

Borisekov Institute of Catalysis SB RAS
Councils of Young Scientists of BIC
Institute of Problems of Hydrocarbons Processing
Russian-French laboratory on Catalysis



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The Year of Russia in France and the Year of France in Russia – 2010

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The Russian-French Workshop on Catalysis, Petrochemistry and Biomass for Young Scientists dedicated to “The Year of Russia in France and the Year of France in Russia – 2010”

Russian-French laboratory on Catalysis



Boreskov Institute of Catalysis SB RAS



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Institute of Problems of Hydrocarbons Processing

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**The Time table of the Russian-French Workshop
18-19 May, 2010**

18 May	
14.30	Opening of the Workshop
14.45	PL 1. Yakovlev
15.15	OP1. Dundich
15.30	OP 2. Delidovich
15.45	OP 3. Chauve
16.00	Coffee brake
16.15	OP 4. Zevak
16.30	OP 5. Shuvaeva
16.45	OP 6. Bourlon
17.00	OP 7. Zakharov
17.15	OP 8. Bouchonneau
17.30	OP 9. Sadykova
17.45	OP 10. de Navacelle
18.00	Poster session
19.00	Picnic

19 May	
9.30	PL 2. Belskaya
10.00	OP 11. Budukva
10.15	OP 12. Elia M.
10.30	OP 13. Potapenko
10.45	OP 14. Udalov
11.00	Coffee brake
11.15	OP 15. Leonova
11.30	OP 16. Mironenko
11.45	OP 17. Savonnet
12.00	OP 18. Kazakov
12.15	OP 19. Pereima
12.30	OP 20. Mondange
12.45	Closing
13.00	Lunch
14.30	Excursion to Omsk



DESIGN OF CATALYTIC PROCESS FOR BIODIESEL AND GREEN DIESEL PRODUCTION

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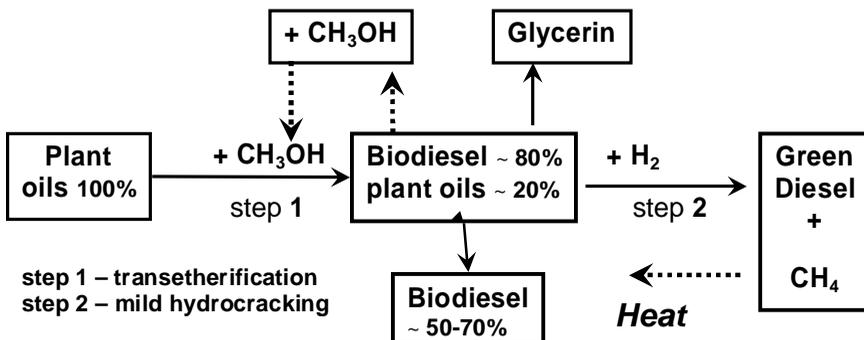
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Biomass is a renewable alternative to fossil raw materials in the production of liquid fuels and chemicals. The objective of this work is to develop two-stage technology for biodiesel and green diesel production from lipidic renewables (plant oils, animal fats, algae lipids). The specificity of the work is development of new effective catalysts, adjusted to renewable feedstock. The technology is based on conjugated catalytic processes of transesterification and mild hydrocracking represented on the scheme below:



Main features of developed technology are:

- biofuel production of two types: biodiesel and green diesel;
- varying of biodiesel and green diesel yields depending needs;
- optimization of hydrogen consumption;
- energy-supply of both stages via burning of gaseous products, produced on 2nd step.

Catalytic characteristics of the technology include application of heterogeneous basic transesterification catalysts under 200-220°C and 2.0 MPa and possibility of multiple catalyst regeneration for the first stage. For the second stage these ones comprise using of non-sulfided and non-noble metal catalysts, mild reaction conditions (300-340°C and 2.0 MPa H_2) and possibility of green diesel production with different cetane number via hydroisomerization catalysts application.

Thus, developed transesterification and mild hydrocracking processes allow to obtain high-clean biodiesel and green diesel with high cetane number, which can be used as improving additive to traditional fossil diesels. Developed new effective catalysts can be used in processing of non-food lipidic renewables.



PLATINUM POLYHYDROXOCOMPLEXES AS
PRECURSORS FOR HYDROCARBONS CONVERSION
CATALYSTS

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Two main mechanisms were determined to be available in surface Pt-species formation: ion-exchanged process in which Pt-complex keeps its nature (A), and the coordinated interaction accompanying by the surface groups entering into coordination sphere (B). Usually the part of coordinately grafted species in the samples prepared from chloride complexes is not more than 30%.

The aim - development of new coordinately grafted catalysts precursors.

Methods and results:

It's shown that the part of complexes (B) may be increased by Pt-hydroxocomplexes using as precursors. The advantage of hydrolyzed Pt-species is a firm metal grafting due to complex's OH-ligands - surface alumina hydroxogroups exchange. Besides, an ability of hydroxocomplexes to form polynuclear structures was shown by RDED method. It's important for active sites geometry formation at the initial stage of synthesis.

It was developed a new method of Pt-hydroxocomplexes direct surface synthesis by thermal hydrolysis of pre-adsorbed chloride precursors. As a result the part of complexes (B) increases up to 80%. The temperature and the exposure time variation regulate A:B ratio.

The surface complexes were investigated by ESDR, EXAFS, TPR, chemisorption methods. The complexes (B) have the average composition $[\text{PtCl}_2(\text{OH})_4]/\text{Al}_2\text{O}_3$. Their high temperature reduction results to Pt-crystallites with specific adsorbed properties, favorable for new hydrocarbon processing catalysts synthesis.

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INVESTIGATION OF CATALYTIC HYDRODEOXYGENATION OF FATTY METHYL ESTERS

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The increasing consumption of fuel has led to a rapid decrease of Earth's fossil reservoirs; therefore, it becomes perspective to produce engine fuels from the renewable sources. With over 10 years of commercial use in Europe, biodiesel has proved its value as a fuel for diesel engines. Biodiesel is usually obtained through transesterification reaction of vegetable oil by methanol. It is a mixture of methyl esters of fatty acids (FAMES).

However, in spite of many its ecological advantages, biodiesel cannot be used in diesel engines, because it has high viscosity, ability to dimerization and low. The main reason for the low operating characteristics of biodiesel is high oxygen content due to the presence of ester groups (11-12 % *wet.*) in its components. That is why the FAMES can be used only in a mixture with the hydrocarbon fuels.

Thus the main aim of the present work is a research and development of biodiesel hydrodeoxygenation process in order to obtain high-cetane hydrocarbons – i.e. "green diesel".

In recent papers, non-sulfided catalysts are reported to be suitable used in this process because of the low sulfur content in the biodiesel [1]. Therefore, the development and research of the new catalysts for biodiesel hydrodeoxygenation (HDO) is also the important aim of the present work.

The reaction was carried out with the commercial biodiesel produced from the colza oil. At the first step a lot of catalysts were tested in biodiesel HDO at the constant conditions. The results of biodiesel hydrodeoxygenation showed that the most active catalysts are Ni-Cu/CeO₂-ZrO₂. The hydrocarbons obtained at the 270-400⁰C and 0,5-1,5 MPa of H₂. The variation of the process conditions and nature of the catalyst modifier enabled to produce different hydrocarbon products.

The obtained experimental data on the examined catalysts stability and selectivity makes it possible to make the conclusions about a possibility of the given process industrial realization.

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CATALYTIC SELECTIVE OXIDATION OF SUGARS OVER Pt, Pd AND Au

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Carbohydrates constitute the major part of the renewable feedstock for chemical industry. Polyoxoacids being sugar oxidation products are widely used for synthesis of pharmaceuticals, food additives, cleaning agents, and other demanded products.

This work was aimed on the revealing the correlations between the catalytic performance of monometallic Pt, Pd and Au catalysts towards oxidation of sugars and nature of active metal, its oxidation state and dispersion. Sugars with different structure and positions of functional groups (glucose, sorbose, lactose) were used as model substrates.

The Pt/Sibunit, Pd/Sibunit, Au/Al₂O₃ and Au/Sibunit catalysts were synthesized, characterized and tested for the oxidation of sugars in aqueous solutions.

Common tendencies were revealed for the oxidation of aldoses (glucose and lactose). The catalytic activity increases in the order: Pt < Pd < Au, at the selectivity to corresponding acids up to 98% at total substrate conversion. Specific catalytic activity of Pt and Au does not depend on the metal mean particle size in the 1-5 nm range for Pt and 2-20 nm for Au. It was found that finely dispersed Pd/C catalysts ($\langle d_{Pd} \rangle = 3$ nm) are easier deactivated than samples with larger metal particles ($\langle d_{Pd} \rangle = 6$ nm) under kinetic controlled conditions. The stability of Pd nanoparticles increases under diffusion control. The dependence of catalytic activity and stability against deactivation on Pd oxidation state was studied by XPS.

The catalytic activity of Pt towards selective oxidation of sorbose exceeds those of Pd and Au. The selectivity of formation of 2-keto-gulonic acid never exceeds 20%. The reaction pathways of catalytic sorbose oxidation were proposed basing on the results of HPLC-MS analysis of the reaction mixture.

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KINETIC MODELLING OF PURE CELLULASES INVOLVED IN ENZYMATIC HYDROLYSIS OF CELLULOSE

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The enzymatic hydrolysis of cellulose is still considered as a main limiting step of the biological production of biofuels from lignocellulosic biomass. This step involves the action of three types of cellulose degrading enzymes acting in a synergic way [1]. Endoglucanases (EC 3.2.1.4) randomly cleave β -1,4 glycosidic linkages of cellulose, Cellobiohydrolases (EC 3.2.1.91) attack cellulose chain ends to produce cellobiose the constitutive unit of cellulose, and β -glucosidases (EC 3.2.1.21) hydrolyses cellobiose into two molecules of glucose. The enzymatic cocktail secreted from *Trichoderma reesei* is mainly used in the industrial process [2] and it is often supplemented by β -glucosidase from *Aspergillus niger*. Modeling enzymatic hydrolysis kinetics is usually used to predict cellulases action and to design optimized process reactor. Zhang and Lynd [3], and more recently Bansal et al [4], have reviewed the different kinetic models described in the literature. They distinguish different classes such as Michaelis-Menten, adsorption or soluble substrates models. However, only few models integrate the characteristics of each enzymes family and most of them directly model the enzymatic cocktail without taking into account the presence, during the hydrolysis, of an heterogenous and an homogenous phase corresponding respectively to the action of endo-/exocellulase and β -glucosidase.

This work aims to develop a full kinetic model integrating the own properties of each enzyme and theirs synergisms. Classical Michaelis-Menten model with competitive inhibition by glucose will be used to describe β -glucosidase activity on soluble substrate. A model based on Langmuir assumptions will be chosen to predict the hydrolysis on the solid substrate by cellobiohydrolases. The characterization of pure enzymes activity allows the predictive modelling and a better understanding of the mechanisms involved in the saccharification of cellulosic substrate.

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NANOCRYSTALLINE CeO₂-ZrO₂ SOLID SOLUTION
PROMOTED BY Pt AND Ni: SYNTHESIS, PROPERTIES
AND CATALYTIC PERFORMANCE IN SYNGAS
GENERATION

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Nanocrystalline doped ceria-zirconia promoted by precious metals or Ni is a perspective material for such catalytic processes as transformation of hydrocarbons into syngas by partial oxidation, autothermal or dry reforming, water gas shift reaction, internal reforming of fuels on solid oxide fuel cells anodes, etc.

In this work, nanocrystalline ceria-zirconia samples doped with Pr, La or Sm were synthesized by Pechini method. Pt (1-5 wt.%) and/or Ni (2-8 wt.%) were supported by the incipient wetness impregnation. Structural and surface properties of samples have been studied by TEM with EDX, XRD and XPS. The oxygen mobility and reactivity were characterized by oxygen isotope exchange (including ¹⁸O SSITKA), CH₄ and H₂ TPR, temperature-programmed reoxidation by CO₂. Catalytic properties of samples were estimated in the reaction of CH₄ dry reforming (DR) in the temperature range 600- 900°C at short contact times

Applied preparation procedures result in pronounced interaction between nanocrystalline active components including incorporation of Ni or Pt cations into the surface/subsurface layers of fluorite-like oxides in oxidized state, formation of Pt-Ni alloy nanoparticles in reduced state, the latter being in a strong epitaxy with support as well as decorated by its fragments. The rate of CH₄ DR was found to be controlled by the oxygen mobility in complex oxide, size/composition of supported metal/alloy clusters and support acid-base properties (control CO₂ activation and bonding strength/reactivity of surface carbonates).

This work was carried out in frames of Russian-French Associated European Laboratory on catalysis. Support by OCMOL FP7 and RFBR-CNRS 09-03-93112 Projects.



INFLUENCE OF CALCINATION TEMPERATURE ON THE STABILITY OF $\text{Fe}_2\text{O}_3/\text{SiO}_2$ CATALYSTS AGAINST SULFIDATION

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Silica-supported iron-containing catalysts are highly efficient for the environmentally valuable reaction of H_2S oxidation to sulfur, for example, Fe oxide catalyst is used commercially as catalyst for the SUPERCLAUS[®] process. It is known that the formation of iron disulfide phase due to the interaction with H_2S from the reaction medium is accompanied by an appearance of SO_2 among the reaction products that decreases the selectivity towards sulfur. Thus, the stability of the active phase against sulfidation in the reaction conditions is crucial for the development of the selective catalyst for the oxidation of hydrogen sulfide to sulfur.

The aim of this topic is to study the effect of the calcination temperature on the catalytic activity of Fe-containing silica-supported catalysts prepared using the iron (II) sulfate precursor that received few attention despite it is needed in properly utilization as the main component of steel-picking chemical waste.

The samples were prepared by dry wetness impregnation of silica with an aqueous solution of Fe (II) sulfate with subsequent drying at 110°C and calcination at $400\text{--}900^\circ\text{C}$. The nature of the iron-containing species was studied by DTG, XRD, XPS and Mössbauer spectroscopy.

The comparison of the steady-state reaction rates of the H_2S conversion let us to conclude, that the increase in the calcination temperature led to the rising of the H_2S oxidation rate. The 100% selectivity in the oxidation of hydrogen sulfide to sulfur was observed for all studied samples. The sample calcinated at 900°C revealed highest activity and stability in the reaction of H_2S oxidation. According to the XRD and Mossbauer's spectroscopy data the increase of calcination temperature up to 900°C led to the formation of thermal stable $\epsilon\text{-Fe}_2\text{O}_3$ phase.

Thus, the increase in the calcination temperature of supported iron oxide catalysts prepared by impregnation of silica with aqueous solution of iron (II) sulfate improves their activity and stability against sulfidation due to formation of $\epsilon\text{-Fe}_2\text{O}_3$ phase.

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ULTRASONIC AND ^{27}Al MAS NMR INVESTIGATIONS OF ALUMINOSILICATE GEOPOLYMER PASTES FROM MIXING TO SETTING

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Global warming is one of the most worrying world's problems for the future. Anthropogenic greenhouse gas emissions, particularly CO_2 , are considered as the main cause of this phenomenon. Geological storage of carbon dioxide is considered as a mitigation option in the fight against global warming [1]. Nevertheless, the feasibility of this method involves that CO_2 confinement must be ensured for thousand years. To guaranty well integrity used for CO_2 storage, it's necessary to identify and design new cementing materials able to withstand chemical attack due to acidic fluids.

Geopolymers appear as a potential alternative to the conventional cement materials. Alkali aluminosilicate materials also called geopolymers, after Davidovits [2], are amorphous materials produced from metakaolin or fly-ash reacting with alkali hydroxide/alkali silicate solution.

The mechanical and chemical evolution of these materials from mixing to setting is still not well known. Using ultrasonic shear wave reflections enables to monitor *in situ* the evolution of the shear modulus of geopolymer paste during the setting. This non destructive method provides useful information about the viscoelastic behaviour of geopolymers and allows to determine their setting time. ^{27}Al MAS NMR enables to follow the evolution of the aluminium nuclei environment during the geopolymerisation. This method provides information about the advancement of the reaction. Therefore, these methods allow to correlate the mechanical evolution to the chemical evolution of geopolymers.

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GEOCHEMICAL PETROLEUM INDICATORS IN OIL AND GAS HYDROGEOLOGY

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Petroleum field searching methods by hydrogeological data along with geophysical and geochemical methods become increasingly more actual. That is produced higher requests to evolving and interpretation criteria of hydrogeological anomalies and determination of research area prospects.

Research objects of present work are Paleozoic and Jurassic underground waters and brines in west part of Tomsk region. Data contents results from about 5,000 analyses.

Geochemistry features of underground waters and brines have been studied. Especially, salinity changes along the area have been investigated, relationship between salinity and contents of main cations, anions and micro constituents has been determined, distribution of chemical compounds has been mapped, main lateral and sequence regularities of geochemical indicators changing have been recorded.

A large number of hydro-geochemical indicators involve use of mathematic methods. Correlation analysis has been determined strong positive connections between salinity and concentrations of some geochemical compounds in underground waters. Cluster analysis has been reflected compounds accumulation features.

Data analyses on empty and oil-bearing structures have been allowed to construct probability plots for local structure yields.

Consequently, complex interpretation of hydro-geochemical data allows giving petroleum exploration direction with highly validity.



THE DEVELOPMENT OF NON CONVENTIONAL OIL
SUPPLY UNDER PRICE UNCERTAINTY: APPLICATION
TO THE CANADIAN OIL SANDS

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The aim of this study is to model the development of the non conventional Canadian crude oil under uncertainty, by taking into account various scenarii on crude oil price anticipations and increasing environmental cost.

First, a linear programming approach was chosen to determine the long term equilibrium of non conventional crude oil supply in response to a crude oil demand scenario in the North American market. The optimization consists in maximizing the profit function, under a set of technical, capacity and finite stock constraints. The model is solved with the Cplex solver implemented in the GAMS software.

Second, a dynamic programming approach was selected to analyse the impact of volatile crude oil price on non conventional resources development. Introducing directly probabilized price scenarii at each time period (decisional tree) in the linear programming model would have significantly increased the size of the model. Even with the minimum number (two) of scenarii per time period, the high number of periods (n) increases exponentially the scenarii number and the size of the model (2^n). On the contrary, a dynamic programming approach allows us to introduce multiple decision steps, on the condition that we use only limited state variables (in our case a reserve and a capital state variables are sufficient). A backward recursive algorithm is then used to determine the optimal extraction trajectory under a volatile crude oil price scenario.



THE NATURE OF HYDROGEOCHEMICAL ZONALITY
OF OXFORDIAN REGIONAL RESERVOIRS
GROUNDWATER OF OB-IRTYSH INTERFLUVE SOUTH
REGIONS

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This paper considers the J_1 groundwater horizon of Oxfordian regional reservoirs of Ob-Irtysh interfluvial south regions and its seal layers.

In upper Jurassic complex of the studied area background water is presented by sodium chloride and chloride - hydrocarbonate solutions with mineralization 20 g/dm^3 . On this background areas with higher and lower mineralization are broadly presented.

To clarify the reasons of appearance of these anomalies paleohydrogeochemical maps for the Oxford and Volga time have been constructed with superposition of the data of modern groundwater's composition. This data analysis revealed considerable distinctions in composition of modern and syngenetic groundwater. During the Oxford and Volga ages on territories of the south of the West-Siberian pool mainly marine regime of sedimentation occurred. Hence, background waters of the Oxford regional reservoir having a chemical composition and level of the general mineralization close to the level of normal sea water salinity, appear to inherit their composition from syngenetic waters of sea pool. This implies that abnormal mineralization levels appear in the course of pool evolution as a result of elision water exchange and interstratal overflows.

Consolidation of seal layers rocks, thermal dehydration and mineralogical transformation of clay sediments favor continuous supply of soft solutions onto a collector. These processes, apparently, are also the cause of occurrence of lowered mineralization groundwaters anomalies of the Oxford regional reservoir.

The carried out comparative analysis of Oxford regional tank groundwater's hydrogeochemistry and groundwater of lower-middle Jurassic and Paleozoic complexes has allowed to confirm the presence of anomalies of interlayer flow types on Bakljansky, Verh-Tarsky, Nizhne-Tabagansky and other areas. Similarity of groundwater's composition of above-listed complexes is confirmed by close levels of total mineralization, pH, and macro- and microcomponents content.

Interlayer flows occurrence is caused by the fragmentation mode of the lower-middle Jurassic sediments distribution in the south of the Western-Siberian megapool.



CHALLENGES AND FUTURE DEVELOPMENTS OF THE REFINING INDUSTRY IN THE PETROLEUM PRODUCING COUNTRIES

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In the past years several ‘mega-projects’ in refining and basic petrochemicals have been announced by petroleum producing countries, such as Saudi Arabia and Kuwait. These projects when and if completed will add some 1,400 thousand barrels per day of refining capacity in an already surplus market. The question of vertical integration in the producing countries is not new, many authors have presented elements in favour or against its implementation. Since the 1970s and throughout the decades, authors have updated the pros and cons for the then current economical and political context. Due to the evolving petroleum market, some reasons have become outdated and new have arisen. This article is an update of the different incentives and limits to vertical integration by the petroleum producing countries, given the current evolutions and future prospects for supply, demand and environmental regulation of world petroleum markets.

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THE DEVELOPMENT OF NOVEL HYDROTREATING CATALYSTS

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The development of the modern hydrotreating processes for the gasoline, kerosene and diesel oil fractions is determined by the demand of reduction of S-, N- organic compounds due to the strict environmental standards for motor fuels. Nowadays the standards Euro-4 and Euro-5 are accepted worldwide. Modern hydrotreating catalysts are used for the production of the fuels meeting the mentioned conditions.

The following approaches are applied for the development of such catalysts:

1) Synthesis of the modified support with the defined optimal textural properties and grains size and shape for the specified feed type. The stated approach is based on the fact that the hetero-organic compounds of various sorts of feedstock have different average sizes of the molecules. Therefore it is of great importance to use the optimal pore size to achieve the high degree of hydrotreating. Modification of the support allows to reduce the strong interactions between the support and active phase of the catalysts [2].

2) Synthesis of the active component precursor in the solution (molecular design) followed by the impregnation. The precursor is the bimetallic Co(Ni)-Mo complex stabilized with the chelate ligands; the complex is based on the molybdenum polyanion coordinated with Co^{2+} and Ni^{2+} cations. The structure of this complex allows to modify the nature and the ratio between the metals in the catalyst. One of the main advantages of this complex is its stability and ability to keep the structure being dissolved and also on the surface of the $\gamma\text{-Al}_2\text{O}_3$ support after impregnation and the catalyst drying [3]. Using such complex makes it possible to obtain (Ni)-Co-Mo-S type II phase which possess a high activity in the hydrotreating reaction.

The present work reviews the main approaches to the development of the novel hydrotreating catalysts. The using of bimetallic Co-Mo complexes such as $[\text{Mo}_2\text{O}_4(\text{C}_2\text{O}_4)_2(\text{H}_2\text{O})_2]$, $\text{Co}[\text{Mo}_3\text{O}_4(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_3]$ and $\text{Co}_2[\text{Mo}_4\text{O}_{11}(\text{C}_6\text{H}_5\text{O}_7)_2]$ which are the starting materials in the synthesis of the active catalysts have been discussed.

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STATIONARY THERMAL STABILITY ANALYSIS OF A GAS OIL HYDROTREATING REACTOR

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Safety is a high-priority topic for the chemical industry to minimize the frequency and severity of accidents while keeping the productivity and quality of the production. The processes that may undergo reaction thermal runaways are at the heart of these risks. The comprehensive study of such highly reactive systems is necessary to achieve their safe and productive operation as well as for safe new designs.

In refining and petrochemistry field the thermal runaway risk is real and has already been observed at industrial scale. Some examples of processes that may undergo a runaway are: selective hydrogenations, Fischer-Tropsch synthesis, H-Oil, l'hydrocracking, Alphabutol and Dimersol beyond others. The consequences of a thermal runaway can be an early deactivation of the catalyst (coking), lost of operability of the unit and very infrequently the reactor explosion. It is obvious that there are safety measures to avoid the danger of explosion. These measures are the advanced control of the unit, the fixing of alarm thresholds, the installation of pressure safety valves and rupture discs. However, the alarm thresholds are fixed rather based on experience and not on a scientific basis. Therefore it is necessary to establish in a rigorous way the safe field of operating conditions for the processes.

The objective of this study is to develop a methodology to determine the operating conditions of reliable operation of chemical reactors in the field of refining and petrochemistry processes.

The methodology consist on stationary and dynamic analysis. The stationary stability analysis is based on the van Heerden criterion and parametric sensitivity analysis. The dynamic analysis applies the perturbation theory to definitely determine if a stationary point is stable according to an eigenvalue analysis.

This work presents a thermal stability study under stationary conditions of gas oils hydrotreating. This process consists on the hydrogenation of unsaturated compounds present in gas oil feeds. Hydrogenation reactions are highly exothermic. Hydrotreating feeds containing high amounts of aromatics such as light cycle oils (80-90 weight %) may lead to a thermal runaway of the reactor. Therefore, a thermal stability study of this process was carried out. A dynamic model that accurately represents an HDT pilot plant was used for the study. The model takes into account a detailed description of the reactive system and the configuration of the pilot plant: three phases (gas-liquid-solid), the kinetics, the flow characterization in the gas and liquid phases. A stationary and dynamic thermal stability analysis was carried out. Such a study is useful to identify the stable/sensitive/unstable operating regions. The resulting reactor operation diagrams are a useful guide for engineers in the reactor design and operation practice.



TRANSFORMATIONS OF SULFUR ORGANIC COMPOUNDS IN CATALYTIC CRACKING CONDITIONS

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With increasingly stringent regulations to engine fuels the sulfur content should be steadily reduced. According to Euro 3 and Euro 4 specifications the gasoline sulfur level should be less than 350 and 50 ppm respectively. The major source of sulfur is fluid catalytic cracking (FCC) naphtha that contributes about 40 % to the gasoline pool and more than 90 % to the total sulfur content. To reduce FCC gasoline sulfur it is required either to remove it from feed or products, or to redistribute sulfur-containing products directly during a catalytic cracking. Last solution of desulfurization is inferred in creating special compositions of cracking catalysts, which promotes transfer of sulfur to gaseous or heavy liquid products.

In FCC feed and products sulfur-containing substances are divided into two groups: nonaromatic and aromatic (various thiophene derivatives). Nonaromatic sulfurorganic compounds at high temperatures of cracking process and in the presence of a great number of acid sites of base catalyst decompose with high selectivity to hydrogen sulfide and corresponding olefine. This process proceeds similarly to dehydration of alcohols. Thiophene ring containing substances are not cracked to H₂S. In this case primary reactions are isomerization and alkylation. One of the possible ways to destruction of aromatic coupling of thiophene ring are hydrogen transfer reactions from hydrogen donors ([H]-donor) molecules. Products of these reactions are cyclic sulfides which easily decompose to hydrogen sulfide and olefine in catalytic cracking conditions. So, it was supposed, that hydrogen transfer ability of hydrocarbon substrates should govern great effect on the selectivity of dearomatization.

As compounds acting as hydrogen donor n-undecane, decalin, cumene were investigated. Sulfur was introduced from 2-methylthiophene, benzothiophene or dibenzothiophene in amount of 1,0 wt. %. The reaction mechanisms of cracking of hydrocarbons from different classes shows that naphthenes are the best [H]-donors and aromatic compounds – the worst.

An equilibrium FCC catalyst and stabilised laboratory samples were used as a catalysts which contain H-ZSM5 zeolite (Si / Al = 30) or mixed Mg, Al - oxide with a spinel structure.

Theoretical conclusions about a possible mechanism of dearomatization of thiophene sulfur were confirmed with experimental data. Increase of [H]-donor activity of hydrocarbon source promotes the raise of both general conversion of aromatic sulfurorganic substances and transfer of sulfur to gaseous products. When H-ZSM-5 zeolite or Mg, Al - spinel additives which possess pronounced acid properties were used the conversion of sulfur substrates and the selectivity to H₂S were higher. At the same time the distribution of sulfur-containing cracking products slightly differs for each additive.



CATALYTIC PYROLYSIS OF HEAVY HYDROCARBON UNDER MICROWAVE HEATING

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It is well known that absorption of microwaves by any substance is sensitive to the nature of irradiated material, so the microwave (MW) power can be used for selective heating of heterogeneous systems. Also microwave heating has some other features, such as heating some substances to high temperatures in a short period of time.

And the first idea of the present work is to heat selectively a catalyst only with the use of microwave technique at comparatively cold ambient medium. In this case we can arrange a fast supply of the heat to catalyst and remove the desired reaction product prior to its secondary conversion to byproducts. This approach was used for the process of hexadecane cracking. It was showed, that on some catalysts the specific feature of the MW-assisted hexadecane pyrolysis is the predominant formation of α -olefins as the main products. One can suppose that under microwaves these catalysts are heated non-uniformly. The presence of small overheated particles promotes the α -olefins formation because of the olefins concentration must increase with the temperature rising. On the other hand, this selectivity is additionally reinforced by the “quenching” effect.

The second idea of the present work is to realize cracking of heavy oil residues inside porous granules of catalyst. The procedure of the cracking is the following: A granule of a MW-absorbing porous material is soaked with the oil residues at temperature when the residue is liquid. Thus we form a solid particle which is easily moved via any kind of reactor and doesn't limit the exchange by gaseous substances with the ambient. Then these particles are heated rapidly to high temperatures by MW.

Our experiments show that in such cases an extremely rapid heating of the porous material leads to the thermal cracking of the substance inside the pores occurred with the formation of coke and some gasified hydrocarbons escape to the gas stream. Note, that in such cases the coking + cracking do not considerably diminish the mobility of the granules which helps a lot at the process design and engineering.



THE EFFECT OF CITRIC ACID ON LOCALIZATION OF ACTIVE COMPONENT AND SUPERIOR ACTIVITY OF Co-Mo HYDROTREATING CATALYSTS

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The hydrotreating catalysts preparation using impregnated solutions of the metals salts stabilized with citric acid (CA) is widely presented in the patents, scientific papers and used in industry. The superior activity of these catalysts is prescribed by some researchers to the Co citrate complex formation, the other authors point out the Mo citrate formation in the impregnation solution, while the interaction between Co and Mo in citrates containing solutions is not revealed. Meanwhile, it is commonly accepted that the proximity of Co(Ni) and Mo in the surface species of the catalyst oxide precursor can be considered as criterion for obtaining high good promoting effect of Co(Ni) atoms. The high activity of the catalysts prepared using CA allows to propose the formation of the compound with close interaction between Co and Mo in the impregnated solution.

Aim of this study was to obtain more insight into the Co-Mo interaction in the citrate solution and its influence on the hydrotreating catalysts active sites genesis. The impregnated solutions were prepared using different above specified initial compounds of Co and Mo, but the concentrations of the Mo, Co and CA in the all cases were the same that used for the catalyst preparation. The different stages of the catalyst genesis were studied using variety of characterization methods, the catalyst activity was studied as well.

The data obtained allow to conclude that much higher activity of the catalysts prepared using citric acid is due to:

(1) CA enables to obtain bimetallic CoMo described by $\text{Co}_2[\text{Mo}_4\text{O}_{11}(\text{C}_6\text{H}_5\text{O}_7)_2] \times x\text{H}_2\text{O}$ formula. The existence of this complex within the impregnated solution ensures the formation of the oxide precursors with close proximity between Co and Mo during its deposition at alumina surface and provides the formation of highly active disperse sulfide particles during the sulfiding step. So, CA assures of stable the vicinal arrangement of Co and Mo during the genesis of catalysts.

(2) The molecular size of the complex with citric ligands that does not allow it to penetrate into the narrow pores of the carrier not available for most S-containing compounds of diesel fuels.

(3) Citric ligands screen the metals from the strong interaction with support.



#16

MODIFICATION OF FUNCTIONAL COVER OF THE γ - Al_2O_3 SURFACE BY USING OF ALUMINIUM OXALATE

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The goal of the presented work was to change the ratio of alumina surface sites at an invariable chemical composition of a surface. To achieve this goal γ - Al_2O_3 was modified with aluminium oxalate complexes (AOC) with subsequent heat treatment in oxidizing atmosphere. Interaction process of modifying ions with support is usually not considered, and the amount of the modifier and its influence on the properties of support are controlled only [1]. Earlier we shown that the maximum amount of AOC deposited on the γ - Al_2O_3 surface is 3 % (with respect to to Al_2O_3) [2]. In the same paper the chemisorption mechanism of AOC was suggested. In the present work the influence of offered modification method on surface properties and the porous structure characteristics of the support is studied.

By infrared spectroscopy it was shown that the supporting of AOC followed by the formation of aluminium oxide compounds on the γ - Al_2O_3 surface leads to some decrease of all absorption bands intensities, especially bands at 3670 and 3775 cm^{-1} . Therefore it was suggested that this types of surface hydroxyl groups participate in chemisorption of AOC (bridged and terminal OH-groups connected with 5-coordinated aluminium atom). Besides, the quantity of weak Lewis acid sites (LAS) decreases (absorption band at 2191 cm^{-1} in IR spectra of adsorbed CO).

Calcined at 550^oC alumina samples were investigated with the low-temperature nitrogen adsorption in order to receive their textural characteristics. It was shown, that modification (supporting of AOC and subsequent heat treatment) does not influence on parameters of support porous structure. Small change of pore size distribution is observed.

In addition, double bond isomerization of hexene-1 was used for an evaluation of influence of the alumina surface modification on its acid-base properties. The formation of aluminium oxide compounds on the γ - Al_2O_3 surface leads to decrease of hexene-1 conversion. The result is in agreement with IR spectroscopy data, i.e. decrease of the LAS quantity leads to decrease of hexene-1 conversion.

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TAILOR-MADE MULTIFUNCTIONAL MOF VIA A GENERIC POST-FUNCTIONALIZATION ROUTE FOR ACID-BASE CATALYSIS

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Thanks to their versatility, their tunability, Metal-Organic Frameworks (MOF), open new perspectives in heterogeneous catalysis. Their basicity/acidity features and their hydrophilicity/hydrophobicity balance can be tuned by post-functionalization methods. This study deals with the development of a soft, generic, one-pot post-functionalization method (Fig 1) for MOF starting from compounds exhibiting an amino group on the linker.

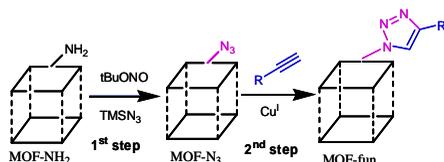


Figure 1: One pot post-functionalization route by click chemistry

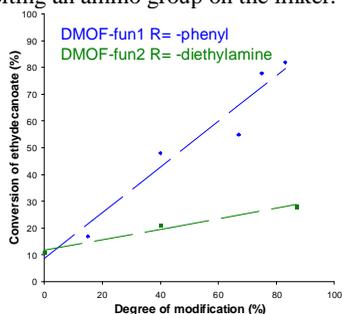


Figure 2: Catalytic results of functionalized-DMOF

This method is applied to MIL-68(In)-NH₂ [1], DMOF-NH₂ [2], CAU-1 [3] and MIL-53(Al)-NH₂ [4] which represent distinct and important classes of MOF. The solids were characterized by XRD, FTIR, ESI-MS, ¹H NMR and by N₂ adsorption.

The effect of functionalization on catalytic performances in the transesterification of ethyldecanoate with methanol is described in Fig 2. A systematic study dealing with the grafting of moieties exhibiting different functions on diverse amino-MOF platforms will be shown.

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OPTIMIZATION OF METAL-ACID PROPERTIES OF
Pt/SO₄²⁻-ZrO₂-Al₂O₃ CATALYST FOR
HYDROISOMERIZATION OF BENZENE-CONTAINING
FRACTIONS

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Production of cleaner fuels implies significant restrictions of benzene content. In a typical refinery up to 85% of benzene comes from reformat. One of the ways to reduce benzene level in gasoline retaining its high octane number is to transform benzene to methylcyclopentane by hydroisomerization. To provide these reactions both metal and acid sites are required. Conventional skeletal isomerization catalyst Pt/SO₄²⁻-ZrO₂ (Pt/SZ) does not suit in this case because of high acidity and depressed hydrogenation activity. Side reactions such as alkanes cracking and naphthenes ring opening readily take place on strong acidic sites. Hydrogenation activity of the catalyst is not enough to eliminate benzene totally. In this work we study the modification of structural, textural, metal-acid and catalytic properties of Pt/SZ by alumina incorporation.

Acidic supports SO₄²⁻-ZrO₂-Al₂O₃ (SZA) were characterized with thermal analysis, BET, XRD and HRTEM. In order to obtain bifunctional catalysts SZA supports were loaded with 0.3 wt% Pt (Pt/SZA). It is shown by IR-spectroscopy of adsorbed pyridine and CO that the number of Bronsted acid sites and medium Lewis acid sites of Pt/SZA catalyst decreases as alumina content grows. Such modification of acidity strongly affects catalytic properties in acid catalyzed reactions and allows attaining high selectivity for n-heptane and cyclohexane isomerization.

As shown by H₂ chemisorption Al₂O₃ enhances hydrogenation activity of Pt/SZ. IR spectroscopy of adsorbed CO revealed that the most part of Pt in alumina-containing catalysts is presented in metallic state.

Incorporation of alumina into Pt/SZ increases benzene conversion from 68 up to 99% during hydroisomerization of n-heptane-benzene mixture at 300°C. At the same time optimized acidity of the catalyst containing 67.8 wt% Al₂O₃ diminishes side reactions and provides selectivities to iso-C₇ and cycloalkanes 93 and 96% respectively. Hydroisomerization of light fraction of reformat confirmed high efficiency of the catalyst with optimized metal-acid properties: the catalyst provides total benzene elimination and selective methylcyclopentane formation.



HIGH-ACTIVE NiW/Al₂O₃ HDS CATALYSTS PREPARED WITH USING COMPLEX BIMETALLIC COMPOUNDS

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NiW/Al₂O₃ hydrotreating catalysts are very promising for HDS of heavy petroleum feeds and ultra-deep HDS of diesel fuel. In the present work NiW/Al₂O₃ HDS catalysts were prepared by impregnation method with solution of bimetallic Ni-W complexes, stabilized by organic ligands. The organic ligands play an important role, on the one hand, they stabilize the bimetallic complex leading to formation the compound with close interaction between nickel and tungsten in the impregnated solution, on the other hand, organic ligands prevent metals from strong interaction with the support leading to completely conversion metals during sulfidation into the active bimetallic sulfide phase.

In aqueous solution were synthesized bimetallic complexes stabilized by citrate ligands, γ -Al₂O₃ was impregnated with the solution, followed by drying at 120°C for 2 hours. The structure of the complexes in the impregnating solutions and on the surface of the support was studied by infrared and ¹⁷O NMR spectroscopy. It was shown that structure of complexes in the solution and on the surface of support is the same. Prepared catalysts were sulfided in H₂S flow at 400°C for 2 hours. Nickel and tungsten structures on sulfided catalysts were characterized by EXAFS and X-ray photoelectron spectroscopy (XPS). It was shown that in sulfided catalysts prepared by impregnation with solution of the bimetallic complexes nickel and tungsten are completely converted into sulphide form, whereas in catalysts prepared by conventional method (by incipient impregnation with an aqueous solution of ammonium metatungstate and nickel nitrate), a significant amount of metals presents in the oxide form and don't convert into the active sulphide bimetallic phase.

Prepared catalysts were tested in the HDS of petroleum distillates. Under the same conditions of the process, catalysts obtained with the use of complex bimetallic compounds showed superior activity in HDS than the conventional NiW/Al₂O₃ catalyst.



SYNTHESIS AND INVESTIGATION OF $Zr_{0.92}Y_{0.08}O_2$ AND ITS COMPOSITES WITH NiO AND FLUORITE LIKE COMPLEX OXIDES

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Nanostructured zirconia-based ceramics are widely studied due to their specific chemical and physical properties including high chemical stability, high temperature insulation ability and ionic conductivity. Zirconium oxide (ZrO_2) is commonly stabilized by the addition of yttrium oxide (Y_2O_3) into its crystal structure. This stabilization permits ion O^{2-} conduction, making Yttrium-Stabilized Zirconia well suited for uses in solid oxide fuel cells. In the field of industrial materials, YSZ is also known for its applications as structural material, sensor, catalyst, refractory material or thermal barrier coating in jet engines and gas turbine.

A wide variety of methods have been used for the production of ultra-fine YSZ powders, such as hydrothermal synthesis, sol-gel, plasma spraying and mechanochemical activation.

In this paper, we will focus on ultra-fine powder of YSZ ($Zr_{0.92}Y_{0.08}O_2$) and composite materials based on YSZ, NiO and SmPrCeZr complex oxide synthesized by the Pechini and coprecipitation methods. Materials are characterized by XRD, TEM and specific surface area measurements. Catalytic properties of composite materials were estimated in the reaction of CH_4 dry reforming (DR) in the temperature range 600- 880°C at short contact times (5 -75 ms). The oxygen mobility and reactivity of composite materials were characterized by CH_4 TPR, while the bonding strength of surface carbonates as intermediates in DR was estimated by TPD CO_2 .

According to XRD data, samples of YSZ synthesized by Pechini route and calcined at 400-600°C in the air flow correspond to single phase fluorite- like solid solution with a cubic structure. All prepared composite materials contain YSZ, NiO and SmPrCeZrO phases.

In DR of CH_4 in stoichiometric feeds, all composite materials demonstrate good and stable performance with high syngas yield and H_2/CO ratio close to 1. Promotion with Pt further increases performance of composites making them highly active even at temperatures below 700 °C.



#1

HYDROISOMERIZATION OF BENZENE AND n-HEPTANE ON PLATINUM MORDENITE CATALYSTS FOR THE ECOLOGICAL FUELS PRODUCTION

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At present in Russia one of the major task for most refiners is the benzene reduction in the gasoline for meeting the new ecological requirements. One of the promising solution of the problem is benzene hydroisomerization usage. In the work a series of H-mordenite-based platinum catalysts were studied in the reaction of the benzene hydroisomerization. This reaction includes the stage of hydrogenation of benzene to cyclohexane (100% conversion on whole specified temperature range) and the stage of isomerization of the latter to methylcyclopentane (MCP). Investigation was carried out on binary mixture of 21 wt% benzene and 79 wt% n-heptane under the following condition: $p = 15$ bar, $T = 200-320^{\circ}\text{C}$, $\text{WHSV} = 2 \text{ h}^{-1}$, $\text{H}_2/\text{hydrocarbon}$ molar ratio = 3.

The research of the effect of zeolite/alumina ratio for mixture transformation parameters showed that the optimum mordenite (MOR) content of the catalyst is about 10-30 wt%, the equilibrium yield of MCP being reached at 280-310°C. If the zeolite content is lower than 10%, the catalytic activity is shifted to not so favourable thermodynamically high temperature zone. Fig. 1 shows the yield of the

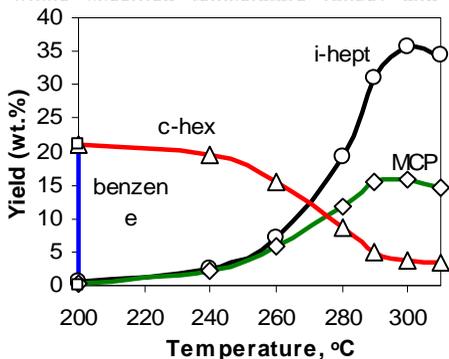


Fig. 1. Product yield vs. temperature on Pt/MOR-30 catalyst

main products of benzene and n-heptane hydroisomerization versus the reaction temperature on the Pt/MOR-30 catalyst with the following composition: Pt = 0.3 wt%, MOR = 30 wt%, $\text{Al}_2\text{O}_3 = 70$ wt%. Catalytic results for Pt/MOR-30 are given in Table 1. The research octane numbers of the feed and the product are 22.6 and 71.1 respectively.

Thus, the feasibility of high selective process of hydroisomerization benzene to methylcyclopentane with reaching the equilibrium yield of the latter on the Pt/mordenite catalysts is shown. In addition, cracking of heptanes does not exceed 10-20 wt%.

Table 1. Catalytic results for Pt/MOR-30

T, °C	c-Hexane conversion, wt%	Selectivity of hydroisomerization of benzene to MCP, wt%	MCP/c-Hexane	n-Heptane conversion, wt%	Selectivity of hydroisomerization of n-heptane, wt%	Yield of the ΣC_7 cracking products, wt%
290	77,1	98,2	3,08	53,4	71,4	10,8
300	82,0	94,1	4,05	69,0	62,1	19,0



INNOVATING *OPERANDO* CHARACTERIZATION OF
COBALT SUPPORTED CATALYST
BY COUPLED XRD-DRIFT MEASUREMENTS

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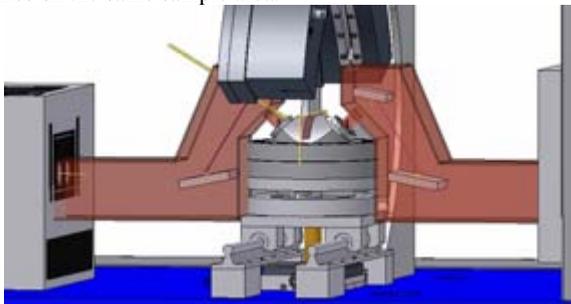
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In order to improve our knowledge on the structural and catalytic properties relationship in supported cobalt catalysts, an innovative characterization method has been developed including *operando* XRD and DRIFT analysis.

In an original in situ cell, infrared and diffraction analysis are performed in perpendicular planes on the same sample area.



Both techniques have been associated to optimize cobalt catalysts characterization under optimistic FT synthesis conditions : internal cell pressure can reach 30 bars and temperatures can reach up to 600°C. Gaseous reactants will travel through the cell via a fixed bed reactor.

Structural modification of the catalyst and products formation on its surface will be followed during the reaction [1-2].

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DOES OPEC STILL EXIST (AS A CARTEL) ? AN
HISTORICAL AND ECONOMETRICAL VIEW SINCE 1973

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If the end of the 1990's experienced a huge drop in oil prices after the Asian financial crises (10 \$ per barrel in 1997), the context has radically changed at the beginning of the new century, with a slow and sharp increase of the oil prices during the 2001-2008 period, reaching a maximum during July 2008 at 147 \$ per barrel. This level matched in real terms (deflated by the US CPI) the one observed during the second oil crisis in 1979. Nevertheless the financial crisis and the anticipations of the actors did not prevent the market to collapse at the end of the 2008 year at around 30 \$ per barrel and to increase thereafter to the 70 \$ per barrel level in July 2009. This context of huge instability in the oil market helps us to highlight that all the questions related to the oil prices formation remain. What are the key factors of the oil prices formation? Is the market supply-side driven or demand side driven? Many analysts pointed out the fact that because of emerging countries, such as China, the market was essentially driven by the demand side and forgot that oil market is very particular because of the main production organization, OPEC.

This paper is concerned with the evolution of production behaviour of exporting countries belonging to the OPEC Organization (Algeria, Indonesia, Iran, Iraq, Kuwait, Libya, Nigeria, Qatar, Saudi-Arabia, UAE and Venezuela) and countries which could be considered as "important" players in the market (Mexico, Norway, Russia and UK). Our aim is to study the long-run relationship between the production of each player in the market and the aggregated production of the Organization (OPEC). This allows us to investigate if OPEC acts as a cartel, by testing if the production decisions of the different economies are coordinated and if they have an impact on prices.



MECHANICAL DEGRADATION OF POLYMER USED IN ENHANCED OIL RECOVERY**Dupas A.¹, Hénaut I.¹, Argillier J.-F.¹, Aubry T.²**¹: IFP, Rueil Malmaison, France²: LIMATB, Université de Bretagne Occidentale, Brest, France

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The use of water soluble polymers such as polyacrylamide in enhanced oil recovery (EOR) aims to increase the mobility of the injected fluid during flow by increasing its viscosity. However, harsh injection conditions can cause the degradation of the polymer and hinder its efficiency. In this study, we report observations of this phenomenon as well as the effects of mechanical degradation in EOR. We used aqueous solutions of polyethylene as model polymer with different molecular weights and concentrations. We proceeded to its degradation by a standard capillary system which has been developed by the American Institute of Petroleum (API) . [1] To make sure that polymer solutions are degraded, the critical shear rate is determined. This rate corresponds to the beginning of molecular bond breakage and represents a shear viscosity loss of 10%. As in EOR conditions, the real flow contains shear and extensional components, we measure study of shear and extensional properties in order to know which one is predominant. The extensional properties are determined by the relaxation time using a extensional on-chip viscosimeter. The difference of relaxation time between initial and degraded polymer solutions is around 50%. Consequently, the extensional properties are more affected than the shear viscosity. [2] We also showed that the critical shear rate obtained for semi-dilute polymer solutions is inversely related to the average molecular weight in agreement with literature. [3] [4] As the system used is semi-dilute, the next step will be estimated the influence of concentration on mechanical degradation.

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A DERIVATIVE FREE OPTIMIZATION METHOD FOR RESERVOIR CHARACTERIZATION INVERSE PROBLEM

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Reservoir characterization inverse problem aims at building reservoir models consistent with available production and seismic data for better forecasting of the production of a field.

These observed data (pressures, oil/water/gas rates at the wells and 4D seismic data) are compared with simulated data to determine unknown petrophysical properties of the reservoir.

The underlying optimization problem is usually formulated as the minimization of a least-squares objective function composed of two terms : the production data and the seismic data mismatch. In practice, this problem is often solved by nonlinear optimization methods, such as Sequential Quadratic Programming methods with derivatives approximated by finite differences.

In applications involving 4D seismic data, the use of the classical Gauss-Newton algorithm is often infeasible because the computation of the Jacobian matrix is CPU time consuming and its storage is impossible for large datasets like seismic-related ones.

Consequently, this optimization problem requires dedicated techniques: derivatives are not available, the associated forward problems are CPU time consuming and some constraints may be introduced to handle a priori information. We propose a derivative free optimization method under constraints based on trust region approach coupled with local quadratic interpolating models of the cost function and of non linear constraints. Results obtained with this method on a synthetic reservoir application with the joint inversion of production data and 4D seismic data are presented. Its performance is compared with a classical SQP method (quasi-Newton approach based on classical BFGS approximation of the Hessian of the objective function with derivatives approximated by finite differences) in terms of number of simulations of the forward problem.

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REGULARITIES OF JOINT CONVERSION OF N-HEXADECANE WITH DECALIN AND CUMENE ON BIZEOLITE CRACKING CATALYST

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Catalytic cracking is complex process, which includes many parallel and consecutive reactions. In the literature it is very few information about the joint conversion of hydrocarbons of different types, especially if it relates to transformations of hydrocarbons on bizeolite catalysts under the conditions of deep catalytic cracking.

The purpose of this work is to investigate the regularities of the catalytic cracking of linear alkanes in the presence of naphthenic and aromatic hydrocarbons on bizeolite catalyst.

During the study of the joint transformation of n-hexadecane with decalin it is established that an increase of decalin content in the model mixture does not affect n-hexadecane conversion. In this case observed increase in the yield of arenes and reduction in the formation of olefins is due to an increase in the contribution of the hydrogen transfer reaction. The estimation of the observed activation energy of n-hexadecane cracking shows that this parameter practically does not change during the joint transformation of n-hexadecane with decalin. The value of the observed activation energy for the conversion of n-hexadecane and its mixture with decalin (50:50) amounts 40,3 and 40,9 kJ/mol respectively. It should be noted that the low values of the observed activation energy indicates that cracking reactions proceed in the region of configurative diffusion on zeolites.

Sharp decrease of n-hexadecane conversion is observed with an increase of arene content in the model mixture n-hexadecane-cumene. Suppression of n-hexadecane cracking by cumene is concerned with the selective absorption of aromatic hydrocarbon on the strong acidic sites. As a result, the yield of paraffins and olefins, excluding propylene and butylenes, decreases, and the yield of aromatic hydrocarbons on the contrary increases. The observed activation energy of n-hexadecane cracking substantially grows in the case of the joint conversion of n-hexadecane with cumene (50:50) and its value reaches 64,1 kJ/mol.



CARBONATION OF WELL CEMENT: EXPERIMENT AND MODELLING

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Concerning Carbon Capture and Storage (CCS) [1], research aiming at guaranteeing the absence of CO₂ leakage through the well is done. The possibility of such leaks raises considerable concern about the long term wellbore isolation and the durability of hydrated cement used to isolate the annulus in wells. The thesis aims at developing knowledge and comprehension of the degradation mechanisms of a hardened cement paste due to CO₂-laden fluids, as well as to model the phenomena inducing physico-chemical evolution of cement based materials exposed to such fluids.

Experiments are conducted to investigate, over a short time scale, the degradation of a hardened cement paste exposed to CO₂. The conditions of exposure to CO₂ are 80°C and 50 Bar during 15 days, 1 month and 3 months. The tomography analysis show the carbonated zone size increasing when the time of the test is longer. The mineralogical evolution of the cement samples, from the bulk to the edge, is studied by means of X-ray diffraction and thermogravimetric analysis. Moreover, the repartition of the chemical elements in the samples is studied by Scanning Electron Microscopy.

Then, modelling consists in the adaptation and validation of a thermodynamic database thanks to the acquired thermodynamic data thanks to a detailed literature survey. A second aspect is to use reactive transport modelling to help to design appropriately the leaching experiments (flow rate to be used, localization of the samples inside the cell...). Finally, the last task is to simulate the leaching experiments implementing carbonated fluids in order to reproduce the experimental results.

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SMOOTHING SPLINE ESTIMATION IN HIGH
DIMENSIONAL RESPONSE SURFACE MODELS VIA
ITERATIVE THRESHOLDING REGULARIZATION

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To perform the uncertainty analysis of computer experiments we model the outputs as nonparametric regression models with multivariate design points. Under the framework of Smoothing Spline ANOVA, we propose a new method based on L_{2} kernel estimation combined with L_{1} multidimensional regularization. The formulation of our estimator leads to an iterative thresholding algorithm which is designed to select a parsimonious model representation by selecting a small set of ANOVA terms. Numerical studies on simulated and real data, show that our method gives competitive performance compared to COSSO and some Gaussian processes approaches.



GLOBAL MODELING OF HYDROCRACKING: METHODOLOGY

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Hydrocracking process has become a major operation unit in today's oil refining industry. Such an interest is explained by the increasing demand of middle distillates with excellent product quality. Hydrocracking is a catalytic cracking process converting high-boiling fractions like Vacuum Gas Oil (VGO) into lower-boiling and more valuable fractions like diesel. It is carried out on bifunctional catalyst combining both a metal and an acid phase, in the presence of a high hydrogen partial pressure. To optimize the yield of the desired products and because of the complexity of the feedstock and the reactions, hydrocracking modeling is essential. The developed model considers an hydrotreated feedstock composed of aromatic, naphthenic and paraffinic hydrocarbons. Its purposes are both to realize a relevant molecular reconstruction of the effluents and a global kinetic model taking into account the industrial context.

Analytical techniques are not yet powerful enough to detect and quantify in detail all the components of the effluents. Thus a molecular reconstruction is required. The proposed method is to use analytical results provided by high-temperature two-dimensional gas chromatography (HT-2D-GC)^[1] to create an initial set of molecules. Then, the molar fractions of these molecules are optimized by the maximization entropy method. Finally a detailed and relevant distribution of molecules is obtained.

For the kinetic model, the goals are both to introduce the aromatic and naphthenic hydrocarbons in the model and to consider the reactions in the metal phase and in the acid phase. A reaction mechanism of hydrogenation/dehydrogenation has to be defined and implemented into the kinetic model^[2, 3]. For the acid phase, the kinetic model is based on the Single-Event approach initiated by Froment et al.^[4]. Its biggest interest is to use a limited number of kinetic parameters.

Finally, the global model allows to simulate the hydrocracking process in industrial conditions considering complex feedstock.

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CARBON ADSORBENTS WITH GIVEN POROUS STRUCTURE

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The purpose of this work is research of methods of synthesis of nanoporous carbon materials with controlled pore size distribution and chemical characteristics of the surface, that is necessary for design of effective sorbents used in environment protection, medicine, extracting non-ferrous and rare metals in hydrometallurgical processes, etc. This aim is achieved by using conjugated polymers as carbon precursors. As known, polymers with conjugated double bonds C=C have high thermal stability. On the other hand, these polymers easy form sp^2 carbon structures by macromolecules condensation and aromatization. Therefore, sizes and a positional relationship of the structural elements of obtained carbon material can be determined by original conjugated polymer structure.

This approach has been implemented by the example of thermal dehydrochlorination of chlorine substituted polyenes (polychlorinevinylenes) running even at 200 °C. Initial polychlorinevinylenes were synthesized by chemical dehydrochlorination of available carbochain halogen polymers with high Cl content (e.g. polyvinylidene chloride, chlorinated polyvinyl chloride) in the presence of bases.

The conditions of intramolecular dehydrochlorination were selected using the potentiometric titration. The formation of polychlorinevinylenes in chemical dehydrochlorination is confirmed by the presence of characteristic narrow peaks at 1107 and 1490 cm^{-1} in the Raman spectra. According to TGA, MS data and Raman spectra, thermal dehydrochlorination of polychlorinevinylenes (interchain polycondensation) proceeds in mild conditions and leads to the formation of highly disordered nanostructured sp^2 -carbon material, similar to carbon black.

The selection of the chemical dehydrochlorination conditions (e.g. solvent, dehydrochlorinating agent, temperature) in combination with various conditions of subsequent thermal treatment allows changing greatly the parameters of porous structure of the resulting material. Proposed method has been used to obtain as ultramicroporous carbon with a narrow micropore size distribution so a material with advanced volume of mesopores. High values of specific surface area (up to 1800 m^2/g) and volume of micro- and mesopores (respectively 0,7 and 1,4 cm^3/g) have been achieved.

Besides, it has been shown that the addition of different nanoparticles (carbon nanotubes, carbon nanoglobules, SiO_2 nanoparticles) to polychlorinevinylenes significantly influences to the carbonization process and the development of porous structure in the final material.



INVESTIGATION OF Pt/DEFECT γ - Al_2O_3 SYSTEMS IN REFORMING REACTION

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Effective reforming catalysts include ionic platinum forms (Pt^σ -centers) which are the result of strong interaction between active component precursor and surface OH-groups and defects of γ - Al_2O_3 . Defects are anionic vacancies which can be created on the Al_2O_3 surface by calcination in air of alumina precursor. Therefore an actual task is the development of method for synthesizing of γ - Al_2O_3 with high number of defects.

In this work structural modification of the support was done. That modification consists of the introduction of organic (acetic, oxalic and citric) acids into an aluminum hydroxide mass with formation of basic aluminum salts on the surface of AlOOH primary particles. The thermal decomposition of these salts results in appearance of more defects. Formation of alumina with different physicochemical properties from unmodified alumina is occurred.

The increasing degree of defectiveness was judged on the decrease of true density from helium pycnometer, the increase of intensity vibrations of terminal OH-groups connected with unsaturated-coordination aluminum cations ($\text{Al}^{\text{V}}\text{-OH}$, $\nu = 3775 \text{ cm}^{-1}$) and the volume increase of strong Lewis acid centers ($\nu = 2190 \text{ cm}^{-1}$).

Adsorption and catalytic properties of platinum centers on supports have been investigated. The catalysts on the basis of more defective alumina surface obtain the greater rate of Pt^σ -centers. Hence, increasing catalytic activity A (A) and selectivity S (A) of Pt/defect Al_2O_3 systems in dehydrocyclization reaction of n-heptane is observed (fig. 1).

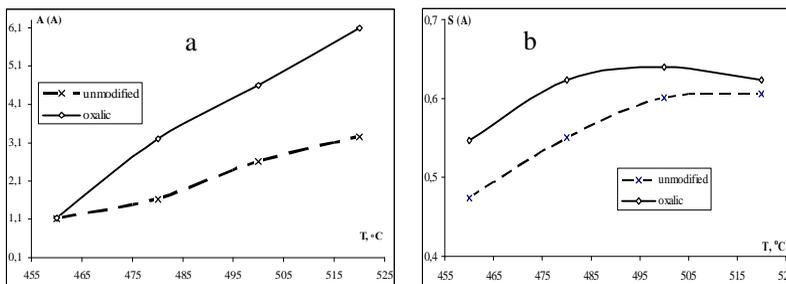


Fig. 1. Comparison of samples 0.5wt% Pt/ Al_2O_3 : a) dependence of aromatization activity on reaction temperature; b) dependence of aromatization selectivity on reaction temperature.



A MODEL FOR CONDUCTIVE FAULTS IN HETEROGENEOUS MEDIA

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Faults have a major impact on fluid migration, because of their permeabilities, which can be much higher, acting as a conduit, or much lower, acting as a barrier, than the surrounding matrix rock, but also because they can connect different stratigraphies, with different properties. Taking into account the influence of faults is an important challenge for reservoir (well development plans), basin (evaluation of the hydrocarbon migration) and CO₂ storage (risk assessment for CO₂ leakage) simulation. Evaluating the influence of faults with homogenization methods shows poor results. Explicit gridding of a fault zone with volumetric elements can be considered for a simple single fault, but becomes rapidly too tedious for a real fault network. Indeed, in the standard Corner Point Grid approach, a fault zone is supposed to be sufficiently thin to be represented as a surface with non-matching interfaces, due to the throw, across the fault. Following this point of view, we study an approach where fluid flow along the fault is modeled by a lower dimensional model, the fault thickness becoming a model parameter. It can be seen as an extension of the Discrete Fracture Model approach. We present here the model and the impact of one parameter that differs among the different authors in the literature.

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