts can significantly reduce the concentration of sulfur in liquid products of the catalytic cracking, which subsequently leads to the use of milder conditions in hydrotreating.

For high sulfur reduction activity, additive should possess: high acidity, stability and sorption activity of organic sulfur compounds [2, 3]. Therefore, the composition of the test additive includes:

- Al-MCM-41 is a mesoporous material with a high specific surface area, adsorption properties and high acidity
- Al_2O_3 - increases acidity and stability of the additive
- Lanthanum and magnesium - increases sulfur reduction activity and acidity.

La and Mg-containing materials based on mesoporous Al-MCM-41/Al_2O_3 with different component ratios: 30/70, 40/60, 50/50 % wt. were synthesized and tested as additives to FCC catalysts. The samples were characterized by TEM, IR spectroscopy, TPD of ammonia, low-temperature adsorption/desorption of nitrogen, ^{27}Al NMR spectroscopy. According to the data obtained from nitrogen adsorption/desorption isotherms, all the materials have ordered mesoporous system.

Cracking of vacuum gas oil was carried out in a micro activity testing (MAT) laboratory system at 500 °C with a catalyst/feedstock ratio 3,4. A commercial microspherical cracking catalyst was used. The fractional composition of liquid cracking products was determined by a simulated distillation. All additives obtained showed a sulfur reduction activity. Increasing of the content of aluminosilicate (Al-MCM-41) from 30 to 50 % wt. and lanthanum from 1 to 4 % wt. leads to decreasing sulfur content in liquid cracking products. In the case of 4%La-1%Mg-Al-MCM-41/Al_2O_3 (Al-MCM-41/Al_2O_3 ratio = 50/50 % wt.) the sulfur content in liquid cracking products decreased up to 35 %, as compared with catalyst without additive. Thus, it was found that bimetallic La, Mg-containing additives based on aluminosilicate Al-MCM-41 supported on Al_2O_3 are highly active in sulfur removal in liquid products of vacuum gas oil catalytic cracking.

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MESO-MACROPOROUS CATALYSTS FOR REMOVAL OF HETEROATOMIC COMPOUNDS FROM MIDDLE DISTILLATES

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One of the most important parametres for efficiency of hydrotreating units is retention of catalyst's activity. There are a lot of contaminations in crude oil and its distillates that may reduce catalyst's activity. Such metals as Ni, V, Na and Fe are well-known catalytic poisons that are treated successfully. However, there are some non-obvious elements that also poison the catalyst. For example As, Si, Cl cause serious damage to the catalytic system. Arsenic is a permanent catalyst poison which means once it is on the catalyst it cannot be removed via regeneration or other means. It is a severe poison since a small amount results in significant activity loss. The arsenic is believed to bind with the metal sulfide sites, and in particular the active nickel on the catalyst forming nickel arsenide [1,2]. Thus it becomes obvious that special guard catalysts or even guard reactors are needed in order to treat poisonous arsenic. Current arsenic removal sorbents are comprised of Ni–Mo supported on Al_2O_3 [3]. However, arsenic can remain in the guard reactor effluent either through incomplete sequestering of the arsenic in the guard reactor or by leaching of arsenic from the sorbent material.

In present work we have synthesised guard layer catalyst that treats arsenic compounds effectively. We used a meso-macroporous material as a support for the catalyst. It is a member of novel class of materials that may help to reduce diffusional limitations for bulky molecules that are presented in middle and heavy distillates of oil.

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PP-11

BIODIESEL OBTAINING UNDER SUPERCRITICAL FLUID CONDITIONS: NON-CATALYTIC AND CATALYTIC REACTION, THE REACTION KINETICS AND THE PROCESS SIMULATION

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An experimental study of non-catalytic and catalytic transesterification reaction of rapeseed oil in ethanol under supercritical fluid conditions was carried out. The ultrasonic treatment of the initial mixture was made. The molar ratio "ethanol - rapeseed oil" varied from 6:1 to 20:1, reaction temperatures from 320 °C to 380 °C at a pressure of 30 MPa. Flow-type installation was used for the experiments. To reduce the parameters of the state and accelerate the reaction rate authors experimentally realized catalytic transesterification reaction using heterogeneous catalysts, carried out under the same regime parameters as in non-catalytic reaction. As heterogeneous catalysts metal oxides (Al_2O_3, ZnO/Al_2O_3, MgO/Al_2O_3 et al.) in granular form are used. For the catalysts preparation, method of impregnating the carrier (Al_2O_3) by immersing the granules in the concentrated solution of the corresponding salts followed by calcinations are used. As a technique for control of the Fatty Acid Ethyl Esters (FAEE) content in biodiesel samples the correlation dependence of FAEE concentrations from the values of the kinematic viscosity was proposed.

In order to optimize the biodiesel fuel production process, transesterification reaction kinetics equations are compiled and the kinetic rate constants are determined.

The prospect of commercialization of biodiesel production process involves the simulation of the process on the basis of data on the content of biodiesel in the reaction product and the reaction kinetics. As the simulation program technological production simulator VMGSim was chosen. When as the starting materials in the simulation ethanol and triolein (the main component of rapeseed oil) are used; glycerol and ethyloleate - as a reaction products. As the thermodynamic model - Advanced Peng-Robinson are used. The values obtained for the concentrations of reactants and products, calculated in VMGSim, showed the possibility of the process scalability.

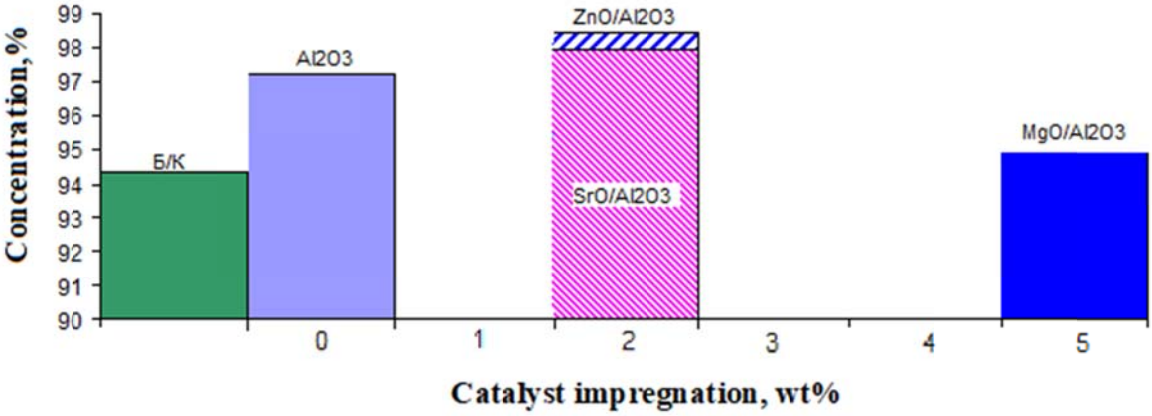

Fig. 1. The concentration of FAEE in the reaction product using catalysts with different degrees of impregnation: T = 638 K, P = 30 MPa, molar ratio "ethanol/rapeseed oil" - 18:1

PP-12

DEVELOPMENT SYSTEM OF GUARD CATALYSTS AND MATERIALS FOR COMPLEX HYDROTREATING OF DISTILLATE FEED

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Metals, resins, and asphalts in hydrocarbon feeds are a serious problem, which causes irreversible hydrotreating catalysts deactivation. Using of guard bed in reactors of hydroprocesses improves dispensing, protects main bed catalyst from fouling and reduces coke formation from polymerization products, therefore decreases reactor pressure drop. From there guard bed using provides maximal activity of main bed catalyst and enhance unit's cycle length.

VNII NP JSC has carried out research for the development of hydrotreating process for hydrocarbon feeds containing secondary distillates using sorbing catalytic materials, which provides removing of mechanical impurities, arsenic, silicon, nickel, vanadium. Stacked bed comprise CoMo/Al_2O_3 or NiMo/Al_2O_3 main catalyst bed, which takes 85-90 % of the reaction zone and guard catalysts and materials – 10-15 %. The balance between catalysts and materials can vary in dependence on raw feed quality.

In this work we used the stacked bed with guard bed which comprises four types of materials and catalysts given in top-down sequence:

1) Inert mechanical trap;
2) Ni/Mo catalyst supported on the high-porous cellular material, which is characterized by 80 % of free volume;
3) Mesoporous sorbing catalytic material with surface area higher than 350 m^2/g and pore volume 0.65 cm^3/g and Ni/Mo oxides content up to 20 % wt.
4) Demetallation catalyst with Co/Mo oxides contents up to 12 % wt. with surface area higher than 180 m^2/g and pore volume 0.48 cm^3/g.

With described stacked bed hydrotreating of mixed feedstock was carried under following conditions: LHSV 0.7 h^{-1}, temperature 360 °C, hydrogen pressure 10 MPa, and hydrogen to feedstock ratio 500 nm^3/m^3. Feedstock mixture comprises 50 % straight-run diesel and 50 % secondary middle distillates (20 % light cycle oil, 20 % delayed coking gasoil, 10 % delayed coking gasoline) and contains 3 ppm As, 5 ppm Si, 0.3 ppm Ni and V. Hydrotreated product contains 5 ppm S, 4 % wt. polyaromatics and the total content of As, Si, Ni, and V lower than 0.4 ppm.

Using guard bed material and catalysts in stacked bed with main bed catalyst for hydrotreating mixed feeds with high polyaromatics and unsaturated hydrocarbon content allows not only obtaining a product with required quality but prolong catalysts cycle.

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PP-13

INTELLECTUAL TECHNOLOGY OF LOW-HARDENING HYDROCARBON FUEL PRODUCTION

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Intellectual technology of low-hardening hydrocarbon fuel production by account for chemical interactions between hydrocarbons, as in the stage of catalytic hydrocarbon processing in catalytic cracking, hydrodeparaffinization and hydrocracking, and at the mixing stage provides high economy effectiveness, what is in the line with the tasks within directions of scientific and development strategies in Russian Federation. Predictive mathematical models are created, adequate to real processes, with the use of which it is possible to define necessary conditions for maximum catalyst's potential using, as well as the raw materials resource while optimizing the formulas for mixing high-energy low-solidifying hydrocarbon fuels. It is important to use oil raw materials rationally and catalytic system possibilities in oil refining on the basis of the established physicochemical and macro kinetic regularities of hydrocarbon transformations. Catalyst deactivation is the main problem of energy-saving in the industrial chemistry. To fully prevent catalyst deactivation are not possible, as well as adverse reactions occurring in a process, but it is necessary to carry out systematic investigations of deactivation process with mathematical modelling method application. Rapid and irreversible catalyst deactivation of reforming and platforming processes, fractions cracking of natural hydrocarbons lead to significant increase in the cost of buying and reloading expensive contacts, especially in a case of catalysts which contain such metals as Rhodium, Platinum and Palladium. With mathematical model method using in the base of different factors account, influencing on catalyst deactivation the problem of effectiveness and energy-saving in low-hardening hydrocarbon fuel production is solved. Difficulties of creating and mathematical model using, developed of the data basis, obtained in laboratory conditions, for process improvement, occurring in industrial reactors, it was proposed to use data, obtained in industrial units with account of process technology specific, reactor construction, raw material diversity. A variety of approaches has been used for reaction mechanism clarification, including quantum chemical methods.

SUPPORT EFFECTS ON THE PROPERTIES AND CATALYTIC ACTIVITY OF Co-Mo-S HYDROTREATING CATALYST

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Hydrotreating processes are largely carried out over sulfided Co(Ni)Mo catalysts supported on alumina, which has good thermal, mechanical and textural properties and provides high dispersion of the active metal components. However, the main drawback of alumina is strong interaction with the active components, which hinders the complete sulfidation of supported metals and decreases the number of active sites. There are number of approaches for preparation of hydrotreating catalysts with enhanced activity. Among them, the addition of chelating agents, especially, citric acid as a relatively inexpensive chelating agent, has been widely used in the hydrotreating catalysts preparation. Unlike alumina, carbon materials hydrophobic surface limits the metal support interaction, which facilitates the sulfidation process. Multi-walled carbon-nanotubes (MWCNT) have drawn a lot of attention since their discovery due to their unique properties. In this work the effects of MWCNT and γ-Al_2O_3 supports on the properties and hydrodesulfurization (HDS) activity of corresponding CoMo catalysts prepared with citric acid is studied.

CoMo/MWCNT and CoMo/Al_2O_3 catalysts were prepared by impregnation with aqueous solution prepared from cobalt hydroxide, ammonium heptamolybdate and citric acid. Impregnated catalysts were dried at 120 °C. The catalysts contained 12.0 ± 0.2 wt % of Mo and 3.2 ± 0.1 wt % of Co. The sulfidation of the catalysts was carried out in H_2S flow for 4 h at 200 °C and 400 °C at atmospheric pressure. The catalysts in sulfide form were studied by N_2 physisorption, XPS and HRTEM. The catalysts were tested in simultaneous dibenzothiophene (DBT) HDS and naphthalene hydrogenation in fixed-bed reactor under the following conditions: t = 280 °C, P = 3.5 MPa, LHSV 20 h^{-1}, H_2/feed = 500 nm^3/m^3.

Figure 1 shows HRTEM data for sulfide CoMo/MWCNT and CoMo/Al_2O_3 samples. For both catalysts the unsulfided species of active component are not observed. Active phase is uniformly distributed on Al_2O_3 surface in CoMo/Al_2O_3 catalyst. For CoMo/MWCNT the presence of active phase both inside and outside the CNT channels is observed. It is defined that the average stacking number for CoMo/MWCNT and CoMo/Al_2O_3 samples is close and equal to 1.035±0.015. The average slab length is 2.88 nm for CoMo/Al_2O_3 and 3.75 nm for CoMo/MWCNT.

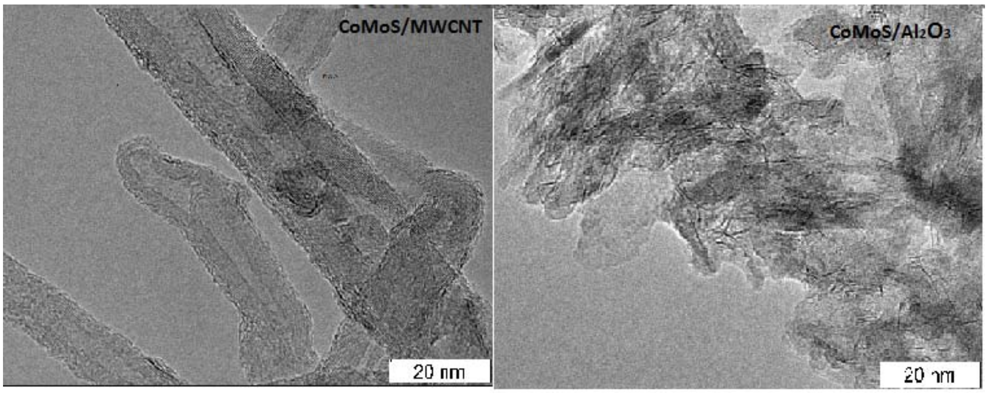

Fig. 1. TEM micrographs of sulfide CoMo/MWCNT and CoMo/Al_2O_3 samples

The formation of active CoMoS phase on the surface of supports was confirmed by XPS. For both catalysts Mo3d spectra contain an intensive peak with binding energy of 229±0.1 eV and Co2p spectra contain an intensive peak with binding energy of 779.0±0.1 eV. According to Mo3d spectra deconvolution the amount of Mo^{4+}, which is related to molybdenum in sulfur surrounding in sulfide catalysts, is higher for CoMo/MWCNT sample: 77 % versus 63 % for CoMo/Al_2O_3. The deconvolution of Co2p spectra shows that the amount of CoMoS phase is 73 % for CoMo/MWCNT and 63 % for CoMo/Al_2O_3.

Table 1. DBT and naphthalene conversion over CoMo/MWCNT and CoMo/Al_2O_3

Sample	**Conversion, %**	
	DBT	**Naphthalene**
CoMo/MWCNT	91.6	12.4
CoMo/Al_2O_3	80.8	8.8

The results of catalysts testing in hydrotreating of model feed (Table 1) show that CoMo/MWCNT has higher activity in HDS of DBT and hydrogenation of naphthalene. The beneficial effect on HDS and hydrogenation activity is provided by the higher proportion of active metals in the form of CoMoS phase in CoMo/MWCNT catalyst.

Acknowledgements

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CHARACTERIZATION AND ACTIVITY OF DISPERSED MoS_2 CATALYSTS FOR HYDROCRACKING OF VACUUM RESIDUE

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Declining availability of conventional light crude oils has drawn much research on the upgrading of the extra heavy oils (API≤15) [1]. Among the heavy oils like petroleum residue and bitumen, vacuum residue (VR) occupying a half of heavier crude oil, has been a target to be upgraded into middle distillates [2]. The heavy oils are, however, rich in asphaltenes which are known as a precursor of coke due to the colloidal instability and aggregation behavior in the refinery processes. Hydrocracking is one of the most promising processes with high conversion rate of heavy oil to distillates. In particular, unsupported oil-dispersible nano-catalyst in VR HCK, in which enhanced VR HCK was for oil-dispersible catalyst system over the supported catalyst system, due to the better accessibility toward active centers of the catalyst [3].

This study presents the hydrocracking and hydrogenation activity of molybdenum sulfide and cobalt-molybdenum sulfide on the slurry phase hydrocracking of VR. The pretreatment was conducted at 10 MPa H_2 and 653~683 K for 1~4 hr and the reaction was tested at 10 MPa H_2 and 693 K for 2~4 hr in an autoclave reactor. The feedstock was prepared by blending a VR (30 g) and precusor catalysts, like $Mo(CO)_6$, or recycled one (360 ppm metal).

The characterization was conducted with X-ray absorption fine structure (XAFS) method. The EXAFS spectra were recorded at beamline 8C and 10C of the Pohang accelerator laboratory and were calculated with feff program (feff, version 8.5) based on the results of DFT simulations (Material studio, Accelrys, version 5.5, DMol module). The optimization of kinetic parameters was conducted using the Matlab with Levenberg-Marquardt algorithm. Differential equation formula were proposed and calculated with Runge-Kutta algorithm.

As the result, nano-sized MoS_2 catalysts with various ranges in size were well synthesized by in-situ method in the presence of $Mo(CO)_6$, VR, H_2 atmosphere. The EXAFS, the TEM and the activity test results confirm that the smaller MoS_2 catalysts gave higher VR hydrocracking activity with less coke formation and low asphaltenes contents but with particle growth in the course of VR HCK. The introduction of Co-doping onto MoS_2 catalysts could enhance the stability during the VR HCK.

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APPLICATION OF MODERN HYDROPROCESSES FOR LOW-VISCOSITY MARINE FUELS PRODUCTION

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Due to the deepening of oil processing refineries began to use the products of deeper processing of petroleum feedstocks, which differ from products of straight distillation 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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APPLICATION OF NOVEL AND EASILY SYNTHESIZED NANOCATALYST FOR UPGRADING OF HEAVY CRUDE OIL

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Nowadays with the high demanding for energy, attention to the source of unconventional oil resources recently became more important. In order to that, with the decreasing of conventional oil resources getting energy from unconventional resources such as heavy crude oil is extremely outstanding process. Nanotech applications in oil-refining industry are the symbol of the-state-of-the-art technological phenomena. Lately, hydrothermal catalytic process in reservoir environments (in-situ upgrading) has got significant considerations. Nanotechnology could also represent a breakthrough element for prospection in oil industry especially refining [1-2].

The goal of this study is to investigate the heavy crude oil upgrading using new novel and low-cost core-shell nanocatalyst and also following and monitoring its stability using EPR spectroscopy techniques [3].

Herein, we presented application of new generation of core-shell $Al_2O_3@MnO_2$ nanoparticles based on facial synthesis method. We have evaluated nanocatalyst efficiency in heavy oil upgrading processes induced by steam injection in the reservoir. For this purpose we have used different methods to monitor crude oil properties before and after upgrading (SARA analysis, elemental analysis, viscosity, NMR and FTIR spectroscopy, gas chromatography, MALDI-TOF mass-spectrometry, etc.). EPR-spectroscopy was applied to understand the catalytic mechanism. Generally, we observed that, applying nanocatalyst into upgrading of heavy crude oil showed reasonable results from the matter of cracking and cleavage of bonds in long chain compounds in heavier crude oil and converted to lighter crude oil with shorter chain compounds.

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DEEP HYDROTREATING OF VACUUM GAS OIL OVER NiW CATALYST SUPPORTED ON MODIFIED MESOPOROUS ALUMINA

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Over the past decades, a tendency to decline in the quality of feedstocks for hydrotreating (HDT) of vacuum gas oil (VGO) requires severe operating conditions. The development of improved HDT catalysts with high stability is among the most desired alternative for deep hydrotreating these kinds of feedstocks. Preparation of highly active catalysts has been possible through a using a more efficient supports.

The aim of the work was the preparation and characterization of mesoporous alumina supports, corresponding NiW catalysts and their performance in VGO HDT.

A mesoporous alumina (*m*-Al_2O_3) was synthesized using a triblock copolymer, Pluronic P123 and aluminum sec-butoxide as the aluminum source. Alumina supports were prepared by peptization of commercial TH-60 powder with addition of mesoporous alumina gel (*mp*-Al_2O_3). NiWS/Al_2O_3 catalysts were synthesized by the incipient wetness method via impregnation of the supports with aqueous solutions containing the required amounts of $H_3PW_{12}O_{40}$ and nickel citrate. The physico-chemical properties of supports and catalysts were studied by low-temperature adsorption of N_2, XRD, TPD-NH_3, XPS and HR TEM. The catalytic properties were determined in the hydrotreating of a straight-run diesel fraction and a VGO.

The *m*-Al_2O_3 sample obtained by hydrolysis of aluminum sec-butoxide had a surface of 637 m^2/g and a high pore volume of 2.71 cm^3/g, with an average pore radius of 35 Å. However, low mechanical strength limits the possibility of using it directly as a support of a hydrotreating catalyst. Therefore, we used a combined method of synthesis. Addition of a gel of mesostructured aluminum hydroxide to a pseudoboehmite powder and further peptization of the mass made it possible to obtain a *mp*-Al_2O_3 sample having an increased specific surface area of 307 m^2/g, a pore radius of 70 Å, and a strength of 1.5 kg/mm^2. The support obtained by peptizing the pseudoboehmite powder was denoted *p*-Al_2O_3.

Sulfided NiW catalysts were characterized by HR TEM and XPS in order to obtain more information about NiWS crystallites. Distributions in stacking degree and slab length of the NiWS particles are presented in Table 1.

Table 1. Composition and morphological characteristics of the NiWS active phase species

Catalyst	Average length (nm)	Average stacking number	Ni fraction (rel. %)			W fraction (rel. %)		
			NiWS	NiS	Ni^{2+}	WS_2	WS_xO_y	W^{6+}
NiW/*p*-Al_2O_3	6.6	2.1	26	52	22	54	9	37
NiW/*mp*-Al_2O_3	3.8	1.8	44	54	2	68	11	21

The average length of NiWS particles on NiW/*mp*-Al_2O_3 was 1.7 times shorter than that of NiW/*p*-Al_2O_3. The use of the *mp*-Al_2O_3 resulted in an increase of tungsten and nickel sulfidation degree and decrease in the amount of W in the oxygen surroundings. Moreover, the Ni percentage in the NiWS phase over NiW/*mp*-Al_2O_3 sample increased to 44 rel. % compared to 26 rel.% over NiW/*p*-Al_2O_3. The results of the evaluation of the catalytic properties of prepared catalysts in VGO HDT showed that the NiWS/*mp*-Al_2O_3 sample exhibited a higher activity in desulfurization, and significantly exceeded the NiWS/*p*-Al_2O_3 sample in the hydrogenation of polyaromatic hydrocarbons. The obtained results are associated with a higher average pore diameter of the support used, which allows for efficient diffusion of heavy polyaromatic molecules to the active sites of the catalyst, as well as a higher dispersion of active phase particles having high hydrogenation activity. The catalysts based modify support exhibited a lesser degree of deactivation and a lower coke content after the tests.

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NOVEL CARBON CARRIERS FOR CATALYSTS

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Catalysis, of course, is one of the most important directions in modern technologies for the synthesis of products of organic chemistry, petrochemistry and gas processing.

However, up to now, the main carriers of catalytic additives have been mineral sorbents: silica gels, alumogels. This is obviously due to the fact that they consist of pure homogeneous components SiO_2 and Al_2O_3, respectively.

It is generally known that impurities, especially the ash elements, are catalytic poisons that reduce the effectiveness of the catalyst. Therefore, carbon sorbents with 5-15 % by weight of ash elements in their composition are not used in the above mentioned technologies. However, in such an important field as a gas-mask technique, carbon sorbents (active carbons) are carriers of catalytic additives, providing effective protection of a person against any types of potent poisonous substances (SDYAV) [1].

In AO "ENPO "Neorganika" there has been developed the technology of unique ashless spherical carbon carrier-catalysts by the method of liquid forming of furfural copolymers with subsequent gas-vapor activation, brand FAS [2].

Active FAS carbons have 100 % qualitative characteristics of the three main properties of carbon sorbents: strength – 100 %, the proportion of sorbing pores in the pore space – 100 %, purity – 100 % (ash content is close to zero).

The table shows the above indicators depending on the degree of activation, expressed by the development of the total pore volume.

Bulk density, g/dm^3	Total pore volume (V_Σ), cm^3/g	Volume of micropores (V_{mi}), cm^3/g, (cm^3/cm^3)	Size of micro pores (N), nm	Volume of mesopores (V_{meso}), cm^3/g, (cm^3 /cm^3)	The volume of macro-pores (V_{macro}), cm^3/g	Ash content, %, GOST 12596 Abrasion resistance, % (GOST 16188)	Abrasion resistance, % (GOST 16188)
605	0,66	0,29 (0,18)	1,21	0,37 (0,22)	0,0	0,03	99,1
574	0,76	0,34 (0,20)	1,28	0,42 (0,24)	0,0	0,01	99,0
509	0,92	0,45 (0,23)	1,45	0,47 (0,24)	0,0	0,03	99,7
470	1,01	0,51 (0,24)	1,50	0,50 (0,23)	0,0	0,06	100
436	1,09	0,56 (0,24)	1,59	0,53 (0,23)	0,0	0,05	98,8
405	1,22	0,66 (0,27)	1,63	0,56 (0,23)	0,0	0,05	99,5
345	1,50	0,80 (0,28)	1,75	0,70 (0,24)	0,0	0,08	98,0

A particularly outstanding feature of active FAS carbons is their uniquely high mechanical compressive strength of 740 ± 40 MPa, which is 3-7 times larger than that of such materials as granite, quartzite, electric coal, and is comparable to the value for cast iron – 400-1000 MPa. This allows the FAS to operate under severe conditions in moving and fluidized beds.

It should be noted that according to GOST 16188-70 the abrasion resistance of silica gels and alumogels, as well as natural and synthetic zeolites is 60-70 %, and for crushing no more than 100 MPa.

Unique properties of FAS sorbents allow using them in any adsorption processes of gas and liquid media purification, human endoecology and nanotechnologies.

Obviously, it is time to actively develop catalysts based on FAS sorbents for oil refining, petrochemicals, gas processing and various technologies of organic synthesis.

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MICROTUBULAR SOLID OXIDE ELECTROLYZER CELL FOR HYDROGEN PRODUCTION

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Alternative methods of power generation attract more attention in recent years. This interest is caused, from one side, by reduction of mineral fuels, from other - by economic efficiency of the innovative approaches in the production of electric power and strict ecological requirements for new technologies.

One of directions of alternative energy development are the high temperature electrochemical devices (ECD). Such devices allows to a) effectively (efficiency 60-70 %) transform an organic fuel and hydrogen, in electric power with the use of solid-oxide fuel cells (SOFC) and b) process carbon dioxide and aquatic steam in a synthesis gas ($CO + 2H_2$), utilizing the extrass of greenhouse gases, effectively stocking energy of cheap energy sources, with the use of high temperature solid-oxide electrolyzers (SOE). As known, hydrogen is not only basis of ecofriendly hydrogen energy but also feedstock for the various hydroprocessing technologies, multi-tonnage production of ammonia and methanol and subsequent chemical products.

Structurally SOE/SOFC can be divided into planar and tubular shape. A planar design is widely used in stationary devices, by power from a megawatt and higher, as provides good heat and mass transfer, compactness of assembling and allows to use the standard methods of ceramic treatment. The substantial lack of planar configuration is high requirements to absence of considerable temperature gradients along a membrane, that can result in device destruction during thermal cycling and dramatic changes of temperature. This results in a slow startup speed.

The problem can be solved using microtubular membranes, the advantages of which are improved thermal and mechanical stability, ease of sealing. The rapid launch of high-temperature ECD opens the possibility of developing a promising niche of compact, mobile devices in transport, in the military field and in household appliances.

In this paper, the results of studying the functional properties of microtubular SOEC with new cathode materials are presented. The obtained data indicate the promise of these cathode compositions.

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INVESTIGATION OF MICRO-MESOPOROUS MATERIALS WITH LAMELLAR STRUCTURE AS THE SUPPORT OF HYDROTREATING CATALYSTS

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The development of micro-mesoporous materials as the support of catalysts in middle distillates refining is an actual subject [1–3]. In the course of previous study it was shown that double-templating synthesis of micro-mesoporous materials is an appropriate way to obtain composite materials as the support of diesel fractions hydrotreating catalysts [4]. The hydrogenation of the derivatives of naphthalene molecule proceeds on the external surface and in the mesopores, the mesopore system in the support could contribute mass transfer. In order to obtain the support with acidity of zeolites and pore size distribution of mesoporous materials it was necessary to crystallize both systems under the same conditions [5]. Therefore, MCM–41 and ZSM–5 materials were chosen as micro- and mesoporous systems due to their similar synthesis conditions (hydrothermal synthesis – T°C, τ; pH,). In this study during the crystallization process we observed the absence of ordered hexagonal mesoporous structure due to the structure transformation into lamellar ZSM–5 crystals.

The results from the TEM and XRD analyses confirm the incorporation of Al into zeolite structure. Moreover, ^{27}Al MAS NMR measurements indicate that the framework of aluminum species in ZSM-5/MCM-41 is practically the same as in zeolite structure. The catalytic study shows that this micro-mesoporous material is an excellent support for NiW catalysts and Ru catalysts in the hydrotreating of middle distillates. In this paper, it was shown the synthesis of new catalysts based on micro-mesoporous materials and analysis their activity for hydrogenation and ring-opening of aromatic compounds under various reaction conditions, using light cycle oil (LCO) and naphthalene as a model substrate.

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FEATURES OF THE CONVERSION OF PROPANE ON THE STRUCTURALLY LABILE FORM OF CATALYTIC SYSTEMS

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The oil and gas industry plays a big role in the development of mankind. And it's not just about fuel providing of internal combustion engines. From cosmetics to noise-insulating coatings – the products of the oil refining industry are used everywhere.

One of these products is propane. The most famous applying of propane is a fuel. However, it can also be used for the further synthesis of polypropylene, acrylonitrile and propylene oxide.

Since the importance of propane is obvious, and the ways of its obtaining through recycling of associated petroleum gases need to develop, then the catalytic processes have acquired great importance. Catalysis is an effective method of chemical transformation in industry and is of great importance in the petrochemical, oil refining fields.

It is for these reasons that the purpose of this study was to study the features of propane conversion in the presence of vanadites and rare earth vanadates, namely La, Sm, Er. It should be noted that vanadates of REE have a zircon structure, and vanadites of the REE have a perovskite structure. These types of structures have high thermal stability, and perovskite-like structures also have oxygen conductivity.

Vanadites and Vanadates of the REM (La, Sm, Er) were obtained by the solid-phase synthesis method and have a low specific surface area of about 3 m^2/g and a small pore volume.

The experiments were carried out under steady-state conditions, at atmospheric pressure, in a flow-through catalytic unit with a U-shaped quartz reactor. Propane of high purity (99.98 % by weight) was used as feedstock.

The range of the investigated temperature range for the cracking of propane ranged from 298 K to 1143 K, with a step of 50 K, since an increase in the process temperature above 1143 K leads to instantaneous carbonization of the catalyst due to the formation of resins and heavy hydrocarbons. After the reaction, 0.125 ml of the gas mixture was withdrawn through the sampling device and submitted for analysis to a Crystal 5000M chromatograph equipped with a thermal conductivity detector.

In addition to shifting the degree of semi-transformation to lower temperatures, the selectivity to olefins also changes compared to thermal cracking. In the case of catalytic cracking, the yield of olefins increased in the temperature range 623-1123 K.

At 973 K, $SmVO_3$ has a high ethylene selectivity of the order of 90 %, while its yield is 0.8 μM/g × s, while with thermocracking to 1023 K, no formation of ethylene was observed. A further increase in the cracking temperature results in a slight increase in the selectivity for ethylene to a limit of 91 %. The use of lanthanum vanadite as a catalyst made it possible to achieve an ethylene selectivity of 70 % at a temperature of up to 700 K, but there was an insignificant yield of the target product with a conversion of less than 20 %. The use of erbium vanadite shifts the maximum of ethylene selectivity to even lower temperatures, but the propane conversion at this temperature was only 9 %. The increase in temperature leads to a change in the selectivity for ethylene to propylene. So at a temperature of 900 K, the selectivity to propylene is 30 %, but a sharp drop in the yield of light hydrocarbons is observed.

In samarium vanadate, there is a decrease in the selectivity for the formation of ethylene, in comparison with samarium vanadite, for the most active temperature range. But there is an increase in selectivity in the formation of propylene. There is a tendency to increase the yield of ethylene and propylene from lanthanum to samarium, and then their decline.

The activation energy for thermocracking was 105 kJ/mol, and for the reaction using catalysts, a significant decrease in the activation energy was observed, respectively, for $SmVO_3$, $SmVO_4$, V_2O_3, V_2O_5, $LaVO_3$, $ErVO_4$, $ErVO_3$, $LaVO_4$ was 39, 54, 36, 33, 22, 22, 22, 21 kJ/mol.

PP-23

Co PROMOTED HYDROTREATING CATALYSTS: GENESIS OF THE ACTIVE PHASE FOLLOWED BY IN-SITU XAS ANALYSIS

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The treatment of heavy petroleum feedstock and the presence of environmental standards require a constant search for more effective hydrotreating catalysts. It is well known that the active phase for hydrotreating catalysts is the so-called "CoMoS" phase, typically supported on γ alumina. Catalysts based on heteropolyanions (HPA), used to introduce in the same molecular entity promoter and molybdenum at the oxidic level, have shown a better hydrodesulfurization activity compared to catalysts prepared by co-impregnation with ammonium heptamolybdate and cobalt (II) nitrate [1-3]. This study proposes the monitoring of the activation under H_2/H_2S of promoted hydrotreating catalysts, prepared from HPA or conventional precursors and which have undergone various pretreatments (drying, calcination), by time resolved X-ray absorption spectroscopy (Quick-XAS). The experiments, performed at the ROCK beamline of SOLEIL synchrotron, allow the simultaneous monitoring of Co and Mo local orders [3]. Chemometric method based on multivariate curve regression with alternative least squares (MCR-ALS) [4,5] has been used to obtain the concentration profile and the XAS spectra of the pure species involved in the genesis of the active phase. The use of a new XAS data processing method has made it possible to determine and separate the various intermediate species involved in the sulfidation of molybdenum and cobalt.

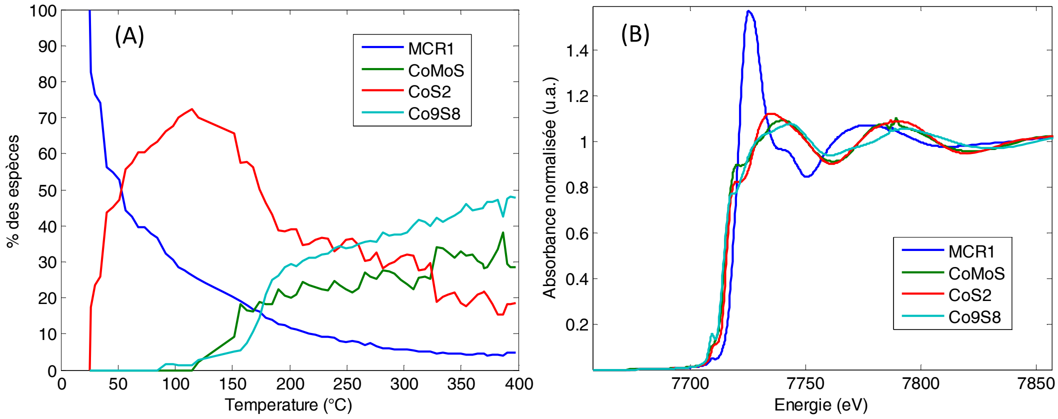

Figure: (A) concentration profiles and (B) XANES spectra obtained by MCR-ALS during the sulfidation of $Co_3Co_2Mo_{10}$-cal at Co K-edge

Sulfidation of molybdenum presented a first oxysulfide intermediate, which structure depends on the catalysts pretreatment, while the second intermediate is identified as MoS_3 on all solids. Regarding cobalt, its sulfidation led to the formation of CoS_2, Co_9S_8 and of a third component exhibiting cobalt-molybdenum contributions and identified as the CoMoS phase, which is an unprecedented result by XAS technique. For the first time, it was thus possible to monitor the percentage of active phase in hydrotreating catalysts as well as its kinetics of formation, depending on the pretreatment of the catalyst.

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PROCESSES OF NON-EXTRACTIONAL DEMERCAPTANIZATION OF OIL AND OIL PRODUCTS

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Demercaptanization (removal) of hydrogen sulphide and light mercaptans or their deactivation is one of the stages of commercial oil preparation. The need to remove these impurities is associated with environmental (high toxicity) and operational (corrosive) aspects.

The need to remove these impurities also applies to heavy oil refining fractions (fuel oil and vacuum gas oils). So, according to European standards, the content of H_2S in fuel oil should be less than 2 ppm.

The main industrial method for removing these compounds is alkaline oxidative demercaptanization, consisting of the stage of sulfur impurities extraction with an aqueous alkali solution followed by the regeneration stage of the extractant. The disadvantage of this technology is the formation of large amounts of sulfur-alkaline waste that requires disposal. The often applied injection method in the formation leads to migration and mixing of toxic waste water with groundwater.

Another method for removing hydrogen sulphide and light mercaptans is a reagent method that does not have these drawbacks. However, it is characterized by rather high absorber costs (10-15 ppm / 1 ppm S). Another approach to demercaptanization processes in which no sulfide-alkaline waste water is formed is the catalytic oxidation of sulfhydryl impurities by oxygen directly in hydrocarbon media. The main oxidation products are non-toxic di- and polysulfides (1):

$$4\,RSH + O_2 \rightarrow 2\,H_2O + 2\,RSSR \qquad (1)$$

It was shown in [1] that metal complexes based on copper salts and nitrogen-containing bases are effective catalysts for the oxidation of hydrogen sulphide and light mercaptans in the process of demercaptanization of oil from various deposits and fuel oil (Table 1, 1-3).

As shown in the table, the catalysts based on water-soluble nitrogenous bases (MEA) are active in the removal of hydrogen sulphide and light mercaptans, but are inactive in the oxidation of thiols from C_3 and higher, which is due to the heterophase nature of the oxidation reaction.

Table 1. Characteristics of the demercaptanization process of oil and petroleum fractions

№	C, g/l	t, h	$[H_2S_0]/[H_2S]$, ppm	$[C_2H_5SH]_0/[C_2H_5SH]$, ppm	gS_{total}/gkt	TON moleS/moleCu
1	0,21	20	150/0	130/34	1,0	40
2	0,061	20	88/0	218/86	3,0	120
3	0,075	4	56/0	58/18	1,0	40
4	0,0038	5	-	*1200/60	250	790
5	0,0324	4,5	-	*1200/0	30	125

1, 2 – oil fields Alibekmola and Chinarevo, catalyst $Cu(CH_3COO)_2/MEA/H_2O/SAS$;
3 – gas condensate fuel oil, $CuCl/MEA/H_2O/SAS$;
4 – vacuum gas oil, $CuCl/C_{22}H_{47}NO_2$ (N-octadecyldiethanolamine)/HCl,
$C_{kt} = 3{,}8*10^{-5}M$, $C_{HCl} = 2{,}8*10^{-4}M$;
5 – vacuum gas oil, $CuCl_2*2H_2O/CuO$/cocamide DEA/H_2O.
* – content of total mercaptans.

To remove heavy thiols proposed catalysts are soluble in hydrocarbons (Tab. 1, 4 and 5). It has been found that the introduction of HCl into the reaction volume significantly increases the activity of catalyst 4 (from TON = 20 to 790). However, the activation of HCl enhances the corrosive activity of the catalyst. The introduction of corrosion inhibitors leads to deactivation of the catalyst. When the inhibitor is introduced into the catalytic system 5 in a ratio of 8/100, corrosion is suppressed while maintaining a high level of activity (TON = 125).

It is shown that the use of the proposed catalysts for non-extraction demercaptanization makes it possible to carry out effective purification of hydrocarbons of various group composition with a sulfur impurity content of 100 to 1000 ppm. In addition, the formation of sulphurous alkaline wastewater is avoided and environmental risks are reduced when transporting and storing petroleum products.

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AQUEOUS-PHASE HYDRODEOXYGENATION OF LIGNIN MONOMER GUAIACOL OVER Ru CATALYSTS SUPPORTED ON MESOPOROUS MATERIALS

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Lignin-cellulose biomass is the perspective renewable carbon-containing feedstock that can be used for both synthesis of hydrocarbon transportation fuels and chemical production. Bio-oil produced by fast pyrolysis of biomass cannot be directly used as transportation fuel because of high water (15-30 wt %) and oxygen contents, poor chemical stability and immiscibility with hydrocarbon fuels [1]. Hydrodeoxygenation (HDO) is a process similar to hydrofining performed to improve the quality of bio-oil for introduction to co-processing in refinery; in the course of this process, phenolics from lignin-derived part of bio-oil are converted into cycloalkanes, which are more effective energy carriers. In addition to high water content, bio-oil contains a large number of low-molecular-weight compounds formed during fast pyrolysis of cellulose – acids (formic, acetic), alcohols (methanol, ethylene glycol), esters (methyl formate), ketones (acetone, hydroxyacetone), aldehydes (formaldehyde, glyoxal) *etc*, up to ~35 wt %, which substantially affects the on catalytic activity and product distribution for HDO of bio-oil-derived phenolic compounds [2].

The HDO of lignin monomer guaiacol (2-methoxyphenol) was investigated over Ru catalysts based on mesoporous zirconium and aluminium silicates using water and methanol/water solution as the solvent (in a 1:1 wt %). As HDO of phenolics will produce water as a by-product, water-resistant catalysts would be promising choice for this type of reaction. Mesoporous aluminosilicate (Al-HMS with Si/Al ratio 10) and mesoporous *m*-ZrO_2-SiO_2 with Si/Zr ratio 1.3 were synthesized. The supported catalysts were prepared by an incipient-wetness impregnation method, characterized with NH_3-TPD, TEM, XPS, N_2 adsorption–desorption methods (Table 1) and tested in the guaiacol HDO at 200 °C and 5 MPa H_2.

Table 1. Physicochemical characteristics of catalysts

Sample	$S_{sp.}$, (m^2/g)	D_{pore},(Å)	Total number of acid sites, (μmol/g NH_3)
Ru/Al-HMS(10)	876	37	286
Ru/*m*-ZrO_2-SiO_2	646	38	451

The main reaction products determined by GC-MS were cyclohexanes (cyclohexane, methylcycloxehane), cyclohexanols (cyclohexanol, methoxycyclohexanol) and phenols (phenol, cresol) (Table 2). It was established that product distribution substantially depends on the properties of the support. Phenols, which are known as coke precursors, were actively formed by more acidic Ru/*m*-ZrO_2-SiO_2 catalyst. The best hydrodeoxygenation activity was achieved on Ru/Al-HMS(10) catalyst in water with high selectivity to cyclohexanes (86 %), which can be the components for a bio-based liquid transportation fuel.

Table 2. Hydrodeoxygenation of guaiacol

	Ru/ Al-HMS(10)	Ru/ *m*-ZrO_2-SiO_2	Ru/ Al-HMS(10)	Ru/ *m*-ZrO_2-SiO_2
Solvent	H_2O : MeOH		H_2O	
Conversion, %	90	79	100	100
	Selectivity, %			
cyclohexanes	72	73	86	42
cyclohexanols	20	9	14	58
phenols	8	18	0	0

The developed Ru-containing catalysts based on mesoporous materials seem to be highly attractive for biorefining application.

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IN SITU REACTIVATION OF SPENT NiMoP/γ-Al_2O_3 FOR HYDRODESULFURIZATION OF STRAIGHT-RUN GAS OIL

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The *In Situ* reactivation of spent NiMoP/γ-Al_2O_3 catalyst has been investigated in the hydrodesulfurization (HDS) of straight-run gas oil. The spent NiMoP/γ-Al_2O_3 was treated by a solution of xylenes and 2,6 bis 1 hydroxy 1,1 diphenyl methyl pyridine as organic additive in order to eliminate the coke impregnated. Then, the catalyst was dried at 120 °C. The catalysts were reactivated *In Situ* with molybdenyl acetylacetonate; the catalysts labeled and pretreatments are shown in **Table 1.** The sulfided catalysts after and before HDS reaction were characterized by nuclear magnetic resonance (NMR), Raman spectroscopy, temperature-programmed reduction (TPR) and X-ray photoelectron spectroscopy (XPS).

The Highest activity of the spent materials was found for the CatAXAceMo **(Table 2).** NMR results suggested that the pretreatment with xylenes and organic additive on the spent catalyst decreased the amount of aromatic coke on the catalytic surface. In this regard, Raman spectroscopy showed a decrease of coke crystallite size in comparison with the catalyst without pretreatments; 13.41 Å vs 20.82 Å [1], respectively. Elemental analysis of CatAxAceMo and CatRef presented 3.14 and 7.60 on C/Al ratio. These results are in agreement with the coke crystal size seen by Raman spectroscopy. On the other hand, the CatAxAceMo displayed higher MoS_2 species than CatRef; 33.2 % vs 9.3 %; respectively. In this sense, the TPR profile of CatAX showed higher H_2S production at low temperature (< 300 °C) than the CatRef. This result could suggest that the pretreatment with xylenes and organic additive favored the production of "coordinatively unsaturated sites" (CUS) related to the catalytic activity in HDS [2]. The increment of sulfurization degree and the decrease of coke on the catalytic surface provoked by the organic additive in the *In Situ* reactivation resulted in a higher gas oil HDS activity.

Table 1. Catalysts and pretreatments

Catalyst	Synthesis conditions	Additive	Xylenes	AceMo
CatRef	NiMoP/γ-Al_2O_3	-	-	-
CatAX	NiMoP/γ-Al_2O_3	X	X	-
CatAceMo	NiMoP/γ-Al_2O_3	-	-	X
CatAXAceMo	NiMoP/γ-Al_2O_3	X	X	X

Table 2. Activation energy, conversion[a] and reaction rate constant at steady state (18 hours) in the HDS of straight-run gas oil over NiMoP/γ-Al_2O_3 sulfided catalysts

	CatRef	CatAX	CatAceMo	CatAXAceMo
Ea (kcal/mol)	27.2	27.1	26.0	34.4
$X_{340\,°C}$ (%)	86.0	86.0	81.9	84.2
$X_{360\,°C}$ (%)	94.9	94.2	92.4	96.4
$X_{380\,°C}$ (%)	98.2	98.2	97.2	98.9
$khds_{340\,°C}$ $(Sw\%)^{-0.5}*h^{-1}$	3.4	3.4	2.7	3.1
$khds_{360\,°C}$ $(Sw\%)^{-0.5}*h^{-1}$	6.9	6.3	5.3	8.7
$khds_{380\,°C}$ $(Sw\%)^{-0.5}*h^{-1}$	13.2	13.2	10.0	17.2

[a]Reaction conditions were: P = 56 kg/cm^2; total reaction time per catalyst ca. 56 h; fixed bed reactor

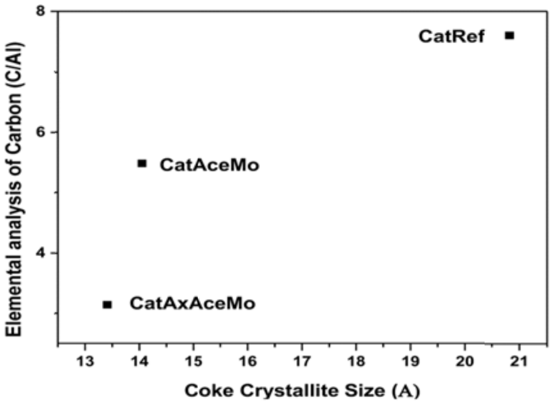

Figure 1. Crystallite size vs Elemental analysis of Carbon

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PP-27

THERMODYNAMIC EQUILIBRIUM OF LIGHT NAPHTHA HYDROISOMERIZATION REACTIONS

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The reaction network for the hidroisomerización of light naphtha has been generated based on a bifunctional mechanism and considering the formation of olefins as intermediaries. There were considered 72 molecular reactions involving 33 different hydrocarbons. The thermodynamic equilibrium of these reactions has been studied with the Peng-Robinson equation in an equilibrium reactor in ASPEN Plus®. To determine the thermodynamic equilibrium in a systematic way, a sensitivity analysis has been carried out based on the selection of different combinations of operating conditions determined from a statistical analysis using the Taguchi method. The results of the simulation consider the performance of isomerate (i-C_5 + i-C_6) and its octane number (RON). Thus, a mathematical model has been obtained that allows to accurately predict the maximum performance of isomerate in thermodynamic equilibrium in the range of operating conditions studied. The maximum isomerate yield thus obtained was 91.58% weight at optimal conditions of temperature, pressure and H_2:HC molar ratio.

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UPGRADING OF CRUDE OIL ASSISTED WITH ANIONIC SURFACTANT AND CARBON PARTICLE CATALYST IN STABLE EMULSION

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The catalytic activity associated to carbon particle (graphite) and anionic surfactant (SDS) in a stable emulsion was studied on the hydrocracking of Maya crude oil. The emulsion was prepared with an oil-water 50/50 wt/wt ratio at 1000 rpm for 1 hr, 2 wt % carbon particles, and anionic surfactant in different concentrations from 0.25-1 M. The time of crude oil precipitations, coalescence, creaming, and the stabilization were measured in the emulsion formation. The characterization of the products was performed by infrared spectroscopy analysis, thermogravimetic analysis, and interfacial tension. The results showed that the hydrocracking reaction was favorable when the emulsion was stable. The thermogravimetric studies showed that the carbon particle was catalytically active from 200 to 700 °C and the thermogravimetric residual was negligible. Due to the instability of the emulsion, the reaction was shown to be highly exothermic and explosive, and hence the reaction was interrupted.

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PP-29

EXPERIMENTAL STUDY OF IN-SITU UPGRADING FOR HEAVY CRUDE OIL USING COPPER-BASED CATALYST UNDER STEAM INJECTION CONDITION

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As light crude oil production approaches peak, attention has been shifted to vast deposits of heavy oil and bitumen to offset the rising fuels demand. However, heavy oil and bitumen are known to constitute high-boiling molecules which gives them characteristic high viscosity, high density/low API gravity, low yields of low-boiling fuel distillates, and high heteroatom content compared to light oil. The main challenges are to find best methods for the production and processing of heavy and extra-heavy oil to get it with lower viscosity and more light fractions [1-2]. Steam injection plays an important role among methods about enhancing oil recovery especially in the extraction of high-viscosity oils and natural bitumens, but with the passage of time efficiency of this method has been decreased, but with the passage of time efficiency of this method has been decreased, so it is necessary to used new method that called steam catalyst co injection that allows to upgrading (partial oil refining in the reservoir).

Recently, hydrothermal catalytic process in reservoir conditions (in-situ upgrading) has got remarkable attentions. In this study, the feasibility of the in-situ upgrading of Ashal’cha crude oil (Tatarstan region Russia) using steam and copper-based catalyst co injection at different temperatures from 200 °C to 375 °C under high pressures for 24 h using a stainless-steel 500-ml batch reactor was investigated.

The results were compared as the changes in the density/API gravity, viscosity, chemical composition (SARA analyses), Fourier Transform Infrared Spectra (FT-IR), elemental analysis (EL), molecular weight analysis and nuclear magnetic resonance (^{13}NMR) of heavy crude oil before and after thermal treatment. In general we can concluded that, the content of resin and asphaltenes is decreased and the average molecular weight of heavy oil is reduced after hydrothermal catalytic process. Whereas saturated and aromatic hydrocarbons increased, due to the destruction of its high molecular weight components [3]. Viscosity and API gravity changes were explored. As it's known, at high temperatures coke should be formed [4]. During the process, especially at high temperatures of 300 °C and more, coke was formed, at which it was reduced with the simultaneous use of steam with the copper-based oil-soluble catalyst.

In this study we used an oil soluble catalyst that, after injection, it well a good distributed in the reservoir, and during the process the catalyst is transformed into nanoparticles. The catalyst was analyzed after hydrothermal catalytic upgrading using XRD and TEM microscopy methods, and it was noticeable that the copper-based oil-soluble catalysts was converted into nanoparticles.

Thus, these results indicated that using copper-based oil-soluble catalysts in hydrothermal catalytic system have a great potential for upgrading of heavy oil.

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DEVELOPMENT OF NANOSTRUCTURED NICKEL PHOSPHIDE FOR HYDROTREATING OF OXYGEN-CONTAINING FEEDSTOCKS

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Hydrotreating processes of feedstocks should constantly be developed because quality of oil feedstocks nowadays decreases as well as environmental requirements to fuels become stricter. In addition, there is a tendency to use non-traditional sources of crude oil as a feedstock. Traditional hydroprocessing catalysts have certain disadvantages so the search for new catalysts always becomes a goal of current interest.

Widely used noble metal catalysts of hydrogenation processes are characterized by high price and inapplicability for feedstocks with high-sulfur content. At the same time, the activity of another class of hydrogenation catalysts, transition metal sulfides, decreases over time in low-sulfur feedstocks. It happens because of substitution of sulfur atoms by oxygen atoms.

An alternative class of hydroprocessing catalysts is a number of transition metal phosphides. These catalysts are explored insufficiently and deserve more attention. It is known that metal-rich phosphides demonstrate high activity in hydrogenation, hydrodesulfurization and hydrodenitrogenation processes [1, 2].

Metal phosphates and organic derivatives of phosphine are often used as phosphorous source for transition metal phosphides, hypophosphites however are used rarely. It is well known that organic derivatives of phosphine can be oxidized to phosphoxides by air oxygen. In order to obtain phosphides from phosphates it needs applying high temperature (600-800 °C), which is difficult to carry out in a laboratory. Hypophosphites don’t have disadvantages mentioned above. They are easily transformed to phosphides at low temperatures under inert or reduction conditions [2].

One of the most active phosphides in hydroprocessing is nickel phosphide Ni_2P. It has higher activity than phosphides of other transition metals like W, Mo, Co, Fe [1].

In present work, synthesis of nickel phosphide *in situ* during the process of hydrogenation/hydrodeoxigenation of guaiacol has been developed. Guaiacol, monomer of lignin, is one of the components of bio-oil. Bio-oil is a perspective fuel, which is obtained from biomass by fast pyrolysis [3]. Because of the large amount of oxygen-containing compounds, bio-oil is not suitable for direct use as a motor fuel, so its hydrotreating is required.

Catalytic tests were carried out at 350-400 °C and at initial pressure of hydrogen of 40-60 atm. Cyclohexane, benzene and phenol were obtained as main products. The qualitative and quantitative composition was determined by GC-FID and GC-MS analyses. Obtained nickel phosphide was analyzed by a set of physico-chemical methods.

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HYDROGENATION AND SULFUR REMOVAL VIA WATER GAS SHIFT USING DISPERSED UNSUPPORTED CATALYSTS

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The depletion of reserves of light petroleum led to the exploration and production of heavy and extraheavy crude oils, characterized by high content ofimpurities as well as producing low yields of distillated fractions [1, 2]. Refineries being increasingly supplied with lower-quality feedstocks. At the same time there are progressively stringent environmental legislations that limit the content of sulfur and aromatics. In this respect the demand for residue and heavy crude oil upgrading by means of hydroprocessing has increased considerably [3], resulted in hydrogen production are becoming ever more important in refinery operations.

At the last few decades a lot of researches are devoted to the development of dispersed catalysts as alternatives to the supported catalysts currently used for upgrading the quality of heavy feedstocks [2, 3]. Dispersed catalyst systems have a number of advantages over the supported ones. Their microsizes provide a high catalytic metal utilization. Thanks to high interaction of oil and hydrogen on the high surface area of the small particles more efficient activation of molecular hydrogen is achieved resulted in high suppressibility of coke formation and stability to deactivation. Also, there are no diffusion limitations making contact of reagent with active metal more difficult as in the case of supported catalysts [3-6].

The requirement to increase hydrogenation processes in refineries, coupled with the need to process heavier crudes and residua, has resulted in increased demand for hydrogen. So, it would be highly beneficial to the industry to develop refinery processes involving in situ hydrogen generation via the water gas shift reaction (WGSR). It is well known, that transition metal sulfides (molybdenum, tungsten) being major components of hydrorefining catalysts are also highly active in water gas shift (WGS) [7, 8]. Thus, the H_2O/CO system can be used as a hydrogen sourse for hydrogenation/hydrodesulfurisation reactions.

The purpose of this work is to examine the efficiency of in situ generated Mo-based dispersed catalysts in WGS and to test its activity in hydrogenation/hydrodesulfurization of model compounds (methylnaphtalenes, bensothiophene and it's derivatives).

The Mo- and W-based dispersed unsupported catalysts, promoted by Ni or Co, obtained in situ by termal decomposition of oil-soluble metal-containing precursors, were characterised by XPS, TEM and elemental analysis.

It was shown, that dispersed unsupported Ni(Co)-Mo(W) catalysts are active in WGS and provide hydrogen generation in H_2O/CO system resulted in hydrogenation of poliaromatics and sulfur-containing substrates.

It is found, that Mo-containing dispersed catalysts promoted by Ni, are most active at the temperature of 380 °C and CO pressure 5 MPa.

Also, the influence of H_2O/CO molar ratio on substrates conversion was studied. It was found, that optimal H_2O/CO ratio is at the range of 1.5-2.0.

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IMPROVED COMBUSTION BEHAVIOR OF HEAVY OILS USING OIL-SOLUBLE METAL-BASED CATALYST IN IN-SITU COMBUSTION PROCESS

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In-situ combustion (ISC) is an effective thermal recovery method for heavy oils. It is widely accepted that the success of an ISC process generally depends on developing a stable combustion front [1-3]. The purpose of this work is to develop oil-soluble metal-based catalyst to enhance the combustion of heavy oils, and thus improve the stability of combustion front.

In this work, oil-soluble metal-based catalyst was synthesized. Its pyrolysis and oxidation behavior at nitrogen and air atmosphere, respectively, were investigated by TG-FTIR and DSC. Its catalytic effect on combustion was evaluated using high-pressure differential scanning calorimetry (HP-DSC) and adiabatic reaction calorimeter (ARC). Kinetic parameters were calculated using different models and model-free methods to quantitively characterize the catalytic effect. Simultaneously, SEM and XRD were employed to analyze the variation of catalysts before and after oxidation with/without crude oils to better understand the catalytic mechanism.

The oil-soluble metal-based catalyst significantly improved the combustion behavior of heavy oils including shifting reaction intervals into lower temperature range, reducing activation energy, improving combustion efficiency of high-temperature oxidation (HTO), and decreasing ignition temperature and induction time. TG-FTIR, DSC, XRD and SEM results showed that before 350 °C the metal-based catalyst was totally decomposed, and metal oxides nanoparticles were in-situ formed. The high catalytic activity can be attributed to the highly dispersed state of copper stearate and in-situ formed metal oxides that increased the dispersed active sites. Simultaneously, the high surface area of in-situ formed metal oxides nanoparticles is believed to play an essential role in the process of coke formation and combustion. Additionally, the organic side chain of oil-soluble metal-based catalyst is also considered to be responsible for reducing the ignition temperature. The significant improvement of the combustion efficiency of HTO and reduction of ignition temperature and induction time indicated that oil-soluble metal-based catalyst not only has a great potential for improving the stability of combustion front, but also can promote ignition process behaving as an initiator in a real ISC process.

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HYDROGEN PRODUCTION BY SORPTION-ENHANCED STEAM REFORMING OF HYDROCARBONS WITH AUTOTHERMAL SORBENT REGENERATION IN A SUPER-ADIABATIC HEAT FRONT OF CATALYTIC COMBUSTION REACTION

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Active development of hydrogen-based energy technologies is in a great extent limited today by availability of efficient and low-cost hydrogen production. The most promising technological way in this direction is application of sorption-enhanced catalytic methane steam reforming. This approach, first formulated even in 19-th century [1], has received a lot of attention in modern practice since 1980-s and now is developing extremely fast by numerous research groups worldwide [2]-[6].

The sorption-enhanced catalytic methane steam reforming concept except usual methane and carbon monoxide steam conversion catalytic reactions, widely applied in conventional technologies

$$CH_4 + H_2O \Leftrightarrow CO + 3\,H_2 \tag{1}$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \tag{2}$$

also includes the adsorption of product CO_2 by solid sorbent:

$$MeO + CO_2 \Rightarrow MeCO_3 \tag{3}$$

leading to favorable equilibrium conditions for reactions (1), (2) and to achievement of high yield of high-purity hydrogen in one conversion stage. After saturation of sorption capacity of the sorbent it is necessary to provide its regeneration according to backward reaction

$$MeCO_3 \Rightarrow MeO + CO_2 \tag{4}$$

Though the research efforts in this area are very intensive and active, the achieved level of process efficiency is still far from ideal. While performance of basic reaction cycle (reactions 1-3) is well studied, the source of most complications is sorbent regeneration reaction stage (4). The method here is “isothermal” sorbent regeneration, meaning external bed heating during regeneration stage, characterized with high level of inefficient energy losses. Moreover, efficient and uniform heating of the bed in this case is possible only in reactors with relatively small diameter and this factor limits the scale of approach application or requires unreasonable complication of reformer design.

Much more promising, but much less studied, regeneration method is adiabatic or autothermal regeneration, meaning heating of the catalyst-sorbent bed by exothermic reaction performed directly inside the bed [7],[8]. In this case CO_2-sorbent regeneration is performed according to reaction (4) with supply of heat, necessary for regeneration, by oxidation of available combustible substances (say, hydrogen or methane) in the air flow directly in the adiabatic sorbent-catalyst bed:

$$H_2 + \frac{1}{2} O_2 \Rightarrow H_2O \quad (5)$$

$$CH_4 + 2O_2 \Rightarrow CO_2 + 2H_2O \quad (6)$$

As shown by mathematical modelling, both process stages may be performed in a periodical “traveling heat wave” regime and in this case, it becomes possible to create at each process stage the axial profiles of catalyst temperature, optimal for performance of next stage. Especially efficient operation mode may be realized by application of counter-current (or reverse flow) operation, when methane/steam and air/fuel mixtures are fed into processor bed in opposite directions.

The evident advantage of the proposed regeneration mode is that combustion heat produced is distributed uniformly around the bed sequence and, therefore, the regeneration efficiency does not depend upon the bed diameter. This circumstance opens the way for creation of cheap and reliable adiabatic packed bed methane processors of unlimited processing capacity instead of either conventional single-tube reactors with external heating with very limited productivity or expensive and complicated multi-tubular reactors for high capacities.

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INVESTIGATION OF $GdCo_xFe_{1–x}O_3$ (x = 0; 0,5; 1) PEROVSKITES AS CATALYSTS FOR SYNGAS PRODUCTION VIA DRY REFORMING OF METHANE

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Natural gas is a clean energy source, and the demand for it is growing steadily. It is considered that natural gas will become the dominant energy source in the early to middle of this century. The main component of natural gas is CH_4, and it is mainly converted to synthesis gas (H_2 + CO), which is directly used as fuel or can be converted to liquid fuel or other chemicals using the synthesis of Fischer-Tropsch method.

Dry reforming of methane (DRM) is considered as an alternative method of synthesis gas production, which has several advantages over those used in industrial steam reforming. DRM advantages are lowering temperature and a substantial pressure drop of the process. It is significantly reduces the economic costs. But the main obstacle to using DRM process in industry is that at present there are practically no catalysts that would not have been subjected to deactivation due to coke formation [1].

The aim of this work was the study of the possible use $GdCo_xFe_{1–x}O_3$ (x=0; 0,5; 1) perovskite-type complex oxides as a catalysts for the dry reforming of methane and the effect of substitution of iron by cobalt in B-site of these oxides on its catalytic performance.

The investigation objects in the syngas production were $GdFeO_3$, $GdCo_{0,5}Fe_{0,5}O_3$ and $GdCoO_3$ complex oxides obtained via sol-gel technology [2]. These samples were characterized by the complex of physico-chemical methods. According to XRD data, all initial samples are single-phase and have a perovskite structure of the ABO_3 type. The data of X-ray photoelectron (XPS) and Mossbauer spectroscopy confirmed the presence of the B-site atoms heterovalent state (Fe^{+3} and Fe^{+4}; Co^{+2} and Co^{+3}) in the perovskite structure. The scanning electron microscopy method was displayed that the samples had a porous structure with a grain size about 200 nm.

All catalytic tests were carried out at atmospheric pressure in the temperature raised from 773 to 1223 K under continuous flow of reactant gases with a CH_4:CO_2 = 1:1 ratio. The exit gases were analyzed by gas chromatography (Crystal 2000M), equipped with a thermal conductivity detector (TCD) and flame ionization detector (FID).

The catalytic activity dependence study of the perovskite-type oxides $GdCo_xFe_{1-x}O_3$ (x = 0; 0,5; 1) on the cobalt proportion in the samples showed that the perovskite with x = 1 possessed the highest catalytic performances: the methane and carbon dioxide conversions were 98 and 99 % at T = 1223 К, respectively (table 1). The determination of products yields (H_2 and CO) showed their increase depending on the cobalt proportion in the order: $GdFeO_3$ < $GdCo_{0,5}Fe_{0,5}O_3$ < $GdCoO_3$.

Table 1. Catalytic performances of the investigated samples at T = 1223 K

Catalysts	***α (CH_4),%***	***α (CO_2), %***	***Y (CO), %***	***Y (H_2), %***	***H_2:CO***	***Carbon balance, %***
$GdCoO_3$	98	99	74	87	1,06	75
$GdCo_{0,5}Fe_{0,5}O_3$	92	99	65	72	1,1	78
$GdFeO_3$	45	60	41	24	0,6	89

This, however, despite the highest catalytic performance, the maximum carbon deposition was observed over $GdCoO_3$ catalyst. But all the same, the gadolinium cobaltite demonstrated its high stability: catalytic properties of this sample were retained during repeated experiments and almost unchanged after 130 operating hours.

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$NiMo/Al_2O_3$ HDS CATALYSTS FROM Mo-BLUE PRECURSOR

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The use of various types of organic additives during hydrodesulfurization (HDS) catalysts preparation has resulted in materials of enhanced S removal activity. Different beneficial effects have been related to chelators addition those mainly being attributed to their strong chemical interaction with the promoters (Ni and Co) [1]. Those complexing organic compounds could enhance molybdenum-promoter interaction during catalyst sulfiding that resulting in materials of increased hydrodesulfurizating activity [1, 2]. Regarding non-chelating ligands as HDS catalysts additive so far no general agreement about the origin of their beneficial influence has been reached. It appears that enhanced HDS activity could be originated by a number of factors [3, 4]. In this work, saccharose (SA) was used as organic additive in simultaneously impregnated phosphorous-doped $NiMo/Al_2O_3$ hydrodesulfurization (HDS) catalysts (Mo, Ni and P at 12, 3, and 1.6 wt%, respectively). One-pot impregnating solutions were prepared by MoO_3 digestion (~353 K) in diluted aqueous H_3PO_4, followed by $2NiCO_3 \cdot 3Ni(OH)_2 \cdot 4H_2O$ addition. Saccharose (SA, SA/Ni=0.5, 1, 2 and 3) was dissolved in originally emerald green-impregnating solutions which changed to cobalt blue by aging at room temperature due to Mo-blue formation by partial molybdenum species reduction. After sulfiding of samples impregnated with SA supported MoS_2 particles of shorter slabs but enhanced stacking were observed. Meanwhile, both Ni dispersion and sulfidability increased with the amount of organic modifier. Enhanced hydrodesulfurization activity in dibenzothiophene (DBT) HDS was registered for catalyst obtained from Mo-blue precursor as to that of corresponding material from emerald-green Ni-Mo-P impregnating solutions (Table 1). However, in solids impregnated at high saccharose content (SA/Ni=3) enhanced mixed “NiMoS” phase formation was not reflected in improved activity (Table 1) probably because excessive amount of carbonaceous deposits from SA residua decomposition could partially plug the porous network of sulfided formulations. That fact seemed to provoke limited accessibility of reactant molecules to surface active sites. Mo-blue precursor seemed to play a decisive role in obtaining HDS catalysts of improved properties. Saccharose results a very convenient additive to produce catalysts of enhanced HDS activity.

Table 1. Pseudo first order intrinsic kinetic constant values in DBT HDS over sulfided catalysts prepared with and without SA

Cat.	$k^1\times10^{-4}$ $\mathrm{m^3\ kg_{cat}^{-1}\ s^{-1}}$	$k^2\times10^{-4}$ $\mathrm{l\ g_{Mo}^{-1}\ s^{-1}}$	$k^3\times10^{-1}$ $\mathrm{l\ mol_{Mo4+}^{-1}\ s^{-1}}$	$k^4\times10^{-23}$ $\mathrm{at._{Mo4+edge}^{-1}\ s^{-1}}$	$k^5\times10^{-23}$ $\mathrm{(NiMoS)_{slabs}^{-1}\ s^{-1}}$
SA(0)	1.35	11.25	1.55	1.29	3.38
SA(1)$_g$*	1.64	13.71	-	-	-
SA(0.5)	2.04	17.00	-	-	-
SA(1)	2.40	20.04	2.66	1.52	5.43
SA(2)	2.19	18.27	2.34	1.18	5.62
SA(3)	0.28	2.32	0.32	0.18	0.38

*: Prepared from emerald-green impregnating solution
k^2: k^1 adjusted by Mo content in formulations
k^3: k^2 adjusted by Mo^{4+} content (as determined by XPS analysis) in sulfided formulations
k^4: k^3 adjusted by atomic Mo^{4+} content at edges (as determined by HR-TEM, in sulfided formulations
k^5: Activity per site, k^4 adjusted by $(NiMoS)_{edge}$ content (as determined by XPS) in sulfided formulations

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VIRTUAL PRESENTATIONS

MICROEMULSION CATALYSTS: HYDROTHERMAL SYNTHESIS AND ACTIVITY IN THE REACTION OF HYDROCRACKING OF HEAVY HYDROCARBONS

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In the last decade, special attention has been paid to the development of nanocatalytic systems, including the development of ultrafine catalyst compositions for catalytic recovery and upgrading of heavy and extra-heavy oil under both in situ and ex situ conditions. This approach, which was originally started in preparative purposes to create new promising materials for nano-reactors, is now being practically implemented in several process technologies (CAPRI processes- CAtalytic upgrading PRocess In-situ, Combined EOR-in-reservoir-upgrading method [1-2]. According to existing estimates, the use of nanotechnology allows to increase the oil recovery factor from 50 %, which is the upper limit using traditional chemical methods of oil production intensification, up to 70 %. In the Russian Federation, the possibilities of using nanoscale and ultradisperse particles of catalysts dispersed in hydrocarbon media for use in slurry and blacking reactors for the hydroconversion of heavy petroleum feedstocks are being actively studied [3].

In this paper, hydrothermal method for preparing microemulsion oxide catalysts based on cobalt and iron nanoparticles for the conversion of heavy hydrocarbons has been described. The method of preparing the catalyst compositions is based on a combination of double emulsion technologies and hydrothermal hydrolysis of iron nitrates and cobalt nitrates under sub-critical conditions at temperatures of 180-220 °C and a pressure of up to 20 atm to obtain nanomaterials with controlled particle sizes of mixed oxides.

The results of studies of the catalytic activity of synthesized catalyst samples in the model reaction of hydrocracking of asphaltenes (the conversion of heavy hydrocarbons into more valuable light hydrocarbons) in the temperature range 623-773 K are presented.

Hydrothermal synthesis was carried out in a laboratory high pressure plant in an inert gas stream using various additives that accelerate hydrolysis. It has been experimentally established that it is optimal to obtain Co_3O_4 with a particle size of

16.2 to 25 nm using Co $(NO_3)_2 * 6H_2O$ cobalt nitrate as a precursor, and $CO(NH_2)_2$ urea as the added component at different molar ratios from 4.0 to 0.15) of nitrate to urea. In the joint hydrolysis of cobalt nitrate and ferric chloride in the presence of carbamide, the maximum yield of hematite with a crystallite size of 20 nm was observed when equimolar ratios of hydrolysable compounds and carbamide were used.

The sedimentation stability of the synthesized microemulsions was determined by centrifugation at 2600 rpm after 24 hours holding at room temperature. To control the dispersion of emulsion size, laser correlation spectroscopy methods (emulsion size determination) and high-resolution electron microscopy (TEM) and XRF (to determine the size of metal oxides after heat treatment of emulsions) were used. It was found that the size of the obtained experimental samples of microemulsions of oxide catalysts is 320-360 nm with the sizes of crystallites of metal oxides of 20-25 nm.

The possibility of choice of regimes of hydrothermal synthesis of nanomaterials with controlled particle sizes of mixed cobalt and iron oxides has been determined and optimal conditions (temperature, pressure, duration of synthesis, content of additives accelerating the hydrolysis of metal salts) for synthesis of active catalytic systems for hydrocracking reaction of heavy hydrocarbons.

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SLURRY CATALYST SYSTEMS FOR HYDROCONVERSION OF HEAVY PETROLEUM FEEDSTOCKS

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Currently, many researchers are involved in studies on heavy oil hydroconversion processes performed in the presence of unsupported catalysts. The most effective unsupported hydroconversion catalysts seems to be ultrafine and nanosize catalyst particles, which can be produced *by thermochemical approach in* reverse emulsions medium [1-3]. Comparison of the existing methods for production of nanoscale metal sulfide particles, mainly MoS_2, shows that the properties of synthesized catalysts can vary considerably depending on the method and synthesis conditions. Reverse emulsions way allows to vary properties of the synthesized particles in a wide range [2, 3]. Our research is focused on the preparation of MoS_2–slurry with particle size in nano-/ultradisperse range. As the catalyst precursors were applied water-soluble metal salts, dissolved in aqueous phase of reverse emulsions. The choice of water-soluble metal salts is mainly justified by their thermal properties, providing precursor transformation to metal oxides and sulfides. The continuous phases of reverse emulsions were represented by individual hydrocarbons and commercial samples of heavy petroleum feedstocks.

The established effects make it possible to develop approaches for production of MoS_2–slurry catalysts with controlled particle size, structure and phase composition. These characteristics are sensitive to procedure scheme and type of sulphiding agent, parameters of the reaction medium and the regime of thermal treatment. At optimal parameters of the emulsion system and synthesis conditions in the medium of high-boiling hydrocarbons, we formed slurry catalysts containing up to 10 % wt. per dispersed phase with the particle size in the nano-/ultra-disperse range (10-300 nm). The catalytic activity nano-/ultra-disperse slurry catalysts is determined by properties of dispersion medium and dispersed phase, which tend to be stabilized by native petroleum surfactants.

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VP-3

THE EFFECT OF HYDROGEN ON THE CONVERSION OF A MIXTURE OF C_7H_{16}:C_4H_{10} ON THE MOR / WO_4^{2-} - ZrO_2 CATALYTIC SYSTEM

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The involvement of gaseous alkanes to the formation of C-C bonds with other alkanes is an actual problem for their aimed utilization. The formation of bimolecular intermediates with the participation of butane molecules is well known. The present report presents the results of a study of conversion of a mixture of n-C_7H_{16}: C_4H_{10} on a composite catalyst, the component of which is the zeolite MOR (M) or Al_2O_3 (A) WO_4^{2-}-ZrO_2 (WZ) and the effect of hydrogen on this transformation.

Conversion of the C_7H_{16}: C_4H_{10} mixture was studied in a flow type quartz reactor under the following conditions: C_7H_{16}:C_4H_{10} = 1:1 (mole) WHSV = 2.0 h^{-1} and GHSV = (250 h^{-1}), H_2/CH = 3, T = 140-200 °C and atmospheric pressure. The reaction products were analyzed by gas chromatography.

Comparative studies have shown that, unlike n-C_4H_{10}, the C_7H_{16} effectively isomerizes on the catalysts used, regardless of the A or M component of the composite catalyst. However, the conversions of the mixture of n-C_7H_{16}:C_4H_{10} on the MWZ and AWZ catalysts differ significantly. Under the influence of n-C_4H_{10} AWZ is deactivated, while MWZ, despite some decrease in activity, maintains its stability (Fig. 1).

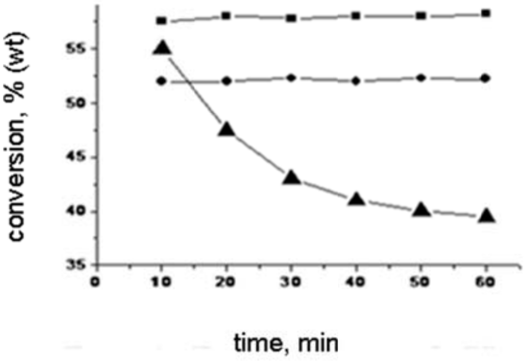

Fig. 1. Effect of n-C_4H_{10} on the conversion of n-C_7H_{16}. T = 200 °C.
A-WZ: ■-н-C_7H_{16}; ●-н-C_7H_{16}; ▲-н-C_4H_{10}

It can be seen from the table that under the influence of n-C_7H_{16} occur both the intensification of the conversion of n-C_4H_{10} and the change in the distribution of the products of its transformation (table).

Table. Effect of temperature on the conversion and distribution of transformation products of a mixture of n-C_7H_{16}:n-C_4H_{10}.The catalyst is M-WZ; n-C_7H_{16}:nC_4H_{10}=1: 0.3

temperature, °C	140	160	180	200
conversion, %				
n-C_7H_{16}	4.2 (4.6)	14.3(15.5)	20.5 (22.3)	52.6 (58.7)
n-C_4H_{10}	4.0 (~1)	11.2(2)	16.3 (3.2)	8.6 (5.0)
Distribution of products, % (by mass)				
C_1-C_2	-	-	-	1.0
C_3	-	-	0.4	13.7
i-C_4	-		1.6	16.4
i-C_5	39.2	30.5	15.3	10.5
n- C_5	0.5	0.6	0.5	0.3
i-C_6	36.1	27.2	14.7	9.0
n-C_6	0.7	0.8	0.6	0.4
i-C_7	20.3	32.5	66.2	48.7
C_{8+}	3.2	3.0	0.7	-

*The individual conversions of n-C_7H_{16} and n-C_4H_{10} are indicated in parentheses

The increase in the yield of C_5-C_6 paraffins and the presence of C_{8+} alkanes in the products of conversion of n-C_7H_{16}: C_4H_{10} mixture suggests that the formation of these compounds is preceded by the formation of a bimolecular intermediate [C_{11}]. The formation of this intermediate occurs with the participation of the WZ centers, whose function is performed by the electrophilic oxygens of the volframate ion;

$$ZWO^{\delta+} + n\text{-}C_7H_{16} \rightarrow ZWO^{\delta-}H\text{-} - C_7^{\delta-}H_{15} \qquad (1)$$

$$ZWO^{\delta-}H\text{-} - C_7^{\delta-}H_{15} + n\text{-}C_4H_{10} \xrightarrow[-H_2O]{} ZW + [C_{11}] \overset{H_2}{\rightarrow} \text{products} \qquad (2)$$

$$ZW + H_2O \rightarrow ZWO^{\delta+} + H_2 \qquad (3)$$

According to this scheme, WZ is partially reduced, and the formed $C_7^{\delta+}$ and $C_4^{\delta-}$ are combined in [C11], which is then hydrocracked with the participation of the zeolite component. In the absence of n-C_4H_{10} scheme (2) is realized with the participation of hydrogen molecules, and the reaction products are iso-C_7H_{16} and hydro decomposition products.

Acknowledgements

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VP-4

INFLUENCE OF HYDROTHERMAL TREATMENT OF THE AMORPHOUS ALUMINUM HYDROXIDE ON CATALYTIC PROPERTIES IN ACID TYPE REACTIONS

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Dehydration products of alcohols such as styrene and ethylene and skeletal isomerization of olefins (isobutylene) are important monomers of rubbers and are used in many petrochemical processes [1-5]. These reactions proceed with the participation of Lewis acid sites of aluminum cations. As catalysts, γ-Al_2O_3 is used with a high concentration of Lewis acidic sites. Industrial γ-Al_2O_3 is produced by dehydration of the corresponding aluminum hydroxide pseudoboehmite [2]. Obtained directly from pseudoboehmite, the alumina catalyst does not have enough of the acidic Lewis centers to conduct these reactions (dehydration and isomerization), so the surface of the alumina is modified to increase it [3]. One way to increase the strength of Lewis acid sites on the surface of aluminum oxide is directed hydrothermal treatment of weakly crystallized (pseudoboehmite) and uncrystallized (amorphous) forms of aluminum hydroxide, which are partially present in industrial aluminum hydroxide samples obtained by "reprecipitation" of Al-containing solutions obtained from gibbsite [4]. Also, during hydrothermal treatment, intensive release of Na, Fe, etc. ions from the catalyst, which are catalytic poisons, occurs [5]. This will yield high-purity alumina catalysts with high Lewis centers on the surface of aluminum oxide and thereby increase the energy efficiency of the processes and the yield of their target products.

The phase composition and kinetics of the transformation of amorphous aluminum hydroxide obtained by different methods and basic aluminum salts under conditions of hydrothermal treatment at temperatures of 110-150 °C, corresponding to saturated water vapor pressures and at different pH values of the aqueous suspension were studied. Hydrothermal treatment was carried out in an autoclave "Limbo li" of the firm "BüchiGlasUster" with automatic regulation of temperature and pressure in a 250 ml stainless steel reactor at a weight ratio of alumina: water = 1: 5

and agitation with a stirrer at 500 rpm the maximum degree of filling of the autoclave is 70 %.

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VP-5

CHANGE OF ASPHALTENE FRACTIONAL COMPOSITION IN HYDROTHERMAL CATALYTIC PROCESS

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In today's world, technologies aimed at the production and processing of heavy crude oil feedstock resulting with lower viscosity and simple fractions. Hydrothermal catalytic process affected the heavier compounds in inside of crude oil. Recently, with the decreasing of conventional oil resources, industries need much more energy from unconventional oil resources. Because of that, in the near future modern oil-producing and oil-refining industries will be linked to the development of the unconventional hydrocarbon resources such as heavy crude oil and natural bitumen.

Asphaltenes extracted from the samples of heavy crude oil and the products of a catalytic and non-catalytic aquathermolysis in the presence of a cobalt-containing catalyst were investigated. Five fractions of asphaltenes [1,2] were received by a fractional precipitation method. In the process of catalytic aquathermolysis [3] an increase of the content of light fractions (saturated hydrocarbons) as a result of intensification of the destructive hydrogenation mostly on the least strong –C–S–C– bonds in resins and asphaltenes molecules was observed. This work revealed a phenomenon of redistribution between fractions of asphaltenes, extracted by solvents of different composition and solvent forces, as well as a decrease in the average molecular mass of asphaltenes for each fraction in the presence of a catalyst.

In this study we investigated the oil-soluble catalysts behavior towarding to cracking of asphaltene into fractions and lighter compounds. Treating asphaltene using cobalt-based catalyst showed that, catalyst is very active and effective in cracking of asphaltene to lighter fractions especially in A1, A2 and A4 fractions.

We can conclude that, using cobalt-based oil-soluble catalyst in in hydrothermal catalytic system overally, increased the amount of lighter fractions of cracked asphaltenes. Also we confirmed these fraction compound structures with the help of IR and MALDI spectroscopies.

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VP-6

SYNTHESIS OF HYDROGENING CATALYSTS ON ALUMINUM OXIDE PREPARED BY ELECTRO-CHEMICAL ANODIZATION

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The membranes of porous Al_2O_3 are an ideal matrix for creating nanodimensionalcomposites [1-2], due to enough regular pore structure with a small dispersion in diameter and distances between the pores. On its basis, homogeneous nanodimensionalmetal and semiconductor structures [3] with new magnetic [4], catalytic [5] and optical [6] properties are successfully created.

Precipitation of transition metal compounds was possible due to the peculiarities of the molecular structure of porous Al_2O_3. To obtain nanocatalysts based on nickel oxide, a porous alumina matrix with pore sizes of about 50 nm and 50 micronsthick was used (Fig. 1)

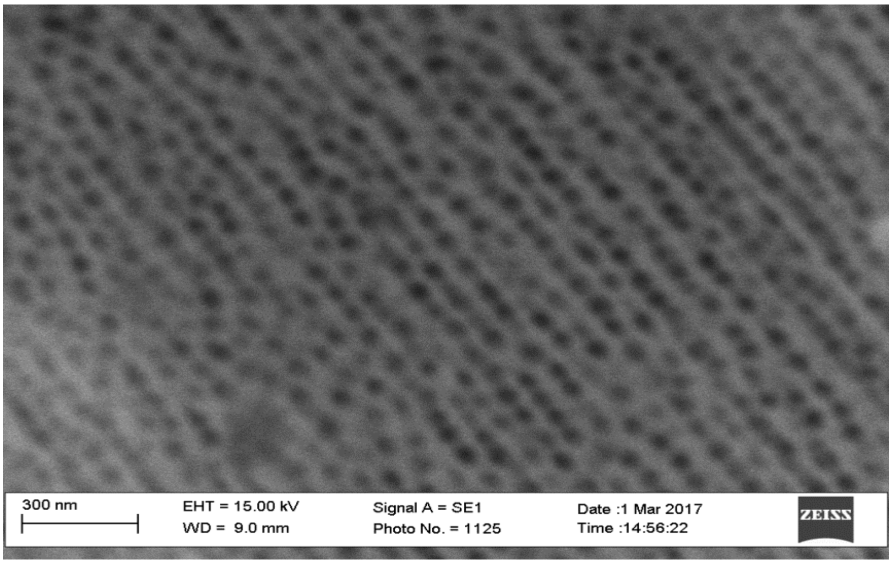

Fig. 1. Image of the plate surface obtained by electrochemical anodization

Our research has shown that the molecular layering method is the most optimal way of obtaining nanocatalystsbased on nickel oxide.

The introduction of nanoparticles of nickel and molybdenum into the alumina matrix was carried out by periodically dipping the porous plate into appropriate solutions with intermediate drying.

Elemental analysis data indicate equal allocation of nickel and molybdenum in a matrix of uniformly porous alumina. A similar picture was observed when molybdenum was applied from an aqueous solution of its salt.

Nanodimensional catalysts were obtainedon the basis of nickel and molybdenum by using a porous alumina matrix. Elemental analysis showed that a spongy structure with a filament size of the order of one nanometers was formed on the surface of the aluminum oxide matrix and this structure contains nanoparticles of nickel and molybdenum.

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VP-7

INFLUENCE OF THE ACTIVATION PROCEDURES ON PHYSICAL-CHEMICAL AND CATALYTIC PROPERTIES OF Pt/WO_x-ZrO_2 CATALYSTS

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

These catalysts are prepared usually by thermal treatment of the zirconium hydroxide precursor impregnated with tungstate anions, followed by promotion with platinum and final calcination [1]. During the operation, the catalytic system undergoes activation and reactivation procedures. These bring about the changes in the state of the catalyst, in its surface properties and catalytic activity, in particular. The study of the effects of the activation and regeneration conditions on the efficiency of the catalyst in the hydrocarbon hydroisomerization is thus an actual research task.

The goal of this paper was to study the effect of the reductive activation and oxidative regeneration conditions on the physical-chemical properties and the efficacy of the Pt/WO_x-ZrO_2 catalysts in the reaction of hydroisomerization of n-heptane-benzene model mixture.

It was found that the procedures of the reductive activation of the parent Pt/WO_x-ZrO_2 catalysts and oxidative reactivation of the spent ones after hydroisomerization reaction under conditions studied hardly affect the phase composition and texture properties of catalysts, however, dramatically affect their surface characteristics, oxidation state and surface-volume distribution of tungsten and platinum components. The optimal reductive activation and oxidative regeneration conditions that ensure the high catalytic activity, selectivity and stability of the Pt/WO_x-ZrO_2 catalysts in the hydroisomerization of both n-heptane and n-heptane-benzene mixture were determined.

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Ni-W AND Co-Mo SULPHIDE CATALYSTS SYNTHESIZED *IN SITU* IN A HYDROCARBON MEDIUM FOR AROMATIC HYDROCARBONS HYDROGENATION

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In recent years, interest in the study of nanosized catalysts has significantly increased because of the possibility of improving the efficiency and selectivity of the catalysts [1]. This fact has given rise to the development of a new approach to the synthesis of catalysts: formation of nanoparticles directly in a hydrocarbon feedstock. Thiosalts are precursors that are often used for the preparation of sulfide [2, 4]. The decomposition of thiosalts in the reaction medium provides a high sulfur content in the final sulfide catalyst and contributes to the production of stable fine particles. In this study, a method for preparation a nickel–tungsten and cobalt-molybdenum sulfide catalysts for aromatics hydrogenation by the decomposition in situ of the synthesized $[(Ph)_3S]_2Ni(WS_4)_2$ and $[(Ph)_3S]_2Co(MoS_4)_2$ precursors in the hydrocarbon feedstock is proposed. Model systems, including mono- and bicyclic aromatics (such as naphthalene, monomethylnaphthalenes, dimethylnaphthalenes etc.) and dibenzothiophene (DBT) are used as feedstock.

Precursors and formed catalysts were analysed by atomic absorption spectroscopy, transmission electron microscopy (TEM) and X-ray photoelectron (XPS) spectroscopy. Catalytic hydrogenation tests were conducted in a steel autoclave in a hydrogen atmosphere under a high pressure (5.0 MPa) and vigorous stirring varying the reaction temperature (350-380 °C), time (3-10 h) and active metals content in the feed. TEM studies have shown that the catalysts particles are nanoplates associated in multilayer agglomerates. XPS data established the formation of catalytically active Ni-W-S and Co-W-S phases. The resulting catalysts exhibits high activity and stability in the hydrogenation of bicyclic hydrocarbons and in the DBT conversion and some trends may be noted:

- naphthalene hydrogenation is preferably in the presence of a nickel-tungsten catalyst;

- it is preferable to conduct the hydrogenation process in the presence of 2.5 % sulphur to increase the number of active sulphide sites;
- the optimum reaction conditions are 350 °C, 5.0 MPa, 5 hours, since in this case of high values of conversion and selectivity of naphthalene on the target products are achieved, the thermodynamic limitations inherent in polycyclic aromatic hydrocarbons are taken into account, and the features of the reaction on the data catalysts;
- the rise of precursor concentration in the feed provides high conversion and selectivity values;
- catalytic system, obtained by the decomposition of the thio-precursor $[(Ph)_3S]_2Ni(WS_4)_2$, showed great activity in the hydrogenation reactions of all the alkyl substituted aromatic mixtures;
- the main products of the hydrogenation reaction of methylnaphthalenes are methyl-substituted tetralins due to the occurrence of steric hindrance to the adsorption of the molecules of the raw material to the surface of the catalyst as a result of migration of substituents within the aromatic medium;
- the total selectivity for decalin in the course of the hydrogenation reaction of methyl-substituted naphthalenes on the Ni-W-S catalyst is several times greater than the selectivities on the Co-Mo-S system;
- the high activity in the hydrogenation reaction of DBT is exhibited by the Co-Mo-S, the maximum conversion is 99.5 %;
- similarly, the activity of the Co-Mo-S composition is manifested during the hydrogenation of 4-methyl DBT. The presence of alkyl radical creates steric hindrance during hydrogenation and lowers the rate of reaction, which is confirmed by a slight fall in conversion to 94 %.

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HYDROCARBON RESINS HYDROGENATION OVER UNSUPPORTED SULFIDE CATALYSTS FORMED FROM OIL-SOLUBLE AND WATER-SOLUBLE PRECURSORS

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Hydrogenation is known to be one of the most forcible methods for hydrocarbon resins quality optimization, that is aimed at improving color, color stability under UV radiation or heating, oxidative stability, toxicity decreasing. Hydrocarbon resin hydrogenation catalysis possesses some special features, that is the possibility of chain scission at high temperature and pressure [1, 2] obvious for all macromolecular materials. One should also mention diffusion limitations, steric hindrance [3], that results in low conversion over conventional supported micro and mesoporous catalysts [4].

In this regard, unsupported metal or sulfide nanoparticles seem to be attractive for hydrogenation of macromolecular compounds: hydrocarbon resins, polystyrene, polybutadiene, etc. In this case not only diffusion limitations would be eliminated, but also sterical hinderance and lack of macromolecules access to catalyst sites would be resolved.

The present research deals with *ex situ* synthesis of sulfide nanoparticles and their catalytic properties evaluation in hydrocarbon resins hydrogenation process. Ni-Mo unsupported catalysts were synthesyzed from oil-soluble (nickel ethylhexanoate and molybdenum carbonyl) and water-soluble (nickel nitrate and ammonium heptamolybdate) precursors. Synthesys ex situ is preferable since sulfide phase formation requires temperature up to 380 °C that causes hydrocarbon resin chain scission. Morphology of the synthesized catalysts were investigated by SEM with surface composition analysis by EDX, TEM, phase composition was analysed by XPS.

Catalytic properties were evaluated in a batch reactor under continuous stirring, initial hydrogen pressure in a range 3 to 6 MPa, in a temperature range 280-360 °C under different hydrocarbon resin concentrations in cyclohexane. Hydrogenation degree was determined from ^{1}H NMR spectra [5, 6], color – by iodine color scale, average molecular weight – by gel permeation chromatography.

For both types of catalysts, that is formed from water and oil-soluble precursors, effect of Mo/Ni ratio, catalyst concentration on activity in aromatic and olefinic moieties hydrogenation was evaluated. As to water-soluble precursors, effect of the amount of surfactant (Span 80) on emulsion dispersity, sulfide particles size and catalyst activity was determined. Hydrocarbon resins were evaluated as surfactants and demonstrated excellent properties as emulsifiers.

The effect of temperature, pressure and hydrocarbon resin solution concentration on the rate of hydrogenation and cracking reactions was estimated. Solution concentration turned out not to influence on degree of hydrogenation over unsupported catalysts, but one cannot mention the same about supported catalysts that suffer diffusion limitations in concentrated solutions (over 20 wt. %). As to unsupported catalysts, hydrogenation can be performed even in very concentrated solutions (40 wt. % and higher). All unsupported catalytic systems were successful in improving color of hydrocarbon resins, as well as color stability during thermal oxidation tests.

The unsupported catalyst activity does not alter much from cycle to cycle despite on some carbon deposition. The morphological characteristics (the number of MoS_2 slabs and their length) of the fresh catalyst and recirculated are quite similar, as well as phase composition (amount of Ni-Mo-S, MoS_2, NiS, etc.).

From this perspective unsupported sulfide catalysts are potentially functional for hydrocarbon resins hydrogenation since particle size can be adjusted well just under synthesis to match different molecular weight polymers.

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SPHERICAL CATALYSTS: TiO_2-SiO_2/NiO, TiO_2-SiO_2/Co_3O_4, TiO_2-SiO_2/Cr_2O_3 FOR OXIDATION OF N-HEPTANE

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In the last two years, several publications on the synthesis and use of spherical oxide materials coated with a layer of TiO_2 were published [1]. Such materials reveal a high catalytic activity in reactions of oxidation and reduction of organic substances [2, 3] which is an important task in industrial processes.

In the presented work, we investigated spherical TiO_2-SiO_2/NiO, TiO_2-SiO_2/Co_3O_4, and TiO_2-SiO_2/Cr_2O_3 materials. The method of preparation consisted of several stages. The first one was the preparation of the spherical substrate by sorption of Ni^{2+}, Co^{2+}, and $Cr_2O_7^{2-}$ ions by polymer material from aqueous solutions. The second stage was the preparation of aggregately stable sols solution on the basis of tetramethoxysilane, tetraethoxysilane, water, and hydrochloric acid, and deposition of sol particles on the spherical substrate during 12 hours. Then, the spherical material was dried at 80 °C for 60 min and was calcined in air by several steps at 100 °C, 150 °C, 250 °C for 30 minutes at each temperature, and further at 500 °C for 60 minutes.

Electronic state of d elements comprising spherical materials was investigated by Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DRS). The UV-Vis DR spectra of all samples were recorded on UV-2501 PC "Shimadzu" spectrophotometer with the ISR-240 A diffuse reflection attachment in the wavelength range of 190-900 nm (11 000-54 000 cm^{-1}). The final UV-Vis DR spectra were represented in coordinates: of function Kubelka-Munk vs. wavenumber.

The catalytic activity of the TiO_2-SiO_2/NiO, TiO_2-SiO_2/Co_3O_4, and TiO_2-SiO_2/Cr_2O_3 samples was measured in the model reaction of n-heptane oxidation. The reaction was performed in a flow catalytic setup using quartz tube reactor with an inner diameter of 4 mm. The feed gas composition was $C_7\%:O_2\% = 1:25$, a feed rate of 4.5 L/h. The size of the catalysts spheres was 0.2-0.5 mm, a charge of catalyst was

0.2 g. Qualitative and quantitative analysis of the starting mixture and the products of the oxidation of n-heptane were performed on Shimadzu FTIR-8300 spectrometer.

An intensed absorption above 27 000 cm^{-1} was observed in the UV-Vis DR spectra of all the samples; the edge of fundamental absorption (28 000-32 000 cm^{-1}) was distinguished corresponding to the band gap of TiO_2. For TiO_2-SiO_2/NiO sample the band of 14 000 cm^{-1} was observed in the UV-Vis DR spectrum, which corresponded to the Ni^{2+} cations in octahedral oxygen coordination, stabilized in the form of NiO. The absorption band at 15 000 cm^{-1} for TiO_2-SiO_2/Co_3O_4 sample corresponded to the Co^{2+} cation in tetrahedral oxygen coordination and probably corresponded to the phase Co_3O_4. For TiO_2-SiO_2/Cr_2O_3 sample, the absorption band at about 16400 cm^{-1} was observed, related to the Cr^{3+} cations in octahedral oxygen coordination, and corresponded to a phase of Cr_2O_3.

Oxidation of n-heptane in the TiO_2-SiO_2/NiO sample started at 300 °C. The formation of products of partial oxidation was observed: ketones and α-olefins up to a temperature of 450 °C. With further increase of temperature, the deep oxidation of n-heptane was observed. The conversion of n-heptane over TiO_2-SiO_2/NiO did not exceed 50 %.

Over TiO_2-SiO_2/Co_3O_4 sample, the oxidation of n-heptane began at 250 °C. In the temperature region of 500-600 °C, the products of deep oxidation of n-heptane (CO_2) and cracking products (α-olefins) were formed. The conversion of n-heptane over TiO_2-SiO_2/Co_3O_4 was 80 % at 600 °C.

Oxidation of n-heptane on TiO_2-SiO_2/Cr_2O_3 sample started at 145 °C. Selectivity of TiO_2-SiO_2/Cr_2O_3 toward products of deep oxidation was 100 %. The degree of conversion of n-heptane reacheed 100 % at 400 °C.

The spherical TiO_2-SiO_2/NiO, TiO_2-SiO_2/Co_3O_4, TiO_2-SiO_2/Cr_2O_3 catalysts revealed a catalytic activity in reactions of deep and partial oxidation of n-heptane. TiO_2-SiO_2/NiO and TiO_2-SiO_2/Co_3O_4 samples were active in both reactions. TiO_2-SiO_2/Cr_2O_3 sample was active only in the reaction of deep oxidation of n-heptane.

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PHOTOCATALYTIC DEGRADATION OF PHENOL UNDER SOLAR LIGHT IN THE PRESENCE OF ZINC OXIDE NANOSHEETS, ANNEALED AT DIFFERENT TEMPERATURES

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Oil industry is one of the most important part of world economy. Technologic processes of oil refinery discharge the water wastes, and they move to nature water reservoirs: ponds, rivers, lakes and etc. Phenol is the most toxic substance, which is consisted in wastewater of oil industry. Purification of sewage can be realize by several approaches, divided into sorption and oxidation ones. Oxidation ones allow to destroy organic pollutants with forming carbon dioxide and water. Phtocatalysis is the oxidation process based on forming electron/hole pair into crystal of semiconductor material under electromagnet irradiation. Photon energy of irradiation and width of band gap play main role in decomposition process. If photon can move through band gap of semiconductor and activate electrons at valence band to move it to conductivity band, photocatalysis would be realized. One of most promising photocatalyst is zinc oxide [1] due low cost and high stable in aggressive solutions. It has band gap about 3.3 eV, that corresponds ultraviolet light. So water treatment with such photocatalysts needs using special lamps, which need additional electricity energy. Solar light is the free course of irradiation but it consists a few volume of UV irradiation so for water purification it is necessary to decrease width of band gap. Reducing of band gap usually is realizing by doping of semiconductor with metal or non-metal atoms. We show that annealing temperature of photocatalyst influences on it activity. Special misfits of crystal cell allow to purify wastewater from phenol under solar light. We prepared zinc oxide nanosheets with wurtzite structure consisted potassium atoms. It's shown that special thermo treatment allows to change photocatalytic properties of zinc oxide.

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VP-12

NON-STATIONARY MODELLING OF DIESEL FUEL HYDROTREATMENT PROCESS WITH THE CATALYST DEACTIVATION

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In acordance with the increasing role of hydrotreating processes in the oil refining industry there arises the need in the development of computer modeling systems that implement mathematical models of hydrotreatment [1].

The main purpose of this study is to model the hydrotreating reactor and catalytic reactions of sulphur compounds widely present in oils including the sulfides, benzothiophenes (BT), and dibenzothiophenes (DBT) – the sulfur compounds which are the most difficult to remove from petroleum products [2]. One of the main applications of this research work is to select and optimize the design of the reactor and to formulate ideas concerning the improvement of the quality of the hydrotreated diesel fuel.

A list of possible reactions is compiled on the basis of experimental data. The change of Gibbs free energy provided by the reactions calculated using software packages HyperChem and Gaussian 09. In previous work [2], studies were conducted to determine the kinetic parameters of the hydrodesulfurization reactions, based on experimental data from laboratory equipment including “Kristal-2000M” chromatograph and laboratory mini-reactor, where the diesel fuel fraction (180..320 °C) with sulphur content 1.4 w % was hydrotreated under next conditions: H_2/feed ratio – 400:1; Pressure – 2 MPa; Temperatures – 330...380 °C. Obtained rate constants and the activation energy (~120 kJ/mole) are incorporated in the mathematical model.

The basis of the developed mathematical model is built on the hydrodesulfurization reaction of individual groups of organic sulfur compounds such as sulfides, benzothiophene, dibenzothiophene. Also, the model takes into account hydrogenolysis reaction products: saturated and aromatic hydrocarbons.

The developed mathematical model based on the law of mass action and is a system of differential equations, which reflect changes in the concentrations of the reactants. Thus, the mathematical model performs a material balance calculation of sulfur compounds during hydrotreating taking the non-stationary process of catalyst coking and deactivation into account.

An experimental data was taken from the monitoring file of hydrodesulfurization unit “LG-24/7” which uses HR-538 catalyst. Monitoring file reflects the state of technological parameters and differing sulfur content of feed.

The developed mathematical model was modernized to calculate activity (Figure 3) of the catalyst at L-24-10/2000 hydrodesulfurization and hydrodeparafinization unit with HR-538 catalyst. To make this possible the mathematical model converted to calculate volume of processed diesel fraction.

The conclusions made based on calculated data. Thus, the catalyst’s activity loss by nearly 1/3 of its extrapolated beginning activity is observed. This could be caused by imperfections in diesel fuel fraction composition and in technological parameters at hydrodesulfurization reactors of “L-24-10/2000” unit.

Developed mathematical model allows making a conclusions on initial reasons which influence the overall process quality and helps in making a decisions in the questions of process optimization.

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VP-13

GLASS-FIBRE CATALYSTS FOR HYDROCRACKING OF HYDROCARBONS

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There is substantial interest in studying of the refining process of heavier fractions of oil to increase the resource of synthetic hydrocarbon fuels, including reactive and diesel fuels,lubricating oils, raw materials for cracking and reforming, etc. In this regard, the application of the hydrocracking process becomes more and more urgent in industry. This process combines catalytic cracking and catalytic hydrogenation, which allows to recycle aromatics to obtain diesel fuel.

It is known [1] that for the recycling oh high-boiling oil fractions, a scheme consisting of several stages is proposed to use: obtaining synthesis – gas, Fischer-Tropsch synthesis, hydrocracking and final purification of reaction products. In each of these stage, a certain of catalysts are used. Depending on the kind of product obtained and its required degree of saturation, the catalysts need to combine certain hydrogenating and acid functions. For instance, for the Fischer-Tropsch synthesis, an iron catalyst proved to be well established. In the case of hydrocracking catalysts may be used, containing both noble metals (Pt, Pd) in which the hydrogenation function exceeds the acidic and cheaper Ni, Mo, W, Co and combinations thereof and compounds, for instance sulphides (WS_2), in which more acid properties are expressed. As carriers used are zeolites, monmorillonite, powders of aluminium oxides, silicon, titanium and others.

In this study, fiberglass fabrics with impregnated and magnetron sputtering in a low- temperature nickel plasma in the hydrocracking reaction were used as an innovation to existing materials [2]. The obtained samples have certain properties: flexibility, thermal stability, good hydro- and gas dynamics.

As result of the studies, the followings results were obtained:

1. Samples of nickel – containing catalysts on a fiberglass basis, obtained by magnetron sputtering and impregnate with subsequent reduction in a hydrogen stream at a temperature range of 400-1000 °C.

2. The cracked paraffins Sasolwax H1 (C_{20}–C_{40}) at a temperature of 315-330 °C and an initial pressure of H_2 of 50 atm. were mainly crushed into C_8–C_{16} fractions.

3. Further distillation at higher temperatures allowed to obtain of gasoline (C_8–C_{12}) and diesel (C_{13}–C_{26}) fractions, and higher-boiling fractions were returned to the system to increase the yields of the target products.

The distribution of the cracked products by fractions for the samples of sputtered nickel catalysts reduced in the hydrogen current at the appropriate temperatures is shown in Fig. 1.

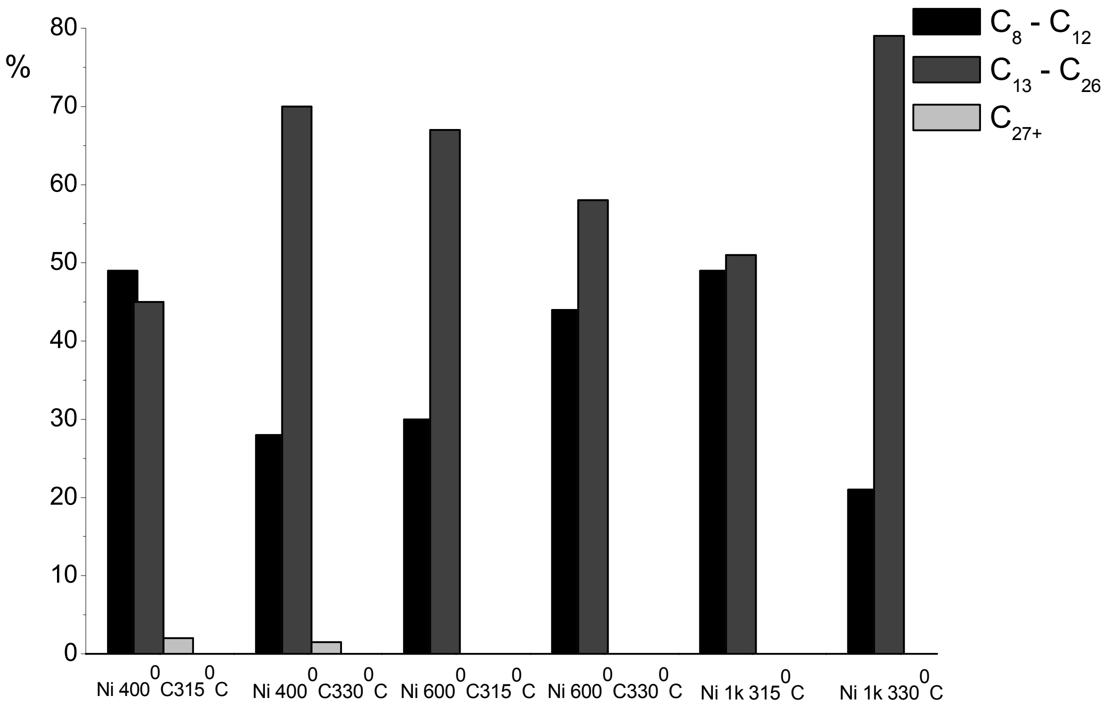

Fig. 1. Distribution of cracked products by fractions

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VP-14

SYNTHESIS AND PHYSICO-CHEMICAL PROPERTIES OF ADSORBENTS OF THE ABSORPTION OF CHLORIDE HYDROGEN

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In the process of selecting the most suitable local raw materials for the preparation of domestic adsorbent – an analogue of imported HCl scavengers from the hydrogen-containing gas of reefing SAS-857 and AxTrap 860, the decisive factor was considered the maximum similarity of physicochemical and adsorption properties in order to avoid additional problems when replacing with another type of adsorbent.

It is very important to consider the possibility of processing the aluminum oxide adsorbent (AASH) used in the process of polyethylene production ("OAASH") at LLC "Shurtan Gas Chemical Plant", with the aim of its further use as a processing facility in the hydrogen chloride absorber, while preserving the spherical shape of the OAAS granules. Also synthesis from aluminum hydroxide and from catalyst carriers production of Novomichurinsk catalyst plant.

A method for modifying spherical OAAS granules has been developed to improve the adsorption capacity in reference to hydrogen chloride. A series of samples from carriers of LLC "NKZ" of the brand AN was synthesized.

The results of a study of the physic-chemical properties of fresh (AASH with AxTrap 860 (France) and AN (Russia)), spent (AASH and SAS-857) and thermoregenerated adsorbents (AASH and SAS-857) are compared.

Based on the results of the study of fresh, spent and synthesized adsorbents during the adsorption of HCl from the hydrogen-containing reforming gas, it was concluded that it is advisable to modify them with alkaline and various modifiers to maximize the sorption capacity of the HCl.

THE ROLE OF CATALYSTS IN THE SYNTHESIS OF ACETYLEN ALCOHOLS AND THEIR VINYL ESTERS BY CATALYTIC METHODS OF PETROLEUM PRODUCTS

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Chemical processing of oil and gas as well as obtaining on the basis of thin organic synthesis products and materials for agriculture, chemical, pharmaceutical, textile, energy, automotive and aircraft industries is highly effective [1].

The high reactivity of C≡C- and C-H bonds in alkynyl makes them participants in the diverse reactions that form the basis of section synthetic organic and industrial chemistry [2].

Recently, scientific investigations on the creation of ecological safety and waste less technologies, also, on the synthesis of economically cheap chemical preparations with higher yield and to introduce them into the practice have been carried out [3].

At present time on the base of aromatic acetylenic alcohols and vinyl esters different solvents, medicine preparates are elaborated production of monomers, biocides and compounds using as crosslinking agents and inhibitors is put right [4].

By action of acetone, methylethylketone, methylpropylketone, diethylketone, methylisopropylketone, pinokaline, acetophenone and croton aldehyde of phenylacetylene (PhA) were obtained by metod Favorskiy falloving aromatic acetylenic alcohols: 2-methyl-4-phenylbut-3-yn-2-ol, 3-methyl-1-phenylpent-1-yn-3-ol, 3-ethyl-1-phenylhex-1-in-3-ol, 3-ethyl-1-phenylpent-1-yn-3-ol, 3,4-dimethyl-1-phenylpent-1-yn-3-ol, 3,4,4-trimethyl-1-phenylpent-1-yn-3-ol, 2,4-diphenylbut-3-yn-2-ol and 1-phenylhex-4-en-1-yn-3-ol and also was proposed [5]:

In composition of molecules of aromatic acetylenic alcohols berides aromatical cycle and triple bound there is OH group in which there is mobile activ atom of hydrogen which is responsible for vinylation reaction of synthesized aromatic acetylenic alcohols by acetylene in different conditions:

a). Homogen-catalytic vinylation of aromatic acetylene alcohols [6]: Process was carried out in solutions of DMSO and DMFA at duration 4-10 h and temperature 80-140 °C in presence of LiOH, NaOH and KOH. At using catalysts with high base KOH (quantity catalyst 10 %) maximal yield of vinyl esters aromatic acetylenic alcohols was determined. At this alcoholyat of potassium in comparison with such of Na and Li is the most active and correspondently in it's presence yields of vinyl esters were high.

b). Reaction of aromatic acetylenic alcohols with acetylene in homogeneous conditions at using of high-base catalytical system MeOH-CsF-DMSO was investigated according [7]. Vinylation of aromatic acetylenic alcohols in the presence of high-base system is characterized by high velocity. At this hydrogen atom of acetylene has stereos- and regeoselectivity owing to which process of exchange has carried out lightly. In systems MeOH-CsF-DMSO during of reaction solvates of metals are formed active metal is conversed in complex with formation of catalytically active centers and increasing of function of catalysts.

c). Synthesis of vinyl esters aromatic acetylenic alcohols on the base of local raw material-acetylene by heterogeneous-catalytical method [8]. Influence of nature of catalysts and molar ratio of initial components was investigated. Systems such as NaOH/$C_{activ.}$ and KOH/$C_{activ.}$ were used as catalysts. Reactions were carried out at 200 °C during 3 h.

With increasing of acetylene content it's diffusion to surface of catalyst has increased and at this at first physical and then chemical adsorption have carried out.

Adsorptive molecule of acetylene has formed with active center of catalyst π-complex transform mating in compound which has reacted with molecules of alcohols with formation of vinyl esters. By alcoholyats aromatic acetylenic alcohols don't saturated by acetylene than catalysts reagated with molecules of aromatic acetylenic alcohols what is prevented carring out of reaction and is a cause of decreasing of vinyl esters yields.

Advantages of geterogenno-catalytical synthesis in comparasion with gomogeneous-catalytical were determined. It is necessary to note that geterogeneous-catalytical method of synthesis of vinyl esters aromatic acetylenic alcohols is more economically cheaper, ecologically safety and at this quantities of by products were increased.

Applications aromatic acetylene alcohols as corrosion protection of biocides in the biological corrosion of steel and metal industry equipment Oil and gas leads to a 80-82 % disinfection of bacteria and fungi and improve the performance properties of metal equipment. The use of vinyl esters of aromatic acetylenic alcohols for complex allocation of sulfur compounds from the oil, petroleum products and natural gas reduces the amount of sulfur compounds to 42-55 %.

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EXHIBITION

EnviroESCA – ROUTINE SURFACE ANALYSIS UNDER ENVIRONMENTAL CONDITIONS

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Since many decades XPS (or ESCA) is the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task existing ESCA tools combine reliable quantitative chemical analysis with comfortable sample handling concepts, integrated into fully automated compact designs. Over the last years it has been possible to develop XPS systems that can work far beyond the standard conditions of high or ultrahigh vacuum. Near Ambient Pressure (NAP) XPS has become a fastly growing field in research inspiring many scientist to transfer the method to completely new fields of application. Thus, by crossing the pressure gap, new insights in complicated materials systems have become possible using either synchrotron radiation or laboratory X-ray monochromators as excitation sources under NAP conditions.

Based on this experience SPECS Surface Nano Analysis GmbH has developed a revolutionary tool to realize the long existing dream in many analytical laboratories: reproducible chemical surface analysis under any environmental condition. EnviroESCA allows for different applications, like extremely fast solid surface analysis of degassing (but also non-degassing) samples, ESCA analysis of liquids or liquid-solid interfaces, chemical analysis of biological samples, materials and device analysis under working conditions.

After introduction of the technological realization a comprehensive survey of results will be given starting from standard solid conductive samples under different pressure conditions, bulk insulators with environmental charge compensation applied, high throughput analysis of batches of similar objects, geological samples, chemical analysis of pharmaceuticals to the comparative analysis of ultrapure liquid water with different aqueous solutions. The application of Near Ambient Pressure XPS to biological specimen from plants and animals, biofilms and bacteria, as well as food samples, which is a completely new field for electron spectroscopic studies of the surface chemical composition, will be presented.

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