CATALYSIS FOR RENEWABLE SOURCES:
FUEL, ENERGY, CHEMICAL

Crete, Greece
September 2-6, 2019

5th International Conference
CATALYSIS FOR RENEWABLE SOURCES: FUEL, ENERGY, CHEMICALS
CRS-5

ABSTRACTS

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V International Conference

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CRS-5

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ABSTRACTS

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Сборник включает тезисы пленарных лекций и устных докладов секций:

- **Section I. CATALYSIS FOR BIOMASS DEPOLYMERIZATION AND DOWN-STREAM UPGRADING**
  Catalytic systems for hemicellulose, cellulose and lignin depolymerization
  Catalytic processing of tall oil and tar
  Selective conversion of biomass derived sugars and phenolics to fuels, chemicals and polymers
  Catalysis in dendrochemistry for valuable products
- **Section II. BIOMASS DERIVATIVES IN PETROCHEMISTRY**
  Catalyst application for clean syn-gas and clean hydrogen production
  Lipids in petrochemical synthesis
  Co-processing of biomass derivatives and oil feedstock
- **Section III. CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION**
  Catalytic interesterification and hydrocracking of lipids to kerosene and diesel fractions
  Catalytic approaches to biomass pyrolysis processes
  Conversion of carbon rich unconventional fossil resources and biomass feedstock into biofuel
- **Section IV. CATALYTIC PROCESSING FOR VALUABLE CHEMICALS PRODUCTION**
  Bio-catalysis for chemicals production
  Lipids conversion to valuable products
  Electrochemical biomass conversion
  Catalytic transformations of CO_2 to lignin cellulose
- **Section V. CATALYSIS FOR ENVIRONMENT AND SUSTAINABILITY**
  Catalytic processes for energy efficiency and ecology
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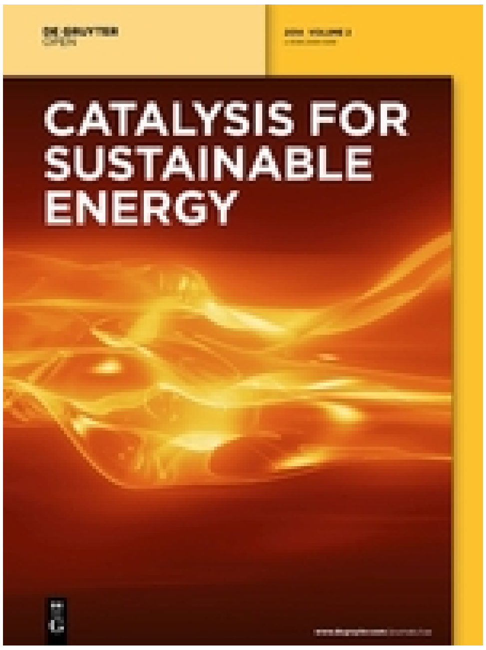

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CATALYSIS FOR SUSTAINABLE ENERGY

PLENARY LECTURES

IN-SITU AND EX-SITU BIOMASS CATALYTIC PYROLYSIS TOWARDS PRODUCTION OF HIGH QUALITY BIO-OIL. THE ROLE OF CATALYST DEACTIVATION

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Introduction

The use of heterogeneous catalysis in biomass fast pyrolysis has been extensively investigated the last years for producing high quality catalytic bio-oil with better properties than the thermal one. Catalytic biomass pyrolysis can be applied in two operating modes: i) in-situ, where the catalytic fast pyrolysis (CFP) takes places in one reactor and ii) ex-situ, where the entire process take place in two reactors connected in series (a first reactor for thermal pyrolysis and a second for the catalytic upgrading of the pyrolysis vapors).

In this study the research work carried out in CPERI the last 10 years (under the EU projects BIOBOOST and CASCATBEL) for both modes of catalytic pyrolysis will be presented and discussed. Emphasis will be given on the catalyst and reactor technologies developed at CPERI which is based on ZSM-5 zeolites and on circulating fluidized bed reactors and also on the catalyst deactivation phenomena that strongly affects the performance of the process.

Experimental

The experimental systems used at CPERI for this work consist of reactor technologies covering all scales from bench, medium up to pilot. For the in-situ mode the continuous pilot scale circulating fluid bed reactor technology will be discussed. For the ex-situ mode the technology developed at CPERI consists of a medium scale continuous fluid bed thermal reactor connected with a fixed or a fluid bed catalytic reactor and of a pilot scale continuous fluid bed thermal reactor connected with a catalytic circulating fluid bed reactor.

Regarding catalytic technologies emphasis was given (for in-situ mode) on new and commercial available zeolitic (acidic) and basic catalysts. For the ex-situ mode different types of ZSM-5 based catalyst (standard, hierarchical and nanocrystalline) were tested. Commercially available catalysts were also tested for a side by side comparison of the performance of the two modes. Full characterization of fresh and deactivated catalyst was carried out using routine and advanced analytical tools. For catalyst deactivation by coke confocal fluorescence microscope aided by UV-Vis and IR microscopy was used.

Results and Conclusions

For the in-situ CFP, bench and pilot scale tests were carried out using several catalysts (E-cat, ZSM-5, Magnesium, Titanium and Nickel oxides etc.). These catalysts were evaluated towards their better selectivity for bio-oil deoxygenation. It was shown that ZSM-5 based catalysts are the best catalyst for the in-situ mode. Regarding operating variable effect, the catalyst to biomass ratio (C/B) was studied on pilot scale. It was found that C/B ratio affects strongly the yield of the produced bio-oil. Finally it was revealed that for in-situ CFP the catalyst is deactivated by two mechanisms: hydrothermally due to the severe conditions in the regenerator and by metal poisoning due to the high ash content of the biomass.

For the ex-situ mode, medium scale tests were performed with three ZSM-5 zeolites with different structure (normal, hierarchical and nanocrystalline) at constant reactors temperatures (500 °C and 450 °C) by varying C/B ratio and time-on-stream. The increase of the C/B ratio enhanced over all catalysts the cracking reactions, leading to reduced bio-oil yield, with however lower oxygen content. In terms of activity, desilication of ZSM-5 led to increased cracking. Comparison of deoxygenation selectivity at constant conversion pointed out to a nanocrystalline ZSM-5 being the most selective catalyst. Catalyst deactivation in ex-situ mode is mainly coming from coke formation and not metals poisoning (as in the in-situ mode). To investigate the coke formation spatial characterization was carried on the used catalysts to determine the location and role of the individual catalyst components (e.g. zeolite and binder) on coke formation. The coke nature proved highly heterogeneous within the catalyst body. Among the series of catalysts selected, those with lower concentration of strong Brønsted acid sites were found to form richer H-content coke, in line with their lower activity. From the work performed till today it was proved that the best ex-situ technology for a potential commercialization should contain a first (fixed or circulating) fluid bed thermal reactor following by a circulating fluid bed catalytic reactor in order to assure the continous catalyst regeneration.

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To all personnel of the laboratory of environmental fuels and hydrocarbons (LEFH) of CPERI/CERTH.

PL-2

STRUCTURALLY - DIMENSIONAL EFFECTS IN SELECTIVE HETEROGENEOUS CATALYSIS OF RENEWABLE BIOMASS INTO IMPORTANT PRODUCTS OF PETROCHEMISTRY

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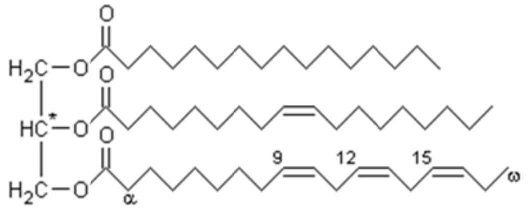
In recent years, much attention has been paid to the use of renewable biomass as an alternative raw material for the production of fuel components, hydrogen and syngas, as well as important monomers. In this direction, a special role is given to catalytic processes using nanoscale catalytic systems that provide highly selective conversion of renewables.

The report presents the results obtained during recent years in the laboratory of Catalytic nanotechnology of A.V. Topchiev Institute of Petrochemical Synthesis RAS concerning with the study of the structural organization of nanoscale metal-containing active components effect on selective conversion of ethanol and fermentation products, fatty acid triglycerides and plasma-catalytic dry reforming of mixed kraft lignin in the main energy carriers and important petrochemical products.

It was found that by increasing the ratio of the active components of Sn/Pt to 5 in Pt-Sn/Al_2O_3 catalysts, the selectivity in the reaction of reducing deoxygenation of a large number of esters, including fatty acid triglycerides, increases in the hydrocarbon components by the number of carbon atoms corresponding to the ether fragments and water [1,2]:



$$\longrightarrow \quad C_3 + C_{18} + nH_2O \qquad (1)$$

The yield of light hydrocarbons C_1, C_2 and carbon oxides CO_2, CO does not exceed 0.5 %. The study of the evolution of the active components structure showed that high selectivity is provided by the formation on the surface of the nanoscale intermetallic particles $PtSn_{3\pm\delta}$ and tin oxides with a size of 2-3 nm.

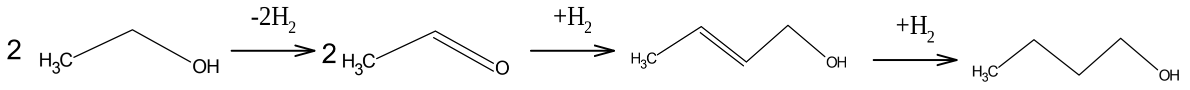
Using a porous hybrid membrane-catalytic converter obtained by self-propagating high-temperature synthesis of Ni(5 % Al)-Co composition, a high conversion is achieved in the process of dry and steam reforming of methane, hydrocarbons, ethanol and fermentation products into synthesis gas, reaching 80-120 m^3 /dm^{3}membr.h. The role of Al on the formation of reforming active components on the inner surface of the converter channels was established. The study evolution structure with use X-Ray and TEMHR showed that in the presence of 5-8 % Al, the formation of the converter proceeds by the so-called mechanism of aluminothermal synthesis, as a result of which aluminum atoms reduce cobalt from its oxide, turning into aluminum oxide particles up to 200 nm in size, on the surface of which highly dispersed intermetallic particles of Ni-Co alloy with a size of 5-8 nm are formed [3,4]:

$$8Al + 3Co_3O_4 \rightarrow 4Al_2O_3 + 9Co \qquad (2)$$

$$Co + Ni \rightarrow [NiCo] / Al_2O_3 \qquad (3)$$

There were presented methods of nickel-and iron-containing components formation on the surface of mixed lignin of wood origin, having by high ability to absorption of microwave irradiation (MWI) with plasma generation and catalytic activity. Dry reforming of organic mass of lignin (OML) proceeds in the mode of plasma stimulated by MWI at the average temperature of the reaction zone 700-800 °C. Conversion to OML reaches 65 % at selectivity in producing syngas of H_2/CO – 1 up to 92 %. Time of carrying out of process is 15 min. With using vibration and messbauer spectroscopy, TEMHR and magnetic measurements have studied evolution of the structural organization of the active components having high ability to absorption of MWI and catalytic activity in dry reforming process [5,6].

High activity (60 %) and selectivity (85-90 %) in reactions of selfcondensation of supercritical ethanol to n-butanol and β-alkylation of isopropanol-2 by ethanol to pentanol-2 were reached in the presence of nanosize bimetallic catalysts such as Au-Ni; Au-Cu and Au-Fe forming on the surface of γ-Al_2O_3 as nano size particles 2-3 nm [5,6]:



It was shown that the role of gold co-reagents is providing by high activity and selectivity of the catalysis consist of in an obstacle of agglomeration of the gold nanoparticles and formation of Au+.

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PL-3

OPPORTUNITIES AND CHALLENGES FOR BIOMASS CONVERSION PROCESSES

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The European Commission, but also many other public and private organizations, believe that biomass for fuels and chemicals production will play a crucial role in meeting Europe's targets to move towards a low carbon economy. Among the main biomass conversion technologies (combustion, gasification, pyrolysis) only pyrolysis converts biomass to high energy density liquids (bio-oil) at high yields and, hence, is the most suitable to fulfil the high future demands for biofuels and biochemicals. However, the presently available reactor technology and seperation technolgies for bio-oils are far from optimal. Most fast pyrolysis reactor designs have not survived the pilot plant stage apart from the rare exception. In this presentation, the focus is on the first principles based design of a new reactor type known as the rotating bed reactor in a static geometry (RBR-SG) [1]. In the Laboratory for Chemical Technology we are currently demonstrating this new disruptive technology for the conversion of biomass to chemicals and fuels via fast pyrolysis [2]. In our integrated approach of the problem, besides reactor engineering, kinetic modelling, Computational Fluid Dynamics, focus is given, on one hand, on the genetic modification of plants [3] to optimise liquids yields and, on the other, on the further purification, fractionation [4] and extraction of valuable compounds from these liquid products. On-line analysis using comprehensive 2D GC [5] and Time of Flight Mass Spectrometry play an essential role to close mass balances and obtain accurate data. Stabliization of the bio-oil [6] or catalytic conversion [7] of the produced bio-oil proved to be challenging because of deactivation.

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PL-4

HYDRODEOXYGENATION OF FATTY ACIDS AND TRIGLYCERIDES TO LIQUID FUELS OVER ZEOLITE-SUPPORTED NICKEL CATALYSTS

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The extensive emission of anthropogenic carbon dioxide resulted from the widespread usage of fossil fuels has been confirmed as the main cause leading to the global warming and extreme weather events. Consequently, the development of economically and environmentally friendly fuel alternatives from renewable resources to replace fossil fuels has become the focus of extensive research works. One of these alternative fuels is fatty acid methyl/ethyl esters (FAME/FAEE), *aka* biodiesel. Biodiesel is obtained mostly via the esterification of free fatty acids (FFAs) or the transesterification of triglycerides including vegetable oils, animal fats and waste cooking oils, in excess methanol or ethanol in presence of proper catalysts. However, the high oxygen content in biodiesel has been detrimental in long-term storage and has limited their applications in cold weather. For example, biodiesel can be clouding and even gel-like to clog the fuel lines during cold months. Furthermore, the application of FAMEs as aviation turbine fuels becomes almost impossible owing to the very low fluidity in cold environment/high altitude. As the result, the catalytic hydrotreatment of these renewable fatty acids and triglycerides is proposed to produce liquid alkane fuels with less oxygen content [1, 2].

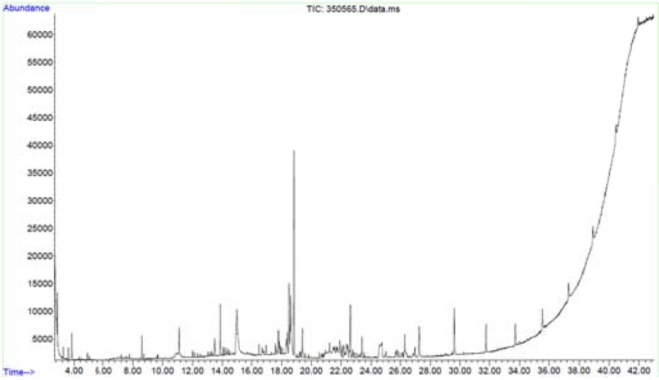

Figure 1. GC/MS chromatogram of liquid products obtained from hydrotreatment of soybean oil

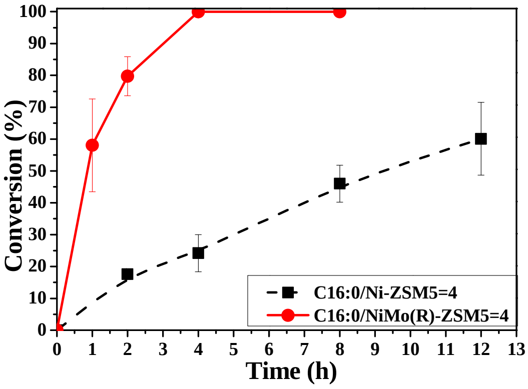

Figure 2. Conversion of palmitic acid in a batch reactor (H_2^0 = 35 bar; T_{rxn} = 573 K; Cat loading = 25 wt % of palmitic acid)

In our group, zeolite-supported Ni-M catalysts (M = none or Mo) were prepared and studied for their applications in the catalytic processing of fatty acids and triglycerides to liquid fuels, mainly via hydrodeoxygenation (HDO) and hydroisomerization (HI) process. In brief, zeolite ZSM-5 from Zeolyst (CBV 3024E) was used as support, and no precious metals were used as active catalysts in this work. A Ni-content about 10 wt % of zeolite ZSM-5 support with various Mo-contents was found on these Ni-Mo/ZSM-5 catalysts. Prior to the hydrogenation reaction, catalysts were generally reduced in the stream of 5 % H_2/Ar (100 mL/min) at 500 °C for at least 3 hours. Both HDO and HI of palmitic acid and soybean oil were carried out at 280-350 °C and under the H_2 pressure up to 70 bar. The GC-MS was employed to qualitatively analyze the products, which include methylbenzene, dimethyl-heptane, tetramethyldecane, *t*-butylphenol etc. (Figure **1**). The catalyzed HDO reaction of palmitic acid was carried out in a batch autoclave (Parr 4560) at 573 K with an initial pressure of hydrogen at 35 bar at this temperature. The loadings of catalyst were maintained as 25 wt % of palmitic acid. With Ni/ZSM5 catalyst, the conversion of palmitic acid reach ca. 60 % in 12 h. In contrast, the complete conversion of palmitic acid was almost achieved, near 99 %, in 4h with Ni-Mo/ZSM-5 catalysts. Presence of molybdenum really improved the HDO reaction of palmitic acid. Furthermore, a significant portion of isomerized alkanes were obtained in the product as revealed by GC-MS (Figure 3). That is, both HDO and HI reactions took place conjointly with Ni-Mo/ZSM-5 catalysts.

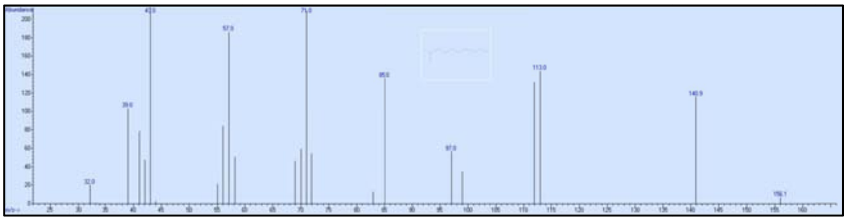

Figure 3. GC/MS chromatogram of 2-methyldecance (rt = 7.25 min) obtained from HDO of palmitic acid

As the HDO of palmitic acid proceeded, the yields of short-chain alkanes would increase (Figure 4). Therefore, an optimal strategy in catalytic hydrotreatment of fatty acids and triglycerides has to be implemented.

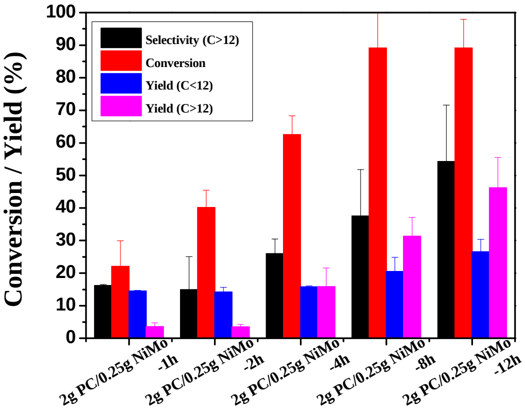

Figure 4. Yields and Selectivity of products from hydrotreatment of palmitic acid in a batch reactor (H_2^0 = 35 bar; T_{rxn} = 573 K; Cat loading = 25 wt %)

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PL-5

MORPHOLOGICALLY-CONTROLLED NANOMATERIALS AND PERIODIC NANOPOROUS MOLECULAR SIEVES FOR SUSTAINABILITY

Parasuraman Selvam

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The discovery of periodic mesoporous materials with one- and three-dimensional nanopore channels in early 1990s has opened wide range of opportunities in ordered porous solids. The development of such materials of well-defined pore geometry with precise and easily controllable pore shape and size is of great importance in many areas of modern science and technology. Microporous, mesoporous and hierarchical porous molecular sieve materials are the new generation ordered nanoporous solids, analogous to microporous (zeolitic) molecular sieves with high surface area, large pore opening and huge pore volumes. On the one hand, the unique flexibility in terms of synthetic conditions, pore size tuning, high surface area, large internal hydroxyl groups, framework substitution, etc. have created new avenues not only in catalysis but also in the areas of advanced energy materials, environmental pollution control strategies and separation processes. However, the preparation and characterization of high quality materials with designed pore structures is of paramount importance for many applications in areas including nanomaterials, catalysis, adsorption and separation. In designing such materials, several characteristics of pore structure may be addressed, which include their shape, size, pore interconnectivity, etc. In this presentation, the recent progress on the development of numerous nanoscale materials including hierarchical micro-meso pore-structures and their applications in heterogeneous catalysis, electrocatalysis, photocatalysis and environmental catalysis will be discussed.

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KEYNOTE LECTURES

BIOMASS-DERIVED FUELS AND CHEMICALS BY ALDOL CONDENSATION

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The conversion of lignocellulose biomass to valuable chemical products, including high-quality transportation fuels, has been attracting an ever-increasing interest. While lignocellulose has a complex composition, it can provide relatively simple molecules which can be considered as starting building blocks for the construction of more complex compounds with tailored properties.

Aldol condensation of lignocellulose-derived aldehydes and ketones is a promising tool to produce compounds with increased molecular weight starting from relatively simple molecules. The (partial) deoxygenation of the condensation products results in the formation of various valuable products including alcohols or even fuel-range hydrocarbons.

This presentation discusses aldol condensation of furfural and acetone or cyclohexanone (used as model compounds) in presence of Mg-Al mixed oxides and the corresponding reconstructed hydrotalcites as solid basic catalysts. Their catalytic performance will be compared with zeolite-based catalysts (having either acidic or basic character). Finally, strategies for deoxygenation of the aldol-condensation products will be briefly discussed as well.

KL-2

SYNTHESIS OF CHEMICALS FROM RENEWABLE FEEDSTOCKS CATALYZED BY HETEROPOLY ACIDS

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Heteropoly acids (HPAs), comprising nanosized oxometal cluster polyanions, have attracted much interest in catalysis, both in academic research and industrial applications, offering significant economic and environmental benefits. The aim of this presentation is to discuss recent developments in catalysis by HPAs for the synthesis of chemicals from renewable feedstocks focussing on reactions of terpenes, glycerol and ethanol.

Terpenes, found in essential oils of plants, represent sustainable and versatile feedstock for the synthesis of flavours, fragrances and medicines (e.g., alpha- and beta-pinene, 350,000 t/y). Acid catalysis plays a key role in terpene chemistry. Traditionally, mineral acids (e.g., H_2SO_4) are used as catalysts in large, over-stoichiometric quantities, with adverse impact on the environment. The development of new acid catalysts for cleaner processing is a challenge. It is demonstrated that HPAs are efficient and environmentally friendly catalysts for acid-catalysed terpene reactions such as hydration, esterification, etherification, cyclization and isomerization in homogeneous and heterogeneous systems. These reactions can provide clean routes to valuable ingredients and intermediates for the fragrance and pharmaceutical industries.

The growing worldwide production of biodiesel has made a large amount of glycerol available as a renewable feedstock for the synthesis of chemicals. Dehydration of glycerol to acrolein is one of the most important routes for the utilisation of glycerol. HPAs are very efficient catalysts for this reaction in the gas phase. Other promising reactions discussed are integrated conversion of glycerol to acrylic acid and acrylonitrile and hydrogenolysis of glycerol to propanediol.

The dehydration of ethanol is of interest to produce ethylene and diethyl ether from non-petroleum renewable feedstock. Ethylene is the feedstock for about 30 % of all petrochemicals, and diethyl ether is a valuable chemical and a green transportation fuel alternative. HPAs are highly efficient catalysts for ethanol dehydration. Hammingbird$^{®}$ is a new sustainable ethylene production process from bioethanol using HPA catalysis.

CATALYSIS FOR BIOMASS CONVERSION

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Today, the use of renewable and sustainable sources to produce energy and chemicals associated with the development of efficient catalysts is an important strategy. In this perspective, sugars derived from biomass, such as glucose and fructose, can be employed as raw materials to produce chemicals, which may complement or replace some petrochemical derivatives and exhibit great industrial potential [1-5].

Thus, the search for active and selective catalysts able to transform sugars into products of interest is increasing. In the literature, the use of inorganic acid catalysts [6], ionic liquids [7,8], Sn(IV) complexes [9,10], silica-included heteropolyacids [2], inorganic and organic potassium salts [11], among others, has been reported for research in biomass conversion. The use of heterogeneous catalysts has many advantages, mainly due to the possibility of recovery and reuse, reducing the costs of the final products [12].

A few examples are available in the literature concerning the use of mixed oxides and their application on biorefinery routes and the use of mixed oxides provides a great variety of Lewis and Bronsted acids present in the materials, which play an important role in the conversion and selectivity of the catalytic systems [13-16].

The present work aims to contribute to the field of sugar conversion and innovative catalyst design, by the systematic synthesis and investigation of robust catalytic systems based on tin mixed oxides at various proportions for application in the conversion of fructose. The goal of this investigation is to obtain important structure-property relationships in order to open new perspectives for modulating the characteristics of mixed oxides systems for use in biorefinery processes.

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KL-4

CHEMO-CATALYTIC CONVERSIONS OF GLYCEROL TO LACTIC ACID

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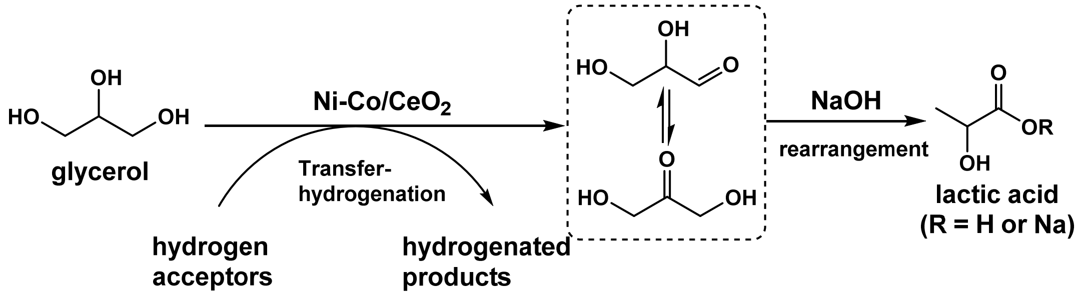
The conversion of glycerol into useful chemical products over heterogeneous catalysts is an important research topic that received increasing attention in recent years. This presentation is focused on the design and development of enhanced catalysts for the conversion of glycerol into lactic acid and lactates. This multi-step reaction requires the combination of two types of catalytic sites: metallic sites for the oxidative dehydrogenation and acid (or base) sites for the rearrangement step (Scheme 1).

Au-based noble metal catalysts combined with Sn-MCM-41-XS were designed, synthesised and tested for the multistep synthesis of methyl lactate from glycerol without adding a base. The best catalytic system consisting of a physical mixture of Au/CuO and Sn-MCM-41-XS gave 66 % selectivity towards methyl lactate at 96 % glycerol conversion after 10.5 h of reaction.

In addition, bimetallic Ni-Co catalysts supported on CeO_2 were prepared and tested. The bimetallic $10NiCo/CeO_2$ catalyst exhibited very high activity (91 % glycerol conversion) and selectivity to lactic acid (94 %) at 160 °C (4.5 h under N_2 atmosphere). The introduction of Co into the catalyst formulation was crucial to obtain finely dispersed bimetallic Ni-Co nanoparticles on CeO_2, which led to increased activity compared to the monometallic Ni or Co counterparts. Moreover, various H_2 acceptors (levulinic acid benzene, nitrobenzene decene and cyclohexene) were hydrogenated with the in situ hydrogen transferred from glycerol and resulted in several useful target products (Scheme 1).



Scheme 1.

KL-5

ADVANCED PHOTO-/ELECTRO-CATALYSTS FOR ENVIRONMENTAL PROTECTION

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This presentation will cover topic of chemically synthesised ligand protected metal colloids and clusters as well as controlled synthesis of oxide nanostructures [1-13]. A selection of fundamental studies of such materials in either pure form or as deposited onto surfaces using a range of techniques such as Far-IR, XPS and HR STEM to understand their unique electronic properties and behaviour on surfaces will follow [14-20]. Correlation of experimental results with DFT calculations helps to advance these studies. Selected examples of applications of such materials as thermal-, photo- and electro- catalysts will be presented.

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KL-6

PLASMONIC NANOMETAL DECORATED PHOTOANODES FOR EFFICIENT PHOTOELECTROCHEMICAL WATER SPLITTING

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Abstract

The design of photo-electrodes with good light absorption, effective photo-generated charge carrier separation and fast charge transportation are key parameters for photoelectrochemical (PEC) water splitting reactions. Development of efficient plasmonic metal-semiconductor hetero-nanostructures has been receiving a great attention to obtain the best PEC performance. In this work, low-cost, visible-light active and environmental-friendly g-C_3N_4/Bi_2S_3/BiNPs nanocomposites were fabricated and tested as photoanodes for Hydrogen generation. Typical results indicated a high photo-current density of 2.85 mA cm^{-2} at 1.23 V versus RHE, which is higher than g-C_3N_4/Bi_2S_3 and pristine g-C_3N_4 photoanodes. In addition, higher solar to hydrogen conversion efficiency was achieved for this quaternary composite photoanode. Further, g-C_3N_4/Bi_2S_3/BiNPs photoanode also demonstrated long-term stability. It has been concluded that the introduction of plasmonic Bi metal and Bi_2S_3 QDs enhances the electron transport in the photoelectrode and improves the PEC performance for hydrogen generation. Thus, the new composite reported here has superior PEC performance because it provides an economical and feasible route to fabricate SPR-enhanced composite photocatalysts using earth abundant Bi material instead of noble metals.

Experimental

g-C_3N_4 was prepared by a calcination method, whereas, BiNPs was synthesized by chemical reduction method followed by Bi_2S_3 QDs was fabricated by SILAR method. Various physico-chemical techniques were used to ensure the formation of the catalyst materials.

Results and discussion

The PEC activity of photoanodes such as pristine g-C_3N_4, g-C_3N_4/Bi_2S_3 and g-C_3N_4/Bi_2S_3/BiNPs were evaluated for water splitting by linear sweep voltammetry (LSV) (Figure 1a), which indicated that all samples have no photoactivity under dark conditions. Upon chopped light illumination, g-C_3N_4, g-C_3N_4/Bi_2S_3 and

$g\text{-}C_3N_4/Bi_2S_3/BiNPs$ composites showed photocurrent density of 0.74, 1.25 and 2.85 mA cm^{-2} respectively, at 1.23 versus RHE (Figure 1a). The $g\text{-}C_3N_4/Bi_2S_3/BiNPs$ composite showed the highest photocurrent density and also exhibited the higher solar to Hydrogen conversion (STH) efficiency (1.12 % at 0.65 V versus RHE) as shown in Figure 1b. The best performance of $g\text{-}C_3N_4/Bi_2S_3/BiNPs$ photoanode in PEC water splitting was attributed to the combined action of Bi_2S_3 which improves the absorption in visible region, whereas, SPR-BiNPs extends the absorption to near-infrared region and also facilitates an efficient charge carrier separation [1, 2].

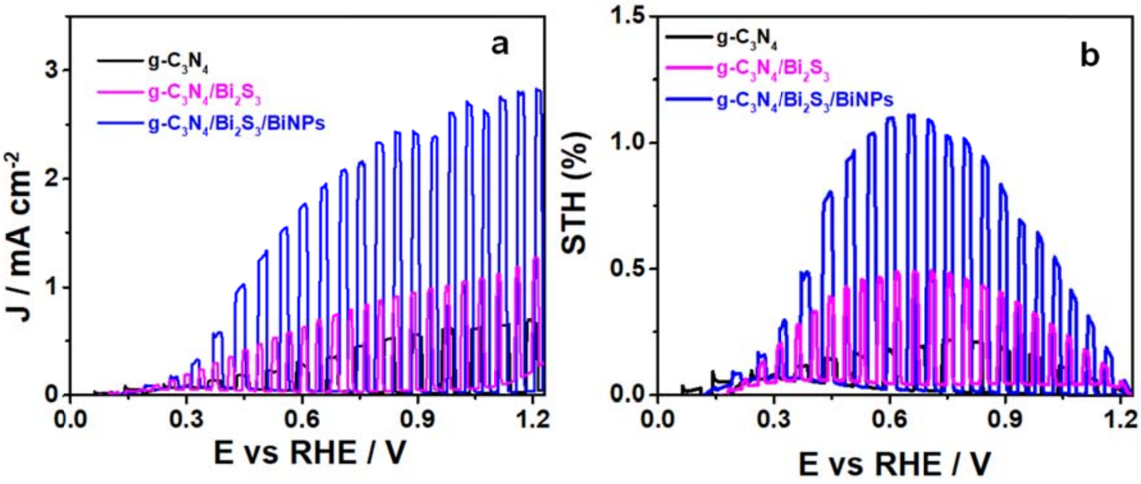

Figure 1. (a) LSV plots and (b) STH efficiencies of photoelectrodes

Conclusions

$g\text{-}C_3N_4/Bi_2S_3/BiNPs$ photoanode was fabricated, characterized and tested for PEC performance. Typical results indicated that extensive characterization indicated the reduced exciton recombination and good PEC performance.

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ORAL PRESENTATIONS

Section I. CATALYSIS FOR BIOMASS DEPOLYMERIZATION AND DOWN-STREAM UPGRADING

Catalytic systems for hemicellulose, cellulose and lignin depolymerization
Catalytic processing of tall oil and tar
Selective conversion of biomass derived sugars and phenolics to fuels, chemicals and polymers
Catalysis in dendrochemistry for valuable products

CATALYTIC HYDROGENOLYSIS OF KRAFT LIGNIN TOWARDS SUBSTITUTED PHENOLICS

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Lignocellulosic biomass composed by cellulose, hemicellulose and lignin can be an alternative source of chemicals and fuels towards the substitution of crude oil derived products. Lignin is an amorphous polymer composed by p-coumaryl, coniferyl, and sinapyl alcohols, linked mainly with β-O-4 ether and C-C bonds. The chemical structure and composition of lignin offers numerous exploitation opportunities towards the production of a vast variety of valuable products. Lignin itself can be used either directly without modification or after chemical modification in the polymer industry and in resins production. Furthermore, lignin can be depolymerized into monomers, which can be further upgraded to value added chemicals [1].

In the present work, reductive lignin depolymerization was carried out by the use of gaseous H_2 and/or hydrogen donor solvents (i.e. ethanol) to induce tranfer hydrogenolysis/hydrogenation reactions, on transition metal (Ni, Cu) and noble metal (Pt, Ru) catalysts supported on micro/mesoporous carbons. The feedstock was kraft lignin which is the by-product of the pulp and paper industry being produced in Mtons annually worldwide. The aim was the production of a stable bio-oil rich in alkoxy-phenol monomers. The effects of catalyst support (acidity/basicity), type of metal and preparation method, reductive reaction conditions (molecular hydrogen and/or transfer hydrogenation), solvent type with regard to lignin solubility and inhibition of re-polymerization reactions were thoroughly investigated.

Representative characterization results (Figure 1) concerning the 3 and 5 wt. % noble (Ru, Pt) metal supported showed that they exhibited a micro/mesoporous texture with high surface area (800-1000 m^2/g), and high metal dispersion as no XRD reflections owned to metallic Ru or Pt could be detected. Only in the case of 5 % Pt/AC catalysts, low intensity XRD peaks corresponding to metallic Pt metallic could identified.

OP-I-1

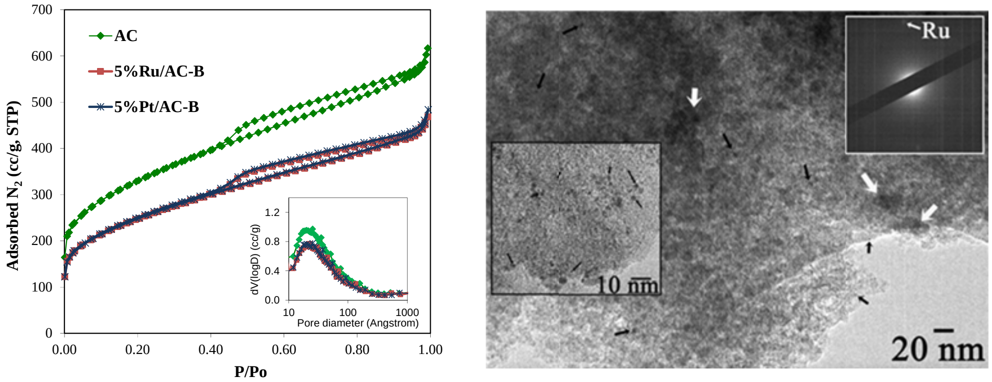

Figure 1. Representative XRD patterns and TEM images (for 5 % Ru/AC-H) catalysts; where (B) denotes the catalysts that have been reduced with $NaBH_4$ and (H) those reduced at 350 °C with H_2

Indicative results of the lignin hydrogenolysis experiments (220 °C, 3 hrs, 30 bars H_2 initial pressure, ethanol medium) are shown in Figure 2. The bio-oil produced by the noble metal catalysts comprised mainly of guaiacol type alkoxy-phenols with one alkoxy group, in accordance with the origin of the kraft lignin used (i.e. from softwood – spruce). Other minor components were acids and ketones. The conversion level reached ~85 % with the Pt catalysts exhibiting marginally higher activity than the corresponding Ru catalysts. Higher metal content (3 vs. 5 %) and reduction with H_2 (instead of $NaBH_4$) sightly favored conversion and phenolic monomer abundance.

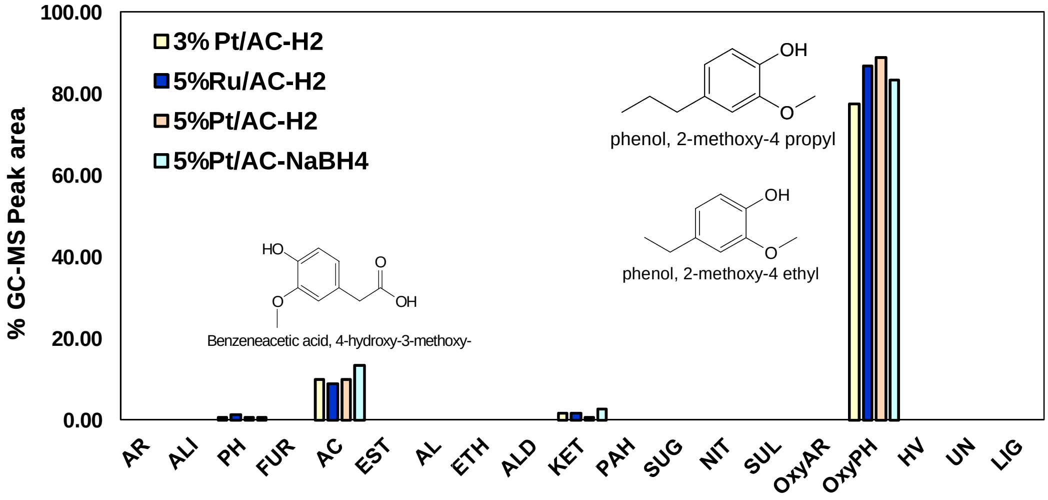

Figure 2. Representantive results of Kraft lignin hydrogenolysis with (Ru,Pt)/AC catalysts

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Acknowledgements

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WILL THE "SLEEPING GIANT" OF SUSTAINABLE CHEMISTRY AWAKEN?

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Integration of renewable bioresources for sustainable applications is one of the key challenges of modern chemical science and technology. The most perspective approach to the synthetic utilization of plant biomass involves the catalytic conversion of carbohydrates to low-molecular-weight building blocks, which are defined as bio-based platform chemicals. 5-(Hydroxymethyl)furfural (HMF) is one of the key platform chemical that has been referred to as a “Sleeping Giant” of sustainable chemistry. Low stability and difficult isolation process limits utilization of HMF as a reagent in organic synthesis (Figure 1, a) [1]. This presentation will describe the main difficulties associated with the large scale production of HMF. An efficient approach to the preparation of stable HMF derivatives by direct conversion of modified carbohydrates will also be discussed (Figure 1, b) [1,2].

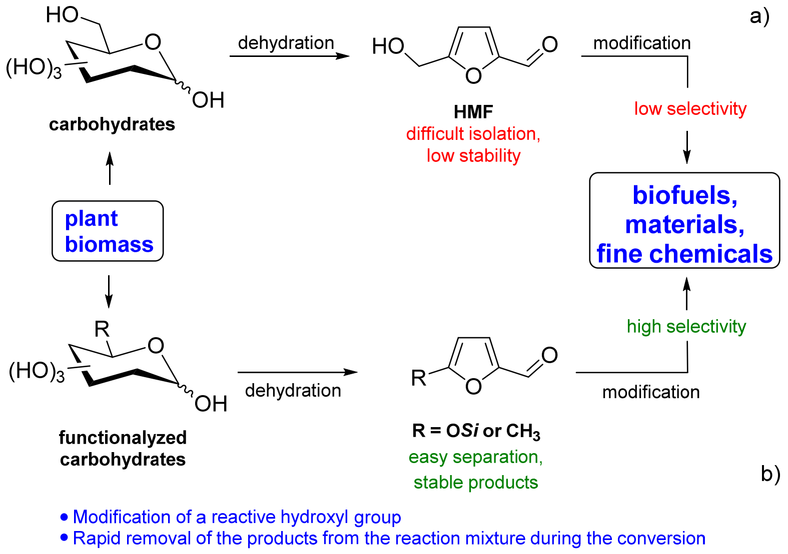

Figure 1. a) general route to plant biomass utilization in organic synthesis; b) our approach based on conversion of modified carbohydrates

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OP-I-3

CATALYTIC UPGRADING OF OLIVE MILL WASTE BIOMASS OVER OXIDE KETONIZATION CATALYSTS

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Olive processing is among the most important traditional agro-activities of the Mediterranean area, however olive oil production, using either the traditional or the modern three-phase process generates large quantities of wastewater (olive mill wastewater: OMWW), rich in phenolic compounds and thus not easily biodegradable. OMWW, characterized by an offensive smell, are in addition difficult to manage due to the high water content, which seriously limits the possibility of energy recovery applications, while their high COD to BOD ratio (from 2.5 to 5) hinders their direct biological treatment. The most common disposal method of OMWW includes storage ponds, where most of the water is evaporated generating a residual sludge (OMWWS) that is then sent to landfills. However, this method requires large land areas, produces bad odor, causes soil infiltration, and insect infestation [1].

Fast pyrolysis is a promising alternative to the current waste (OMWWS) disposal problem that can convert waste biomass feedstock to a liquid fuel product, called bio-oil, along with biochar and non-condensable gases. Pyrolysis of OMWWS using red mud was recently investigated leading to the production of a bio-oil of improved quality (low viscosity, low density, much lower oxygen content, high HHV and especially high aliphatic hydrocarbon content as compared to most lignocellulosic biomass pyrolysis oils) [1, 2]. We have also recently explored the catalytic pyrolysis of OMWWS studying the effect of either an acidic (ZSM-5) or a basic (MgO) catalyst on the yield and composition of the bio-oil produced. In both cases, in situ catalytic upgrading of pyrolysis vapors led to a lower oxygen content (<4 % O_2 in the organic phase) as compared to thermal pyrolysis. Yield and quality of the produced bio-oils strongly depended on the catalyst used. Thus, acidic ZSM-5 zeolite catalyzed cracking and aromatization reactions, resulting in a bio-oil enriched in aromatics, while basic MgO catalyzed decarboxylation of fatty acids yielding a bio-oil composed mostly of aliphatic hydrocarbons. Finally, Co-promoted catalysts (5 % Co either on

ZSM-5 or MgO) led to additional variation of bio-oil quality, mostly enhancing ketonization reactions [3].

In the present work, we studied the effect of a series of Fe and Mn oxide catalysts, based on alumina, silica and magnesia supports, in the catalytic pyrolysis of OMWWS in order to explore the catalyst effect on the yield and composition of the bio-oil produced, mainly focusing on using low-cost catalytic materials. Ferric oxide, aluminum oxide, magnesium oxide, and silicon oxide, are among the major components of red mud, an effective catalyst used in the pyrolysis of OMWWS [1,3] Use of each catalytic oxide separately can elucidate its specific effect on the OMWWS upgrading via the pyrolysis process. Furthermore the catalysts under study were selected as OMWWS is mainly composed of paraffins and fatty acids and these materials are expected to enhance ketonization reactions.

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ADVANCED GREEN APPROACHES FOR THE SYNTHESIS OF HYDRODEOXYGENATION Ni-Cu-CONTAINING CATALYSTS

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The development of new and improvement of existing catalytic processes for the conversion of renewable energy sources is an important, actual and challenging task, both in terms of ecology and energy. The composition, structure, and morphology of the catalysts developed for particular process allow scientists to tune its selectivity, control the product composition, and perform the reaction under suitable conditions, which can significantly increase the efficiency, economic viability and ecological compatibility of the process. However, the conventional methods of the catalysts synthesis often cannot be attributed to environmental processes, because the most of them lead to the formation of a large amount of waste. For example, the use of nitrates as precursors leads to emissions of harmful nitrogen oxides, which are formed during the calcination step.

One of the alternative way to overcome the above difficulties is the SCF based methods [1], in particular the precipitation in Supercritical AntiSolvent ($scCO_2$) – SAS. It’s well-known that the supercritical carbon dioxide (SC CO_2) is an attractive media for various physicochemical processes due to its availability, low price, inertness, non-toxicity, safety, ease of recycling, and low critical parameters (T_c = 303.9 K, P_c = 7,38 MPa). When the SAS method is used, the fast diffusion of $scCO_2$ leads to high supersaturation and, as result, to the precipitation of amorphous powder that allows us to obtain well mixed systems. These systems have a highly defective structure, which can demonstrate high catalytic activity [2].

In this paper we follow the principles of green chemistry not only for the hydrodeoxygenation process of model biofuel compounds, but also for the synthesis of the appropriate catalysts. The previously developed approaches for the catalysts synthesis via SAS based method [3, 4] are used to obtain Ni-Cu-containing catalysts for the hydrodeoxygenation of anisole – a model compound of biofuel. It was shown that these approaches allow us to increase the dispersion of the active metal phase, as well as to obtain active bimetallic alloys with a certain composition avoiding phase separation. The characteristics of the catalysts make these “green” catalysts perspective for the hydrodeoxygenation of biofuel and other renewable sources.

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Acknowledgments

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OP-I-5

CATALYTIC HYDROGENOLYSIS OF SOFTWOOD SAWDUST

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This work relates to the field of catalysis in alternative energy. The object of research is lignin, which structure makes it a suitable raw material for producing of biofuels and other valuable chemical compounds [1-3]. This paper presents the results of a study of the process of the hydrogenolysis of lignin with obtaining components of biofuels with the use of catalytic system 5 % Pt/HPS. Catalytic systems on the basis of hypercrosslinked polystyrene (HPS) has not been studied earlier in the process of hydrogenolysis of lignin.

Catalyst 5 % Pd/HPS was synthesized as follows: the HPS with the mean particle size of 80 μm was preliminary washed with water and acetone and dried in vacuum. Then it was treated with a solution of the calculated amount (5 wt. % of metal) of metal precursor (hexachloroplatinic acid) in a complex solvent THF – methanol – water at room temperature for 10 minutes. Then it was dried at 80 °C for 40 minutes and washed by sodium hydrocarbonate aqueous solution and water until the absence of chloride-anion reaction in the scouring waters. The washed catalysts were dried at 80 °C for 90 minutes and reduced at 300 °C for 3 hours. The process of hydrogenolysis was carried out for 4 hours in the reactor in a hydrogen atmosphere under the following conditions: substrate weight – 1.0 g, catalyst weight – 0.1 g, temperature – 250 °C, hydrogen partial pressure – 1 MPa, solvent volume – 30 mL. The following polar solvents were 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.

In order to study the solvent influence on sawdust processing, three solvents (ethanol, propanol-2, and water) were used for softwood sawdust hydrogenolysis in the presence of the 5 % Pd/HPS catalyst. The substrate conversion values were 45 % in a water medium, 50 % in propanol-2 and 37 % in ethanol. While the hydrogenolysis was carried out in a water medium the highest yield of phenolic compounds was obtained. It can be explained by the higher polarity of water in comparison with the other solvents used. However, we focused on the production of hydrocarbons, thus, depending on the desirable products propanol-2 was chosen as the solvent showing the highest substrate conversion and product yield.

Polymer based catalyst provides high substrate conversion. This can be due to the higher surface area and the higher active metal concentration on the catalyst surface. Also, it is notable, that Pt-containing catalyst result in the lowest formation of oxygen containing products (phenols and methoxycyclohexane). The highest conversion (68 %) and the highest selectivity towards the oxygen free hydrocarbons (96 %) were achieved while using Pt catalyst based on HPS in 2 hours.

In order to detect the other hydrogenolysis products, the liquid phase was analyzed using HPLC. The analysis showed the presence of mono- and disaccharides as well as the sugar alcohols in the liquid samples obtained during the reaction. These compounds seem to be the products of the conversion of cellulose containing in the sawdust (~47 wt. %). It is noteworthy that the yield of aromatic and cyclic products corresponds to the concentration of lignin in the raw material (~22 wt. %).

Among the products obtained during hydrogenolysis of lignin-containing raw materials fuel-like aromatic and cyclic hydrocarbon (benzene, toluene, and cyclohexane), as well as phenolic compounds are the most promising. The latter can be used as additives to conventional fuels and fuels derived from biomass. Moreover, a number of cyclic and aromatic hydrocarbons may also be used in various fields of fine chemicals production as solvents and reagents.

The use of catalytic system based on platinum group metals allows obtaining a high yield of valuable products. The highest selectivity towards the oxygen free hydrocarbons (96 %) at the maximal conversion (68 %) of lignin-containing material was reached in the presence of 5 % Pt/MN-270 catalyst. Moreover, the synthesized polymer based catalysts showed high stability in the hydrogenolysis process (up to 5 consecutive cycles without any regeneration).

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OP-I-6

BIOMASS DERIVED PHENOLICS CONVERSION TO C_{10}-C_{13} RANGE FUEL PRECURSORS OVER STRONG LEWIS ACIDIC CATALYSTS

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Liquid bio-oil formed from pyrolysis of lignocellulosic biomass needs further upgradation by C-C bond formation reaction between the phenolic compounds and small oxygenates to retain the maximum amount of carbon in the fuel range (C_{10}-C_{13}), prior to hydrodeoxygenation step. Herein, a promising model alkylation reaction between *iso*-propanol and *m*-cresol were investigated using different metal ion-exchanged zeolites as solid acid catalysts. Zn-HY zeolite exhibited higher catalytic activity as compared to Zn-HZSM5, Zn-HBEA, Zn-HMCM22, and other metal ion-exchanged HY zeolites. Catalytic activity was observed to increase with increase in zinc content in case of HY zeolite which can be correlated with its strong Lewis acidity. Further, Design of Experiment (DoE) through Response Surface Methodology (RSM) was applied for a comprehensive investigation and optimization of important process parameters like reaction temperature (200-300 °C), WHSV (1.68-3.92 h^{-1}), *iso*-propanol:*m*-cresol mole ratio (1:1 - 3:1), and catalyst loading (0.5-1.5 g). Coefficient of determination value (R^2) of 98.65 % for conversion of *m*-cresol and 98.37 % for selectivity to thymol were obtained when the experimental data were fitted to a second-order polynomial equation using multiple regression analysis. A *m*-cresol conversion of 92 % and selectivity to thymol of 71 % was obtained over 0.99 mol g^{-1} zinc loaded Zn-HY-III at optimal reaction conditions.

What will the audience take away from your presentation?

- Insights into the upgradation of pyrolysis bio-oil to obtain biofuel as alternate renewable energy sources.
- The experimental and statistical study of the model alkylation reaction between *m*-cresol and *iso*-propanol is helpful in the analysis of similar class of biomass-derived phenolic compounds.

- Retention of small oxygenates present in bio-oil by C-C coupling in this alkylation reaction which otherwise would be lost during direct hydrodeoxygenation step. Therefore, selective production of C_{10}-C_{13} range fuel precursors and reduction of carbon fraction loss during hydrodeoxygenation can be achieved.
- This study helps to ascertain the effect of the nature and strength of superficial acid sites as well as their pore size on the catalytic activity and product distribution as well as Response Surface Methodology (RSM) approach optimize the important process parameters with reduced number of experiments for the scale up of the process.

SYNCHROTRON X-RAY DIAGNOSTICS OF HETEROGENEOUS CATALYSTS AND CATALYTIC PROCESSES

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Among various functional materials heterogeneous catalysts seem to be most sophisticate systems regarding both their synthesis and study of their structure and properties. The spesific features of heterogeneous catalysts are usually as follows: 1) multicomponent composition; 2) low content of active component; 3) small particle size and structure imperfection of active component; 4) complex interaction of active component and support. And finally, structure and phase composition of the catalyst at ambient pressure and temperature may differ from that under working conditions, so *In Situ* and *Operando* experimental modes are of great importance.

The most wide distributed methods of X-ray diagnostics of heterogeneous catalysts and catalytic systems are X-ray Diffraction (XRD) and its modifications, X-ray Absorption and Emission Spectroscopy (XAS/XES) and X-ray Photoelectron Spectroscopy (XPS) [1, 2]. One can see a rapid development of modern methods of diagnostics such as X-ray Inelastic Scattering (RIXS/RXES), X-ray Microscopy/Microtomography and Coherent Diffraction Visualization [3]. All these experimental techniques will be realized at Siberian Circular Source of Photons SKIF.

SKIF will be Fourth Generation synchrotron source which will provide extremely brilliant radiation and will allow the above mentioned techniques to be available since 2024. The report covers a review of SKIF experimental opportunities for the study of spatial and electronic structure, phase composition and morphology of heterogeneous catalysts taking into account their specific features at most high scientific level. The attention is paid to complex studies of catalytic system involving different X-ray techniques especially *In Situ* and *Operando* modes.

In the last few years there is the growth of applications of current synchrotron facilities to the study of catalytic transformation of biomass [4]. Some examples of exciting synchrotron research of catalytic conversion of biomass to chemicals and fuels as well as SKIF potential for these studies will be given in the report.

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ORAL PRESENTATIONS

Section III. CATALYTIC PROCESSES FOR BIOFUELS PRODUCTION

Catalytic interesterification and hydrocracking of lipids to kerosene and diesel fractions
Catalytic approaches to biomass pyrolysis processes
Conversion of carbon rich unconventional fossil resources and biomass feedstock into biofuel

INNOVATIVE HEFA AND ATJ PROCESSES TO RENEWABLE HYDROCARBONS

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Air transport accounts for approximately 2 % of global greenhouse gas (GHG) emissions, and exponential growth in the sector can increase this share significantly. Revenue passenger kilometers increased by 66.8 % in ten years (2005-2015), up 7.4 % only from 2014 to 2015. This growth increased the consumption of fossil jet fuel and, thereby, GHG emissions. In 2009, the International Civil Aviation Organization (ICAO) adopted the target of achieving carbon neutral growth from 2020 on-ward and reducing net emissions by 50 % by 2050 (compared to the 2005 levels). In addition, the ICAO approved the Carbon Offsetting and Reduction Scheme for International Aviation (CORSIA), which compensates for any annual increase in international aviation carbon emissions above the 2020 levels. In Brazil, the growth of jet fuel consumption also raises concerns. Therefore, national commitment to reduce GHG emissions was assumed through the Nationally Determined Contribution (NDC) during the 21st Conference on Climate Change (COP 21). Brazil pledged to reduce its emissions by 37 % by 2030 and 43 % by 2030 (compared to 2005). There are several ASTM certified processes to produce biojet fuel. Once Brazil is the second largest ethanol producer as well as the second largest biodiesel producer, Hydroprocessed Esters and Fatty Acids (HEFA) [1] and Alcohol to Jet (ATJ) processes are the main candidates to low temperature renewable hydrocarbons that can be used as green diesel and biojet fuel. In this work, we present new results using nickel based catalysts for HEFA process and ZSM-5 mesoporous catalyst for ATJ process [2-3]. HZSM-5 zeolites provided by PROCAT (Rio de Janeiro, Brazil) have framework SAR (SiO_2/Al_2O_3) values equals to 20 and 50. In order to increase the zeolites pore sizes, two hierarchical zeolites were synthesized by means of HZSM-5 dessilication. Thus, a screening of catalyst (all four zeolites) and variables has been performed, focused on reach determining the adequate conditions for the optimization study. The ethanol conversion was carried out in an automated continuous flow catalytic evaluation unity (Microactivity Effi reactor – PID Eng&

Tech), the reaction products were collected by an inline separator, the gaseous products were analyzed by an inline GC-BID, the organic liquid products were analyzed by a GC-FID and the aqueous products were analyzed by HPLC-RID. Similar unity and analytical apparatus were used for hydrodeoxygenation of soybean esters and soybean fatty acids, both supplied by Granol S.A. HEFA catalysts were: Ni/H-Beta, Ni/HY, Ni-Mo/Al_2O_3 and sulfided Ni-Mo/Al_2O_3. All catalyst were prepared by impregnation. the catalysts were sulfided in situ at 673 K for 2 h in a stream of 15 vol. % of H_2S in H_2 under atmospheric pressure. Ethanol to Hydrocarbons reactions on ZSM-5 catalysts allowed a very interesting selectivity adjustment combining temperature, pressure, WHSV and mesoporous catalyst, obviously. Aromatics can be obtained at least 50 % selectivity. In this case, ethylene yield is significantly reduced. Modelling presents very good adjustment between predicted and experimental results. Table 2 shows very good results obtained with sulfided Ni-Mo/alumina catalyst. In the non-sulfided catalysts tested, Ni/H-Beta presented good results. Thus, Nickel/zeolite based catalyst can be an alternative to sulfided nickel ones as well as noble metal catalysts.

Table 1. Ethanol to Hydrocarbons**.** Design variables, levels planned (HZSM-5, SAR 50)

Parameter	**Unit**	**Object**	**Limit (-)**	**Limit (+)**	**Optim.**
Temp.	°C	(Range)	400	450	450
WHSV	h^{-1}	(Range)	5	15	5
Pressure	bar	(Range)	20	30	20
BTEX	%	Maximize	0	45	54.8
C2=	%	Minimize	0	98.2	7.5

Table 2. HDO of Soybean Fatty Acids (340 °C, 70 bar, 7 h)

Catalyst	**Conversion (%)**	**Selectivity (%)**		
		Fatty alcohols	Hydrocarbons	Wax esters
7.1%Ni-36.7%Mo/Al_2O_3 (Sulf.)	*98.3*	*0.9*	*99.1*	-
10%Ni/H-Beta	70.0	*1.0*	*99.0*	-
10%Ni/HY	*56.6*	-	*95.4*	*4.6*
13.2%Ni-47.3%Mo/Al_2O_3	64.4	*6.1*	*56.2*	*37.7*

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FCC & Hydroprocessing Catalysts

Gazprom Neft PJSC
Mikhail Antonov
2019

Dr. Mikhail Antonov, Director for Oil Refining

FCC & HYDROPROCESSING CATALYSTS

Gazprom Neft PJSC, St. Petersburg, Russia

PRESENTATION

Dr.-Ing. Alexandros Yfantis, President & Managing Director

TECHNICAL BIOENEGRY CRETE (TBC)

SYCHEM Company, Athens, Greece

CATALYTIC PROCESSING OF NATIVE AND ORGANOSOLV LIGNINS OF ASPEN-WOOD TO LIQUID BIOFUELS IN SUPERCRITICAL ETHANOL

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This presentation describes the green processing of wood sawdust and ethanol-lignin to liquid biofuels in supercritical ethanol in the presence of solid catalysts. The choice of ethanol is due to the fact that the value of its critical temperature (243 °C) is close to the temperature of intensive thermal degradation of lignin. Besides, lignin is a waste of ethanol obtaining from wood and that allows its one-site valorization without the use of additional reagents and transport costs.

The mechanical treatment of the mixture of aspen wood – high-silica zeolite catalysts in a planetary activator mill decreases the size and shape of wood particles, the degree of cellulose crystallinity and contributes more homogeneous distribution of zeolite catalyst in the reaction mixture. All these factors increase the yield of bio-liquids, obtained by thermal conversion of activated wood in supercritical ethanol.

The influence of conditions of wood–zeolite catalyst mixtures conversion in supercritical ethanol on the yield and composition of the resulting products was established (Table).

Table. The effect of zeolite catalysts on the conversion of aspen-wood and on the yield of products (270 °C, 6.4-7.5 MPa)

Catalyst	Conversion, wt. %	Yield of fractions of liquid products, wt. %		Solid products, wt. %	Gas, wt. %
		b.p. < 180 °C	b.p. > 180 °C		
Without catalyst	73	24.8	51.0	27.3	2.6
H-HSZ-30	86	62.7	24.1	13.9	3.0
H-HSZ-100	82	55.8	26.1	18.1	3.3

Among the studied catalysts, the highest activity demonstrates the catalyst with a ratio Si/Al of 30, which has the most high concentration of acidic sites. In the presence of this catalyst the yield of liquid products achieves to 84 wt. % at ethanol pressure of 6.4 MPa and 89 wt. % at pressure 21.0 MPa. Liquid products are represented mainly by compounds, formed from wood polysaccharides: 5-HMF, furfural, levulinic acid, ethyl ester, propanoic ester, 2-hydroxy- ethyl ester. The solid residue contains predominantly cellulose and lignin.

The possible mechanism of activated wood thermal conversion to bio-liquids in supercritical ethanol includes, at first the stages of wood hemicelluloses depolymerization and of extraction of soluble ethanol-lignin from wood. Then the initially formed soluble organic products undergo further transformations to bio-liquids over zeolite catalyst.

In the absence of catalysts the conversion of supercritical ethanol is not observed to a temperature of 300 °C. However, at these conditions the Ni-containing catalysts intensify the conversion of ethanol and ethanol-lignin.

The influence of a composition of Ni-containing catalysts on the thermal conversion of ethanol-lignin in supercritical ethanol was studied. The highest conversion of lignin (to 93 wt. %) and the highest yield of liquid products (to 90 wt. %) were achieved at 300 °C in the presence of catalyst NiCuMo/SiO_2 (Fig.). This catalyst reduces the content of phenol and benzene derivatives and increases the content of esters, aldehydes and ketons in hexane-soluble products obtained from lignin.

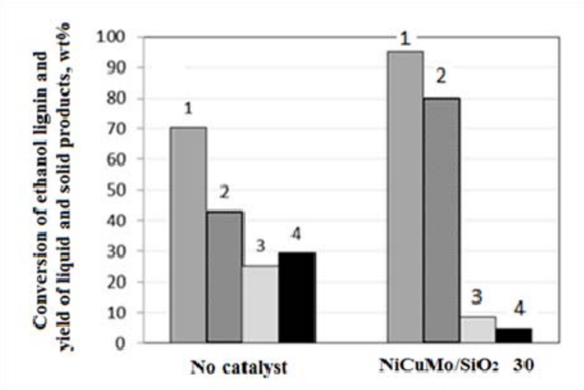

Fig. Influence of catalyst NiCuMo/SiO_2 on the conversion of ethanol-lignin in supercritical ethanol and on the yield of liquid and solid products at 300 °C, 11.6 MPa: 1 – conversion; 2 – products soluble in benzene; 3 – products soluble in ethanol; 4 – solid product

The scheme of catalytic biorefinery of wood was suggested which makes possible to process the woody biomass to liquid biofuels by environmentally friendly way.

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CATALYTIC CONVERSION OF VANILLIN A BIO-OIL MODEL COMPOUND TO CREOSOL A POTENTIAL FUTURE FUEL

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Summary

In this work, Taguchi method of experimental design was applied to optimise the processing parameters for hydrodeoxygenation (HDO) of a bio-oil model compound. Literature studies on the same model compound were conducted at different processing conditions, leading to conflicting product distribution. Hence, optimisation of the reaction system to maximise conversion is reported in this work. At the derived optimum condition, 98.8 % conversion and 23.0 % selectivity towards the product of interest creosol was achieved.

Introduction

Perpetual decline in the capacity of reserves responsible for producing fossil derived fuels and increased awareness on environmental implication of consuming these fuels escalates the need for sustainable renewable energy sources as alternative fuel. For this reason, the production of bio-oils from lignocellulosic biomass has been a subject of intense research lately. Crude bio-oil produced from lignocellulosic biomass via fast pyrolysis cannot be used directly as fuel in conventional engines without prior upgrading because it contain significantly high oxygen and moisture content which makes it chemically and thermally very unstable [1]. Hydrodeoxygenation (HDO) is the most promising available technology for upgrading crude bio-oil [2]. However, the complexity of bio-oil and associated reaction network has shifted research attention to bio-oil model compounds HDO. In this work, the effect of reaction media, catalyst active element, support and influence of process parameters on HDO reaction was probed using vanillin a bio-oil model compound.

Experimental

In a typical experiment, 100 mL stainless batch autoclave was charged with fresh Pd/C catalyst and 0.075 dm^3 solution containing 740 mg of vanillin. Inert atmosphere was created by flushing the system three times with N_2 gas and the autoclave content was stirred at 150 rpm during heating to the desired temperature (318-

338 K). Finally, the system was pressurised to the desired reaction pressure (1-3 MPa) and stirring speed set to the desired value (500-900 rpm). Liquid samples collected from the reaction was analysed via an automated Trace gas chromatography (GC) equipped with flame ionization detector (FID) and a mild polar capillary column (ZB-wax) (250 μm × 0.25 μm × 30 m). The HDO reaction of vanillin was carried out in six different solvents.

Results and Discussion

The effect of changes in the process parameter was evaluated via the Taguchi method over the following ranges: Temperature (318-338 K), Hydrogen gas pressure (1-3 MPa), Catalyst loading (0.1-0.5 kgm^{-3}) and agitation speed (500-900 rpm). Figure 1a shows that changes in the process parameter affected both conversion and product selectivity. While from Figure 1b, it can be seen that ethylacetate solvent produced the highest conversion and cyclohexane solvent gave the highest creosol selectivity.

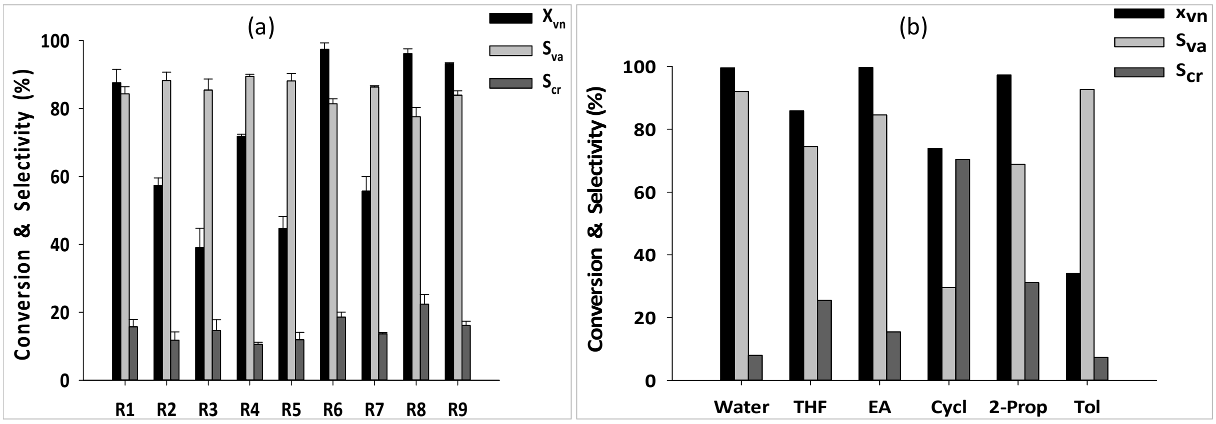

Figure 1. Conversion and selectivity (a) L9 orthogonal array results and (b) effect of solvent [Note R, X, S, vn, va, cr , Tol , EA, Cycl, and 2-Prop represent experimental number, conversion, selectivity, vanillin , vanillyl alcohol, creosol, toluene, ethylacetate, cyclohexane and 2-propanol respectively.]

Conclusion

The optimum condition derived from the Taguchi analysis is: temperature 338 K, pressure 3 MPa, catalyst loading 0.5 kgm^{-3} and agitation speed 500 rpm. It was found that the use of ethylacetate as reaction media favours the conversion of vanillin. However, cyclohexane favours creosol formation from the reaction.

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HYDROTREATMENT OF FAST PYROLYSIS OIL AND ITS MODEL COMPOUNDS OVER Cr-MODIFIED CATALYSTS WITH HIGH Ni CONTENT

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Fast pyrolysis is one of the effective methods for renewable bio-oil production. However, a high oxygen content (about 20-40 wt. %) in pyrolysis liquid causes a high acidity, low calorific value and tendency to polymerization of initial feedstock. Therefore, catalytic hydrotreatment of bio-oil is of particular interest in order to hydrogenate the feedstock and reduce its oxygen content. This process presents a key step to obtain effective biofuel blends and chemicals from biomass.

Recently high activity of silica-stabilized Ni-Cu catalysts has been demonstrated in hydrotreatment of pyrolysis oil [1]. Subsequently, P- and Mo-modified catalysts with high activity, stability to coke formation and acid resistance were developed [2]. However, such catalysts have low specific surface area due to formation of phosphides, phosphates, and Ni-Mo alloys.

In this study, we propose multicomponent Ni-containing catalysts modified by chromium. It is known that Ni-Cr alloys have high corrosion resistance [3], which is an important requirement for bio-oil processing catalysts. In addition, high reduction temperature of the catalysts allows one to convert toxic form of Cr^{6+} into less toxic Cr^{3+}, thus decreasing the negative impact on the environment.

Hydrogenation of anisole as a model compound of lignin fraction of bio-oil was carried out at 320 °C and 6 MPa hydrogen pressure in a batch reactor. It was shown that Ni-containing catalyst with 10 wt. % chromium reduced at 500 °C possessed the highest activity among Cr-, Mo-, and P-modified Ni-SiO_2 catalysts tested in anisole hydrogenation. At the same time, Cr-containing catalysts showed low activity at 100 °C and 6.0 MPa in hydrogenation of furfural being a model compound of carbohydrate fraction of fast pyrolysis oil. It should be noted that Cr addition into Ni-SiO_2 reduces the formation of by-products. As an example, the catalyst $NiCr_{10}$-SiO_2 is very selective with respect to tetrahydrofurfuryl alcohol (95 %), while Mo-containing catalysts lead to hydrogenation of furfural into furfuryl alcohol (80 %). Thus, Cr-modified catalyst demonstrates high activity towards stabilization of bio-oil constituents via hydrogenation of aromatic species. Moreover, the dissolution of samples containing 10 wt. % of Cr in model acidic environment was considerably less than that of unmodified Ni, NiCu and NiCuMo-containing catalysts.

As the next step, the activity of the catalysts in the hydrotreatment of pyrolysis liquid was studied in a batch reactor. Among all these experiments, the formation of “organic phase” and more dense “aqueous phase” was observed. In the case of Cr-containing system, a higher yield of products in the aqueous phase was observed which could be explained by the peculiarities of the formation of catalytically active phases (formation of coordinatively unsaturated Cr^{3+} centers). The advantage of this system is also a reduced yield of gaseous products, including light hydrocarbons C_xH_y. This is of particular interest from the view point of target hydrogen consumption in order to convert compounds in the liquid phase. In addition, the $NiCuMoCr\text{-}SiO_2$ catalyst is characterized by a lower yield of CO_2 (about 2 wt. %), which indicates smaller contribution of non-catalytic thermal transformations of the pyrolysis oil components into the overall hydrotreatment process.

In general, the effective hydrogenation and hydrodeoxygenation of less polar components (lignin derivatives) forming the “organic phase” is observed in the presence of $NiCuMoP\text{-}SiO_2$ catalyst, as evidenced by the higher H/C atomic ratio and lower O/C ratio. The reverse trend is observed for water-soluble products with higher polarity (hemi/cellulose derivatives) in case of $NiCuMoCr\text{-}SiO_2$.

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HIGH STABLE MULTICOMPONENT Co-BASED SUPPORTED CATALYSTS FOR SYNGAS PRODUCTION FROM BIOGAS

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Introduction

Syngas is a crucial intermediate resource for production of high-valuable products. Nowadays several efforts are actually focused towards the development of processes and catalysts for the syngas production from bio-fuels. Among them, biogas is considered a versatile renewable source for energy and chemical production. Biogas depending on its origin essentially consists of CH_4 (55-65 vol. %) and CO_2 (30-45 vol. %). Actually, biogas represents a feed for producing syngas by CO_2 reforming of methane (Eq.1) or so called dry reforming of methane (DRM).

$$CH_4+CO_2 \rightarrow 2CO + 2H_2 \qquad \text{(Eq. 1)}$$

Since the CH_4 to CO_2 ratio in biogas is about 1.5, reforming of biogas alone can lead to significant coke formation. To overcome carbon formation, the ratio of H/C or O/C in the initial feed should be increased. For this reason adding oxygen-containing agent such as an additional CO_2 or steam to provide dry or steam reforming of biogas respectively will facilitate carbon removal. The carbonization of catalysts for these processes is a main challenge, which is not yet solved. This work deals with the design and synthesis of the high active and stable catalyst based on Co and supported on a matrix composed of alumina modified with zirconia and rare-earth metal oxide for biogas conversion with producing synthesis gas.

Experimental

The multicomponent 5 % Co-M/Al_2O_3-ZrO_2-R catalysts, where M is a noble metal and R is rare-earth metal were synthesized by impregnation and tested in dry and steam reforming of biogas. The processes were carried out in a quarts flow reactor supplied with programmed heating and controlled feed velocity. The dry (DR) and steam (SR) reforming of biogas have been studied under atmospheric pressure, gas hourly space velocity (GHSV) – 1000 h^{-1} with using a model biogas with adjusted feed ratio of CH_4/CO_2 to 1:1 and varying temperature within 300-750 °C. The 0.1-1 vol. part of steam has been added to a feed for providing steam reforming of biogas. To elucidate the stability the 5 % Co-M/Al_2O_3-ZrO_2-CeO_2 catalyst was continuously tested for a long-term period: 400 hours in DR reforming of biogas and 100 hours steam reforming. The catalysts were characterised by BET, SEM, TEM, and TPR methods.

Results and discussion

The catalysts perform a high activity in both dry and steam reforming of a model biogas. Methane is almost completely converted at 750-800 °C depending on the catalyst composition and process type. Adding steam in amount 10-50 vol. % to a model biogas always leads to decrease in temperature of methane complete conversion and enriching syngas with hydrogen over the synthesized catalysts.

The 5 % Co-M/Al_2O_3-ZrO_2-CeO_2 catalyst showed a high stable activity for all period of testing in both processes: 400 hours and 100 hours in dry and steam reforming of biogas respectively. Dependence of conversion extent both of methane and carbon dioxide on time on stream is presented in Fig. 1. Under conditions t = 700 °C, P = 1 atm, GHSV = 1000 h^{-1}, CH_4:CO_2 = 1:1, methane conversion was varied within 96.0-96.6 %, while the extent of carbon dioxide conversion was insignificantly less and varied within 90.4-92.3 %. The ratio of H_2/CO in the syngas formed was 0.9. In steam reforming of biogas (CH_4:CO_2:H_2O = 1:1:1), H_2/CO ratio was increased to 1.3.

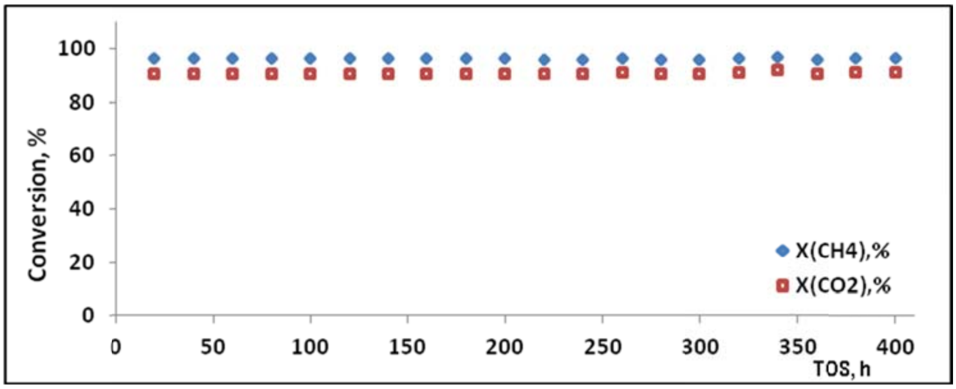

Figure 1. Dependence of conversion of CO_2 and CH_4 on process duration over the 5 % Co-M/Al_2O_3-ZrO_2-CeO_2 (t = 700 °C, P = 1 atm, GHSV = 1000 h^{-1}, CH_4/CO_2 = 1:1)

Conclusion

The 5 % Co-M/Al_2O_3-ZrO_2-R catalysts developed performs the high activity and stability in syngas production from a biogas. The synthesis gas composition can be controlled by adjusting the composition of the feed.

Acknowledgments

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BIFUNCTIONAL Ni-BASED CATALYSTS FOR ONE-POT PRODUCTION OF ISO-ALKANES FROM VEGETABLE OILS

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Introduction

Development of processes of diesel and jet fuel components production from vegetable feedstocks is of considerable interest. Today, the processing of, for example, lipidic raw materials requires a multi-stage treatment in order to remove oxygen to produce alkanes by hydrotreating (hydrodeoxygenation, hydrodecarboxylation, hydrodecarbonylation), as well as their subsequent isomerization [1]. Despite the fact that now there exist examples of technologies on implemented isomerized alkanes obtaining from the lipidic feedstocks, optimization ways of getting component motor fuels from such raw materials remain important. Processing of vegetable oils in two separate stages is a significant disadvantage, giving rise to an increased cost and reduced yield of the target products. Thus, of interest is a developing of catalysts active in the both hydrotreating and isomerization, which enable to process vegetable oils in a single step [2]. These catalysts should have non-sulfided nature, low cost, high activity to deoxygenation and selectivity to the fuel iso-alkanes in comparison with cracking products. Taking into account the above requirements, the most attractive are non-sulfided Ni-based catalysts, which are often modified with other transition metals (e.g., Mo) as well as P [3,4]. Nowadays bifunctional catalysts for one-pot isomerized alkanes production from lipidic feedstocks are high of interest.

Thence, the goal of this work is a development of modified non-sulfided Ni-based catalysts having bifunctional nature to produce isomerized fuel alkanes. Model compounds, a mixture of esters (methylpalmitate dissolved in ethylcaprate) and vegetable oils has been used.

Results

On the first stage a series of nickel-based catalysts were synthesized by wet impregnation using alumina as a support. The Ni-based catalyst was promoted by Cu and/or Mo, W and phosphorus. Activity of these catalysts were studied using fixed bed catalytic reactor (275-315 °C, 10 MPa, WHSV = 0,5-5 h^{-1}). It was shown that the modification by copper decreases activity of the Ni-based catalysts in the esters hydrodeoxygenation and as a result – methane formation suppression was observed. Modification of Ni-based catalysts by Mo and W changes selectivity on products and enables to save the length of alkanes and increase the selectivity of alkanes with length equal to the length of fatty acids in the initial esters.

On the second stage, silica mixed alumina-silica oxide and different type of zeolites were used as supports. The main difference in activity in hydrodeoxygenation of esters of the Ni-based catalysts supported by different supports, which have different acid-base properties, was selectivity to isomerized alkanes and alkanes formed through hydrocracking of longer C-C chain alkanes.

The most active Ni-based catalysts supported on alumina and zeolites were tested in the sunflower and soya bean oil conversion with using of a batch reactor.

The reduced catalysts were investigated by XRD, XPS, FTIR and TEM. H_2 - TPR study of the modified samples showed shifting of hydrogen uptake peaks to lower temperatures region in the case of Cu modified catalysts, and to higher temperatures region in the case of Mo and W modified catalysts. XRD showed that there exist changes in metallic Ni lattice after promotion by Cu, W and Mo. It was shown by XPS that W and Mo presented in the oxide form on the surface of the catalysts.

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A FAST ABLATIVE PYROLYSIS PLANT FOR BIOMASS PROCESSING INTO BIOCHAR AND BIOOIL

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Industrial companies, forestry, and agriculture annually produce a large number of lignocellulosic biomass wastes. These wastes mostly aren't used because of different technological and economic factors.

Fast pyrolysis is one of the economically efficient technologies for processing of lignocellulosic feedstock to organic liquid. Liquid products obtained by fast pyrolysis have energy density 12 times larger than initial biomass and can be effectively transported for further treatment.

We have developed and constructed an FPP02 mobile fast ablative pyrolysis plant for decentralized processing of lignocellulosic biomass wastes for small-scale enterprises. Estimated capacity of the plant was 4000 dry tonnes per year, but it can be scaled up to 30,000 dry tones. The plant consists of 8 transportable modules which can be transported in 5 ship containers. Each of these modules has the overall dimensions equal to those of a sea container. Also, the plant can be completed with a drying module. The modular construction allows fast setting and running of the plant. The plant has continuous operation mode. The products of the plant are biooil and biochar; pyrolysis gases are burned in an energy module of the plant.

The technology has been tested since 2007 on a pilot plant for more than 3000 h. During this R&D work, different feedstock types have been tested: wood, lignin, peat, sewage sludge, grain wastes, wastes railroad sleepers, etc.

Table. Mass balances of processing of different materials

Material	Liquid	Char	Gas
Wood wastes	65	15	20
Lignite	18	64	18
Peat	40	43	17
Wheat straw	56	19	25
Chicken litter	57	20	23
Grain wastes	52	23	25
Sewage sludge	39	40	21

Biooil can be used in different applications. It is an alternative fuel for small-scale energy production, a substitute for fuel oil in boilers and gas turbines. Biooil can be used as a component for adhesives for composite materials: production of biopolymers, substitution of phenol in PFR, substitution of polyol in polyurethanes up to 30 %. This material can be applied as a feedstock for road construction – an addition to bitumen as an adhesive, up to 30 %. Also, biooil can be used as a feedstock for the chemical industry in the separation of valued chemicals (acetic acid, furfural, levoglucosan), rectification, production of oils and engine fuels.

The second product of the process – biochar – also has a wide application field. It can be used as a fuel, in a form of char briquettes, as an additive for soil improvement, as a component for feeding animals and so on.

Tests of the FPP02 plant have been conducted. The capacity of 4000 dry tones of feedstock per year has been confirmed. The yield of biooil from birch wood was about 56 %. The yield of biochar was about 20 %. Specific energy consumption of the plant was comparatively low, about 33.6 kW·h per dry ton.

The mobility and the low installation time have been reached by the application of an original reactor based on ablative fast pyrolysis. The reactor is heated by hot flue gases from an energy module of the plant.

Economical estimations of the technology show that it is cost-effective and has a payback period up to 3 years depending on the local conditions.

CATALYTIC UPGRADING OF PYROLYSIS LIQUID FROM SEWAGE SLUDGE: EFFECT OF PROCESS TEMPERATURE

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Utilization of sewage sludge (SS) from municipal and industrial wastewater treatment plants is of great importance, both from a fundamental and practical point of view. With the increased sludge production throughout the world, the necessity of an economic and environmentally sustainable treatment process is an important matter to be addressed. Currently, SS is primarily disposed via landfilling and incineration. At the same time, there is a growing need to reduce the use of SS as landfill material because of land availability and environmental protection issues related to high concentration of pathogens and heavy metals in SS. Incineration, on the other hand, is still practiced in many parts of the world. However, this is not an environmentally friendly method because the produced pollution often exceeds permissible limits [1].

It is to be emphasized that due to the carbon-rich organic fraction and thus high-energy potential the sludge might be of particular importance for the needs of the fuel and energy sector [2]. Recently, there has been an interest in thermal treatment techniques, such as pyrolysis, as alternative methods to handle this waste stream [3]. SS pyrolysis produces a liquid bio-oil being a complex mixture of water, liquid hydrocarbons (aromatic and aliphatic), and S- and N-containing compounds derived from the degradation of organic constituents of SS. Organic phase of bio-oil has substantial heating value (30-40 MJ kg^{-1}) and can be used as a fuel [4]. However, water content, high S and N contents and presence of potential toxic compounds (i.e. polyaromatic hydrocarbons, heavy metals) pose challenges for direct use of bio-oil as a fuel source. At that, the integration of the liquid viscous product obtained via pyrolysis of SS into the existing oil-refining complex could be considered as one of promising options. In contrast to SS pyrolysis, the information related to upgrading of pyrolysis liquid via catalytic hydrotreatment is scarcely represented in the literature. However, it is particularly important to understand the reaction ability of different types of chemical species in pyrolysis oil during this processing, especially their mutual influence, as well as to gain knowledge on the influence of process parameters and catalyst nature.

The report will focus on studying the effect of temperature on catalytic hydrotreatment of SS pyrolysis liquid supplied by LLC EnergoLesProm (Kazan, Russia), dark non-transparent viscous substance with a well-recognized smell of burning. Hydrotreatment experimentations were carried out in a batch setup manufactured by Autoclave Engineers Company (USA), equipped with a stainless steel reactor of EZE-Seal type and 300 cm^3 volume. Prior each test the catalyst in a powder form was placed into the reactor with subsequent addition of certain amount of pyrolysis liquid, which was slightly pre-heated in a water bath to increase the fluidity. The reactor was weighed carefully after each step. Two types of catalysts were considered in the study: a) sol-gel catalytic system with high metal loading (about 50 wt % of Ni) modified by phosphorus and denoted as $NiCuMo\text{-}P\text{-}SiO_2$, and b) Ni/ZSM-5 catalyst obtained by wetness impregnation technique with 15 wt % of metal in the composition. The former catalyst has shown promising stability and activity results in catalytic hydrotreatment of pyrolysis oil obtained from lignocellulosic biomass, recently studied in our group [5]. The process conditions were as follows in the present study: temperature 200, 250, 300, 350, and 390 °C, H_2 pressure – 60 MPa (RT), catalyst/feed ratio (by weight) – 1/30, the reaction duration – 3 h.

A wide range of physicochemical tools has been used to study both fresh and spent catalysts, such as XRD, TPR, CO chemisorption, etc. The SS pyrolysis oil and products obtained in catalytic experimentations were studied properly as well, using GPC, KF Titration, XRF, HCNS-elemental analysis, GC-MS, etc. The results obtained as well as correlations defined between catalyst nature and product peculiarities will be discussed in detail during the talk.

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CATALYTIC CO-PYROLYSIS OF AGRICULTURAL RESIDUES AND WASTE POLYSTYRENE FOR THE PRODUCTION OF ADVANCED BIO-OILS IN A PILOT SCALE AUGER REACTOR

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The appropriate use of renewable sources emerges as a critical stage to minimize the environmental impact caused by the use of fossil fuels. Particularly, the use of lignocellulosic biomass, the only carbon-containing renewable source that not compete with food market and can produce biofuels similar to fossil fuels, emerge as one of the leading opportunities. In this sense, pyrolysis rises as a potential approach because it is the only thermochemical process that can produce a liquid biofuel (bio-oil) in a simple way and solid and gas fractions that can be used as energy sources to support the process. Nevertheless, in order to further process in future biorefineries to introduce bio-oils in current energy market, their quality needs to be upgraded. For that, the develop of these upgrading strategies at higher scales (≥ TRL-5) seems necessary in a short term.

Introducing different low-cost catalysts and/or incorporating different polymer residues to the process are some of the new, simple and low-cost strategies to directly obtain advanced bio-oils to be used for this purpose. The co-pyrolysis of grape seeds (GS) and polystyrene (PS), both showed in Figure 1, has been demonstrated to be a promising route for the production of drop-in fuels in a lab-scale [1]. On the other hand, the incorporation of calcium-based catalysts to the catalytic pyrolysis and co-pyrolysis processes has been evidenced as a promising application as well [2, 3]. Thus, and in the absence of works at higher scales, this research trends to demonstrate the potential of this combined process at in relevant environment (TRL-5). For that, the experiments has been carried out in an auger reactor pilot plant, operating at atmospheric pressure. GS and PS were mixed previously to ensure a good homogeneity in the sample keeping low percentages of PS (up to 20 wt %), and the calcium-based catalysts were fed in a separated hopper. It is worth of mention that the efficient and economical use of the products plays a fundamental role in heat integration. Thus, catalysts were diluted with sand, keeping a (sand + catalyst) to biomass ratio of 3:1. This solid inventory would be the required as heat carrier for a self-sustainable from an energetic point of view [2]. Thus, biomass and sand + catalysts mass flows of 2 kg/h and 6 kg/h were fed to the auger reactor at 500 °C, respectively.

Figure 1. Grape seeds residue (left) and waste polystyrene destined for food packaging (right)

The results confirm that a two well-defined phase distribution in the resulting bio-oil is obtained. Although the organic yield was slightly lower when the catalysts were added, this phase present better properties in terms of lower oxygen content and high heating value. Moreover, a greater proportion of aromatic compounds was produced finding relevant positive synergetic effects. Thus, this phase results as a promising product to be processed in further biorefineries or be considered as a real drop-in fuel.

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THE POSSIBILITY OF UTILIZATION OF RENEWABLE SOURCES OF HYDROCARBON GASES IN SMALL-SCALE PRODUCTION OF LIQUID FUELS

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One of the main problems in the use of different renewable sources in production of energy or chemicals is the low volume of virtually any renewable source, which makes it economically inefficient or even impossible to use well-established industrial technologies. Therefore, the use of renewable sources often requires the development of special small-scale technologies.

One of the main renewable sources of hydrocarbon gases is biogas, which is produced and widely used both in developed and undeveloped counties. It consists of methane with significant admixture of carbon dioxide and nitrogen and is mainly used as a gas fuel. The problem arises if it is not possible to use the entire volume of such fuel only on the spot. In principal, the best solution would be to convert the excess biogas into any liquid fuel, for example, using the Fisher-Tropsch (FT) catalytic process. The problem is that FT-technology requires preliminary conversion of biogas into syngas. And modern technologies of syngas production are too complex, cumbersome and expensive for small-scale applications.

Recently, we have developed a new type of so-called “matrix” converters [1-3] providing effective small-scale conversion of various hydrocarbons, including biogas with a concentration of CO_2 up to 50 %, into syngas [4]. Matrix converters provide stable and cheap small-scale production of syngas using atmospheric air as an oxidizer. But in this case the produced syngas will be strongly diluted by nitrogen and CO_2, which are initially represented in biogas. Fortunately, several approaches to the use of nitrogen-containing syngas in the cascade FT-process have been developed, which can be applied in combination with the matrix conversion of biogas.

The possibility of production of synthetic FT hydrocarbons from nitrogen-diluted syngas was studied at the semi-industrial level in [5, 6] and recently analyzed in

[7, 8]. The use of nitrogen-diluted syngas has a number of advantages because the heat capacity and thermal conductivity of the system is higher, making it more stable and less prone to overheating. This makes it possible to increase the activity of the catalyst and thereby abandon the recirculation of unreacted synthesis gas in favor of a cascade scheme consisting of several successive reactors.

Synthesis of hydrocarbons from nitrogen-diluted syngas using iron catalysts was studied in [5, 6]. Similar investigations with cobalt catalyst $Co–Pt–ZrO_2/Al_2O_3$ are described in [8]. The favorable effect of pressure increase up to 2.5 MPa on the process is shown. The conversion of CO per pass through reactor was 36.3 % with Anderson–Schulz–Flory distribution coefficient α up to 0.89. In [7, 8] the possibility of small-scale production of methanol and dimethyl ether (DME) from nitrogen-diluted syngas was also considered.

Thus, the coupled processes of matrix conversion of biogas into syngas and the subsequent cascade synthesis of hydrocarbons from nitrogen-diluted syngas open up a real possibility for small-scale use of biogas and other renewable resources of hydrocarbon gases.

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CO_2-TO-FUELS *VIA* COPPER-CERIA BASED CATALYTIC HYDROGENATION

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The utilization of CO_2 as starting material for the synthesis of high performing fuels and hydrocarbon products (oils, solvents, chemicals, etc.), using cheap and renewable hydrogen, appears nowadays one of the most promising strategic route for a "greener economy" [1-2]. In this scenario, many transition metals are differently active catalytic materials in the CO_2 hydrogenation reaction, at temperature ranging 180-360 °C and pressure up to 100 bar. In particular, the chemistry of copper has been investigated, being among the most performing catalytic elements in the conversion of the refinery syngas (CO/H_2; 1/2) into methanol.

Therefore, a series of catalytic formulation based on compositions of metal oxides (Cu, Zn and Ce) have been prepared and tested in the CO_2 hydrogenation to methanol, aiming to ascertain the effect of the catalytic formulation on catalytic performance. The list of catalysts with related chemical composition and physical properties is reported in Table 1. As shown, the bulk catalysts have been prepared at different formulation, varying copper oxide loading from 15.0 wt. % to 45.0 wt. % and achieving weigh ratio ZnO-to-CuO and CeO_2-to-CuO ranging between 0.0-1.0 and 0.9-5.7, respectively. As valuable effect of chemical formulation, a detectable increase of the value of the total surface area has been observed with the progressive enrichment of both CuO and ZnO content.

Table 1. List of catalysts with chemical-physical properties

	Chemical composition (wt.%)				**S.A.BET**	**P.V.**
	CuO	ZnO	CeO_2	K_2O	**($m^2 \cdot g_{cat}^{-1}$)**	**($cm^3 \cdot g_{cat}^{-1}$)**
CC	15.3	-	84.7	1.1	78	0.23
C1Z1C	15.1	14.8	70.1	1.0	156	0.33
C2Z1C	29.7	14.7	55.6	0.9	171	0.39
C3Z1C	45.2	15.1	39.7	1.0	189	0.53

As a rule, CO_2 hydrogenation increases at the growing of both copper content and temperature, while selectivity to methanol declines with Cu loading and temperature, Figure 1A-B. Then, the results of catalytic measurements at different temperatures shed light on the constructive synergism occurring between copper and zinc oxide at the electronic level. Indeed, the catalytic performance results improved by ZnO both in term of hydrogen conversion and methanol selectivity, in the whole range of temperature. Therefore, acting as promoter of the catalytic activity of Cu, the effect ZnO even reflects the “dual site” nature of copper-based systems in the catalytic hydrogenation of CO_2 and the key role played by the “interfacial area metal-oxide” [3-5]. In this respect, the higher catalytic performance reached by C3Z1C system, also outlines the greatest equilibrium occurring between the different active sites Cu° and Cu^+-ZnO, necessary for hydrogen and CO_2 chemisorption, respectively, Figure 1C-D.

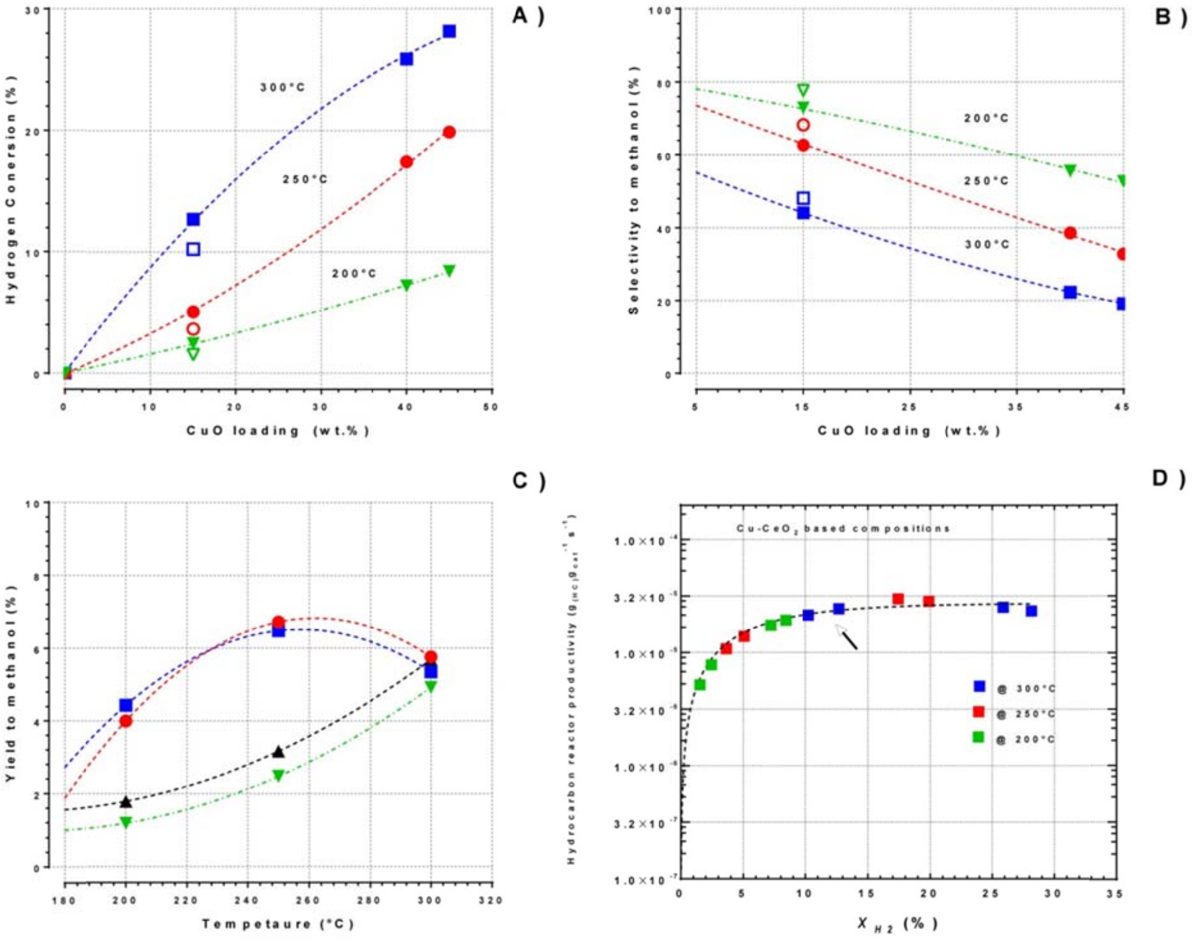

Figure 1. Catalytic performance of the various catalysts

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OP-III-12

HYDROGENATION OF ABIES WOOD AND ETHANOL-LIGNIN TO LIQUID BIOFUELS IN SUPERCRITICAL ETHANOL OVER BIFUNCTIONAL Ru/C CATALYST

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A comparative study was carried out of the processes of catalytic hydrogenation of abies wood and ethanol-lignin in order to establish the influence of the catalyst, as well as carbohydrate components on the conversion of lignin, gaseous, liquid, solid products and molecular weight distribution of liquid products.

The effect of a bifunctional catalyst containing ruthenium nanoparticles supported on mesoporous graphite-like carbon Sibunit on the yield and composition of products in the processes of hydrogenation of abies wood and abies ethanol-lignin in supercritical ethanol at 250 °C was established.

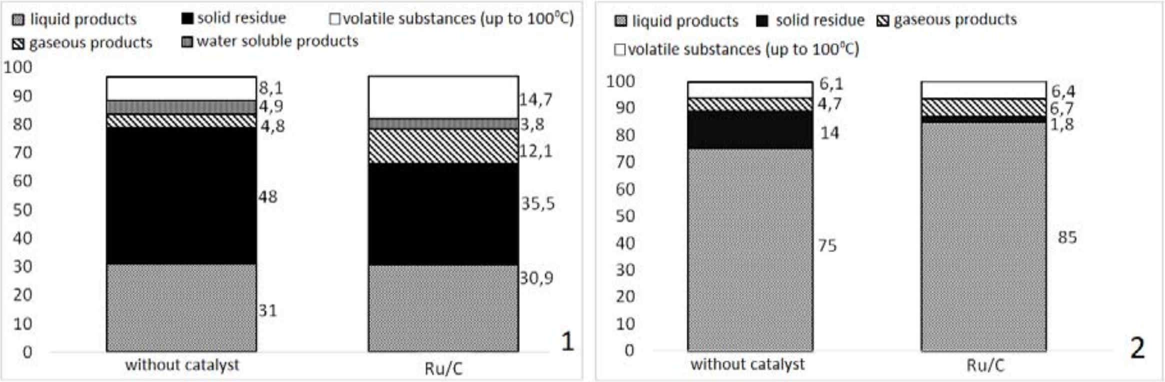

Fig. 1. The yield of products of hydrogenation of abies wood (1) and ethanol-lignin (2) at 250 °C, process time 3 hours and a working pressure of 9.0 MPa

In the process of non-catalytic hydrogenation of ethanol lignin the conversion of lignin was 85 wt. %, the yield of liquid and solid products was 75 wt. % and 14 wt. %, respectively (fig. 1). The conversion of ethanol lignin in the presence of a Ru/C catalyst increased to 98 wt. %, the yield of liquid products to 85 wt. % and the yield of solid product decreased to 2.8 wt. %. Simultaneously, the yield of gaseous products increased by 1.5 times due to the intensification on acid and metal catalyst active sites decarboxylation, decarbonylation and hydrocracking reactions leading to release of CO_2, CO, and CH_4.

In the presence of ruthenium catalyst the yield of liquid products remained almost unchanged and the yield of solid product was reduced by 12.5 wt. %. At the same time, an increase in the yield of gaseous products by around 2.5 times was observed.

The cellulose content in the solid product over the ruthenium catalyst increased up to 70.1 wt. % while the lignin content was reduced to 27.5 wt. %. The hemicelluloses content in solid products did not exceed 2-3 wt. %.

The carbohydrate part of abies wood is chemically bound with native lignin; this prevents lignin dissolution in ethanol. Therefore, the native lignin conversion to liquid products was significantly reduced compared to isolated abies ethanol lignin. Contrariwise, the hydrogen content in the liquid products of reductive fractionation of abies wood, which are mainly formed from native lignin, increases compared to isolated ethanol-lignin.

The catalyst intensified the hydrodeoxygenation reaction. Analysis of the molecular weight distribution demonstrated that the products of non-catalytic conversion have an average molecular weight (Mw) 1174 g/mol and polydipersity 2.275. In the presence of the catalyst, a decrease in the average molecular weight of the liquid products to 827 g/mol with a simultaneous decrease in the polydispersity to 1.914 were observed. On the molecular weight distribution curve the liquid product obtained over the catalyst has the peak in the region of 193 g/mol. This peak can be attributed to the monomeric products of lignin depolymerization. The peaks in the region of 426 g/mol and 1300-1500 g/mol can be attributed to dimeric and oligomeric products.

Thus, the use of Ru/C catalyst in the process of abies wood hydrogenation allows us not only to increase the lignin conversion, but also to steer the composition of liquid products towards the preferred formation of monomers and dimers. The catalyst also makes possible to achive the reductive fractionation of wood biomass to a solid product with a high cellulose content (more than 70 wt. %), liquid and gaseous products from lignin and hemicelluloses.

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INFLUENCES OF SUPPORTED CATALYST SYNTHESIS METHOD ON FISCHER-TROPSCH SYSTEM PERFORMANCES

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The present study investigates the conversion of producer gas from biomass gasification for the production of liquid biofuels. The motivation comes from the need to decrease the carbon footprint of the transportation sector, which account for one third of the total world energy consumptions [1]. In this regard, biomass gasification coupled to a Fischer-Tropsch (FT) system is taken into account. It was recently demonstrated that biomass based FT process can be economically sustainable even at scales of 500-1000 kg/h of biomass throughput [2,3].

Since FT synthesis is a catalytically driven reaction, the catalyst properties play a crucial role in determining the hydrocarbon yields and spectrum. In this regard, the current work investigates two catalyst synthesis methods, wet impregnation (WI) and combustion synthesis (CS), to design catalysts for high conversion and high selectivity to C_{5+} hydrocarbons. Our earlier work [4] demonstrated how the CS method can enhance the synthesis of hydrocarbons fractions ranging from gasoline to diesel and waxes. The catalyst synthesis procedure is described elsewhere [5], except that the CS method utilized herein employed lean stoichiometry with the cobalt nitrate-citric acid reaction. Six distinct alumina supported cobalt catalysts were prepared with 15 %, 20 % and 25 % cobalt loading; three were synthesized with the WI method and three with the CS method. They were tested in a fixed bed reactor at an operating pressure of 3 MPa and temperature of 503 K. The syngas gas composition was simulated with a pressurized cylinder containing 67 % H_2, 32 % CO and 1 % Ar. The products mainly comprise C_1 - C_5 paraffinic gasses and condensate composed of water, waxes (C_{24+}) and other hydrocarbons (C_6 - C_{23}).

The preliminary results show that with the CS catalyst it is possible to achieve higher CO conversion and C_{5+} selectivity compared to the WI catalysts. The yield (kg) of liquid fuels (C_{5+}) per kg of syngas is in a range between 0.28 and 0.49 for weight hourly space velocity (WHSV) of 2610 and 873.3 milliliters per hours per grams of catalyst (mL/(h*g_{cat})), respectively. The spectrum of liquid products broadly varies between C_{10} - C_{16} hydrocarbons and fractions of waxes.

The results of this work could be useful to increase the interest in the production of renewable fuels that can be used for the transportation sector. Moreover, the combination of the catalysis experience with the expertise of the authors in biomass gasification processes [6,7] allows for a more comprehensive approach to biomass-to-liquid (BtL) experimental analysis.

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ORAL PRESENTATIONS

Section IV. CATALYTIC PROCESSING FOR VALUABLE CHEMICALS PRODUCTION

Bio-catalysis for chemicals production
Lipids conversion to valuable products
Electrochemical biomass conversion
Catalytic transformations of CO_2 to lignin cellulose

EFFICIENT CATALYTIC CONVERSION OF MEVALONOLACTONE TO ISOPRENE OVER SiO_2/Al_2O_3 CATALYSTS

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Introduction

Isoprene is a petrochemical commodity used in the production of a wide variety of products, ranging from tires to roofing materials and specialty adhesives. Isoprene is predominantly produced in 2-5 % yield as a by-product of ethylene production by naphtha or gas oil cracking. Currently, substantial research and development efforts are devoted in finding alternatives to the petrochemical production of isoprene. To date, neither direct chemical synthesis nor bioengineering based processes are able to meet this need. Within the frame of the Horizon2020 project BioCatPolymers, we investigate a novel hybrid bio/thermochemical process for the hydrolysis of residual biomass to sugars and their efficient fermentation to mevalonolactone (MVL), followed by fast and selective thermocatalytic processing of MVL to bio-isoprene. Mevalonolactone is efficiently converted to bio-isoprene via acid catalyzed dehydration and decarboxylation over solid acid catalysts. In this work, we study the effect of SiO_2 content in a series of SiO_2/Al_2O_3 catalysts on the reaction pathway and the selectivity of the MVL to isoprene conversion.

Experimental

Commercial aluminosilicates with SiO_2 content ranging from 0 to 90 wt % (herein labeled as SiAl-x, where x is the wt % SiO_2 content) were used for this study (supplied by Sasol and Grace). The surface area and porosity were analyzed with BET, while the total acidity was measured with FTIR-pyridine. TPD studies of MVL-saturated samples were performed in a fixed-bed reactor equipped with mass spectrometer. The pre-saturated samples were heated to 800 °C at a rate of 5 °C/min under He flow with continuous analysis of the reactor effluent with MS. The thermochemical reaction of MVL to isoprene was performed on a fully automated laboratory scale fixed bed reactor unit, with a 70 wt % aqueous feed of MVL at temperature range 200-325 °C, using WHSV $2\ h^{-1}$. Full analysis of all liquids, gaseous and solid products of the reaction was performed with appropriate analytical methods.

Results and Conclusions

The physicochemical properties of the aluminosilicates depend strongly on the SiO_2 content. The surface area increases with SiO_2, ranging from 200 m^2/g for pure Al_2O_3 to 579 m^2/g for SiAl-90. Besides surface area, acidity also increases with the SiO_2 content. SiAl-90, SiAl-40 and SiAl-20 contain both Brönsted and Lewis acid sites, with B/L ratio 0.07, 0.12 and 0.04, respectively. Further decrease of SiO_2 results in elimination of the Brönsted acid sites and lower Lewis acidic sites.

The desorption of isoprene during the TPD measurements of the MVL-saturated samples is shown in Fig. 1a. Isoprene desorbs in the 200-500 °C range, together with CO_2 (not shown). The increase in the SiO_2 content clearly favors isoprene formation and decreases the maximum desorption temperature, suggesting both increased activity and selectivity for the SiO_2-rich samples. The SiAl-90 catalyst with the highest isoprene desorption was also tested in the fixed bed reactor unit. MVL conversion increases progressively with temperature, while a maximum isoprene yield of ~ 28 wt % is recorded at 225 °C (Fig. 1b). Higher temperatures lead to increased production of smaller olefins, such as i-butene and pentenes, which could be a result of secondary reactions of the formed isoprene and/or other reaction intermediates, such as alcohols, ketones and aldehydes, detected in the liquid product of the reaction. Further investigation is on-going to elucidate the reaction mechanism and the nature of the active sites.

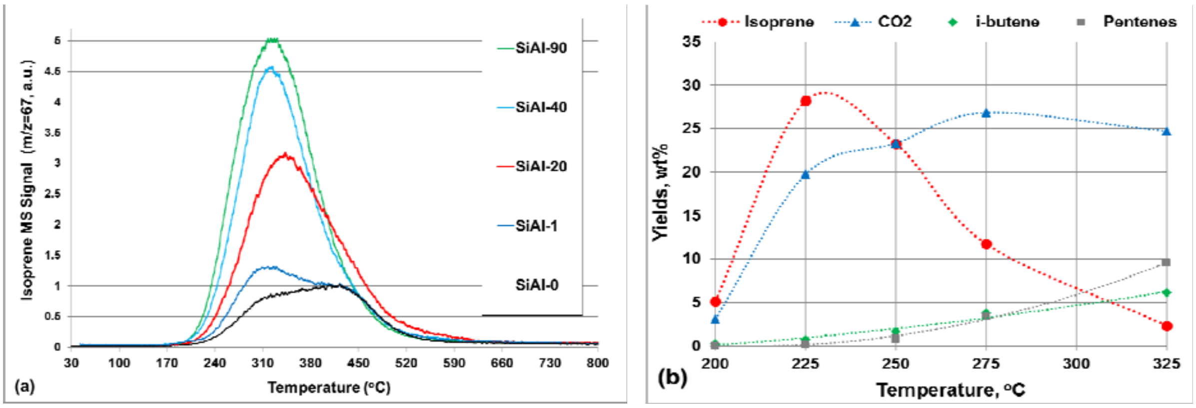

Figure 1. (a) Isoprene desorption over MVL-saturated SiAl-x samples in TPD studies and (b) Yield to gases as a function of temperature in MVL to isoprene reaction over SiAl-90

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HYDROLYSIS-HYDROGENOLYSIS OF CELLULOSE TO ETHYLENE GLYCOL AND PROPYLENE GLYCOL OVER BIFUNCTIONAL CATALYSTS

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Ethylene glycol (EG) and 1,2-propylene glycol (PG) are important glycols, widely used for the synthesis of polyesters. Cellulose, being the main component of lignocellulosic biomass, is the best raw material for the synthesis of lower glycols. The one-pot process for the hydrolysis-hydrogenolysis of cellulose over bifunctional catalysts baring acid-base and metal active sites is a promising method for convertion of cellulose to lower polyols.

This study was aimed at the design of bifunctional catalysts for this process based on highly dispersed Ru or Ni anchored on different solid supports: acidic cesium salts of heteropolyacids (Ru/Cs-CPA) and basic tungsten carbide (W_nC) containing mainly W_2C.

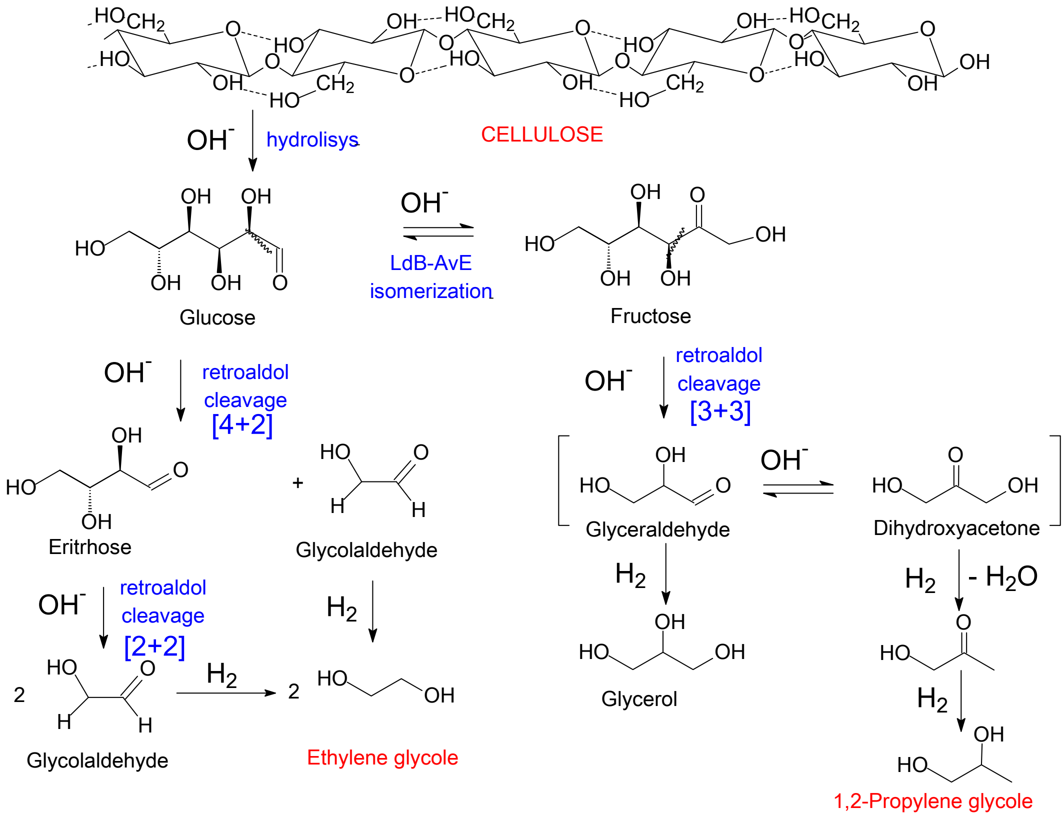
$Cs_3HSiW_{12}O_{40}$ were synthesized from $H_4SiW_{12}O_{40}$ and Cs_2CO_3. Catalytic systems based on tungsten carbide W_2C were obtained by the method of self-propagating high-temperature synthesis from a mechanochemically activated mixture of tungsten oxide, metallic magnesium, carbon black and $CaCO_3$. The phase composition of the formed materials was shown to depend on the amount of $CaCO_3$. Bifunctional catalysts were prepared by the incipient wetness impregnation of the supports by aqueous solutions of $Ru(NO)(NO_3)_3$ or $Ni(NO_3)_2$ with following reduction in H_2. Catalysts were charactrized by HRTEM, XRD, FTIR, . DR UV-VIS, N_2-adsoption.

The catalytic properties of the materials were investigated in the hydrolysis-hydrogenation of mechanically activated microcrystalline cellulose at 245 °C and 5 MPa of H_2 under vigorous stirring in the presence of $Ca(OH)_2$. Reaction products were analyzed by HPLC (Shimadzu Prominence LC-20) equipped with Rezex RPM-Monosaccharide Pb^{2+} column.

In the presence of 1 % Ru/CsHPA the yields of 25 mol. % EG and 11 mol. % PG were obtained (the selectivities of the EG and PG formation were 60 and 27 mol. %, respectively). Catalyst of 3 % Ru/CsPPA shown lower activity, which was accounted for by a decrease in the number of Bronsted acid centers on the surface of the catalyst.

It was established that in the presence of W_nC the main reaction products were EG and PG with a ratio of PG/EG – 1.5-1.8. The deposition of nickel nanoparticles on the W_nC surface increased the reaction rate and product yields. The maximum total yield of diols was 47.1 mol. %.

In general, the total yields of the EG and PG achieved in this work are comparable to the results described in the studies published by other leading research teams. The main achievement of our work is to switch the reaction to obtain propylene glycol as the main product. The mechanism of this process will be discussed in the lecture according the following scheme.



Scheme. Reaction mechanism of cellulose one-pot hydrolysis-hydrogenolysis to ethylene glycol and 1,2-propylene glycol

Acknowledgements

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OP-IV-3

SYNTHESIS OF CHIRAL AMINES *VIA* THE COUPLING OF TRANSAMINASE AND OPPENAUER REACTIONS

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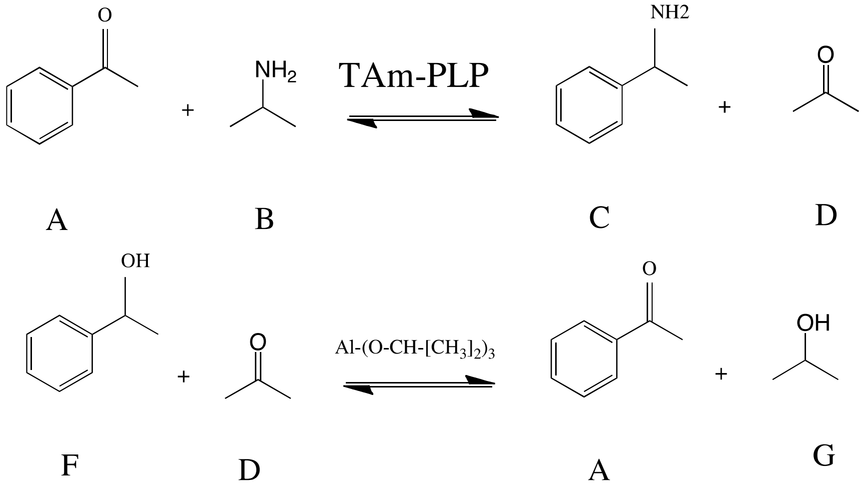
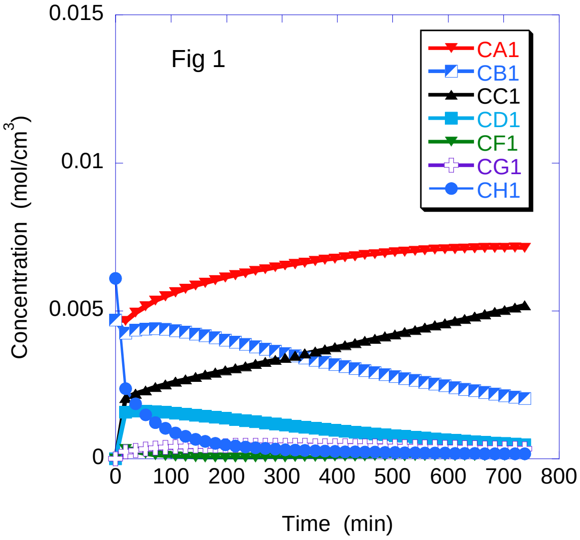
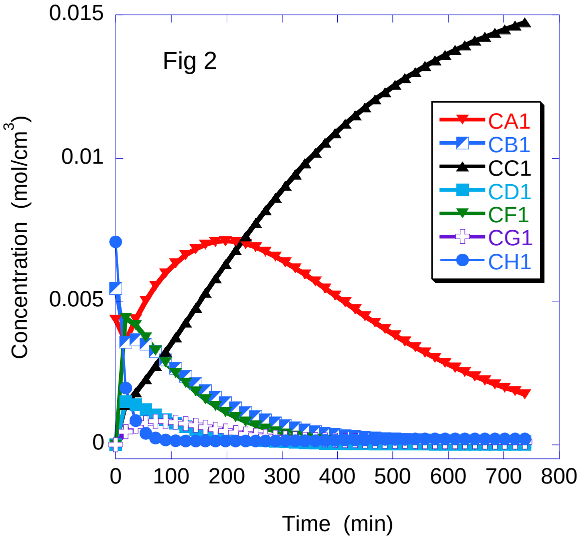
Chiral amines are important building blocks in stereoselective synthesis and commonly found subunits in chiral drugs [1]. The synthesis of chiral amines *via* transaminase reactions are, in most cases, thermodynamically hampered, producing low yields due to unfavorable chemical equilibrium. To overcome this, the simultaneous elimination of one of the by-products from the reacting mixture is performed by the coupling of two favourable chemical reactions, in which one of the products of the first reaction becomes the reactant of the second one, and *vice versa*, in such a way that the chemical equilibrium for both reactions is shifted towards the product side. In this theoretical work we consider the synthesis of a chiral amine (A), which can be extended to the production of different chiral amines provided two conditions are fulfilled: 1) one of the reactants in the ω-transaminase reaction should be 2-propylamine (B), which yields acetone (D) as one of the products, which in turn becomes a reactant in the second reaction, *ie* the Oppenauer oxidation of a secondary alcohol, 2) the secondary alcohol (F) has to be the precursor of the ketone in the ω-transaminase reaction, using aluminium isopropoxide as catalyst, which is regenerated by the acetone. In this way this reaction coupling changes the unfavorable equilibrium in both reactions, producing larger yields of the chiral amine (as shown beneath), producing isopropyl alcohol (G) by the second reaction.



OP-IV-3

Another important condition that needs to be fulfilled for this process to be successful is that the Oppenauer reaction has to be performed in an anhydrous medium, otherwise the aluminium isopropoxide will decompose to aluminium hydroxide (an inert) in the presence of water. This problem could be resolved by performing each reaction in a different CSTR, and both reactors are interconnected by a hydrophobic permeable membrane [4]. In this work we use a detailed kinetic model for each reaction, and mass balances are performed for each reactor interconnected via multicomponent diffusion at the permeable membrane. Figures 1 and 2 compare product distribution and the yields of the desired chiral amine (S)-phenylethilamine (C) from model simulations of the batch isothermal operation <u>in absence</u> and <u>in the presence</u> of the reaction coupling with the Oppenauer reaction, showing a nearly three times improvement in the yield of the chiral amine.





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BIOCATALYTICAL INTERESTERIFICATION OF VEGETABLE OIL TRIGLYCERIDES AND ESTERIFICATION OF FATTY ACIDS FOR PRODUCTION OF VALUABLE CHEMICALS

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The heterogeneous lipase-active biocatalysts have great commercial potential for industrial implementation, in particular in organic synthesis of valuable chemicals such as methyl/ethyl esters of vegetable oils' fatty acids (biodiesel) and other marketable esters used in perfume and cosmetics industry as fragrances, emollients and non-ionic surfactants. The "green" processes of bioconversion of vegetable oils' triglycerides and fatty acids, such as enzymatic interesterification and esterification are carry out with unique 100%-selectivity in non-conventional anhydrous media of organic solvents at very low temperature (20-50 °C). In order to prepare the commercially attractive biocatalysts, lipases are adsorbed on inorganic supports, commonly on silica-based ones. Due chemical inertness and high mechanical strength of silica granules the bio-processes are effectively organized in periodic or continuous modes using stirred-tank, packed-bed or vortex reactors.

In this research the lipase-active biocatalysts were prepared by impregnating of mesoporous silica with solutions containing recombinant r*Pichia*/lip lipase. After impregnation, the biocatalyst was dried under ambient conditions. During drying, the lipase molecules lost their hydrated shells, and "induced" adsorption of the enzyme on the silica surface occurred. Interesterification of vegetable oils with ethyl acetate was carried out in order to obtain components of biodiesel (ethyl esters of sunflower oil's fatty acids) and vitamin F (ethyl ester of linseed oil's omega-3,6 unsaturated fatty acids) [1]. Esterification of various saturated fatty acids with aliphatic alcohols differing by a number of carbon atoms from 2 to 16, as well as isomerism of carbon skeleton (*n*-, *iso*-) and position of OH-group (*prim-, sec-, tert-*) was systematically studied in order to determine the specificity of biocatalysis by immobilized recombinant r*Pichia*/lip lipase [2]. Both processes were carried out in periodic mode at 20-40 °C.

According to the composed matrix of relative esterification reaction rates for various pair of substrates (acid plus alcohol), the specificity of immobilized r*Pichia*/lip lipase was found to be broad [2]. The high reaction rates were observed for saturated fatty acids with 7 or more carbon atoms (till 18) which were reacted with primary alcohols with 3 or more carbon atoms. Maximum rate was measured in the reaction of esterification of heptanoic (enanthic, C7:0) acid with butanol (C4). The kinetics of enzymatic esterification was satisfactorily described by the classical hyperbolic Michaelis-Menten equation. For example, the kinetic parameters of the synthesis butyl heptanoate, such as Michaelis constant and maximal reaction rate, were determined to be equal to 0.22 $mol \cdot L^{-1}$ and 66.7 $\mu mol \cdot L^{-1} \cdot s^{-1}$, respectively.

Maximal conversion of the fatty acids was 80-90 %. The final products (esters) were purified by traditional vacuum distillation but without removal of water formed during esterification. The purity of the final product, for example isopentyl decanoate, estimated by two-dimensional GL-chromatography was 99.0 % content of the ester as a main substance [1, 2].

Activities of the prepared lipase-active biocatalysts (calculated per 1 g) were high enough and equal to 20-70 mmoles of the ester formed for 1 min. Also, these biocatalysts had a very high operational stability that is the most important characteristic for their practical application. The biocatalysts did not change their stationary activity during 500-1000 h of the operation in non-conventional media of organic solvents (hexane and diethyl ether). Based on the values of measured enzymatic activity and stability under studied conditions, the productivity was evaluated as ≥2 tons of final product per 1 kg of dry biocatalyst.

In conclusion, immobilized r*Pichia*/lip lipase is a promising lipase-active heterogeneous biocatalyst for organic synthetic chemistry, and biocatalytical esterification of various organic acids, in particular fatty acids of vegetable oils, is an innovative alternative method for the production of valuable market-oriented esters.

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ADDING VALUE TO BIOMASS THROUGH CATALYTIC TRANSFORMATION

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Chemistry has been the driving force behind progress for centuries - resulting in our lives becoming easier, more comfortable and healthier. These improvements however came at an environmental cost, which is associated with the way we have been using our resources and sourcing our energy. A global shift towards sustainable ways of doing chemistry is necessary to make sure that we continue to meet the needs of our society for chemicals and products, without jeopardizing those needs for future generations.

This transformation requires constant innovation and new technologies, but also support of all stakeholders - from academy, industry, policy-makers and society.

VTT Technical Centre of Finland actively participates in all areas of sustainable development - with special emphasis on climate action and sustainability. We recognize the value that sustainable chemical technologies provide and we actively pursue the development of new bio-based monomers, bio-oils and biofuels, biochemicals, evaluating waste streams as new raw materials sources, carbon capture and reuse, wood-based high value products, bio-based packaging or innovations such as thermoplastic cellulose. In many of our processes and research, catalysis is the key enabler for technologies - making the process commercially viable - reducing costs, increasing energy efficiency and product selectivity. The presentation will highlight VTT's expertise and catalytic technologies related to biomass, waste and CO_2 conversion to added-value chemicals - including liquid hydrocarbons, waxes and aromatics.

OP-IV-6

CATALYSTS AND DESSICANTS BASED ON ACTIVE ALUMINA

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New environmentally appropriate technology for production of active alumina via fast thermal treatment of gibbsite (Gb) being in contact with heated and revolving surfaces in reactor TSEFLAR was developed in BIC SB RAS. Energy consumption for thermal treatment is about 1 kWt per 1 kg of Gb that is twice lower than energy consumption in known analogical flash process.

Obtained product of centrifuged thermal activation of GB (CTA Gb) $Al_2O_3•nH_2O$ (n = 0.25-0.5) is X-ray amorphous and consists of pseudomorphic aggregates (~100 μm) of highly dispersed (2-4 nm) particles. Due to high value of specific surface area (~250 m^2/g) and disordered structure product possess high chemical activity; its solubility is tenfold higher than solubility of Gb.

Based on CTA product a row of effective desiccants and catalysts of different forms, textural characteristics, alumina structural modifications (γ,η,χ) and surface acid-based properties was prepared by variation of the preparation conditions (hydration conditions, nature of peptizing electrolyte, granulation method, calcination conditions and so on) for environmental and sustainability.

Hydration of CTA product in the alkali solutions leads to formation of bayerite containing mixed hydroxide. Granules obtained by extrusion molding of plastic paste prepared from as prepared hydroxide after its mixing with nitric acid solution, after their thermal treatment were characterized with higher dynamic capacity as compared with other alumina desiccants due to higher concentration of strong basic surface sites. As prepared modified with Na cations desiccant is stable in the adsorption-regeneration cycles and to condensed moisture (>99.8%). It was shown that even after regeneration at lower temperature (up to 110 °C) desiccant is characterized with high dynamic capacity. In pilot plant conditions (that modeled real conditions) the dew point temperature about –80 °C was reached with developed desiccant. Due to possibility to vary regeneration temperature in wide interval (110-350 °C) without strong change in dynamic capacity it opens new possibilities to increase the efficiency of the process using desiccant in multi layers with zeolite or silicagel.

Hydration of CTA product in the acid solutions leads to formation of pseudo boehmite containing hydroxide. Prepared from such hydroxide alumina was characterized with higher surface Lewis acidity as compared with precipitated analogue. Ring-shaped granules prepared from acid-modified alumina showed excellent activity in the process of catalytic dehydration of “green” ethanol to ethylene in wall-heated tubular reactor.

Improved catalyst for Claus process obtained by plate granulation of CTA product with special textural additives was characterized with higher catalytic activity; an experimental-industrial catalyst butch made in OOO “Novomichurinsk catalyst plant” is running at OOO “Gasprom producing Orenburg” during 6 years (usually catalysts run 4 years). OOO SPK “Sintez” business under license agreement (2010) deliver industrial batches of active and durable microsphere alumochromium catalyst KDM for C_4-C_5 dehydration.

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OP-IV-7

MoP AS A HIGH-PERFORMANCE CATALYST FOR THE DEHYDRATION OF GLYCEROL TO ACROLEIN

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Acrolein is an important intermediate for the chemical and agricultural industries, which can be directly converted into acrylic acid and DL-methionine [1]. Catalytic dehydration of glycerol to acrolein possesses the potential to valorize the glut of crude glycerol issuing from biodiesel production. The catalytic conversion of glycerol into acrolein can be made in solid acid catalysts including metal phosphates, metal sulfates, heteropolyacids (HPA) and zeolites. Transition metal phosphides, especially for MoP-base catalysts, possess weak, medium, and strong acid sites, suitable for the dehydration of glycerol [2].

The unsupported MoP catalysts were prepared by temperature-programmed reduction (H_2-TPR). XRD measurement and TEM observation revealed that MoP (PDF 65-6487) crystal phase was obtained. Moreover, after the 60-h run, the MoP phase hardly changed. The NH_3-TPD profiles indicated that unsupported MoP presented weak acidity, weaker than that of HZSM-5.

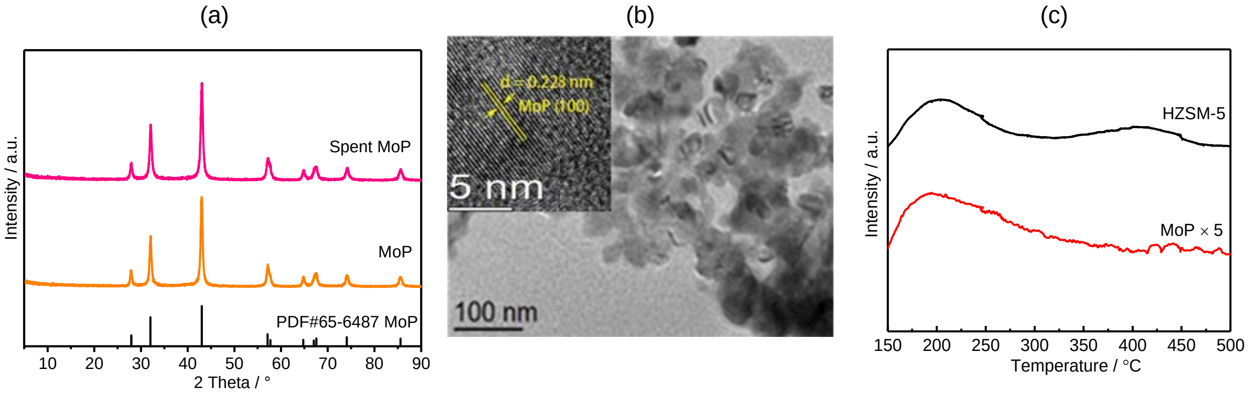

Fig. 1. Characterization of unsupported MoP catalyst: (a) XRD, (b) TEM, and (c) NH_3-TPD

Inherently, glycerol dehydration is a multistep process involving many reactions, leading to complicated active intermediates, which causes rapid coking on the surface of the catalysts [3]. In practice, the coking will suppress the chemical process, leading to lower glycerol conversion and acrolein selectivity. At low reaction temperature, the coke formed slowly and the long contact time of glycerol resulted in higher acrolein yield. The stability of the unsupported MoP catalyst was investigated. It is shown that at lower reaction temperature (240 °C), the selectivity of acrolein was up to 89.0 % and kept constant in the 60-h run (Fig. 2).

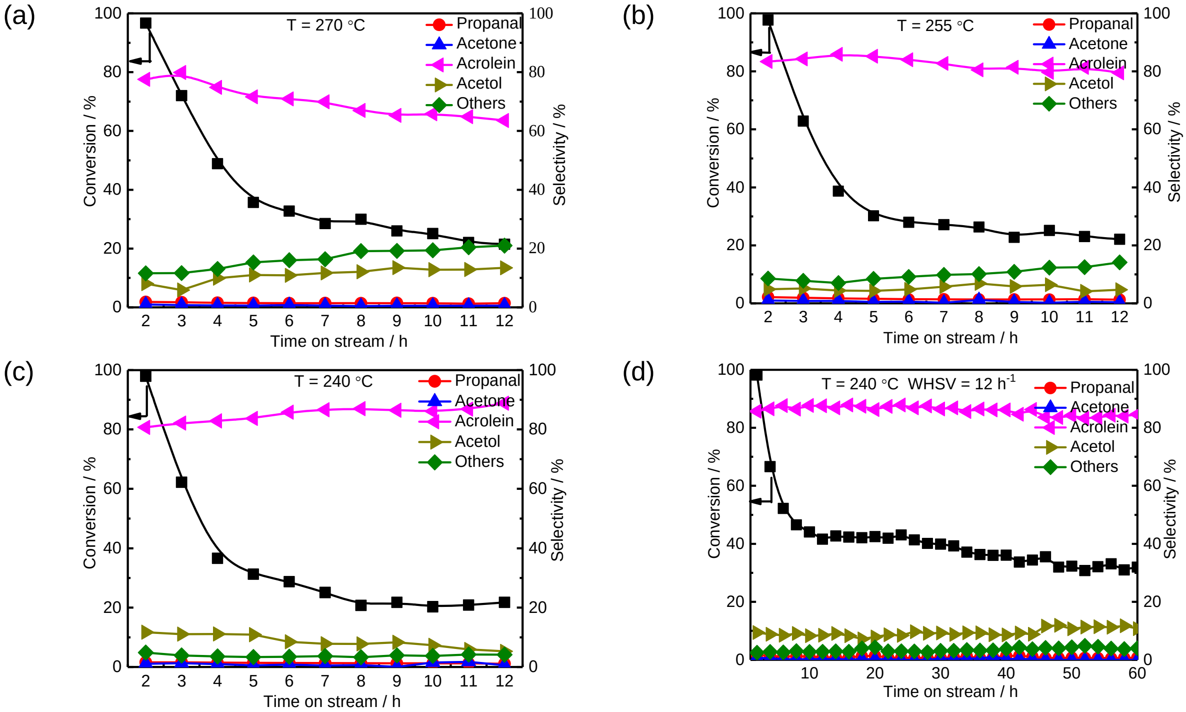

Fig. 2. Catalytic performance of unsupported MoP catalyst in dehydration of glycerol to acrolein Reaction conditions: (a-c) T = 240-270 °C, P = 0.1 MPa, m_{cat} = 0.3 g, $WHSV$ = 20 h^{-1}, G/L = 300; (d) T = 240 °C, P = 0.1 MPa, m_{cat} = 0.5 g, $WHSV$ = 12 h^{-1}, G/L = 100

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OP-IV-8

SYNTHESIS AND CHARACTERIZATION OF LIPID EXTRACTED ALGAE DERIVED NANO - CATALYST FOR BIODIESEL PRODUCTION

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Introduction

The inefficient use of algae biomass due to the unutilized residue and high production cost have affected the commercialization and economical sustainability of algal biofuel technology [1, 2]. The use of residual algal biomass after lipid extraction for other applications can reduce the overall process cost of producing biodiesel from algal biomass [3]. Biodiesel is produced by transesterification, a process enhanced catalytically. Heterogeneous catalyst are gaining interest for the conversion of oil to biodiesel due to their advantage resulting from ease of separation of the spent catalyst and the products/unconverted reactants giving room for possible catalyst reuse, eliminating the need for the neutralization of homogeneous catalysts and the removal of the associated wastewater thereby lowering their production cost [4]. In the last two decades, nanotechnology has developed with its application in almost all branches of science and technology. In this study, lipid extracted algae derived heterogeneous nano catalyst was synthesized and the effect of metal doping and changing the magnetic property to the catalyst for conversion of *Scenedesmus obliquus* lipids to biodiesel was investigated. In addition, the developed catalysts were characterized by X-ray diffraction (XRD), high-resolution scanning electron microscopy (HRSEM), energy dispersive X-ray spectroscopy (EDS) and thermogravimetric analysis (TGA/DSC).

Methods

Algae residue obtained after lipid extraction was calcined at 500 °C for 2 hrs to obtain biochar (C). Magnetic core was prepared by co-precipitation method based on procedure reported by [5] with some modifications. Nano-magnetic catalyst (Ni doped magnetic biochar) was prepared by an excessive impregnation method. Ni doping was carried out by adding the calcined biochar and magnetic biochar support into nickel nitrate nitrate solution, vigorously mixed using ultrasonic sonicator (SONIC –

150W ultrasonic homogenizer, power 150 W, frequency 20-25 kHz). The dried mixture was calcined at 500 °C for 8 h to obtain Ni/C and Ni/ Fe_3O_4-C. The developed catalyst systems were characterized for their surface morphology, crystalline nature and thermal stability using HRSEM/EDS, XRD and TGA/DSC respectively. The performance of the synthesized catalyst was investigated via catalysed transesterification process for the conversion of microalgal lipids to fatty acid methyl esters (FAME) using the method reported by [6].

Results

The crystallinity of the samples was investigated by XRD as indicated in Figure 1a.

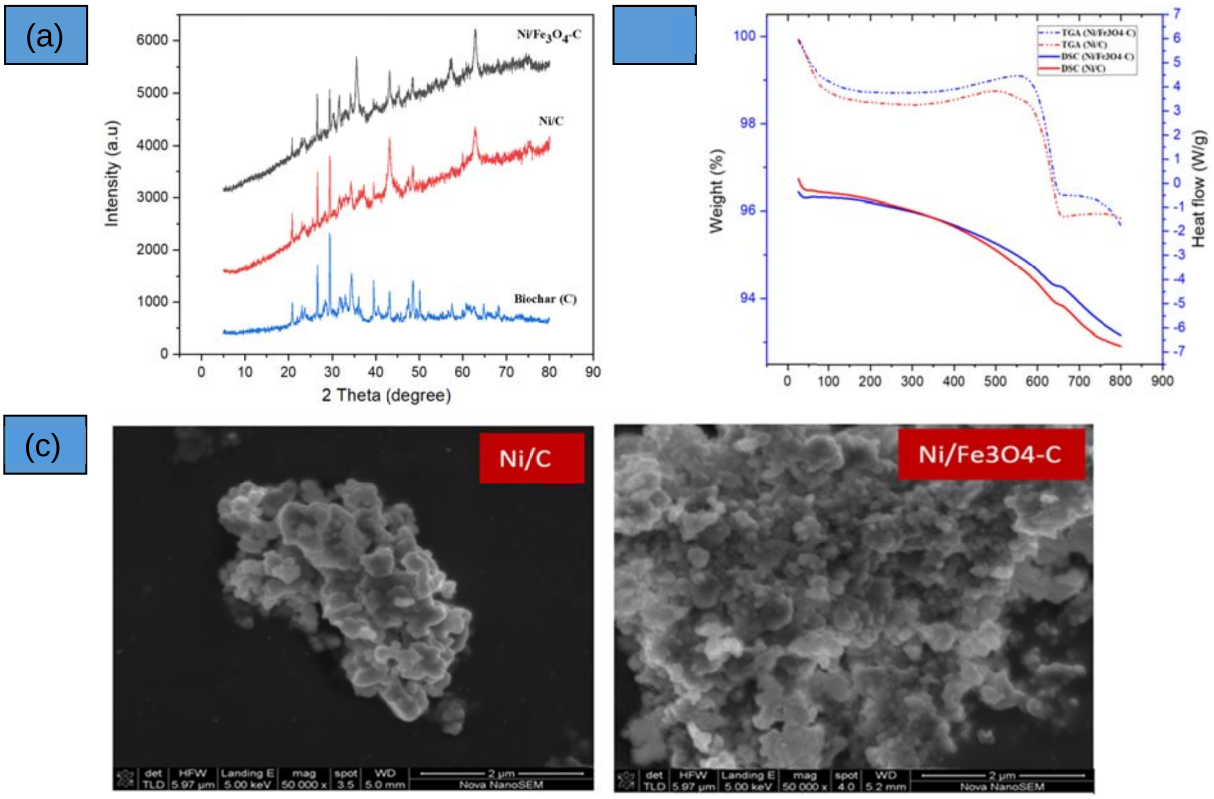

Figure 1. (a) XRD of the synthesized nanocatalysts (b) TGA/DSC of synthesized nanocatalysts (c) SEM images of synthesized nanocatalysts

The XRD result shows a high crystallinity of the synthesized catalysts with average crystallite size in the range of 10-33 nm. Some of the peaks on the biochar were superimposed with nickel doping and additional peaks were observed with the presence of magnetite. As shown in Figure 1b, the synthesized catalysts were thermally stable within the temperature range of 110-600 °C and the surface morphology of the samples were shown in Figure 1c. The EDS result confirms the presence of precious metals in the biochar which could be responsible for its catalytic activity. The catalyst performance result showed that better conversion was achieved with biochar catalyst (96.43 %) and Ni/C catalysts (98.5 %) compared to Ni/Fe_3O_4-C catalyst with conversion of 95.12 % when carried out at 60 °C, with methanol to oil molar ratio of 30:1 and catalyst amount of 15 % (weight/oil weight). The EDS results confirms the presence of precious metals in the biochar which could be responsible.

Conclusion

Magnetic and non-magnetic nano-catalysts were successfully synthesized using lipid extracted algae (residual biomass). The characterization results confirmed the synthesized catalyst were thermally stable, highly crystalline with average crystallite size in the range of 10-33 nm. Biodiesel yield of 95 to 98.5 % was achieved using nano catalysts at 60 °C, with methanol to oil molar ratio of 30:1 and catalyst amount of 15 % (wt/oil wt). Though the performance of the synthesized catalysts were found to be close and adequate, catalyst separation and recovery was much better with the magnetic nano-catalyst (Ni/Fe_3O_4-C) when compared to the non-magnetic (Ni/C). The developed nano magnetic catalyst can be effectively reused for up to 5 batches of conversion reactions without significant loss in its activity.

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ONE-STEP GLYCEROL HYDRODEOXYGENATION TO PROPYLENE OVER Mo-BASED CATALYSTS

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Introduction

Propylene, one of the chemicals produced in large volume, is conventionally produced as a byproduct of steam cracking and fluidized catalytic cracking (FCC) of naphtha and gasoline in petrochemical industry. As an important raw material for the production of industrial products and chemical intermediates, it is important to develop more sustainable ways. Biomass derived intermediates, such glycerol, can serve as feedstock for olefin production, following alternative reaction pathways. Propylene can be formed via complete de-oxygenation of glycerol, along with the formation of a C=C bond, a novel research subject that has not yet been thoroughly explored in the open literature. This study refers to one-step selectively glycerol hydro-deoxygenation reaction (HDO) to propylene over Mo-based catalysts. Typically, glycerol de-oxygenation takes place in liquid phase, at 300 °C, for 2 hr and under 8.0 MPa H_2, using water as a solvent [1]. Up to now, Mo and Fe–Mo catalysts, supported on black carbon, proved to be selective towards C–O bond cleavage, converting glycerol to propylene with satisfied yields [1]. This work focusses on the effect of dopants (Pd, Ir, Co) and supports (black carbon, ZrO_2, CeO_2-ZrO_2, Al_2O_3, HZSM-5) on the performance of Mo-based catalysts in hydrodeoxygenation of glycerol to propylene.

Results and Discussion

Mo/C catalysts have been proved to be efficient materials for glycerol HDO, obtaining 68 % glycerol conversion with 70 % selectivity to propylene for 2 h reaction time [2]. C_3H_6 is the main product formed and the only one in gas phase, while 1-propanol, 2-propenol and 1,2-propanediol are the main products in the liquid phase (though with significantly lower selectivity, 4-7 %), maintaining at the same time the 3C atoms on the glycerol molecule. The addition of Fe has a negative effect on Mo/C acidity leading to lower glycerol conversion values (48.9 %). However, Fe-Mo/C performance increases after 6hr reaction time, showing 89 % and 76.1 % conversion and selectivity to propylene, respectively [1]. The investigation of the operating conditions effect over the Fe-Mo/C catalyst showed that temperature and especially H_2 pressure increment favor glycerol conversion towards propylene, suppressing the formation of partially de-oxygenated products [1]. In addition, mechanistic tests showed that propylene formation mainly proceeds via glycerol conversion to 2-propenol and subsequent conversion of the latter to propylene. The presence of H_2 is a key parameter as it suppresses the 2-propenol to propanal isomerization, leading to increased concentration of 2-propenol, thus enabling its subsequent conversion to propylene. However, the low contribution to propylene formation of a secondary route which involves the successive hydrodeoxygenations of glycerol to 1,2-propanediol and 2-propanol and the dehydration of the latter, could not be excluded [2]. The reduced states of MoO_3, Mo^{+4} and Mo^{+5} are considered as the active sites for the selective conversion of glycerol to C_3H_6, as indicated by XRD and XPS measurements. Most likely, the formation of Mo^{+4} and Mo^{+5} species drives the reaction to the desired product formation through two consecutive reverse Mars–van Krevelen mechanistic cycles [2].

In order to improve the catalytic performance (increase catalyst acidity as well as hydrogenation rate), bifunctional catalysts with both metal and medium to strong acids sites are to be prepared. Apart from black carbon other materials with varying acidity like ZrO_2, CeO_2-ZrO_2, sulfated ZrO_2, Al_2O_3 and H-ZSM-5 will be used as supports for Mo catalysts or added mechanically mixed as co-catalysts. Efforts will be also devoted to strengthen the metallic function of Mo species by adding Pd, Ir, or Co. The preparation of the catalysts and their evaluation in the selective de-oxygenation of glycerol to propylene is in progress.

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SELECTIVE HYDROGENATION OF FURFURAL TO FURFURYL ALCOHOL OVER Cu-Fe-CONTAINING CATALYSTS

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Currently, there is an active interest related to the processing of non-edible plant materials into valuable chemical compounds. One of the promising areas is the production of various useful substances from furfural - a product of acid hydrolysis of hemicellulose [1]. The main direction in the processing of furfural is its hydrogenation to furfuryl alcohol (FA). FA may be used in chemical industry as follows: a solvent and film-forming agent in petrochemistry, in the production of glass fibers, paint, polymer concrete, in the synthesis of different derivatives of furan [2].

The copper-chrome systems are commonly used for the conversion of furfural [3]. But the main disadvantage of the such catalysts is the toxicity of chromium compounds. The catalysts based on noble metals may also be used, but they are very expensive and have a low selectivity towards furfuryl alcohol. Therefore, the non-toxic and stable catalysts with a low cost and a high activity resulted in increased yield and selectivity towards furfuryl alcohol are to be developed.

Cu- and Fe-containing and stabilized by Al_2O_3 catalysts with different content of metals were studied in the reaction of selective hydrogenation of furfural to FA. The catalysts were prepared by fusing the copper, iron and aluminum nitrates followed by reduction at 250 °C. The hydrogenation of furfural in isopropanol was carried out in a batch reactor at 100 °C and a hydrogen pressure of 6.0 MPa. It was shown that the catalyst $Cu_{20}Fe_{66}Al_{14}$ has the highest activity, the conversion and selectivity to FA were 96 and 97 mol. %, respectively. Also this catalyst results in 100 % conversion of solvent-free furfural with 95 mol. % selectivity for FA in a flow reactor at 160 °C and a hydrogen pressure of 5 MPa. At the same time, $Cu_{20}Fe_{66}Al_{14}$ catalyst does not lose its activity during continuous operation for 30 hours. According to the data of physicochemical methods, high values of furfural conversion and FA selectivity achieved in the presence of copper-iron-containing catalysts are due to the presence of stabilized highly dispersed particles of copper formed in the presence of mixed spinel. Thus, copper-iron-containing catalysts can be used as highly selective catalysts for the process of hydrogenation of furfural to furfuryl alcohol, which allows us to obtain the target product in high yield for a long time.

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BIO-CATALYSIS FOR DESIGNING LIGNIN STRUCTURES - MONOLIGNOLS OXI-(CO)POLYMERIZATION USING ENZYME CATALYST

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Lignin is one of the most abundant green polymer in the world together with the cellulose and hemicellulose. Beside the natural sources exploited up to maximum limit today, the pulp-paper as well as bio-refining industries are generous providers of lignin resources. As a consequence, new perspectives of lignin valorization are absolutely required.

We studied the construction of lignin-composites using monolignol fractions (e.g. sinapyl alcohol, SA or coniferyl alcohol, CA) based on the fact that lignin can be efficiently converted into a mixture of mono-/oligo-mers with the ability to be recombined into artificial lignin [1,2]. A novel and practical one-pot system was developed for artificial lignin-composites production. Monolignols (SA/CA) were linked together with caffeic acid (CafAc) in a polymeric net similar with natural lignin based on oxi-(co)polymerization process with H_2O_2 as oxidation reagent and peroxidase enzyme as biocatalyst.

Oxi-copolymerization process has been developed in a heterogeneous system, i.e. SA/CA dissolved in liquid phase, while CafAc was attached on acrylic particles (S_{C2}/S_{C6}-CafAc). S_{C2}/S_{C6}-CafAc-L_1 bio-composite was produced from CA, while SA oxi-copolymerization led to S_{C2}/S_{C6}-CafAc-L_2. Different conversions were achieved for both functionalized supports demonstrating that the solid support together with type of monolignol affected the co-polymerization process (maximum conversion of 71.1 % and 49.8 %, for SA and CA).

Designed composites were investigated using different characterization techniques, e.g. FTIR, TPD-NH_3, TGA, contact angel and SEM. FTIR spectra offered clear evidence of the artificial lignin deposition on the beads, while TPD-NH_3 analysis allowed to evaluate the bio-composite acidity. The acidity for SA-based bio-composite was higher than for CA-based bio-composite. Also, the artificial lignin attachment improved the thermo-stability of the composites compared to original/functionalized support.

Investigation of surface hydrophobicity for the new bio-composites was performed using contact angle measurements of distilled water drop on prepared surfaces. The contact angel of the bio-composites reached to 63° for CA-based polymer or 18° for SA-based polymer. Obviously, the results indicated an enhancement of the hydrophobicity for the oxi-copolymer belonged to CA monolignol. Similar hydrophobicity was reported in the literature for natural lignin attached on silica surfaces [2]. Moreover, it has to be mentioned that the artificial lignin prepared by oxi-copolymerization is more hydrophobic than some natural lignins (e.g. soda lignin from *Triticum sp* and *Saccharum officiarum* with 35° contact angel) [2].

Beside of an innovative system for bio-composite preparation with green chemical aspects, this work gives a new alternative for valorization of lignin residues. Versatility as well as green aspects of the polymeric structure on the bio-composite surface allow easy adjustment of proposed bio-composites to different applications. In this direction, we can mention the use of bio-composites as support or carrier for biomolecules (e.g. enzymes and whole cell) when specific properties of support/carrier are requested.

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THE TREATMENT OF THE LIGNOCELLULOSIC BIOMASS FOR OBTAINING TO THE ORGANIC SYNTHESIS PRODUCTS

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The increasing interest to the biomass as a source of chemicals and energy has recently arisen due to the limited fossil fuel resources and the demand for new clean chemical processes [1]. The research on the development of alternative liquid transport fuels has considerably increased in recent years influenced by the implementation of legislation and directives on alternative energy. To achieve these aims in an ethical, environmental and economical manner the use of lignocellulosic biomass or agri-waste for the production of second-generation biofuels is proposed [2]. Chemicals derived from biomass have recently attracted a considerable interest [3]. The production of biofuels from hemicellulose requires acid hydrolysis to open the biomass structure giving large quantities of xylose [4]. The synthesis of furfural (FF) as a by-product of this biofuel production process has developed an additional important research area [5]. Furfural is one of the key derivatives which can be obtained from renewable biomass for the production of different important fine chemicals [6].

Selective hydrogenation of furfural has attracted much attention to the production of furfuryl alcohol (FA), methyl furan, tetrahydrofurfuryl alcohol, and others. Furfuryl alcohol is widely used in chemical industry, mainly for the production of special resins, polymers, and coatings on their basis, which is 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-dihydropyran and an intermediate in the synthesis of lysine, vitamin C, various lubricants and plasticizers. There are two ways of producing furfuryl alcohol: through hydrogenation of furfural, gas phase hydrogenation and liquid phase hydrogenation. In industry, furfuryl alcohol is obtained by catalytic hydrogenation of furfural in a liquid or vapor phase. 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 [2].

This report is more devoted to the hydrogenation of FF to FA with Pd-containing catalysts stabilized by hypercrosslinked polystyrene (HPS). FF is one of the major ingredients of bio-oil produced by biomass pyrolysis, while FA is a source of value-added chemicals, thus, creating an effective path from biomass to important compounds. Different metal precursors were used for the catalysts synthesis. The nature of the precursor influences the size of metal nanoparticles and their catalytic properties.

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ORAL PRESENTATIONS

Section V. CATALYSIS FOR ENVIRONMENT AND SUSTAINABILITY

Catalytic processes for energy efficiency and ecology
Catalytic processing of waste
Photo-catalysis for environmental protection

OP-V-1

PHOTOCATALYTIC ABATEMENT OF VOCs VIA TiO_2-BASED MATERIALS

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Introduction

One of the most common materials used in photocatalytic processes is the TiO_2. However, it is a photocatalyst with a good efficiency only in the UV-range. For this reason, TiO_2 is started to study with dopants, metals and non-metals [1]. The idea is to move its application range in the UV-Vis light thanks to the modification on its bang gap energy and the reduction of electron-hole pair recombination.

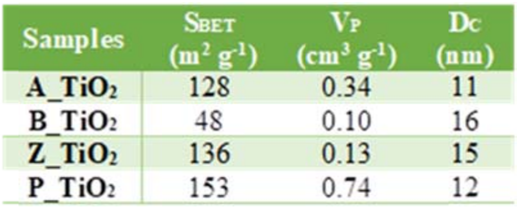
Materials and methods

In this study were synthesized four different TiO_2 samples (two pure and two doped with zirconium and phosphorus). One pure TiO_2 was synthesized with a longer method and the sample was labelled as “A_TiO_2” [2]. The other with a shorter preparation procedure, labelled herein as “B_TiO_2 [3]. The zirconium-doped TiO_2, labelled as “Z_TiO_2”, was synthesized following the procedure of B_TiO_2 but a zirconium precursor (zirconium nitrate) was added in order to have Zr/Ti = 20 atomic %. The phosphorus-based sample, herein labelled as “P_TiO_2”, followed the procedure of A_TiO_2 but was added a phosphorus precursor (phosphoric acid) in order to have P/Ti = 5 atomic %. All the four samples were study by complementary technique in order to investigate their physico-chemical properties (N_2 physisorption, FESEM). At the end, the samples were tested for propylene and ethylene oxidation under UV-Vis light source at these conditions: 0.5 g of photocatalyst, 500 ppmv of propylene (or ethylene), 10 % of oxygen.

Results and discussion

In **Table 1** were reported the results from N_2 physisorption. The doped samples have high surfaces area compared to the pure TiO_2 samples. The crystallite dimensions of the doped samples are 12 nm (P_TiO_2) and 15 nm (Z_TiO_2). On **Figure 1** are reported the FESEM images of the sample studied. The Z_TiO_2 seems to have more compact particles compared to the others. The P_TiO_2 is more porous: this was confirmed previously by N_2 physisorption.

Table 1. Textural properties derived by the N_2 physisorption results



Samples	S_{BET} ($m^2\,g^{-1}$)	V_P ($cm^3\,g^{-1}$)	D_C (nm)
A_TiO_2	128	0.34	11
B_TiO_2	48	0.10	16
Z_TiO_2	136	0.13	15
P_TiO_2	153	0.74	12

Then, the catalysts were studied for propylene and ethylene oxidation reactions. In **Figure 2** were summarized the results. The most promising catalyst is the TiO_2 doped with phosphorus for both propylene and ethylene oxidation. The reason could be the high surface area of this sample. The effect of dopants could be clearly seen during the ethylene oxidation: they exhibit a synergistic role with TiO_2. The reason could be explained by the insertion of these dopants in TiO_2 structure. This phenomenon generates variations in charge transfer electron state and, as a consequence, these two catalysts exhibit better photocatalytic performances.

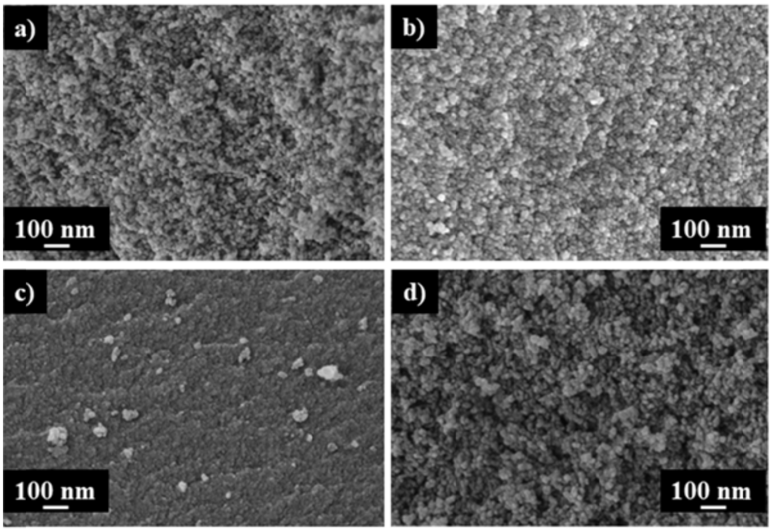


Figure 1. FESEM images of a) A_TiO_2, b) B_TiO_2, c) Z_TiO_2 and d) P_TiO_2

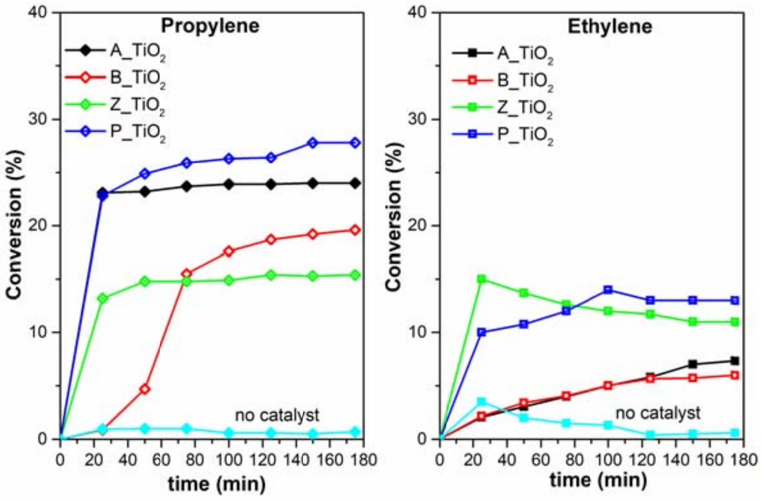


Figure 2. Catalytic activity under UV-Vis source after 3 h of test

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EFFECTIVE LOW-TEMPERATURE CATALYTIC METHANE COMBUSTION OVER Mn-CeO$_2$ CATALYTIC COMPOSITIONS

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Methane is currently considered the second most damaging greenhouse gas, since it has a GWP (*Global Warming Potential*) ranging from 28 to 36 over 100 years, being also the precursor for stratospheric ozone formation. Methane level in the atmosphere has been esteemed to be over 2000 ppb in 2020 [1-2]. Furthermore, the greater exploitation of the natural gas in the last decades has exponentially increasing the emissions of unburned methane. The catalytic combustion of methane over noble metals catalysts is nowadays one of the most effective and efficient technology of abatement, even at low operative temperatures [3-4]. However, noble metals heavy soffer from catalyst disactivation and high cost. On this account, cheaper transition metal oxides (TMOs), such as MnO$_x$ based materials, represent a suitable alternative to noble metals, since they exhibit excellent oxidation functionality and good stability, even tuneable by the synthesis protocol and the addition of promoters [5-6].

Therefore, the present study is aimed to prove the catalytic behaviour in the methane combustion, up to 600 °C, of a series of nanocomposite materials, based on MnCeO$_2$ compositions ($0.3<Mn_{at}/Ce_{at}<9$), with enhanced textural, redox and catalytic properties (Table 1), prepared via a new eco-friendly synthes route [7-10].

Table 1. List of catalysts with chemical-physical properties

Sample	Chemical Composition			Physical Properties		
	Mn/Ce (at/at)	MnO$_x$ (wt%)	CeO$_2$ (wt%)	SA$_{BET}$ (m^2/g)	PV (cm^3/g)	APD (nm)
M9C1	9.00-8.65	77.7	17.6	89	0.42	30
M5C1	5.00-4.66	66.9	28.4	110	0.43	25
M2C1	2.00-2.04	49.8	48.1	142	0.45	21
M1C1	1.00-1.02	33.9	65.8	171	0.47	20
M3C4	0.75-0.75	27.5	72.5	162	0.48	20
M1C2	0.50-0.45	18.6	81.4	179	0.43	16
M1C3	0.33-0.31	13.5	86.5	171	0.32	15

As shown in Figure 1A, all MnCeO$_x$ formulations prove a high activity in the catalytic oxidation of methane, reporting ignition temperatures (T$_{in}$) and temperatures of half conversion (T$_{50}$) below 260 °C and 550 °C, respectively. Then, the presence of CeO$_2$ has a strong promoting effect on manganese oxide activity. Indeed, both the T$_{in}$

and T_{50} decrease linearly with the CeO_2 content, moving from 257 °C to 217 °C (T_{in}) and from 537°C to 470°C (T_{50}) at the varying from 20 % to 80 % of ceria.

Indeed, as structural promoter, CeO_2 ensures a larger surface exposure, a higher dispersion and a greater reducibility, thus reflecting an enhanced catalytic behavior. The promoting effect of CeO_2 is even better evidenced by the exponential relationship between reaction rate (@ 500 °C) and CeO_2 content, reaching about 6.10^{-5} $mol \cdot g_{Mn}^{-1} \cdot s^{-1}$ at 80 % of ceria (M1C2 system), Figure 1B.

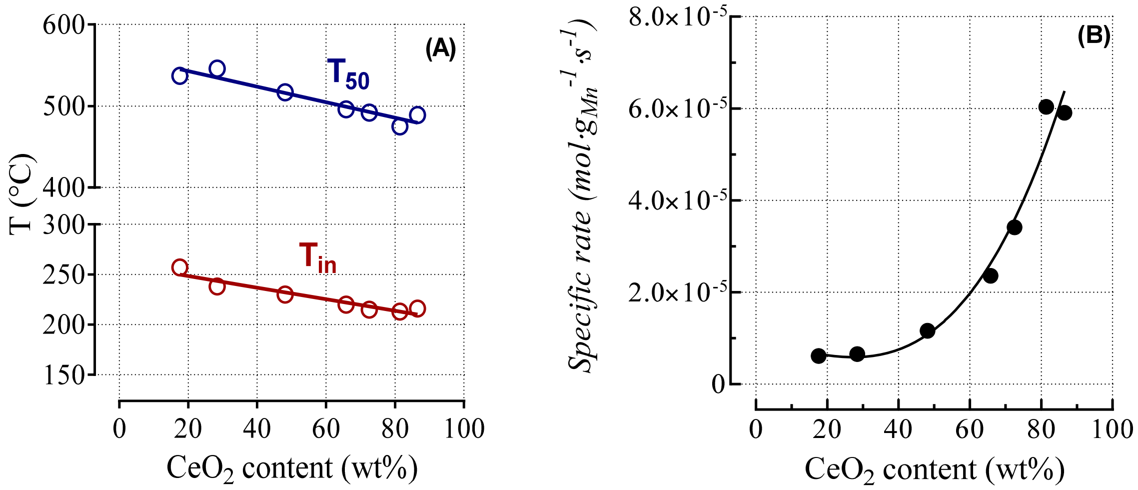

Figure 1. Characteristic methane reaction temperatures (A) and specific reaction rates at 500 °C (B) as function of CeO_2 content

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THERMAL-CATALYTIC DESTRUCTION OF POLYOLEPHIN POLYMERS IN PRESENCE OF $LaVO_3$ AND $LaVO_4$

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The research of the pyrolysis process of polyolefin polymers is an essential point in the creation of modern technologies for recycling of plastic waste. The composition of the initial mixture, the temperature mode and the properties of the environment make a significant contribution to the regularities of the thermal destruction processes. The additional use of catalysts can intensify the pyrolysis process in significant measure and contribute to the expansion of the range of final products. The choice of vanadites of rare-earth metals is based on the catalytic effect of metal cations on the pyrolysis processes of organic raw materials. In this case, carbocations with hydride ion transfer can be formed on the Lewis acid sites of the catalyst. These carbocations are capable of participating in isomerization and cracking reactions at catalytic sites, which should increase the reaction rate of thermal decomposition of the polymer mixture [1].

Orthovanadate of lanthanum of composition $LaVO_4$ are resulted from the solid-phase high-temperature reaction, the lanthanum vanadite from the lanthanum vanadate under high-temperature in current hydrogen reduction. The sole exception is $LaVO_3$, which refers to the tetragonal system. Lanthanum orthovanadate has a monazite-type structure.

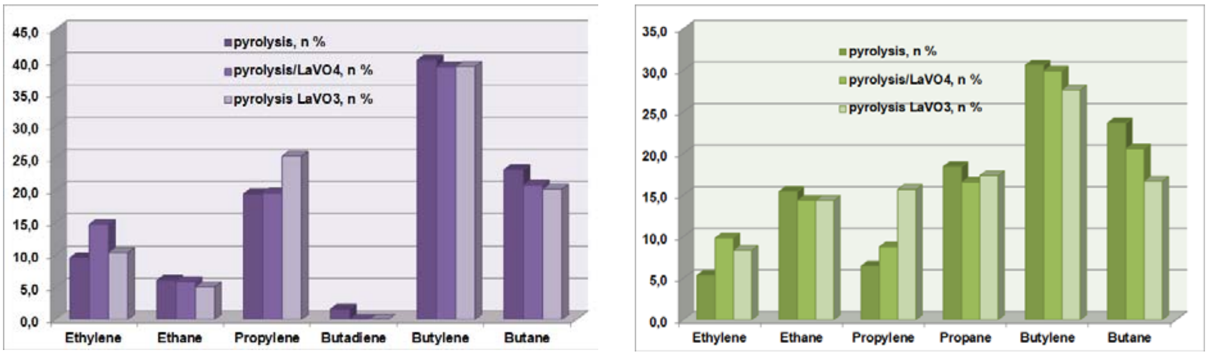
From the pore size distribution curves, the calculated specific surface area by the BJH method and method using desorption isotherm branches in the capillary condensation region, the pore size distribution. Vanadites and vanadates have a very non-porous surface character ~ 3.5 m^2/g. The domain of mesopores is of particular interest for samples. Due to good access to the volume of the catalyst, the bulk products of pyrolysis.

For pyrolysis the prereduced polymer was weighed, loaded into the reactor and placed in an electric furnace. Heating was carried out until the reactor temperature reached 700 K. Formed during pyrolysis products were quantitatively determined by gas-liquid chromatography. Thus, the composition of the reaction products in the case of catalytic and non-catalytic pyrolysis was determined (**table 1**).

Table 1. Yield of thermal decomposition products of polyethylene (PE) and polypropylene (PP)

Process	Yield, % mass.					
	Gas phase		Liquid fraction		Solid residue	
	PE	PP	PE	PP	PE	PP
Pyrolysis	10.4	11.1	89.5	88.7	0.1	0.1
Pyrolysis /$LaVO_4$	13.1	16.7	86.8	83.3	0.1	0.1
Pyrolysis /$LaVO_3$	14.0	16.9	86.9	83.0	0.1	0.1

We noted the entrainment of the gaseous fraction both in the presence of $LaVO_4$ and $LaVO_3$ for catalytic pyrolysis. The composition of the gaseous fraction to produce light olefins is of particular interest. From figure 1 it can be seen that the presence of catalysts alters the quantitative composition of the gaseous fraction. So the use of lanthanum vanadate leads to a significant increase in the yield of ethylene from 5.4 mol. % to 9.8 mol. %. during the pyrolysis of polyethylene and from 9.6 mol. % to 10.4 mol. % in the case of pyrolysis of polypropylene. The use of lanthanum vanadate contributes to an increase in the yield of propylene from 6.5 mol. % to 15.7 mol. % in the case of pyrolysis of polyethylene and from 19.5 mol. % to 25.3 mol. % in the case of pyrolysis of polypropylene.



a b

Figures 1. The composition of the gas fraction during the pyrolysis of a-polypropylene, b-polyethylene

The use of lanthanum vanadite and lanthanum vanadate provokes the formation of light olefins in the gas phase. It should be noted that in the presence of vanadate, the level of ethylene increases, and in the presence of vanadite, an increase in propylene is observed.

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OP-V-4

ENHANCED CATALYTIC PERFORMANCE FOR CO_2 METHANATION ON Ni/OCF CATALYST POWERED BY INDUCTION HEATING

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Power-to-gas (PtG) technology is a strategy to convert and store intermittent renewable energy sources (RES), *i.e.* solar and wind, into easily long-term storable and transportable chemical energy. In this process, hydrogen produced electrolysis from RES electricity is further react with CO_2 to produce synthetic natural gas [1]. The reaction is highly exothermic, therefore, a fine control of the reaction conditions is mandatory to avoid the generation of temperature gradient (hot spots) inside the catalyst bed which can decrease the process selectivity and the catalyst life-time [2]. To this aim, the rational use of thermally and electrically conductive supports, *i.e.* carbon nanotubes (CNTs) [3], along with alternative heating systems, *i.e.* magnetic induction heating (IH), can markedly enhance the catalytic performance. IH has incomparable advantages regarding the high energy efficiency, fast heating/cooling and accurate control capabilities, which has become one promising heating technology in many fields [4, 5].

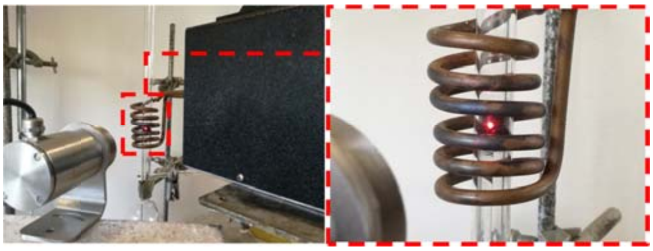

Figure 1. Quartz tubular reactor placed inside the coils of the inductive heater along with the laser pyrometer for the real time control of the reaction temperature

This contribution describes a highly efficient and robust catalyst for CO_2 methanation, using nickel nanoparticles (Ni-NPs) deposited on thermally conductive macroscopic oxidized carbon felt (OCF) combined with IH technical setup. The inherent electrical conductivity of OCF has been successfully exploited for transferring heat to the system by electromagnetic IH [6]. At odds with the classical thermal heating, IH allows the electromagnetic energy to be directly converted into heat by the susceptor (OCF) and Ni NPs (active sites). Such an alternative heating scheme allows rapid adjustment of the reaction temperature (*i.e.* hundred degrees per minute), with great potentials for large scale and rapid manufacturing processes. Most importantly, the temperature control at the catalyst bed has been systematically monitored by a laser pyrometer in almost real time thus ensuring an extremely fast response to any temperature deviation inside the catalyst bed (Figure 1). As a matter of fact, temperature fluctuations (mainly temperature runaway caused by the released heat), frequently encountered in real systems (as the consequence of a discontinuous supply of reagents loads), can be finely controlled thus allowing the reactor to be operated under virtually isothermal conditions. The Ni/OCF catalyst displayed noticeable enhanced catalytic performance with CO_2 conversion up to 74 % and CH_4 selectivity close to 97 % at 320 °C under IH mode compared with that heated by conventional external furnace, which are comparable to the state-of-the-art.

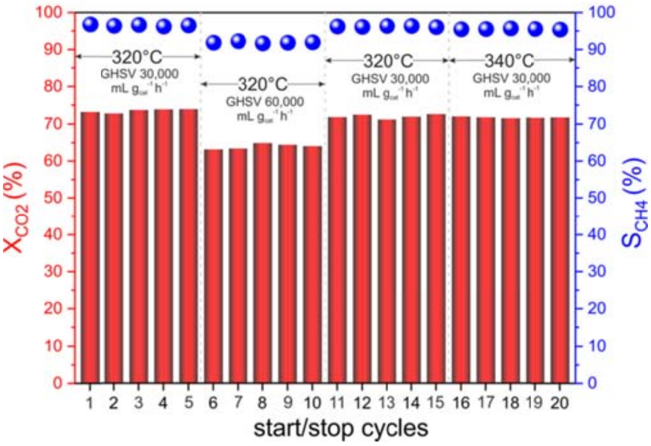

Figure 2. Catalytic performance of Ni/OCF with successive start/stop cycles operated under different opertion conditions

The catalyst has shown excellent stability when forced dynamic operational conditions are applied. Several and sequential start/stop cycles have been run to mimic the process discontinuity under conditions close to those operated in real plants, including changes in the target reaction temperature and GHSV (Figure 2), thus unveiling the extremely high stability of the catalyst under harsh conditions. Long term stability test has also proved this point. Besides the fabrication of such an outstanding catalyst, our research also indicate the promising prospect of IH in terms of energy efficiency and suitability to intermittent operation, especially for PtG system and its intergration in biogas plants. Methanation of the feedstock with similar compositions as biogas need to be further investigated in the near future.

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ECO-FRIENDLY PARTIAL DEAROMATIZATION OF PAHs IN TRANSFER HYDROGENATION CATALYZED BY RANEY® NICKEL

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Depletion of non-renewable natural resources causes rapidly growing interest to their deeper conversion that also complies with the principles of green chemistry. Therefore, deep and environmentally safe processing of condensed polyaromatic hydrocarbons (PAH) of heavy oil fractions or coals [1,2] is under high attentiondemands. Selective partial or total catalytic reduction/hydrogenation of condensed aromatic rings is a challenging and perspective way forward [3,4]. Among numerous catalysts using for the reduction of aromatics, heterogeneous catalysts based on metal nickel has undisputable advantage due to its moderate cost and high availability.

Transfer hydrogenation reaction (TH) is considered to be eco-friendly approach being real alternatives to conventional hydrogenation processes. For the last few years, Ni-based heterogeneous catalysts have been widely studied in TH [5,6]. Importantly, both conventional hydrogenation and TH are proceeded under the similar reaction conditions, however, eco-friendly and available H-donors (aliphatic alcohols, formic acid *etc*.) provide significant advantages for TH. The perspectives of TH in the reduction of different aromatic compounds (benzenes, biphenyls, naphthalenes, anthracenes, phenanthrenes and so on) are considered in this study, where Raney® nickel and 2-propanol are used as a catalyst and H-donor, respectively.

Two series of reactions are made: at 150 °C and 11 atm (self-pressure of 2-propanol) in autoclave and at 82 °C and 1 atm in glass reactor.

Benzene is fully reduced to cyclohexane at 150 °C for 5 hours. This reaction is used as principal point: the reduction/hydrogenation of PAHs is usually accompanied by dearomatization process. Similar conversion of naphthalene at 150 °C achieves 100 % even after 1 hour to form tetralin that is slowly reduced further to decalin (8 % after 5 hours). At 82 °C for 3 hours, naphthalene is totally transformed into tetralin. The similar results are observed for non-condensed biphenyl, which is fully converted to cyclohexylbenzene for 6 h at 82 °C and 1 h at 150 °C, respectively. At the same time, the reactivity of cyclohexylbenzene remains low enough under the same conditions. Thus, products of partial reduction (tetralin and cylohexylbenzene) can be obtained by TH with excellent yield. This is a very promising result for both industrial and laboratory practice [7].

At 150 °C, the TH reaction of both anthracene and phenanthrene occurs similar to naphthalene and includes two parallel ways presented on Figure 1. In both cases the reaction stops after reduction of two aromatic rings. Such partially hydrogenated hydrocarbons are shown to be quite stable in time: ~3 % of perhydroanthracene were observed after 24 h of the reaction.

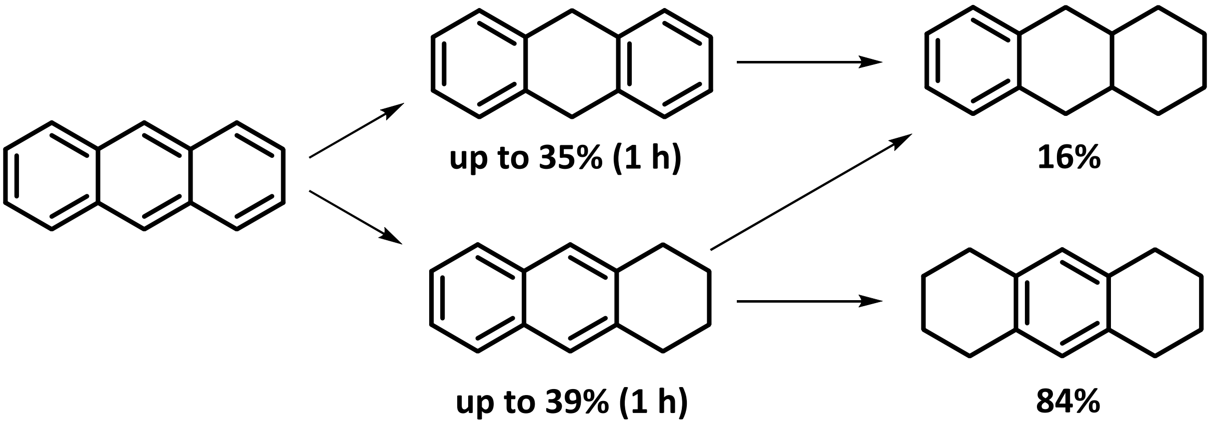

Figure 1. Reaction pathways of anthracene

Interestingly, at 82 °C the reactivity of phenanthrene is noticeably low. Conversion of anthracene achieves 100 % for 2 hours, whereas for phenantherene it is only 59 %.

In conclusion, high potential of Raney® nickel as a catalyst for partial hydrogenation/dearomatization under TH conditions is demonstrated. The process occurs as step-by-step pathway with alternate reduction of aromatic rings. As expected, aliphatic substituents in aromatic ring inhibit TH, therefore reactivity of partially reduced products is noticeably lower. At the same time, the presence of additional aromatic systems adjacent to each other leads to the increase of conversion even if these systems are not conjugated.

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CATALYTIC REACTIVE DISTILLATION OF POLYETHYLENE

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Introduction

Polyethylene (PE) is one of the most ubiquitous plastics in modern society [1]. Due to its particular properties and the fact that its properties can be tailored for a large variety of applications, large quantities of polyethylene plastics are found in single use items [2]. Although PE can be replaced in some of the applications, there are many others where PE is likely to be required for hygienic purpose, for example. It is, thus, very likely that the amount of plastic waste that is generate is still very significant and suitable ways to deal with this waste are required.

Recycling is always considered to be the better option [2, 3] but mechanical, or secondary recycling, often leads to poor quality material and the use of tertiary, or chemical recycling, methods are a very good alternative to convert waste plastic into useful feedstock material for the petrochemical industry [4, 5].

Experimental

In this work a reactive distillation approach was used to pyrolyse PE. Two different arrangements were set-up: one in which a cooling system was placed just at the outlet of the reactor, so that only gas phase products could exit the reactor and the second one where a liquid collection system was placed between the reactor and the cooling system.

The studies were conducted using both high- and low-density polyethylene and the thermal pyrolysis mode was compared with pyrolysis assisted by the use of an HZSM-5 catalyst.

Gas and liquid products (when applicable) were analysed by gas-chromatography and solid products were analysed by thermal analysis coupled with differential scanning calorimetry.

Results

The reaction produced gas and liquid phase hydrocarbons, as well as, in most cases, significant amounts of solid products, in the form of waxes.

Below 450 °C thermal pyrolysis did not produce any gas or liquid phase products.

Figure 1 shows results for LDPE, for both the thermal (non-catalytic) and catalytic processes in the reactor with liquid collection.

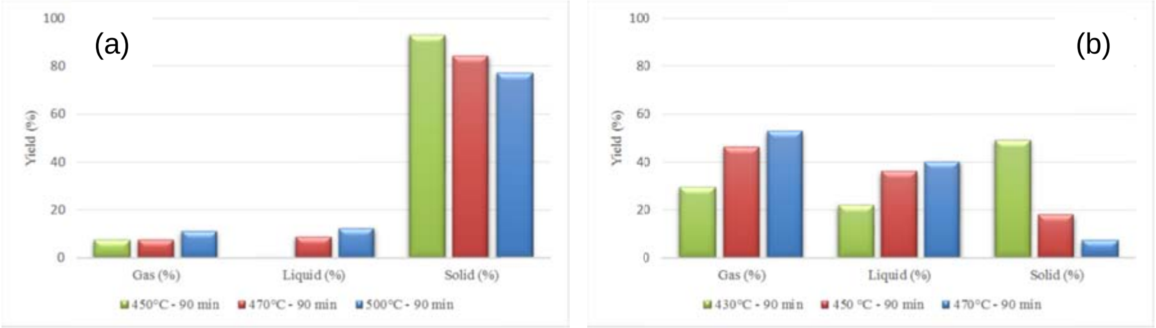

Figure 1. Overall product distribution for the thermal (a) and catalytic (b) pyrolysis of LDPE at different temperatures

These results clearly show that the use of HZSM-5 greatly improves the pyrolysis process, as it can be seen in figure 1. Although even at relatively high temperatures thermal pyrolysis only provided a modest conversion into gas and liquid products, the conversion increased very significantly with the addition of the catalysts, with an almost full conversion at 470 °C. This was the case also for HDPE.

Conclusions

The results show that the reactive distillation approach can, by careful regulation of the reaction conditions, direct the production towards different products, ranging from gas to solids and, thus, allowing one to optimize the product distribution according to the needs, as all of these products can be valuable as feedstock chemicals.

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SUPERCRITICAL CONVERSION OF FATTY ACIDS IN THE PRESENCE OF POLYMERIC CATALYSTS SYNTHESIZED BY HYDROTHERMAL DEPOSITION

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The limitation of fossil energy sources leads to the growth of the interest to renewable fuels. Biomass is the most permissive resource for the production of energy [1]. Different compounds of plant biomass such as cellulose, lignin, hemicelluloses, and vegetable oils have attracted great attention of the researchers [2]. Nowadays triglycerides are one of the most available renewable feedstock for the production of biofuels [3]. Deoxygenation of vegetable oils and their components is one of the alternatives to classical transesterification resulting in the first generation of biodiesel. This process allows solving the main problems of the classical transesterification resulting in the production of fuels with lower acidity, lower viscosity and higher cetane number (up to 99) [4]. The oxygen removal from the triglycerides through deoxygenation proceeds over conventional NiMo/Al_2O_3, CoMo/Al_2O_3 [5] or noble metal (Pt/C, Pd/C) [4] catalysts. However, in order to obtain saturated oxygen-free compounds, the use of a sufficiently high amount of hydrogen is required. The high hydrogen consumption leads to a sufficient increase in the deoxygenation cost making the resulted fuel uncompetitive [6].

Here we report the novel method for the conversion of fatty acids into hydrocarbon fuel without hydrogen consumption. The deoxygenation of stearic acid as a model compound was performed in the medium of supercritical n-hexane in the presence of Ni-containing catalysts synthesized by a hydrothermal deposition method [7]. We studied the influence of the support as well as the metal loading on the yield of target products of stearic acid conversion into hydrocarbons. Ni was supported on the three different supports: anhydrous microporous silica (SiO_2, Reachim, Russia), anhydrous alumina (Al_2O_3, Kupavna reactive, Russia), and non-functionalized hypercrosslinked polystyrene (HPS, Purolight Inc., UK). All the supports were preliminarily dried at 70 °C for 90 min. After the choice -of the optimal support, the Ni loading was varied from 5 to 20 wt. %.

In order to evaluate the influence of the support, three types of porous materials were chosen: microporous silica, alumina, and HPS. The HPS–based catalyst provides a higher rate of stearic acid conversion. The highest selectivity to n-heptadecane (over 90 wt. %) was observed while using Ni/HPS catalyst. This catalyst also showed high stability.

The study of the Ni loading influence showed that the increase in Ni content leads to an increase in the deoxygenation rate. However, the study of the influence of Ni content on the n-heptadecane yield showed that the concentration of Ni above 10 wt. % does not affect the target product yield. Thus, the increase in the Ni content is not preferable from the point of view of the process cost.

For a better understanding of the obtained results, the physical-chemical analysis of the catalysts was performed. It was shown that the hydrothermal synthesis of the catalysts leads to the decrease in the micropore surface area forming mesopores with the diameter above 10 nm. Such mesoporous materials are more preferable for the conversion of large molecules (e.g. stearic acid and triglycerides). HPS-based catalyst has the highest surface area which allows higher adsorption of the substrate molecules and, thus, higher conversion rate.

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STRUCTURED CATALYSTS FOR TRANSFORMATION OF BIOGAS/BIOFUELS INTO SYNGAS WITH MESOPOROUS NANOCOMPOSITE ACTIVE COMPONENTS LOADED ON HEAT-CONDUCTING SUBSTRATES: DESIGN AND PERFORMANCE

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Design of efficient, inexpensive and stable to coking catalysts for transformation of natural gas/biogas/biofuels into syngas and hydrogen in the intermediate temperature range (600-800 °C) is a vital problem of sustainable and renewable energy field. In can be solved by design of active components with developed surface area able to efficiently activate fuel molecules and possessing high mobility and reactivity of surface oxygen species as well as a low surface acidity required to prevent coking. Their supporting on structured heat-conducting substrates ensures their operation with high space velocities in real feeds.

This work presents results of research aimed at design and characterization of such catalysts performance in transformation of biogas (CH_4 + CO_2) and biofuels (ethanol, ethyl acetate, glycerol, etc.) into syngas. As a support the ordered mesoporous $MgAl_2O_4$ prepared by the one-pot evaporation induced self-assembly (EISA) method [1] has been used. Nanocomposite active components containing 20 % $PrNi_{0.9}Ru_{0.1}O_3$, 2 % wt Ni + 2 % wt Ru + 10 % $MnCr_2O_4$ or 5 % wt Ni + + 1 % wt Ru + 10 % $Ce_{0.35}Zr_{0.35}Pr_{0.3}O_2$ were loaded on the support by the incipient impregnation with corresponding solutions, containing in some cases acetylacetone as a complexing agent. $MgAl_2O_4$ support and catalysts were calcined under air at 700 °C. The textural, structural, surface properties of samples and their reactivity have been characterized by N_2 adsorption-desorption analysis, BET, XRD, TEM with EDX, XPS, FTIRS of CO test molecule, H_2 and EtOH TPR. The catalytic properties of these active components in methane dry reforming, ethanol ethyl acetate and glycerol autothermal reforming were tested using tubular plug-flow reactors at short contact times as earlier described [2, 3].

Active components were loaded on structured substrates (Ni-Al (C) foams; Fechraloy foils/honeycombs, gauzes and microchannel platelets, etc.) from suspensions with addition of surfactants, total loading up to 10-20 wt. % [2,3]. Structured catalysts were tested in ATR of concentrated feeds using axial or radial reactors including those equipped with the internal heat exchangers [4].

$MgAl_2O_4$ has the ordered mesoporous structure with 2D hexagonal cylindrical-like pores, SSA 290 m^2/g, pore volume 0.63 cm^3/g and a narrow pore size distribution with the mean size 12 nm. The catalysts retained mesoporous structure with SSA decreasing to 100-210 m^2/g. FTIRS spectra of adsorbed CO demonstrated suppression of support acidity and a high dispersion of Ni-Ru nanoparticles even in reduced catalysts with broad variation of the density of accessible metal sites and the ratio of terminal/bridging carbonyl bands intensity reflecting population of isolated/clustered sites [2, 3]. H_2 and EtOH TPR data revealed a high reactivity of all catalysts. In all studied reactions developed catalysts demonstrated a high and stable performance exceeding that for catalysts on Mg-doped alumina support [2] due to a high dispersion of active component, high reactivity and hampering of coking due to a low acidity. Specific catalytic activity correlates with the number of metal surface sites estimated by FTIRS of adsorbed CO.

In pilot tests of optimized structured catalysts in real feeds at short contact times, a high yield of syngas approaching equilibrium at ~ 700 °C was demonstrated in steam, dry, partial oxidation and mixed reforming of biofuels. Suppression of surface acidity and O_2 addition to the feed decrease C_2H_4 content, thus preventing coking even for such fuels as glycerol. Mathematical modeling demonstrated absence of any heat transfer limitations due to a high thermal conductivity of substrates. For radial – type reactors equipped with the internal heat exchanger partial oxidation or oxy-steam reforming of the mixture of natural gas and liquid biofuels (ethanol, glycerol, etc) allow to operate at inlet temperatures not exceeding 50-100 °C and producing up to 20 m^3/h of syngas with the equilibrium composition. Stable performance was confirmed for more than 200 h time-on-stream.

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REVERSE MICROEMULSION SYNTHESIZED METAL CARBIDES FOR CATALYTIC PROCESSING OF BIOGENIC CO_2-RICH STREAMS

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Introduction: Recently, CO_2 utilization has attracted significant interest as an alternative approach to CO_2 storage [1]. Converting CO_2, which is contained in many biogenic waste streams (biogas, landfilll gas, fermentation off-gas), into synthetic fuels is an attractive pathway to reduce our dependence on fossil fuels. Thermocatalytic hydrogenation (e.g., reverse water gas shift (RWGS) and Sabatier reaction) provides advantages of fast reaction rates and high conversion efficiencies, thus allowing for compact, high-throughput operation [1-7]. The required H_2 can be generated via water electrolysis using renewable electricity (hydro, wind, and solar) or surplus power. One of the key elements in the developing technologies for thermocatalytic CO_2 conversion is the catalyst.

Transition metal carbides have reently attracted attention as promising catalytic materials due to their electronic structure similar to that of platinum group metals, low cost, and excellent stability at elevated temperatures [8]. However, synthesizing supported transition metal carbide nanoparticles is challenging as the preparation procedure requires high temperature thermochemical treatment that leads to low specific surface area. In this study, high surface are, supported transition metal carbides were synthesized via the reverse microemulsion (RME) method, characterized by a variety of analytical techniques, and evaluated for catalytic performance in high temperature CO_2 hydrogenation.

Materials and Methods: $MoO_3/\gamma\text{-}Al_2O_3$ and $CoO/\gamma\text{-}Al_2O_3$ nanoparticles were prepared in reverse microemulsions of water/cyclohexane/Triton X-100/2-propanol. These materials were converted into carbides by reduction in the CH_4/H_2 atmosphere (Figure 1a). The synthesized catalysts were characterized by XRD, BET, ICP-OES, HRSEM, TEM, TPR-FTIR, TGA-FTIR, and *in situ* FTIR. Catalytic activity, selectivity, and stability were analyzed over the range of temperatures, pressures, and space velocities.

Results and Discussion: Catalyst characterization confirmed the composition (ICP-OES) and indicated an exceptionally high specific surface area (BET), 200-

300 m^2/g. Crystalline phases were identified by XRD, e.g., Figure 1b shows XRD patterns of MoO_3/γ-Al_2O_3 and Mo_2C/γ-Al_2O_3. Both the MoO_3/γ-Al_2O_3 and Mo_2C/γ-Al_2O_3 were 100 % selective to CO formation, Figure 1c, attaining nearly equilibrium RWGS CO_2 conversion. The Co_2C/γ-Al_2O_3 catalyst, on the other hand, was highly selective to CH_4 formation with CO_2 conversions exceeding 90 % under optimal conditions. Both the Mo_2C/γ-Al_2O_3 and Co_2C/γ-Al_2O_3 catalysts were stable over 100 h on stream.

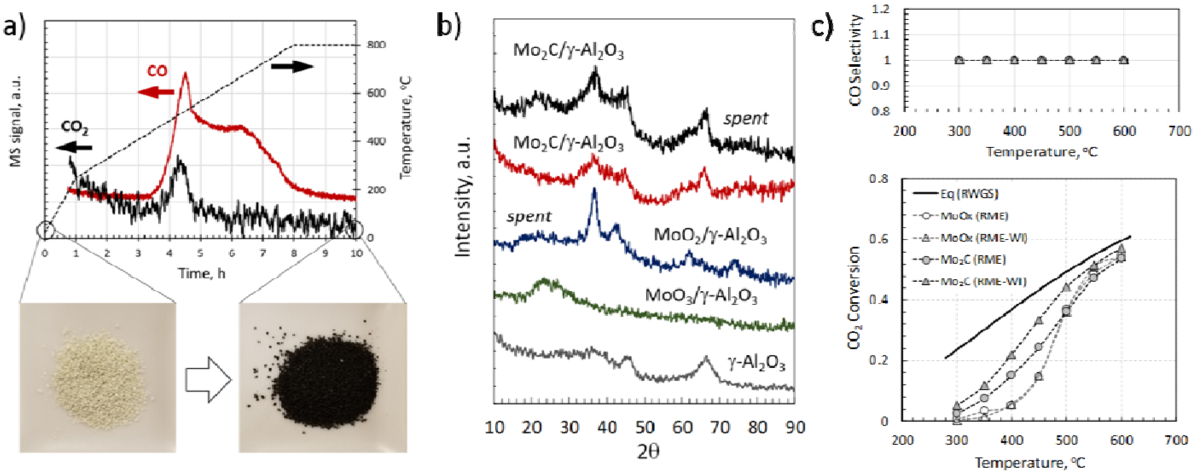

Figure 1. A typical carburization profile (a), XRD patterns (b) and catalytic performance (c) of the $MoOx/\gamma$-Al_2O_3 and Mo_2C/γ-Al_2O_3 catalysts

Significance: We report a versatile method for synthesis of high surface area, supported transition metal carbides. Depending on the selection of a transition metal, these catalysts can be used for various reaction pathways, which can be utilized for chemical synthesis allowing resource management and economic gain.

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CATALYSTS FOR HYDROGEN EVOLUTION BY HYDROTERMOLYSIS AND PHOTOCATALYTIC HYDROLYSIS OF AMMONIA BORANE

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Today, hydrogen storage is one of the most important issues that hinder the development of a hydrogen economy. Many studies searching for effective storage materials are in progress but none has reached the technical criteria that could make them viable from the technological and commercial points of view. According to many researchers, hydrogen generators based on catalytic hydrolysis of hydrides are offered as promising compact and portable devices that were employed with proton-exchange fuel cells. Ammonia borane (NH_3BH_3, AB), a promising stable H_2 storage material, is the object of intense studies now. NH_3BH_3 contains 19.6 wt % H. Today, most of the published papers about NH_3BH_3 deal with improvement of catalytic materials.

In this study, a catalytic hydrothermolysis of AB was investigated. In this process the highly exothermal hydrolysis of a part of NH_3BH_3 (1st step) is coupled to its thermolysis (2nd step). This leads to the high efficiency of this process. Note that catalytic route of hydrothermolysis of AB has not been studied in the literature yet.

It was shown that addition of metal chloride solution (M = Co, Ni, Cu, Fe) to a solid-state bed of AB particles leads to formation *in situ* a catalytically active nanosized phase. Measurements of the temperature of the reaction layer together with the amount of evolved hydrogen and ATR-FTIR study of products have shown that at external heating 85 °C there was acceleration of the 1st step, which resulted in a stronger heating of the reaction layer and a start of 2nd step. The H_2 generation rate and H_2 yield depend on the temperature of external heating, the mole ratios AB/MCl_2 and AB/H_2O and the nature of M. High values of H_2 storage capacity (7.5 wt %) and average H_2 generation rate (39 $ml \cdot g_{composition}^{-1} min^{-1}$) were achieved at 85 °C in this study. Note that organization of hydrogen production by supplying a limited quantity of catalyst precursor solution to the NH_3BH_3 provides for stability of NH_3BH_3 in the cartridge.

Nowadays, one more process of interest is the photocatalytic hydrolysis of AB under visible and UV light. In this study, TiO_2 (anatase), $K_xH_{2-x}Ti_6O_{13}$ and Ag/TiO_2

were used as photocatalysts. The kinetics of hydrogen generation were studied. It was found that anatase and polytitanate nanostructures being in contact provide for higher activity compared with the phases used separately. Ag content in Ag/TiO_2 was optimized and the high value of photonic efficiency of the process (50.6 %) was reached. The fact established at the first time that it is possible to control the hydrogen generation from AB by the light irradiation (λ = 365, 450 nm) if Ag content in Ag/TiO_2 catalyst is less than 0.1 wt. %.

Acknowledgements

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OP-V-11

HYDROCRACKING OF HDPE WITH MICRO AND MESOPOROUS CATALYSTS BY THERMOGRAVIMETRIC ANALYSIS

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Due to the continuously growing production of plastic materials, plastic waste suffered a dramatic increase and become one of the biggest environmental problems nowadays. Chemical recycling, is a promising route to solve this problem.[1][2] and cracking technology (including both thermal and catalytic processes) is being widely used to convert plastic waste into valuable products, like fuels. In the case of the catalytic cracking a wide variety of heterogeneous catalysts can be applied (ex: mesoporous silicas, silica-alumina and zeolites) [3] and the great majority of the studies reported in literature have been performed under nitrogen or air atmosphere. However, the chemical transformation of plastics by catalytic cracking under hydrogen pressure (hydrocracking) presents many advantages when compared with alternative thermal-catalytic routes. The capability to process a wide range of feedstocks the possibility to obtain more stable and valuable products and to reduce the coke precursors, which are responsible for the catalyst deactivation, are the most significant ones. [4]

Therefore, the aim of this study is to evaluate how materials with different structural and chemical features such as porosity and/or presence of acid or metal sites may influence the cracking of HDPE under hydrogen atmosphere both in terms of energy requirements and products distribution. In this study mesoporous silica (MCM-41 and SBA-15) and HZSM-5 type zeolite (Si/Al ratio of 11,5 and 40) are tested as catalysts and thermogravimetric analysis (TGA) is used to obtain the degradation profile of HDPE with temperature for the various systems. The sample preparation method, the catalyst amount and the incorporation of metallic function (Pt and Ni) are other parameters also analyzed in this study. Results give an indication of the required energy to perform polymer cracking and are used as a first tool for the screening of potential catalysts for polymer hydrocracking. Studies under inert conditions are very common in literature but, data is scarce in what concerns polymer conversion under a reducing hydrogen environment. [4]

It is shown that when MCM-41 and SBA-15 mesoporous silicas are added to HDPE no significant changes are observed either in terms of the degradation profile. On the contrary, the use of HZSM-5 (Si/Al = 11,5) allows to decrease the onset of HDPE degradation temperature around 115 °C. A diminishment of heavy products (>C28) is also observed when compared to neat HDPE. A further shift to lower degradation temperatures is verified upon increase of the HZSM-5 amount or addition of a metal source (Pt or Ni). The sample preparation methodology also affects the degradation profile. An intimate mixing of the polymer with the catalyst (achieved by a pre-melting step) decreases significantly the onset degradation temperature.

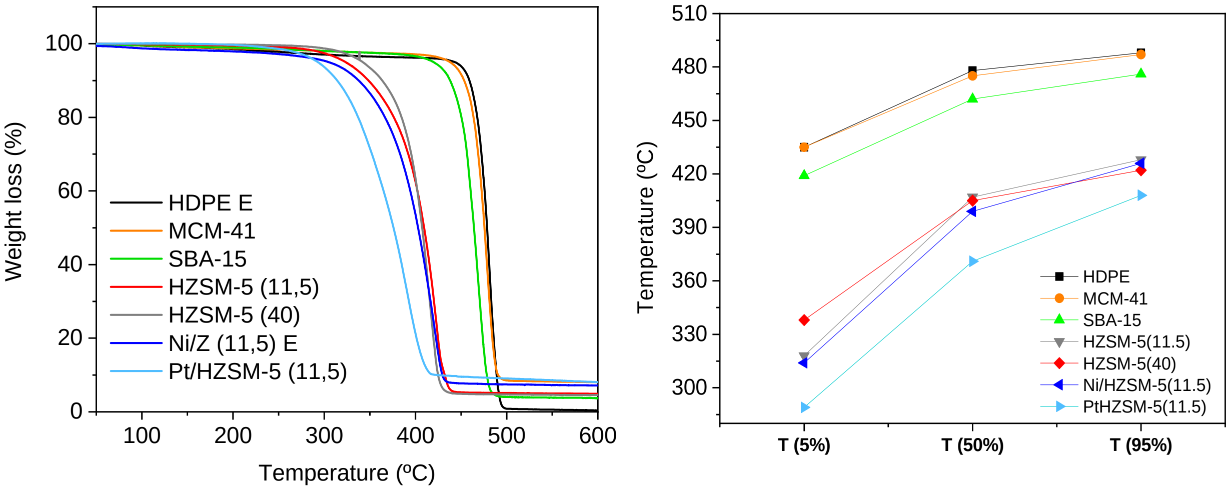

Figure 1. Weight loss curves and 5, 50 and 95 % degradation temperatures for HDPE hydrocracking using distinct catalysts

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COMBUSTION OF RENEWABLE WASTES IN A FLUIDIZED BED OF CATALYST – ECOLOGICAL AND ECONOMIC BENEFITS

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Today, one of the acute problems facing humanity is the formation of a huge amount of waste. Among them are the so-called renewable wastes – from agriculture, animal husbandry, utilities (sewage sludge). Effective utilization of such materials is in itself an urgent task, attracting the attention of the world scientific community. In turn, the possibility of obtaining additional benefits in the form of, for example, thermal energy or the production of new materials, makes work in this area extremely attractive.

Most of the currently existing methods for such types of waste processing have a number of significant drawbacks, such as low efficiency, the formation of significant amounts of pollutants, the high operating cost of the process, etc. Moreover, in some countries, the main part of such waste is sent to landfill, which creates even more environmental problems and limits the use of land allocated for storage.

In the Boreskov institute of catalysis has been developed and successfully applied the technology for the processing of fuels and wastes, which consists in combustion of raw materials in a fluidized bed of catalyst. The implementation of this technology makes it possible to avoid most of the drawbacks characteristic of traditional combustion methods (layered, flare, and in a fluidized bed of inert material). Moreover, the technology is universal and can be used for solid, liquid and gaseous materials, including those with high ash content, humidity and volatile content.

This paper demonstrates the effectiveness of the use of fluidized bed combustion technology in the utilization of renewable waste, in particular sewage sludge from municipal wastewater.

Acknowledgements

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OP-V-13

SYNTHESIS OF MODIFIED TiO_2-BASED CATALYSTS FOR THE PHOTOCATALYTIC PRODUCTION OF SOLAR FUELS

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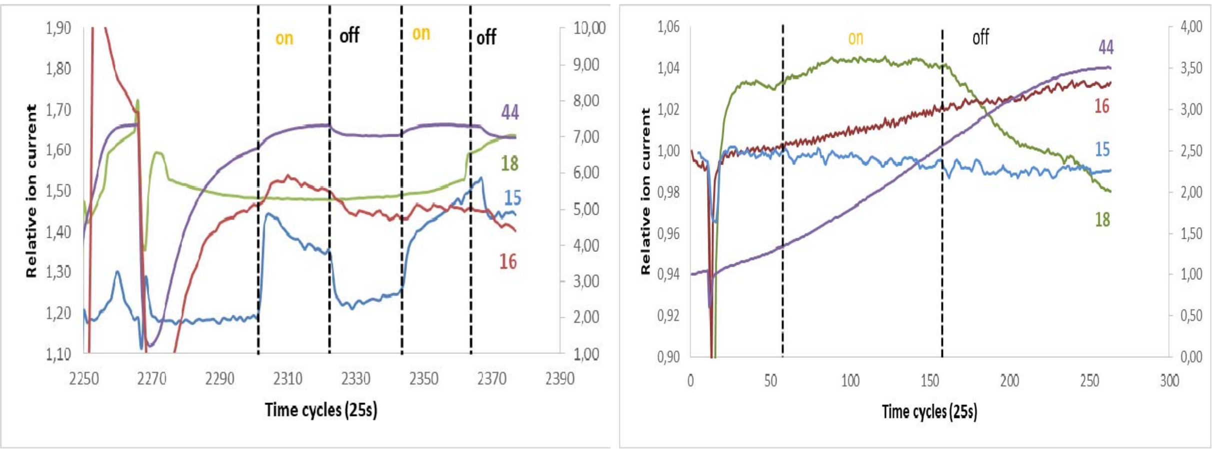
The production of liquid hydrocarbons by processing syngas, a mixture of carbon monoxide and hydrogen obtained by coal or biomass gasification, is a suitable substituent for oil refining. However, this process, known as Fisher-Tropch synthesis, requires temperatures usually higher than 250 °C and pressures ranging from one to several tens of atmospheres. A more sustainable and ideal alternative would be the syngas convertion in liquid fuels using sunlight and a suitable photocatalyst. TiO_2 has been extensively studied in the field of photocatalysis and showed several advantages over other semiconductor materials [1]. Nonetheless, in order to enhance the reactivity of TiO_2 towards visible light, the TiO_2 must be modified to reduce its band-gap and so, its response under sunlight. One of the strategies can be doping with transistor metals.

This work focuses on the photocatalytic transformation of syngas using metal doped TiO_2 to produce hydrocarbons under visible light radiation. The doping materials used were iron and cobalt. The materials were prepared by hydrothermal synthesis and incipient wetness impregnation of titanium dioxide (P25). Diferent metal loadings were also analized (1, 3 and 5 wt. %). Besides the synthesis of the photocatalysts, this work also focuses on optimizing the setup of the gas phase photocatalytic reactor. This includes finding an optimal way of coating the photocatalyst on the glass tube of the reactor as well as optimizing the contact area between the light radiation and the coated photocatalyst.

Both, hydrothermal and impregnated catalysts have lower band-gap (Eg) than pure TiO_2. This Eg decrease is independent of the metal used as doping agent but dependent of the metal loading. The lowest Eg was obtained for 5 wt. % of metal loading achieving band gaps as low as 2.6 eV. These Eg values obtained from diffuse reflectance spectra indicate that the performance of doped samples under visible radiation can be enhanced relative to pure TiO_2 phases.

The catalysts solutions, dispersed in ethanol, were coated droplet wise on the outside of small glass tubes (D = 1.3 cm; L = 7 cm). In some cases, Mowiol additive was added to the solution to improve the dispersion of the catalyst. After coating, the tubes were reduced with a hydrogen stream at 400 °C. The coated tubes were placed in a quartz reactor symmetrically surrounded by 6 UV light lamps (16 Watts each) or visible light lamps (14 Watts each). During catalytic tests performed with CO/H_2 mixture (20 cc/min) in argon (230 cc/min) the products were analysed on-line by mass spectrometry. Figures 1 a) and b) show results obtained with P25-Fe and P25-Co catalysts, respectively.



a) b)

Figure 1. Photocatalytic tests performed with a) P-25-Fe(5) under UV radiation and b) P-25-Co(5) under visible radiation. Curves 15, 16 and 18 correspond to the left axis, curve 44 to the right axis

During experiment a) the UV lights are turned on and off. During experiment b) the reactant stream was pre-heated up to 200 °C and visible light lamps were used. Both catalysts are clearly active resulting in methane (curve 16) and water (curve 18) formation. Consequently the water converts into carbon dioxide (curve 44). This work succeeded in transforming syngas into hydrocarbons using visible light radiation. This work in under progress.

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NOVEL MULTIFUNCTIONAL PHOTOCATALYSTS FOR ENVIRONMENTAL PROTECTION AND HUMAN HEALTH CARE

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Heterogeneous photocatalysis is one of the important fields in scientific research as an effective method for transformation of light energy to carry out useful chemical processes. Since 1972, when Fujishima and Honda have published their study about the electrochemical water splitting using a semiconductor electrode in *Nature*, titanium dioxide has been attracting great interest of researchers all over the world as a high active and stable photocatalyst for various photocatalytic processes. One of the most important features of TiO_2 is a capability to degrade micropollutants by their complete oxidation under irradiation in oxygen-containing mediums. This behavior allows for using the TiO_2-mediated photocatalytic oxidation (PCO) as an effective and environment friendly method for the purification of air and water. But there are some hindrances for active expand of TiO_2 photocatalysts.

The first is related to a wide band gap of TiO_2 (e.g., 3.2 eV for anatase) that corresponds to the fundamental ability for absorption of UV light only. This fact hinders its application under solar light due to the solar radiation spectrum has less than 5% of radiation in that region compared to all the radiation with wavelengths less than 780 nm. The second is related to the formation of reaction intermediates, which are the products of incomplete oxidation. Typically, these intermediates stay on the photocatalyst surface, but for certain types of pollutants or at a very high concentration of pollutant they may desorb and be detected in the gas phase. The formation of gas-phase intermediates (e.g., aldehydes, acids) is an essential problem of the PCO method, because the intermediates may be even more harmful than the starting pollutant [1]. In addition to organic intermediates, CO can be formed in the gas phase during the photocatalytic oxidation of VOCs as the final by-product [2]. Therefore, the development of new photocatalysts is required for solving the problems mentioned above.

In this study, the multifunctional photocatalysts, which consist of the several components, were synthesized and investigated. For this purpose, TiO_2 was doped with nitrogen to extend the photocatalytic activity to visible light and was deposited on the surface of zeolite followed by the deposition of palladium nanoparticles to prevent the formation of harmful intermediates and carbon monoxide during the PCO process.

Despite the superiority of titanium alkoxide precursors in scientific papers, one of the two main ways for TiO_2 production in industry is sulfate technology using the natural mineral ilmenite ($FeTiO_3$) that results in the formation of titanyl sulfate ($TiOSO_4$) followed by its hydrolysis to metatitanic acid ($TiO_2 \times H_2O$). Therefore, we are focused in this study on the investigation of N-doped TiO_2 prepared using titanyl sulfate as a titanium precursor and ammonium hydroxide as a nitrogen source. In contrary on the titanium alkoxides, titanyl sulfate is much cheaper and can be easily dissolved and hydrolyzed in water mediums without organic solvents. The preparation conditions, including the calcination temperature, pH, and the duration of precipitation are optimized to obtain the photocatalysts with a high photoactivity both under UV and visible light. Activity under UV monotonically increases as the calcination temperature increases due to enhancing the crystallinity of TiO_2. Under visible light, the activity has a domed-shape dependence on the calcination temperature due to changing the chemical state of nitrogen. Zeolite acted as a support for TiO_2 substantially increases the adsorption capacity of the composite photocatalyst that leads to decreasing the concentration of intermediates, which are desorbed from the photocatalyst surface and released to the gas phase, and, consequently, the total hazard during the PCO process [3]. Additionally, the deposition of palladium on the surface of TiO_2-N/zeolite suppresses the formation of CO as a by-product during PCO [4].

The multifunctional Pd/TiO_2-N/zeolite photocatalyst allows for suppressing the secondary pollution with harmful intermediates and CO substantially. Therefore, the development of composite photocatalytically active materials is a promising way to enhance the efficiency of air purification devices and to increase the safety of photocatalytic technology for the environmental applications and human health care.

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OP-V-15

GLUTATHION-S-TRANSFERASE CATALYSED REACTION BETWEEN GLUTATHIONE AND 1-CHLORO-2,4-DINITROBENZENE FOR DISCRIMINATION OF PESTICIDE CLASSES

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Glutathione S-transferases (GSTs; EC 2.5.1.18) are a multigenicfamily of cytosolic proteins with multifunctional biological roles,widely distributed throughout the body and found in the liver, kidney, brain, pancreas, testis, heart, lung, small intestine, skeletalmuscles, prostate and spleen [1]. The important biological function of GSTs is their catalytic action in detoxification reaction. The *in vivo* detoxification mechanism of GST has been utilized in biomedical diagnosis of drug resistance in cancer patients. GST catalyzes the conjugation reaction between reduced glutathione and 1-chloro-2,4-dinitrobenzene. Presence of pesticide in the reaction mixture inhibits the catalytic efficiency of the enzyme. Based on this we have studied the inhibition characteristics of four different classes of pesticides namely organochlorine, organothiophosphate, phenolic and benzimidazole towards the reaction while the enzyme was in immobilized state in graphene oxide gelatin matrix [2]. The trend of inhibition appears to be competitive for organochlorines, non-competitive for organothiophosphates and mixed type for phenolic and benzimidazole classes.

The apparent Michaelis-Menten constant for the immobilized glutathione-S-transferase in the said matrix was found to be 0.083 mmolL^{-1} and0.15 mmolL^{-1} respectively for glutathione and 1-Chloro-2,4 dinitrobenzene. Substrate specificity found to be 2.56×10^{7} $s^{-1}M^{-1}$ for glutathione and 2.15×10^{7} $s^{-1}M^{-1}$ for 1-Chloro-2,4-dinitrobenzene.

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POSTER PRESENTATIONS

HYDROGENATION OF LEVULINIC ACID TO GAMMA-VALEROLACTONE USING POLYMER-SUPPORTED PARTICLES OF RUTHENIUM DIOXIDE

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Biofuels are mainly produced from sugars, starches and vegetable oils; however, the limited availability of starting materials (due to restricted amounts of fertile soils) and competition with food from feedstocks are limiting factors for their production [1]. The advanced biofuels can be produced from lignocellulosic biomass, one of the most inexpensive and abundant raw materials. Levulinic acid (LA) is a substance, which can be obtained from cellulosic biomass via acid hydrolysis [2]. At present, the process of biofuels production on the basis of levulinic acid (LA) is of great importance. LA can be transformed into 2-methyltetrahydrofurane (2-MTHF), which is a fuel additive. Although there is a possibility of direct LA transformation to 2-MTHF, improved yields can be achieved by indirect pathways, which proceed through the production of gamma-valerolactone (GVL) as an intermediate. Thus hydrogenation of LA to gamma-valerolactone (GVL) is one of the most promising reactions in the field of biomass valorization to fine chemicals and liquid transportation fuels [3].

Due to the high demand for GVL, its efficient production is currently a topic of intensive research. Investigations are mainly focused on hydrogenation of LA and its esters by molecular hydrogen in the presence of metal catalysts. Application of supported metal catalysts is especially advantageous, owing to the simplicity of product recovery and catalyst recycling [4]. 5 %-Ru/C [5], 10 %-Pd/C and Raney Ni [6] are the most widespread heterogeneous catalysts of the GVL synthesis from LA. Currently, the conventional catalyst of the LA hydrogenation is 5 %-Ru/C [7], the use of which allows achieving high yields of GVL.

In order to achieve high degrees of the LA conversion, the use of ruthenium nanoparticles (NPs) with high surface areas is important. It allows competing with and surpassing the traditional industrial catalysts such as Ru/C. However, for successful use of Ru NPs in the LA hydrogenation the former should be stabilized. A successful solution to this problem, i.e., providing control over the size and size distribution of catalytically active metal NPs, is possible via the use of stabilizing agents, the most promising among which are porous polymers.

Nowadays conformational rigid hyper-cross-linked polymeric materials are the most promising organic supports, which are able to control the size and dispersion of catalytically active NPs and to prevent their aggregation and leaching. Despite the fact that recently the catalysts based on hyper-cross-linked polymers are widely used in reactions of fine organic synthesis, there are no data on the use of polymer-stabilized Ru-containing NPs in the hydrogenation of LA to GVL.

This work is devoted to the use of ruthenium-containing catalysts based on hyper-cross-linked polystyrene (HPS) in the hydrogenation of LA to GVL. Ru-containing NPs immobilized in HPS were synthesized at the variation of Ru loading and type of HPS (functionalized or without functional groups). Hydrogenation of LA was carried out in Parr Series 5000 Multiple Reactor System in an aqueous medium at the variation of reaction temperature and hydrogen partial pressure. Samples of the reaction mixture were analyzed via HPLC method.

Synthesized catalysts were found to be highly active in the hydrogenation of LA to GVL. For example, the use of HPS of MN100 type (functionalized with amino groups) as a support for the development of the catalysts allowed more than 99 % yield of GVL for 120 min of reaction duration at mild reaction conditions (90 °C, 2 MPa of hydrogen partial pressure) in an aqueous medium. It is noteworthy that NPs of hydrated RuO_2, which were located on the surface of the polymeric matrix and in its pores as grape-like aggregates, was found to be an active phase of HPS-based Ru catalysts.

Moreover, for the most active HPS-based catalyst, main kinetic parameters (apparent activation energy, reaction orders) were calculated and formal kinetic modeling was carried out for a deeper understanding of the observed kinetic behavior.

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CATALYTIC CONDENSATION OF BIOMASS DERIVATIVES TOWARDS EPOXY RESIN MONOMERS

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Bisphenol A is an important platofrm chemical since the diglycidyl ether of bisphenol A (DGEBA) is the most used epoxy resin for the manufacturing of high performance polymers and composites used coatings, adhesives or structural parts. However, bisphenol A is considered to affect the endocrine system due to its structural similarity with the estrogens. Since bisphenol A is produced from aceton and phenol that derive from petroleum it would be of high importance to find a safer substitute for bisphenol A that can be synthesized from natural resources. Diphenolic acid (DPA) is regarded as a possible substitute due to its structural similarity with bisphenol A [1]. Diphenolic acid can be synthesized by the condensation reaction of levulinic acid with phenol, both deriving from lignocellulosic biomass, according to the following scheme:

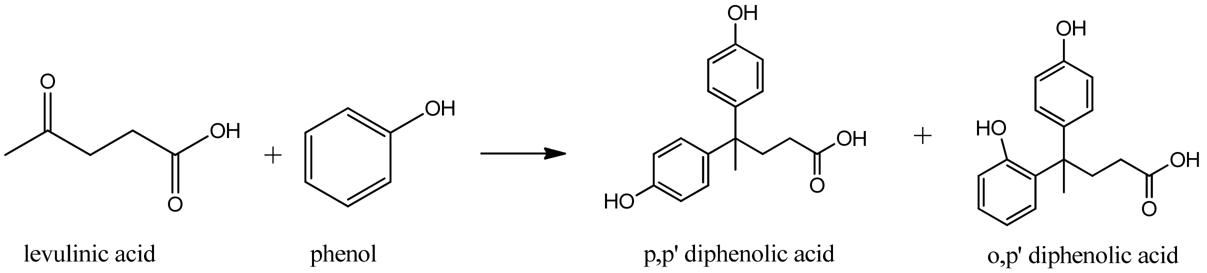

Figure 1. Condensation reaction of levulinic acid and phenol towars diphenolic acid

The selectivity towards p,p' diphenolic acid is of critical importance since only that isomer, after esterification and glycidilation, will produce a biopolymer monomer that will have similar structure as DGEBA. Levulinic acid is produced from biomass carbohydrates whereas phenol could be replaced by natural phenols deriving from lignin, leading to greener fully bio-based epoxy resins [2].

In the present work, we studied the use of different acids as catalysts for the production of diphenolic acid by levulinic acid and phenol. Traditional inorganic acids (HCl, H_2SO_4), solid acids with Brønsted acidity (ZSM-5, Al-ZSM-5, USY, Amberlite resin) and heteropoly acids (HPAs) ($H_4SiMo_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$) were studied as catalysts in the above reaction. The heteropoly acids, mainly the $H_4SiW_{12}O_{40}$ and $H_3PW_{12}O_{40}$, and the respective catalysts with HPA supported on various porous materials (i.e. SBA-15, TiO_2, ZrO_2, SiO_2-Al_2O_3, exhibited the highest yields towards the production of p,p’ diphenolic acid. Tungstosilic acid catalysts were more active than phosphotungstic acid catalysts with similar selectivity towards p,p’ diphenolic acid.

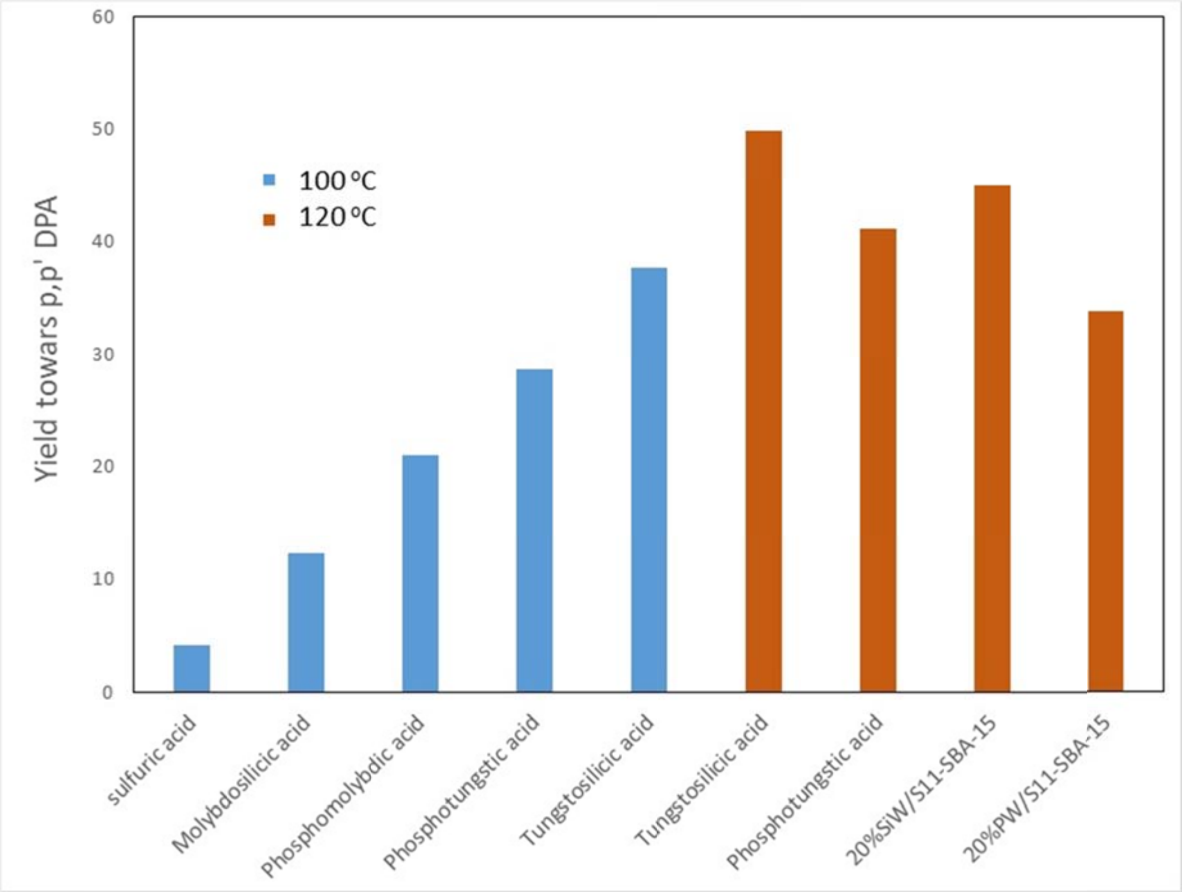

Figure 2. Yield towards p, p’ diphenolic acid (0.15 g HPAs, 0.75 g of supported HPAs, 1.12 g H_2SO_4, 24 h, 10 mmol levulinic acid, 28 mmol phenol)

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A COMPOSITE MATERIALS FOR CATALYTIC REFORMING METHANE TO SYNTHESIS GAS

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Due to the rapid development of technology and production, the demand for traditional energy sources is increasing exponentially. Of course, at present, the main sources of energy are still oil, natural gas and coal. But, the search for new sources of energy is relevant, both for developing Kazakhstan and for the whole world. However, alternative energy sources in the world energy sector are beginning to acquire serious positions each time, based on the use of bioenergy raw materials of different nature [1].

Synthesis gas - by its specificity, it can be quite considered as an alternative source of energy and raw materials. It is a mixture of gases, the main components of which are CO and H_2. Mostly used for the synthesis of various chemical compounds. Synthesis - gas is produced by the conversion of natural gas or oil products and on a small scale by chemical processing of wood, as well as by gasification of coal. Synthesis gas is also obtained along with the target product acetylene during the oxidative pyrolysis of natural gas. The main directions of synthesis gas processing: production of H_2 and methanol; small amounts of it are used in oxo-synthesis and Fischer-Tropsch synthesis.

In modern science, research is of strategic importance in the field of producing synthesis gas under more favorable conditions and also aims at developing various catalysts for the integrated purification of gas emissions from industry [2-4]. The production of various catalysts with different combinations of metals and compounds by means of self-propagating high-temperature synthesis is known from the literature. This article describes the research to obtain new catalysts, which vary the following metal composition: Ni, Al, Pt. Glycine and urea were used as organic additives. Ni-Al-Pt catalysts were prepared by the method of self-propagating high-temperature synthesis. The optimum metal content in the catalyst was determined by varying the ratio of elements in the samples. The conditions for the conversion of methane to synthesis gas are determined. It was found that the highest results on oxidative conversion to synthesis gas can be obtained at 900 °C and a space velocity of 2500 h^{-1} for a catalyst of 25 % Ni + 25 % Al + Pt (0.05 %) – 50 % glycine catalyst. The catalysts were investigated by a complex of physicochemical methods. It was found that when tested in a flow catalytic installation, significant changes occur in the structure of the catalyst. The catalyst has been shown to contain simple and mixed oxides, metal aluminates and a spinel-type structure. The presence of such a variety of structures contributes to the formation of active centers, which favorably affects the oxidative conversion of methane. In addition, elastic carbon nanotubes wrapped in a helix with a diameter of 40–50–70 nm were found in the structure of spent catalysts.

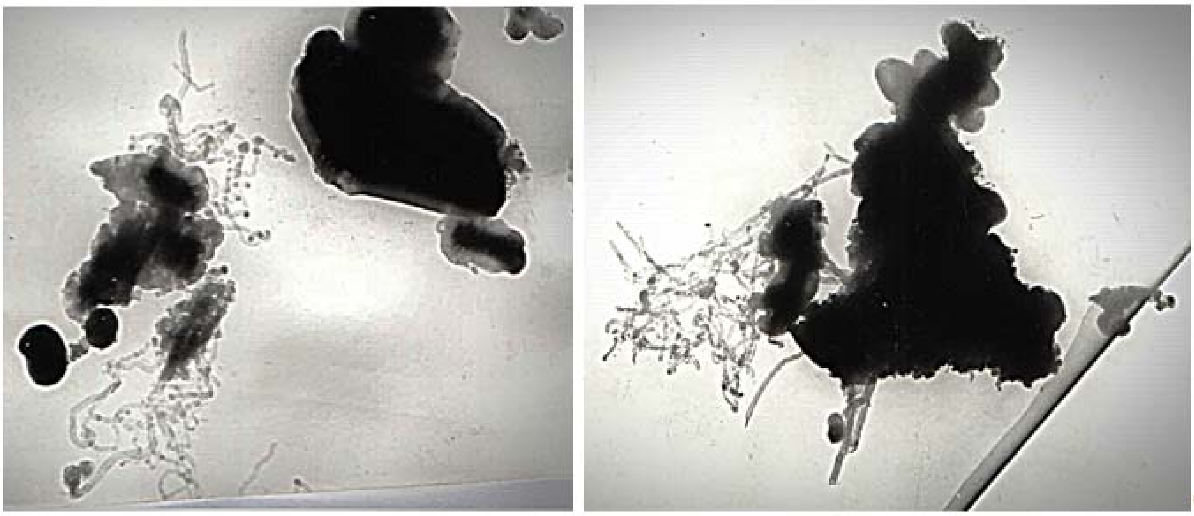

Figure 1. TEM images of the 25 % Ni – 25 % Al - Pt(0.05 %)-50 % glycine catalyst after tests

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PP-4

ZEOLITE-ASSISTED ETHERIFICATION OF GLYCEROL WITH SHORT-CHAIN ALCOHOLS IN A TANDEM REACTOR-MEMBRANE SETUP

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The increase in biodiesel production results in the accumulation of glycerol in large quantities, being the 10 wt % of byproduct of the transesterification reaction for biodiesel production. Although the glycerol has many commercial applications in cosmetic and pharmaceutical industries, the development of new efficient ways of converting it to added values products is necessary to support the eco sustainability of the global process of biomass transportation. On this account, glycerol etherification represents an important approach to directly afford compounds that can be used as fuel additives, intermediates in the pharmaceutical industry, non-ionic surfactants or agrochemicals. Specifically, an appealing strategy is represented by the transformation of glycerol into oxygenated fuel additives to gain benefits both in terms of environmental compliance and efficiency of diesel engines. To date, the catalytic etherification of glycerol has been studied using isobutylene or tert-butyl alcohol [1], but in this study the use of bio-butanol or bio-ethanol was exploited.

$\mathrm{GLY + BUT \leftrightarrows MBGs + H_2O}$ (1a) $\mathrm{GLY + ET \leftrightarrows MEGs + H_2O}$ (1b)
$\mathrm{MBGs + BUT \leftrightarrows DBGs + H_2O}$ (2a) $\mathrm{MEGs + ET \leftrightarrows DEGs + H_2O}$ (2b)
$\mathrm{DBGs + BUT \leftrightarrows TBG + H_2O}$ (3a) $\mathrm{DEG + ET \leftrightarrows TEG + H_2O}$ (3b)

The mono-butyl glyceryl ether (MBGs) and mono-ethyl glyceryl ether (MEGs) could be used as green solvent for catalysis or as precursor for surfactants synthesis and intermediates for the production of chemicals, but they are not suitable in diesel formulation. On the contrary, the *di*- and *tri*- polybutyl substituted ethers (DBGs and TBG) and the *di*- and *tri*- polyethyl substituted ethers (DEGs and TEG) could have a large potential for diesel formulation contributing to decrease the emission of PM, hydrocarbons, CO and unregulated aldehyde if used as additives. Likewise, during the reaction, water is formed as by-product competing with reactants on the active site adsorption and preventing the total glycerol conversion and formation of desired poly-substituted ethers [2]. To overcome thermodynamics limits and thus to enhance the poly-substituted ethers productivity, the reaction has been studied by exploiting a batch reactor assisted by a tubular water-permselective membrane under a temperature range between 70 and 200 °C [3]. By recirculating the gas phase through the permselective membrane (vapor permeation configuration), the water was continuously and selectively removed thus shifting the equilibrium towards products. So, results indicate that both in the presence of butanol or ethanol, it is possible to perform glycerol etherification, with good selectivity to polyethers. Specifically, by employing the permselective membrane at 140 °C, with A-15 as catalyst, glycerol conversion, in presence of butanol, is redoubled, by almost reaching the 100 %, but, at the same time, many new byproducts are formed, likely due to the dehydration of butanol. By using the zeolite-based catalysts, the positive effect of the membrane is less evident because of the lower amount of water formed which could result more difficult to be removed. Anyhow, in this case, with butanol, even if the catalysts are not so active to allow operation at low temperature, an encouraging value of 8.7 % polyethers yield was obtained by modulating reaction conditions and optimizing the surface area of membrane/volume of gas ratio (0.7 cm^{-1}) (see Table 1).

Table 1. Effect of permeoselective membrane: t, 6 h; T = 180 °C; cat = 16-25 mesh, 20 wt %. X_{Gly} = glycerol conversion; Y_{D-T} = DBGs and TBG yield

X_{gly} (%)	S/V[a]	Selectivity (%)								Y_{D-T} (%)
		Sub-1	**1-MBG**	**2-MBG**	**Sub-2**	**1,3-DBG**	**1,2-DBG**	**TBG**	**Ex***	
58.3	-	7.8	60.7	11.6	6.9	2.5	0.8	0.9	8.7	6.5
68.3	1.62	8.9	60.5	11.2	8.0	2.6	0.9	1.1	6.8	8.7
70.0	0.7	9.0	59.5	10.9	8.1	2.3	0.9	1.0	8.8	8.6

[a] S/V = surface area of membrane/volume of gas phase.
Sub-1 or sub-2 = *mono*- or *di*-substituted compounds, with a branched chain.
Ex = extra compounds not easily identified.

As regards the use of ethanol as reactant, the reaction is under study by using hybrid Hyflon-zeolite catalysts in order to exploit their good selectivity towards polyethers products already verified in previously study of glycerol etherification with tert-butyl alcohol [1].

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EFFECT OF CARBON NANOTUBE ADMIXTURE ON ANTHRACENE COKING

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The coking process is one of the most economically feasible ways of processing heavy petroleum residues, which makes it possible to additionally obtain valuable petroleum products at the lowest possible cost, thereby increasing the depth of oil refining. Delayed coking is the most common coking process. The study of the processes occurring during the delayed coking of heavy petroleum residues is of great theoretical and practical importance, since their knowledge makes it possible to control the process aimed at obtaining carbon materials with predetermined properties. In particular, considerable attention is paid to the modification and carbonization of the surface of carbon nanomaterials in order to improve the interaction between reinforcing additives and the matrix. A large pile of hydrocarbons contained in the feedstock behave in different manners depending on the coking temperature. Aromatic and polyaromatic hydrocarbons are the most prone to condensation and coke formation reactions. In this work, the fused-ring aromatic compound anthracene was used as a model feedstock.

In this study we investigated the mechanism of coking of anthracene, a fused-ring aromatic hydrocarbon, and the effect of carbon nanotubes (CNTs) on the morphology and crystal structure of the resulting coke.

The anthracene coking process has been investigated in the temperature range of 400-600 °C. Anthracene coking was carried out in an autoclave at temperatures of 400-600 °C and pressures of 2-4 atm. Anthracene was loaded into an autoclave basket, and the autoclave was placed in an oven to heat the sample to a predetermined temperature. After reaching the set temperature, the sample was held for 2 h. Samples were investigated by high-resolution transmission electron microscopy (HR-TEM) using a JEM-2010 instrument. The phase composition of the samples was investigated using the X-ray diffraction technique.

It has been shown that the intermolecular interaction of two anthracene molecules resulting in the elimination of hydrogen and the formation of a C–C bond between the middle rings begins at a temperature of 450 °C. Increasing the coking temperature to 500-600 °C leads to the formation of poorly crystallized graphite. In the case of pure anthracene, the formation of micron-sized spherical carbon particles occurs. The addition of carbon nanotubes to anthracene leads to the formation of the carbon “fur coat” covering their surface. The thickness of the carbon “coat” depends on the temperature of coking. The amorphous carbon layer observed on the surface of carbon nanotubes has a thickness of 1-2 nm in the case of coking temperature of 450 °C or 10-15 nm in the case of coking at 600 °C.

Acknowledgements

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MAGNETIC NANOADSORBENT BASED ON CARBONACEOUS Fe_3O_4 NANOCOMPOSITE FOR PHARMACEUTICAL WASTEWATER TREATMENT

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In this study, activated carbon-Fe_3O_4 magnetic (AC-Fe_3O_4) nanocomposite was used as an adsorbent for the removal of promazine drug from water. The characteristics of the magnetic adsorbent were evaluated by Raman, BET, XRD, TEM and XPS. The nanocomposite exhibited high adsorptive capacity, easy magnetic separation and reusability. The results showed that the adsorption equilibrium was rapidly attained after 6 min with almost complete elimination (99.9 %) of promazine. Adsorption isotherm and kinetics were performed and in a batch system and the obtained the results corresponded to Langmuir isotherm and pseudo second-order-kinetic models, respectively.

PP-7

VALORIZATION OF LIGNIN BY DEVELOPMENT OF SELECTIVE ENZYMATIC DEGRADATION, CHEMICAL CATALYSIS AND SEPARATION OF INNOVATIVE CHEMICAL BIO-AROMATICS

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Lignin, a main constituent of lignocellulosic biomass, is the only large-volume renewable feedstock that is composed of aromatics [1]. Traditionally, most large-scale industrial processes that use plant polysaccharides have burned lignin to generate the power needed to productively transform biomass. Currently, most integrated biologically based biorefinery concepts comprise four major core sections: feedstock harvest and storage, pretreatment, enzymatic hydrolysis, and sugar fermentation to biofuels [2-4]. Catalysis is regarded as a key enabling technology for biomass conversion in general and for fulfilling the promise of lignin valorization in particular. The chemical study on this topic is scattered, however, and focuses primarily on engineering and biology aspects of lignin rather than specifically on catalytic conversion or catalyst development, which is essential for efficient and selective lignin valorization processes [5-6]. Due to its highly irregular polymeric structure, lignin is quite resistant to enzymatic hydrolysis and therefore the novel approach of combining enzymatic and chemical depolymerization might be very promising. This report is an interdisciplinary approach using enzyme-catalyzed reactions (e.g. “enzyme cocktail”: fungal esterases in combination with oxidative enzymes) and chemical catalysis reactions (e.g. liquefaction and hydrogenolysis using heterogeneous catalysts under quite mild conditions regarding temperature and pressure) that will lead to new monomers, oligomers and small polymer mixtures (cross-linkers, antioxidants, fillers, monomer building blocks etc.) that can be applied in several applications (wood panels, textile, inks, coatings, emulsifiers, adhesives, resins, polymers etc.).

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PP-8

CARBON-BASED METAL-FREE CATALYST FOR SELECTIVE OXIDATION OF H_2S IN THE PRESENCE OF AROMATICS

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The acid gas containing trace amount of H_2S from the crude natural gas or from biogas is nowadays treated by selective oxidation process [1,2]. The presence of benzene, toluene, and xylene (BTX) in the acid gas effluent, even in very small concentrations, can alter the chemical kinetics of H_2S oxidation significantly and often causes rapid catalyst deactivation due to hydrocarbon deposition, especially for the metal-based catalysts. In order to reduce such deactivation problem the BTX compounds were removed through enrichment/combustion process before the H_2S processing. It is of interest to develop new catalyst with high resistance towards BTX deactivation process in order to reduce the overall cost of the process.

Our previous work has shown that the “metal-free” consisting of nitrogen-doped mesoporous carbon coated on silicon carbide (NMC@SiC) catalyst displayed a high desulfurization performance under reaction conditions similar to those operated in industrial plants [3,4,5]. In this contribution, the NMC@SiC catalyst was evaluated for desulfurization process with the present of a relatively large amount of toluene in the feed gas. The catalytic results indicate that the NMC@SiC catalyst exhibits an extremely high desulfurization performance compared to the Fe_2O_3(3 %)@SiO_2 catalyst in the presence of toluene (0.5 vol. %) in the feed gas, keeping the same sulfur selectivity (**Fig.1**). The NMC@SiC catalyst also displays an extremely high stability as a function of time on stream which indicates the low influence of toluene on H_2S conversion. On the contrary, Fe_2O_3(3 %)@SiO_2 catalyst displays a fast deactivation which could be attributed to the coke deposition derived from toluene. Indeed, coke formation from acid sites induced aromatic condensation process is a well known process which progressively blocks the active sites. The high activity and stability of the NMC@SiC catalyst could be attributed to the high nitrogen content in the NMC phase and it basic character which allow one to perform desulfurization process on one hand, and to prevent acid induced condensation of the aromatic to generate pseudo-carbon on the catalyst surface. It is expected that such metal-free and basic catalyst could be efficiently used for performing direct selective oxidation of H_2S containing in the biogas effluent before it subsequence processing.

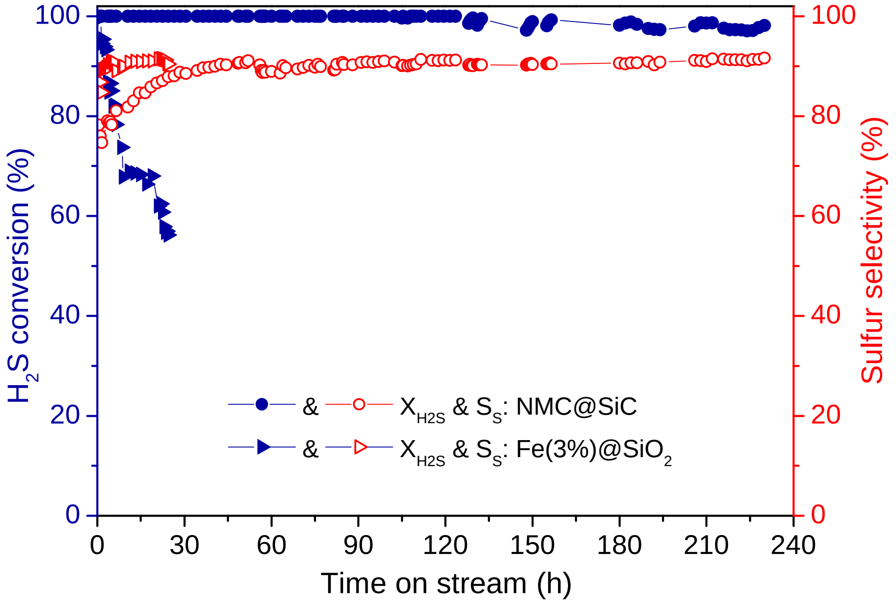

Figure 1. Desulfurization performance on the NMC@SiC and Fe_2O_3(3 %)@SiO_2 catalysts. Reaction conditions: reaction temperature = 210 °C, GHSV = 2400 h^{-1}, [H_2S] = 1 vol. %, [O_2] = 2.5 vol. %, [H_2O] = 30 vol. %., [Toluene] = 0.5 vol. %

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PP-9

THE DEVELOPMENT OF NANOSCALE, MAGNETICALLY CONTROLLED CATALYSTS FOR THE OXIDATION OF METHANOL TO FORMALDEHYDE ON THE BASIS OF THE ENERGY ASH OF THE TPP

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Based upon the energetic ashes of the cenospheres a process of preparation of ferro-molybdene catalyst for methanol to formaldehyde oxidation was developed. As opposed to oxide Fe-Mo catalyst used in the world practice, developed under the program a nano-scale Fe-Mo magnetically controlled catalyst dispersed in the aluminosilicate matrix is effective and stable in the temperature interval >400 °C.

In this study, the conditions for the preparation of modified nanoscale methanol oxidation catalysts have been optimized. As a matrix for catalysts, a stable composition, selected after a three-stage separation was used, containing mass. %: SiO_2 – 48,0; Al_2O_3 – 35,0; Fe_2O_3 – 5,8; Phase composition is represented by quartz and mullite.

The catalyst is not sintered at a temperature of > 500 °C, has a compressive strength of 150-280 kg/cm^2. Mössbauer studies of cenospheres showed that the iron catalyst included in the composition of magnetite. Evacuation of the aqueous suspensions of the products of three-stage fractionation of the cenospheres made it possible to isolate perforated cenospheres from each of them with a different output.

The obtained results showed that large fractions of non-magnetic cenospheres -0.4 + 0.2 and -0.2 + 0.16 mm are characterized by the highest content of perforated cenospheres in products with a bulk weight of 0,32 g/cm^3, while in fine fractions -0.16 + 0.1 and -0.1 + 0.063 mm of perforated cenospheres are most common in heavy products with a bulk weight of 0.49 g/cm^3. As for the magnetic cenospheres, the maximum content of perforated products, exceeding 2-3 times their content in non-magnetic fractions, differs all fractions with a bulk density of 0.52 g/cm^3, while in the fraction -0.16 + 0.1 mm perforated cenospheres of the specified density reaches 50 % wt. Additional processing of such globules with a hydrofluoric acid-based reagent removes the glass-crystalline nanoscale (30-50 nm) shell from the cenosphere surface, as a result of which the porous structure formed by gas occlusions becomes open for the injection of the highly specific active component into the internal volume of the globules.

Impregnation of perforated products of narrow fractions of microspheres with ammonium molybdenum leads to the formation of an iron-molybdenum catalyst.

The obtained catalysts were studied by IR spectroscopy using the infrared spectrometer Vertex-70v (Bruker). In the IR spectra of the aluminosilicate catalyst, intense absorption bands characteristic of the Si–O, Al–O, Si–O–Al groups are observed. The absorption bands in the low-frequency region of the spectrum indicate the presence of Fe^{3+} and Mo^{6+} in oxides. The specific surface area of catalysts, calculated from the total isotherms of low-temperature nitrogen adsorption by the BET method, measured on the BelSorp device (BelJapan Inc.) is 14.7-15.8 m^2/g - for an aluminosilicate catalyst. The integral pore volume of the catalyst calcined at 400 °C is 0.57 ml/g. The optimal size of the active particles of the developed catalysts is 40-50 nm.

ONE-POT PROCESSES OF NAPHTHOQUINONES SYNTHESES IN THE PRESENCE OF HETEROPOLY ACID SOLUTIONS AS BIFUNCTIONAL CATALYSTS

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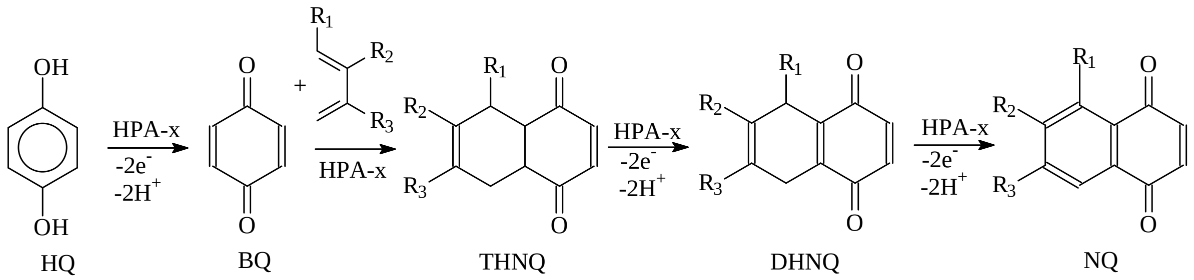
At present, 1,4-naphthoquinone (NQ) and its derivatives are successfully used to produce 9,10-anthraquinone, as polymerization regulators, stabilizers of transformer oils and in dyes manufacture [1]. In addition, many NQ derivatives have a variety of biological activity [2]. A growing demand for NQ and its derivatives cannot be provided with existing technologies of their manufacture. Catalytic oxidation of naphthalene by air results NQ yield only 36 % and 64 % phthalic anhydride.

Another oxidizers (for example, chromic anhydride) are either toxic or produce a lot of wastes. Thus there is a problem of creating a new environmentally friendly process of NQ derivatives production.

For this purpose heteropoly acids (HPA) can be used. Now processes using aqueous solutions of Mo-V-P heteropoly acids $H_{3+x}PV^{V}_{x}Mo_{12-x}O_{40}$ are widespread [3]. Unlike many other oxidizing agents, the vanadium-containing HPA solutions are able to be regenerated by O_2. Thus they can catalyze the oxidation of various substrates by O_2. In the presence of HPA solutions these processes consist of two stages carried out in separate reactors **1** and **2**. In the 1st stage a substrate is oxidized by HPA. In the 2nd stage HPA is regenerated by O_2. Thus vanadium-containing HPA solutions may be considered are *reversible oxidants*. Furthermore, aqueous HPA solutions are strong Brønsted acids and can be used as acid catalysts. Therefore, HPA solutions can be *bifunctional* (i.e. oxidative and acidic) catalysts.

We have developed new processes of NQ derivatives production from hydroquinone (HQ) in the presence of HPA solutions [3]. At that, we have combined *in a single technological stage* three types of reactions occurring at room temperature and atmospheric pressure: 1) oxidation of HQ by HPA to benzoquinone (BQ); 2) the acidic-catalyzed Diels-Alder reaction of 1,3-dienes with BQ giving substituted 1a,4a-tetrahydro-1,4-naphthoquinone (THNQ); 3) the sequential oxidation of THNQ by HPA with the formation of substituted 5,8-dihydro-NQ (DHNQ) and then substituted NQ. Thus, our *one-pot* processes are described by scheme 1.



Scheme 1. Preparation of substituted NQ in the presence of HPA solutions

Such *one-pot* processes were studied. Results are presented in the Table.

№	Substituents	Yield of substituted NQ, %	Content main product in precipitate, %
1	R_1= H; R_2=CH_3; R_3 = H	63	98
2	R_2 = R_3 = H, R_1= CH_3	62	97
3	R_2 = R_3 = CH_3, R_1 = H	72	90
4	R_1 = R_2 = R_3 = H	41	45*
Conditions: 2×10^{-3} mol HQ, 10 mL 0,25 M $H_7PMo_8V_4O_{40}$ (HPA-4) water solution, volume ratio HPA-4: 1,4-dioxane 1:1, reaction time 30 h, temperature 20 °C. HQ conversion ≥ 99 %.			

*Main product is 1,4,4a,9a-tetrahydro-9,10-anthraquinone.

The similar reaction between HQ and 1,3-cyclohexadiene (molar ratio 1:1) in the presence of HPA-4 was studied. Main product was Diels-Alder adduct – 1a,4a-dihydro-5,8-endoethylene-NQ (yield 84 %).

HPA-**4** solutions [4] are stable at elevated temperatures (160-170 °C) and can be fast regenerated by air O_2. This feature of the HPA-**4** solutions has ensured high productivity of the processes depicted in the Scheme 1.

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DEVELOPMENT OF CATALYSTS ON THE BASIS OF WASTE HEAT GENERATION FOR ENERGY EFFICIENCY AND ECOLOGY

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In the work, a microspherical aluminosilicate catalyst obtained from the cenospheres of Almaty CHP-2 operating on high-ash Ekibastuz coal was used to obtain olefins by means of temperature treatment of liquid or gaseous hydrocarbon raw materials. Stabilization of the composition and structure of the cenospheres was carried out in a column pulsation apparatus with a pneumatic pulsator and swirling partitions. The speed of the upward water flow, amplitude and pulsations frequency were kept in range to define the fraction composition. In the lower part of column circular electromagnet is located, providing required range of magnetic field strength in the upstream flow section. Selected and stabilized by composition Fe_3O_4 microspherical aluminosilicates for preparation of mixed catalytic composites Fe_3O_4-MnO, Fe_3O_4-Cr_2O_3, Fe_3O_4-MoO_3 to the process of dehydrogenation of alkanes were prepared by impregnation of microspherical aluminosilicate with appropriate salts Mn^{2+}, Cr^{3+}, Mo^{6+}, dried at a temperature of 110 °C and calcined at a temperature of 1200 °C.

The morphology of the narrow fractions shell of the initial and acid-etched cenospheres was studied in details by scanning electron microscopy. It is shown, that with increase of aluminum oxide content in initial cenospheres the shell thickness and porosity decrease. At the same time on the outer and inner surfaces there is a thin film hiding the structure of the inner part of the shell with a large number of gas inclusions. Nanoscale inclusions soluble in mineral acids (silicate phases of iron, magnetite, etc.) are precursors of nanoscale pores in the structure of the cenosphere shell as a result of their etching by the corresponding acids. The texture characteristics measurement of the products of cenospheres etched with hydrochloric acid showed that this method of processing leads to the formation of a pore structure characterized by a specific surface area of 30-50 m^2/g and the distribution of pores by size with a maximum at 3,5 nm for all samples. The volume distribution of the pore sizes for samples with an iron content 7 wt. % Fe (S^{Ar} = 28 m^2/g) and 2,6 wt. % Fe (S^{Ar} = 50 m^2/g) is shown. It should be noted that for compositions with a high iron content (10,0 wt. % Fe_2O_3) this distribution covers pores up to 50 nm in size and has additional peaks at 4,5 and 7 nm. At low iron content (3,7 wt. % Fe_2O_3) the contribution of pores in the range of 4,5-10 nm is significantly reduced, and the distribution becomes close to monomodal with D_{max} = 3,5 nm. The study of the cenospheres surface etched with hydrochloric acid by scanning electron microscopy indicates the formation of open pores of 50-100 nm on the outer surface of the cenospheres.

When exposed to electromagnetic fields of ultra-high frequency (EMF microwave) on the feedstock and catalyst, most of the energy, due to the presence of dielectric losses, is absorbed and redistributed, transforming into heat, increasing the temperature of the feedstock and catalyst. Part of energy not absorbed by the feedstock and the catalyst is absorbed by the magnetic microspheres inside it. It is known that when the temperature of the initial feedstock and the catalyst is increased the effect of "self-clarification" is observed – a decrease in dielectric losses, which improves the electromagnetic waves energy permeability conditions in the feedstock and catalyst. Hence most of the energy is able to penetrate without loss into the depths of the feedstock and the catalyst, influencing directly on the magnetic microspheres in it. The effect on the magnetic microspheres in the carrier is carried out until the moment of particles activation due to a change in the power or exposure time, or by a combination of these factors. Thus, by changing the composition, the amount of added magnetic microspheres, the exposure zone and object (feedstock, catalyst, etc.) of exposure to EMF, the output of the target products changes.

According to chromatographic analysis, in the mixture of products of hexadecane processing reaction in the presence of a catalyst and EMF microwave (minus unreacted hexadecane) the content of alpha-olefins CnH2n ($1 < n < 15$) is about 90 %.

PP-12

STEAM REFORMING OF BIOGAS OVER Fe-Co BASED ALUMINA SUPPORTED CATALYSTS

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There are several technologies to produce syngas via methane reforming. Among them Dry Reforming of methane (DRM) (Eq.1) is an attractive way to utilize the main greenhouse gases (Eq. 1). More importantly, the biogas mainly composed of carbon dioxide and methane is a cheap renewable source for DRM. Besides hydrogen enriched syngas can be produced from biogas by reforming with added steam, which makes the reaction more desirable for commercialization.

$$CH_4 + CO_2 + H_2O \leftrightarrow xH_2 + yCO \qquad \text{(Eq. 1)}$$

Despite its considerable environmental potentials, both dry and steam reforming of biogas not considered an industrially mature process. The principal reason for this is the carbon-forming reaction, which quickly deactivates conventional reforming catalysts. Ni-based catalysts are commonly used ones and widely investigated. Fe- and Co-containing catalysts are less studied.

In the present work, the of Fe-Co based alumina supported catalysts were synthesized and their performance in steam reforming of a model biogas was studied. The effect of metal amounts on the catalyst behavior has been investigated.

The polymetallic Fe-Co-containing catalysts were prepared by impregnating alumina with an aqueous solution of Fe, Co, and Pt compounds followed by thermal treatment. Total content of Fe and Co was varied within 5-10 wt. %. The mass ratio of Fe:Co was kept as 1:1. The trimetallic catalysts were synthesized by adding of 0.25 wt. % of Pt to the Fe-Co/Al_2O_3.

The physicochemical properties of the catalysts were studied using TEM, SEM, BET, TPR-H_2, Mossbauer spectroscopy, and XRD.

Steam reforming of a model biogas was carried out in a laboratory flow quarts reactor supplied with programmed heating, controlled feeding velocity, and syringe pump. Process was operated under the atmospheric pressure and varying the gas hourly space velocity (GHSV) and temperature within 1000-1500 h^{-1} and 400-800 °C respectively. A model biogas with adjusted feed ratio of CH_4/CO_2 to 1:1 was used. The 0.1-1 vol. part of steam was added to a feed for providing steam reforming of biogas. The catalyst volume was 6 ml, process duration – 6-50 hours. The initial and final reaction products were on-line analyzed using the GC's.

The 10 % Fe-Co(1:1)-0.25 % Pt/Al_2O_3 catalyst performed the higher activity. At 700 °C, GHSV = 1200 h^{-1}, $CH_4/CO_2/H_2O$ = 1/1/0.2 methane conversion was 92.9, while extent of carbon dioxide was less and reached 80.5 %. Syngas formed was enriched with hydrogen, a ratio of H_2/CO = 1.3. The catalyst kept almost the same activity for 20 hours. During the next 30 hours the methane conversion was slowly decreased from 92.0 to 82 %.

By Messbauer spectroscopy, the formation of the bimetallic Fe-Co, Fe-Pt, and possibly trimetallic Fe-Co-Pt clusters were shown. The bi- and trimetallic Fe-Co catalysts are much higher active than the monometallic Co- and Fe-supported catalysts.

The results obtained demostrate that the multicomponent catalysts based on Fe and Co with additive of noble metal and supported on alumina perform the high activity in steam reforming of methane.

Acknowledgments

The authors wish to thank the Ministry of Education and Science of the Republic of Kazakhstan for sponsoring this research (Programme # PCF_BR05236739).

PP-13

TECHNO-ECONOMIC AND ENVIRONMENTAL IMPACT ANALYSIS OF THE INTEGRATED BIOETHANOL-BIODIESEL PROCESS AND BIOMASS THERMOCHEMICAL CONVERSION

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Ethanol and biodiesel agroindustries are the main sources of renewable fuel in Brazil. They produce high amounts of residual biomass that can be recycled to generate products with higher added value. The aim of this work was to evaluate the techno-economic and environmental feasibility of the integrated process of ethanol, biodiesel and thermochemical transformation of biomass. In addition, technical scenary of this integrated process (Fig. 1) was designed considering all residues, i.e., vinasse, crude glycerin and the pyrolytic aqueous phase containing C1-C4 chemicals, as raw materials for biomethane production by anaerobic digestion. Although the results of the research are preliminary, they are quite attractive since the economic results showed an Internal Rate of Return of 16.84%, payback discounted of 7.35 years and Net Present Value of $53.83 millions (Table 1).

Table 1. Results of the economic criteria of Scenarios I and II

Economic Indicator	Scenario I	Scenario II
Total Capital Investment ($)	14.416.669,22	57.846.758,95
Annual Costs with Raw Materials ($)	114.162.920,87	114.162.920,87
Annual Production Costs ($)	135.417.566,82	142.562.993,03
Recipe ($/year)	141.233.953,53	157.857.869,72
Gross Profit ($/year)	5.816.386,71	15.294.876,70
Taxes (35% on Gross Profit)	2035735,35	5.353.206,84
Net Profit ($/year)	3.780.651,36	9.941.669,85
Simple Payback (years)	3.73	5.69
Discounted Payback (years)	4.24	7.35
Net Present Value ($)	27.748.672,99	53.826.185,88
Minimum attractiveness rate (adopted)	6.52	6.52
Internal Rate of Return (%)	26.60	16.84

The attained results were compared with a real industrial process for bioetanol production. The main variables that affecting the profitability were: the prices of sugarcane, anhydrous ethanol, biodiesel and degummed soybean oil, with the potential to make the Net Present Value negative, when a variation of -30 to 30 % of its values (Fig. 1). Both scenarios presented potential mitigation of environmental impacts (Fig. 2), since that reduce the Potential Environmental Impact (PEI) of the generation of the chemicals by their chemical transformation in these processes according to the results attained from Chemical Process Simulation for Waste Reduction (WAR Algorithm) developed by United States Environmental Protection Agency (EPA).

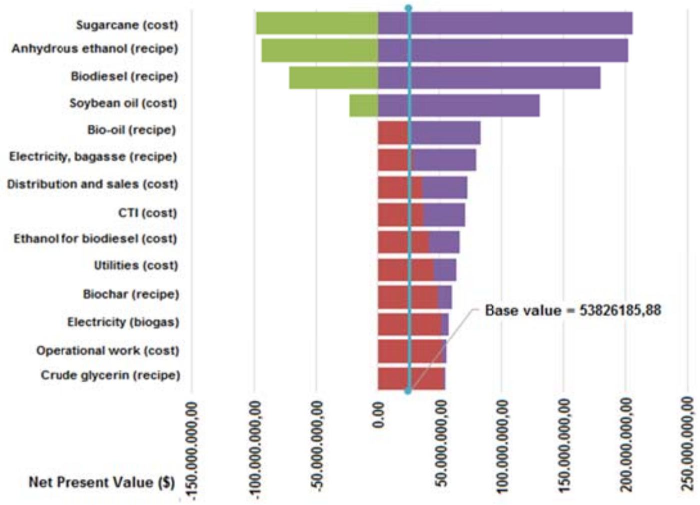
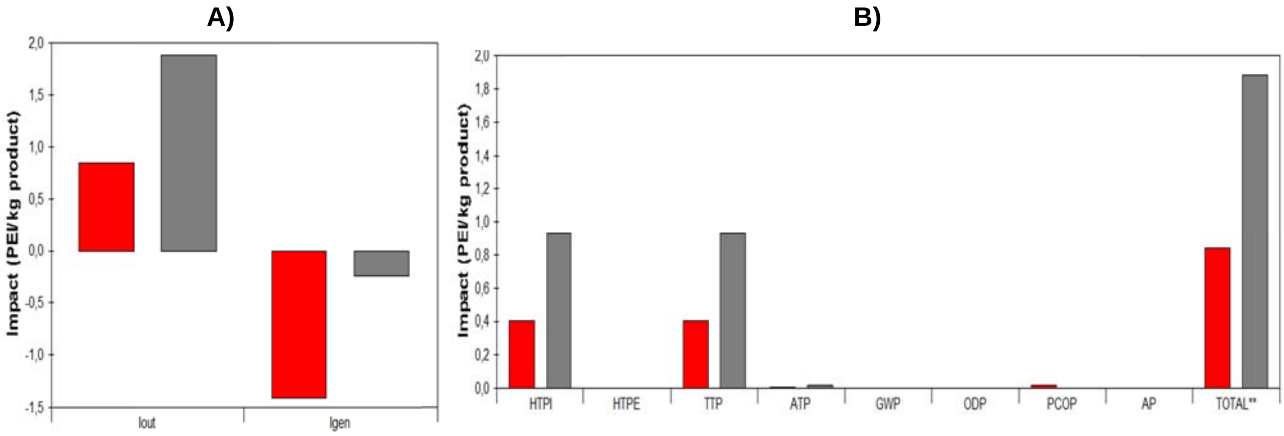


Figure 1. Sensitivity analysis as a function of NPV.
Symbols:
🟩 Negative NPV;
🟪 Positive NPV;
🟥 Interval between zero NPV and lowest NPV


A)

B)

Figure 2. Potential Environmental Impact (PEI) for integrated process under study (A – PEI/mass and B – PEI/categories). Symbols: 🟥 Real process and ◼ integrated process

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PP-14

POSSIBILITY OF USING BIODIESEL FUEL IN REGIONS WITH A COLD CLIMATE

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Biofuel production is a relatively new industrial field, which has bright future. Production process is not new, however, due to the number of circumstances it has not gone any further.

Any vegetable oil, hard animal oil, waste of fat-and-oil production and slaughterhouse waste can be used for production of biodiesel fuel. Any vegetable oil is a mix of triglycerides that are esters bonded with molecules of glycerin [1]. Glycerin adds viscosity and density to the oil. The aim of the biodiesel production is to extract glycerin and replace it by alcohols. To achieve this aim the transesterification reaction was carried out, where vegetable oil reacted with a monobasic alcohol. The exchange between alcohols and esters is called alcoholysis. The reaction can be catalyzed. Otherwise, it is very slow even when it is heated up to 250 °C. The reaction gets slower with the increase in molecular weight of the alcohol. For example, conversion level of the sunflower oil using ethyl alcohol is 35.3 %, and its conversion level using amyl alcohol is 11.5 %. However, the position of the equilibrium can be changedby variations in relationship between triglycerides and alcohol or by removing one of the resulting products, for example, glycerin, from the reaction site [2,3].

Esters were obtained from Camelina oil and n-butanol (Sample 1) [4], and from Camelina oil and isopropanol (Sample 2). Transesterification reaction was catalyzed by sulfuric acid.

Sample 1 does not comply with GOST 305-82, which is why the further research to improve its cold flow properties was started.

Addition of pour point depressants is the most effective and economically efficient way to improve its cold flow properties. Usually, pour point depressants are added in small dosages, most commonly 0.05-0.10 % mas. This leads to the significant temperature depression and improvement of the oil fluidity under low temperatures [5,6]. Composition of biodiesel fuels is different from petro-diesel fuels; therefore pour point depressants might have a limited impact on the fuel or might not have an impact at all.

The cold flow properties of the obtained samples of the biodiesel fuels were researched. Received values correspond with the idea that pour point depressants do not have an impact on cold flow properties of the biodiesel fuels. Therefore, it can be concluded that it is not practical to add depressants to the biodiesel fuel.

The further research of the depressants was carried out using a biofuel mix, a composition of which is: 5 % of a clean fuel and 95 % of a hydrotreated diesel fuel.

Presence of the bio-fuel in the mixed fuel has an impact on its pour point, however it is not significant. Pour point values, which comply with the GOST 305-82, are achieved using the same amount of depressants as for the hydrotreated diesel fuel.

Therefore, presence of the biodiesel fuel,at the rate of 5 %, in the mixed fuel, which contains hydrotreated diesel fuel, does not have a significant impact on the pour point of the mix, and it is possible to add pour point depressants in optimal concentration of 0.02-0.22 % to the mix of clean diesel fuel and improve its cold flow properties up to the requirements.

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PP-15

TG/DSC ANALYSIS OF THE KINETICS OF CATALYTIC PYROLYSIS OF ALGAL BIOMASS USING HYDROTALCITE

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Introduction

Energy consumption is increasing very rapidly and it is not expected that the overall scenario will change significantly in the near future. Even in the more promising scenario from the International Energy Agency, fossil fuels will be needed in large amounts [1], in particular oil, which is the basis of most of our transportation system.

The major problems that are currently associated with the extensive use of fossil fuels is the emission of CO_2.

A possible way to reduce the CO_2 emissions is to replace fossil fuels by other compatible fuels, in particular biofuels that can be produced from biomass by a variety of processes [2]. Among these, thermochemical processes like pyrolysis, which mimic the way nature produced oil and gas are amongst the most interesting.

Pyrolysis is an energy demanding process and the use of catalysts, although very challenging, is also very promising [3]. Different catalysts have been tried, including zeolites [4], but catalyst deactivation is a very important problem for these catalysts. Hydrotalcites are also very promising catalysts that, due to their properties, in particular their basicity, make them useful for a variety of applications [5].

Experimental

In this work a set of different hydrotalcite catalysts, with different composition, was synthesised by a co-precipitation method. The catalysts prepared had different metal combinations, including Mg/Al/Fe, Ni/Zn, Mg/Al and Zn/Al.

Their activity was tested on a commercial dried *Arthrospira platensis* algal biomass material, which was mixed with the different catalytic materials.

Pyrolysis kinetic experiments were carried-out in a simultaneous TG/DSC apparatus where the temperature was increased at a constant heating rate of 10 °C/min from 40 °C to 800 °C; at 800 °C an isothermal section of 10 minutes was maintained. All pyrolysis experiments were performed under a nitrogen atmosphere. Biomass/Catalyst ratio was between 8.1 and 10.

Results

Figure 1 shows the main results that were obtained during the pyrolysis experiments of the biomass. This figure shows the fraction of mass lost as a function of temperature.

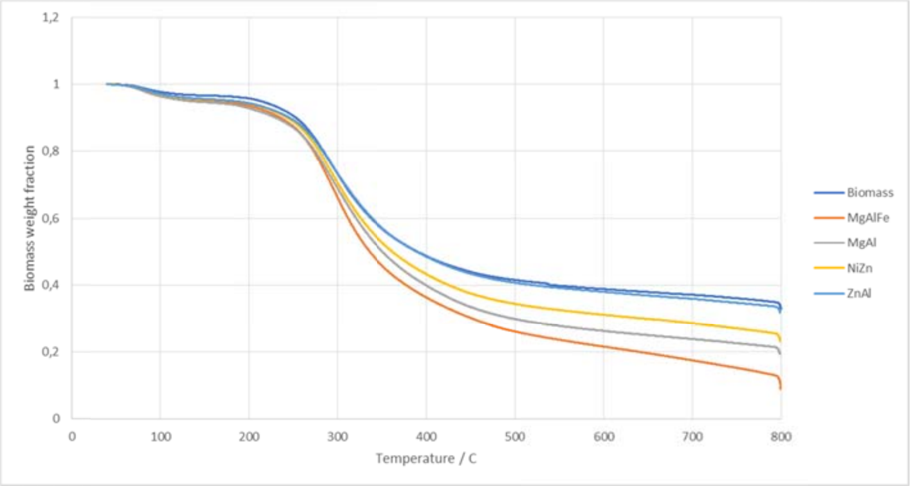

Figure 1. Biomass weight fraction retained as a function of temperature for the pyrolysis experiments using the different catalysts (see text for details)

Conclusions

From figure 1 we can see that some of the catalyst have a significant effect on the mass loss due to pyrolysis. Although the Zn/Al catalyst does not introduce a significant change in the degradation profile when compared to the non-catalysed pyrolysis, all other catalysts significantly increase not only the rate but also the amount of biomass that is pyrolysed. While in the non-catalysed pyrolysis only about 65 % of the mass was lost, for the tri-metallic catalyst around 90 % of the mass is volatilized.

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PP-16

A NOVEL NATURAL SUNLIGHT ACTIVE PHOTOCATALYST OF ZnS BASED HETEROSTRUCTURE FOR WASTEWATER TREATMENT

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Metal doped ZnS modified with carbon nanotubes (SWCNT) as electron mediator was successfully prepared. The as-prepared heterostructure was characterized via UV-Vis, Fluorescence, XRD, XPS and TEM. The morphology of the heterostructure showed uniform spherical nanoparticles with a particle size mean of 5.8 nm for doped ZnS on the SWCNT. The photodegradation of wastewater under natural solar radiation showed an enhanced photocatalytic activity of doped ZnS and SWCNT/doped ZnS are three-fold much greater than that of bare ZnS NPs. Total organic carbon (TOC) was used to further estimate the mineralization capability of the SWCNT/doped ZnS heterostructure (95 % TOC Removal).

COMPOSITE MEMBRANES OF BIOPOLYMER AND ACTIVATED CARBON AS EFFICIENT GREEN CATALYSTS FOR THE TRANSFORMATION OF FURFURAL

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The need for efficient use of resources will necessarily comprise biomass valorization. As a consequence, biomass obtained chemicals became more relevant in the chemical industry. Furfural is one of the platform molecules that can be easily obtain from biomass and from biomass waste and its transformation has gain more relevance in recent years. Thus, the development of suitable and sustainable catalysts is the focus of the present work.

Additionally, totally “green” biomaterials are of extra interest and biopolymers have been considered as one of the most promising materials for this purpose. Biopolymers exhibit characteristics which make them very attractive both for researchers and industries: they are economical, easily available, biodegradable, non-toxic and, with few exceptions, biocompatible. These are promising sustainable materials for heterogeneous catalysis due to the facile degradation of the materials (organic matter) at the end of the life cycle of the catalyst. In addition, biopolymers present a high binding ability to the used catalytic metals due to diverse functional groups, such as hydroxyl, carboxyl and amine groups, insolubility on the majority of organic solvents and may offer the advantage of possible conformational effects related with the polymer structures. Moreover, the biopolymers can be used as catalysts themselves, with functional groups establishing the role of acid or basic catalyst sites [1-4].

In this work we present the synthesis of heterogeneous catalysts based in composite materials of biopolymer κ-carrageenan and activated carbon with acid functional groups aiming the production of “green” catalytic membranes to be used on the acetalization of furfural. Materials with different loadings of activated carbon and with different degrees of reticulation were prepared and tested. The acetalization of furfural was performed in an excess of anhydrous ethanol at 60 °C and the results are presented in figures 1 to 3. The activated carbon (FC) presents conversion values of about 60 %, with only one product detected by GC. When dispersed in the polymer matrix it reaches the same performance only after 3 reutilizations, reflecting the change in the polymer network to accommodate the reagent molecules.

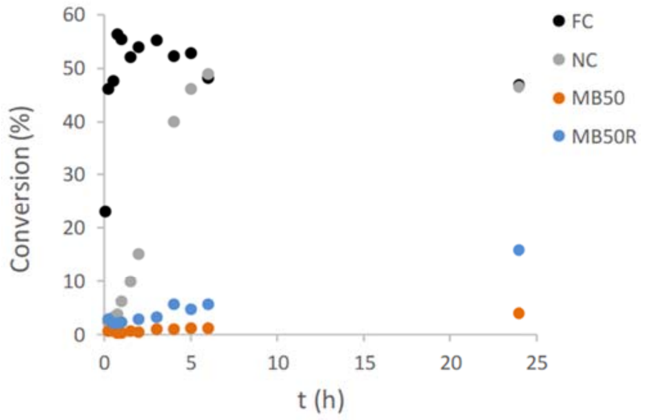

Figure 1. Reaction of acetalization of furfural with ethanol: Conversion (%) in the presence of free catalyst (FC), with no catalyst added (NC), catalyst supported on κ-carrageenan membrane with composition 50 % m/m (MB50) and, catalyst supported on κ-carrageenan reticulated membrane with composition 50 % m/m (MB50R)

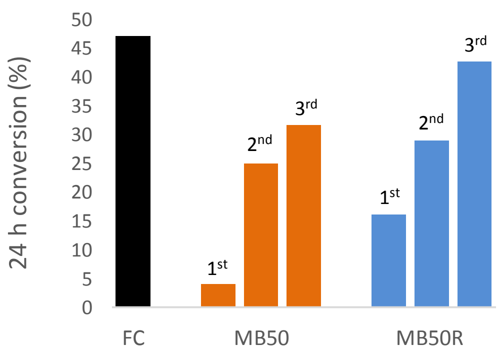

Figure 2. Stability studies of the MB50 and MB50R catalysts on acetalization of furfural with ethanol. Catalytic conversion calculated for 24 hours of reaction in three consecutive experiments. Results are compared with conversion for free catalyst (FC) on 1st use

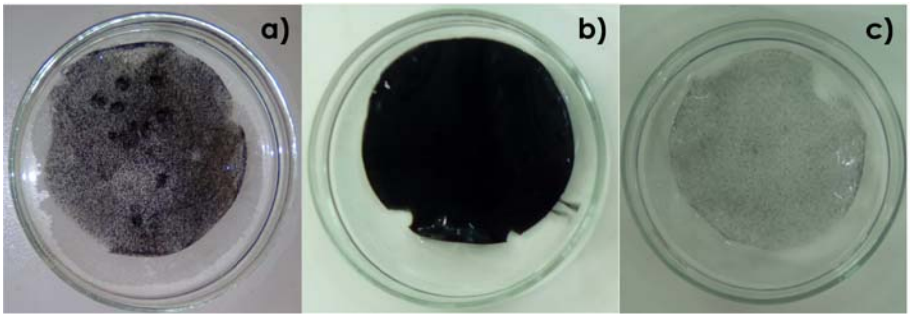

Figure 3. (a) Catalyst supported on κ-carrageenan reticulated membrane with 50 % m/m composition (MB50R), (b) catalyst supported on κ-carrageenan reticulated membrane with 50 % m/m composition and lower dimension of particle size (MB50Rr) and, (c) catalyst supported on κ-carrageenan reticulated membrane with composition 15 % m/m and lower dimension of particle size (MB15R)

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ALKYLATION AND OLIGOMERIZATION C_4-HYDROCARBONS AND FEATURES OF FORMATION OF THE STRUCTURE $MoO_3(WO_3)/ZrO_2$ CATALYSTS

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Tightening the requirements for the environmental safety of motor fuels requires the improvement of existing processes for producing high-octane components for example i-C_4H_{10}-alkylation or $C_4^=$-oligomerization. The catalysts which used for these processes (liquid H_2SO_4 and PO_4-containing solid catalysts respectively) have many drawbacks of both operational and environmental nature. It has been reported that MoO_3/ZrO_2 catalysts displayed catalytic activity in dimerization of alkenes, such as ethylene [1]. $MoO_3(WO_3)/ZrO_2$ systems how catalysts for butene coupling reaction are promising. For a deeper understanding of their properties, it was necessary to study their catalytic and physicochemical properties in a single study.

In this work $MoO_3(WO_3)/ZrO_2$ systems are investigated which were from $ZrO_2 \cdot nH_2O$ powder and different Mo(W)-precursors: ammonia heptamolybdate, $SiMo_{12}$- and PMo_{12}-heteropolyacids. Also influence of method preparation, composition and thermal treatment are investigated. Details of part of the syntheses are given in [2]. Investigation of activity of the resulting catalysts in the process of isobutane alkylation with n-butenes performed on flow unit under the following conditions: t = 80 °C; p = 17 atm. Additionally, the samples were characterized by different physico-chemical methods (DTA-TGA, XRD, N_2 physisorption, FTIR adsorbed pyridine).

It was revealed the genesis of MoO_3/ZrO_2 and WO_3/ZrO_2 systems is in many ways similar to each other. This is manifested mainly in slowing the crystallization of amorphous ZrO_2, and further affects the change in the phase state of ZrO_2. The introduction of $MoO_3(WO_3)$ by impregnation method from HPA strongly stretches the crystallization process by temperature. At the same time, the presence of amorphous ZrO_2 makes a significant contribution to the porous structure (an increase of SSA). The composition and temperature of treatment affect the properties of the resulting catalysts most significantly. Thus, an increase in the content of MoO_3 causes not only the effects described above, but also contributes to a serious reorganization of the acid cover of the surface: the exponential growth of BAS and a non-monotonic change in the content of LAS with a sharp fall at 9 % MoO_3. The method of synthesis by impregnation makes it possible to obtain catalysts with the most developed porous structure and increased high LAS compared to the dry mixing method.

The differences in catalytic properties are largely due to differences in the acidity of the surface. The high content of MoO_3 (introduced by mixing) and a large supply of butenes contributes to the course of the oligomerization reaction. Reducing the supply of butenes and the introduction of $MoO_3(WO_3)$ by impregnation contribute to the flow of alkylation of isobutane.

Table. $MoO_3(WO_3)/ZrO_2$ catalyst activity and selectivity

	4.2 % MoO_3 (mix.)	6.6 % MoO_3 (mix.)	13.2 % MoO_3 (mix.)	9 % MoO_3 (imp.)	18 % WO_3 (imp.)
Isobutane to C_4-olefin ratio	10			19	
Olefin space velocity, $g_{buten}/(g_{cat}\cdot h)$	0.6			0.18	
TOS, min	90	90	90	90	90
1-butene conversion, mol. %	20.6	40.0	50.7	90.2	92.6
ΣC_5-C_7, mol. %	5.5	6.7	7.1	27.6	23.1
C_8, mol. %	**72.9**	**77.1**	**84.4**	**58.3**	**67.8**
icl. TMP+DMG+MG*	10.4	12.9	25.1	49.0	51.8
icl. olefines	62.2	64.1	58.5	9.3	13.9
C_{9+}, mol. %	21.6	16.3	8.5	14.0	9.1

* – trimethylpentanes + dimethylhexanes + methylheptanes.

Controlling the properties of $MoO_3(WO_3)/ZrO_2$ systems by varying the conditions of their preparation allows to regulate their behavior and selectivity towards alkylation or oligomerization. The study of the introduction of various promoters will allow in the future to obtain more stable and selective catalysts.

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Acknowledgments

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SYNTHESIS OF BIFUNCTIONAL CATALYSTS BASED ON PEROXOTUNGSTATE COMPLEXES AND THEIR REACTIVITY TO *GREEN CHEMISTRY* PROCESSES

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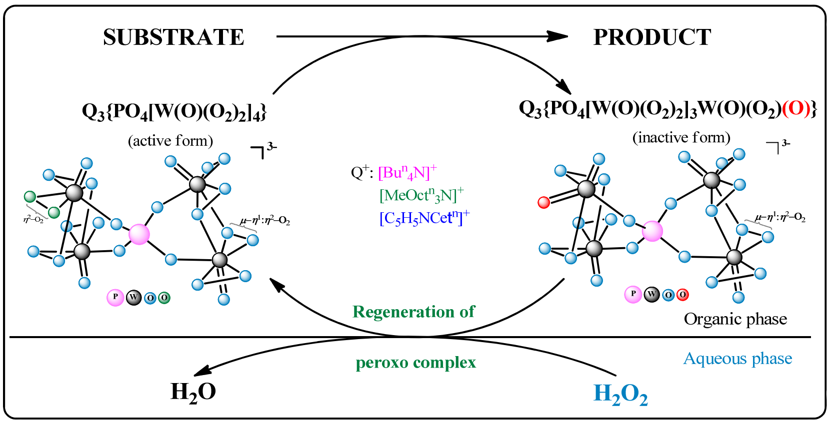
Practicability of the phase transfer catalysis in liquid systems (*aqueous/organic phases*) was demonstrated for oxidation of organic substrates with hydrogen peroxide in the presence of metal complex catalysts based on tungsten peroxocomplexes.

A series of bifunctional catalytic systems were synthesized using tetranuclear peroxopolyoxo complexes of tungsten including quaternary ammonium cations; the cations comprised alkyl substitutes of different chain lengths or both alkyl and aryl substitutes. The precursors used for the catalyst preparation were not only traditional Keggin structure polyoxometallates $[PW_{12}O_{40}]^{3-}$ [1] but also Dawson structures $[P_2W_{18}O_{62}]^{6-}$ with the anion comprising two phosphorus atoms. As a result, the yield of the most active complexes containing tetranuclear anion $\{PO_4[WO(O_2)_2]_4\}^{3-}$ – tetrakis(oxodiperoxotungsto)phosphate – was improved.

The prepared catalysts were tested in the model reaction of oxidation of octene-1 with aqueous 30 % H_2O_2 solution to heptanoic acid [2]. The most promising catalysts were tested for oxidation of isoamyl alcohol and *N*-phosphonomethyliminodiacetic acid with hydrogen peroxide under conditions of phase transfer catalysis.



High product yields (97-99 % heptanoic acid, 95-96 % isovaleric acid, 92-93 % *N*-oxide-*N*-phosphonomethyliminodiacetic acid) were shown to be obtained when the reaction was conducted under conditions of phase transfer catalysis in the presence of bifunctional catalysts based on tetranuclear peroxocomplexes of tungsten comprising a quaternary ammonium cation [3].

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Acknowledgement

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PP-20

Pd-Rh/METAL-FOAM CATALYST DEVELOPMENT FOR BIOGAS CONVERSION

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Sustainable fuels are widely accepted as the solution that can avoid a potential energy crisis in all major sectors including commercial, residential, and transportation and any irrevocable impairment to the climate by global warming potential reduction. Therefore, it is critical to utilize maximum amount of renewable energy. Renewable carbonaceous feedstock (ex. biogas) is a great resource and if remain unused emits significantly high amount of greenhouse gas. Biogas is a distributed resource and available in relatively small amount at asource location.

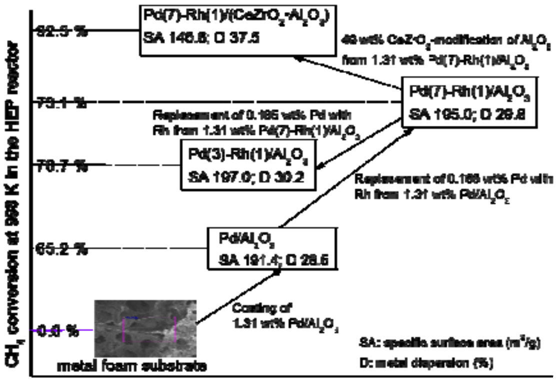
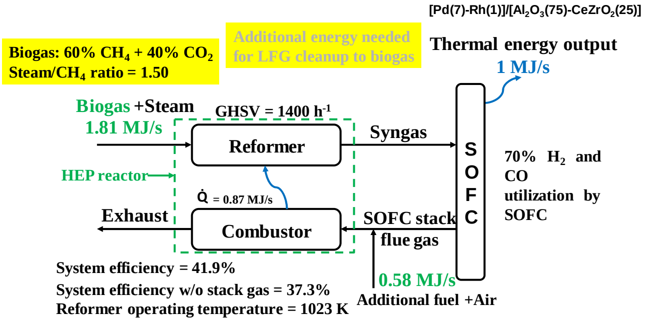


Figure: Catalyst performance with Pd/Rh composition change and CeZrO2 modification

Syngas is attractive from chemical conversion point of view as the reforming of CH_4 with CO_2 and steam utilizes the major components of biogas without CO_2 separation from biogas. A Pd-Rh based bi-metallic catalyst was developed and optimized for steam biogas reforming process with better heat integration by combining with the combustion exhaust flue gas from downstream process utilization. A heat exchanger platform (HEP) reactor is proposed which is a compact fuel processor for combining the steam biogas refomring and combustion forefficientheatsupply.

Metal foam supported catalysts are prepared by incipient wetness impregnation method. Catalysts containing 1.31 wt % (Pd–Rh)/alumina composites on metal foam substrate were tested for steam biogas reforming at 1 atm pressure to study the effects of Pd–Rh composition and $CeZrO_2$-modification of Al_2O_3. Among the catalysts supported on unmodified alumina, [Pd(7)–Rh(1)] catalyst performed slightly better with respect to CH_4 conversion as well as H_2 and CO yields, whereas [Pd(3)–Rh(1)] catalyst performed slightly better for suppression of coke formation. Modification of Al_2O_3 with 49 wt % $CeZrO_2$ improved catalytic activity and metal dispersion of [Pd(7)–Rh(1)] catalyst, despite 25 % loss of BET surface area. For the biogas-reforming reaction at 998 K and GHSV 1,400 h^{-1} with steam/methane (S/C) ratio of 1.50 in the feed, [Pd(7)–Rh(1)]/($CeZrO_2 \cdot Al_2O_3$) exhibited 92 % CH_4 conversion in the microchannel-structured heat exchanger platform reactor, 20 % more than the conversion obtained over [Pd(7)–Rh(1)]/Al_2O_3. H_2 and CO yields were also enhanced by $CeZrO_2$-modification of Al_2O_3. Variation of Pd–Rh composition and $CeZrO_2$-modification of Al_2O_3 did not affect catalytic stability in the feed with S/C = 1.50 for 200 h at 1,023 K and GHSV 20,000 h^{-1}, while $CeZrO_2$-modification of Al_2O_3 improved resistance to deterioration of surface area, pore structure and metal dispersion. Sintering was observed in used catalysts; however there was no clear correlation between the extent of morphological deterioration and the $CeZrO_2/Al_2O_3$ ratio of the catalyst support.

The experimental data show that positive CO_2 conversion was attainable only at temperatures higher than 1073 K, although the equilibrium based simulation predicts positive CO_2 conversion through most of the operating temperature range. Energy efficiency of the overall system was approximately 40 % at temperatures of 948 K and above. Coke formation over the Pd-Rh catalyst was estimated to be 1.05-2.88 % of the carbon input to the system. The results show that the proposed system can provide a viable approach to utilizing distributed renewable methane resources for localized power generation.



$$\text{Overall process efficiency} = \frac{MW\ of\ SOFC}{MJ/s\ of\ CH_{4_{in}} + MJ/s\ of\ additional\ fuel_{in}}$$

Figure: Process efficiency of steam biogas reforming process over Pd/Rh catalyst in the HEP reactor

Acknowledgments

This work was supported by California Energy Commission through Energy Innovation Small Grant No. 57825A/13-08G. Kiseok Kim is grateful to Yeungnam University for the 2015 Research Abroad Grant.

PP-21

THERMOCHEMICAL CONVERSION OF PEANUT SHELL BY FAST PYROLYSIS TO LEVOGLUCOSAN PRODUCTION

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The use of peanut oil has been reported in the literature to produce biofuels [1]. In this work, the pyrolytic sugar Levoglucosan was obtained from peanut shell, seeking the biofuels production, particularly the bioethanol production. Thus, the aim of this work was to improve the levoglucosan production from peanut shell using pretreatments with acetic acid (10 wt %) at 90 °C for 10 min under 200 rpm. Then, treated biomass was sujected to several wash stages with deionized water ut to neutral pH and dried in a vacuum oven at 70 °C up to constant weight. Then, the samples were subjected to fast pyrolysis in a Py-GC/MS [2]. Thus, the impact of the acetic acid on the levoglucosan yield as well as other pyrolytic compounds released during pyrolysis process at different temperatures (from 500 to 600 °C) was reported.

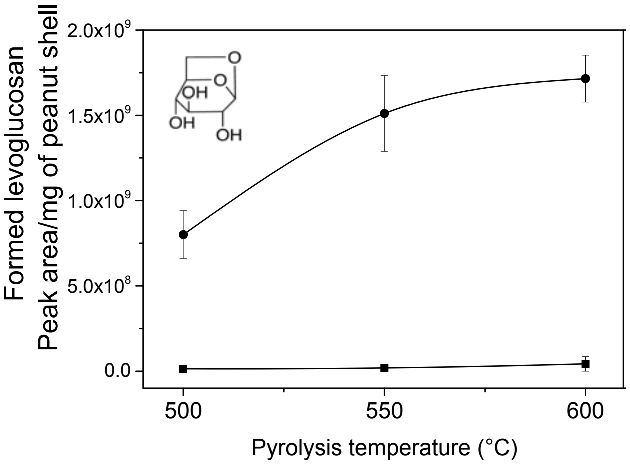

Fig. 1. Yields of levoglucosan from peanut shell under previously acid treatment condition and after fast pyrolysis at different temperature. Symbols; peanut shell: ■ as received; ● acetic acid treatment

The Fig. 1 shows the levoglucosan yield as pyrolysis temperatrure fuction. The best result was attained at 600 °C resulting in high levoglucosan production (around 65 folds) respect to the control experiments (untreated biomass samples) while, the yield of some undesirable compounds decreases as a consequence of the biomass acid washed. probably the high sugar content was attained by the reduction in the alkali and alkaline earth metals (Table 1) as previusly reported [2]. The attained results are very attractive because this pyrolytic sugar exhibits great potential as renewable feedstock for biofuels production and other bioproducts with industrial importance.

Table 1. Results of alkaline and alkaline earth and other elements for biomass determined by ICP method

Chemical elements	Concentration	
	Biomass as received	Biomass treated with acetic acid (10 % em peso)
B (mg/kg)	11.66 ± 4.02	6.32 ± 1.28
Ca (g/kg)	2.22 ± 0.63	1.34 ± 0.02
Cu (mg/kg)	11.57 ± 0.2	13.63 ± 0.17
Fe (mg/kg)	412.25 ± 43.75	154.56 ± 5.94
K (g/kg)	8.30 ± 0.12	0.03 ± 0.00
Mg (g/kg)	1.29 ± 0.04	0.11 ± 0.00
Mn (mg/kg)	25.62 ± 0.67	15.81 ± 0.01
Mo (mg/kg)	0.73 ± 0.01	0.47 ± 0.03
Ni (mg/kg)	0.47 ± 0.07	0.69 ± 0.00
P (g/kg)	0.35 ± 0.00	0.06 ± 0.00
S (g/kg)	0.984 ± 0.00	0.28 ± 0.00
Zn (mg/kg)	14.88 ± 0.00	10.31 ± 3.01

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HIGHLY SELECTIVE CONVERSION OF CO_2 TO CO ON Cu NANOPARTICLES

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Carbon dioxide (CO_2), a key greenhouse gas produced from both anthropogenic and natural sources, has been recently considered to be an important C1 building-block for the synthesis of many industrial fuels and chemicals. Catalytic hydrogenation of CO_2 using a heterogeneous system is regarded as an efficient process for CO_2 valorization. In this regard CO_2 reduction to CO via the reverse water gas shift reaction (RWGSR) has attracted much attention as a viable process for large scale commercial CO_2 utilization. This process can generate syn-gas ($CO+H_2$) which can provide an alternative route to direct CO_2 conversion to methanol and/or liquid HCs from FT reaction [1, 2]. Herein, we report a highly active and selective silica supported copper catalyst with efficient CO_2 reduction to CO in both slurry and fixed-bed reactor systems. The reactions were carried out between 200-400 °C and 5-60 bar pressure with CO_2/H_2 ratio of 1:3. The gaseous phase products were analyzed using TCD while the liquid products were analyzed by using FID detectors. It was found that Cu/SiO_2 catalyst prepared using novel precipitation-hydrothermal method achieved 30% CO_2 conversion with a CO and methanol selectivity of 98 and 2 % respectively. The high catalytic activity could be attributed to its strong metal-support interaction with highly dispersed and stabilized Cu^+ species active for RWGSR. So, it can be concluded that reduction of CO_2 to CO via RWGSR could address the problem of using CO_2 gas in C1 chemistry.

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PP-23

OBTENTION OF NANOSCALE MAGNETIC COMPOSITES ON THE BASE OF Fe_3O_4, $CoFe_2O_4$ STABILIZED BY MICROSPHERICAL ALUMINOSILICATES OF FLY ASH OF CHP

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Nanoscale magnetic composites on the base of Fe_3O_4, $CoFe_2O_4$ stabilized by microspherical aluminosilicates of fly ash of CHP by chemical precipitation and mechanochemical synthesis were obtained. The composition and the process parameters (t°, pH), the influence of ultrasound and magnetic fields are optimized.

The magnetic composites obtained by the Elmor's reaction. $FeCl_3{\cdot}6H_2O$, $CoCl_2$, and $FeCl_2{\cdot}4H_2O$ salts with correlation $Fe^{3+}/Fe^{2+} = 2/1$ were mixed in a reaction vessel in an inert atmosphere. Then NH_4OH (25 %) was added at intensive stirring.

Interaction reactions may be represented as follows:

$$2FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow Fe_3O_4\downarrow + 8NH_4Cl + 4H_2O \qquad (1)$$

$$CoCl_2 + FeCl_3 + FeCl_2 + 8NH_4OH \rightarrow CoFe_2O_4 + 8NH_4Cl + 4H_2O \qquad (2)$$

The macromolecule of the cenospheres binds the particles immediately after the generation of Fe_3O_4 nanoparticles preventing its further growth.

The IR spectrum of the aluminosilicate composite serves as a proof of the coordination sites on the sorbent surface. There is an intense absorption band in the frequency range 1200-1000 cm^{-1}. This interval of frequencies characteristic for the groups Si–O, Al–O, Si–O– Al: ν 1100, 1066, 1022, 1050, 900 cm^{-1}. Absorption bands in the low-frequency region of the spectrum from 668 to 614 cm^{-1} belong to Fe–O in the Fe_2O_3 group.

The study of electronic diffractograms showed that the main phase formed during the chemical coprecipitation in the presence of cenospheres in situ is represented by Fe_3O_4 magnetite.

The Mössbauer spectra of Fe_3O_4 magnetite, measured at room temperature, represent sextets with wide asymmetric lines of magnetically ordered phase.

Mössbauer spectra were measured at a temperature of 5 K for more accurate identification of the phases of iron atoms. In the spectrum, which is a well-resolved sextet, five nonequivalent positions of iron atoms are observed: two positions correspond to trivalent iron atoms in tetrahedral and octahedral environments, the other three positions correspond to divalent iron atoms in the octahedral environment of oxygen atoms to the structural formula of magnetite.

The hysteresis curves are recorded at 300 K and represent closed lines symmetrical to the coordinate system. The shape of the curves proves the ferromagnetic nature of the material, allowing it to be used for magnetic separation.

The study using transmission electron microscopy of nanocomposite obtained by chemical coprecipitation in situ and mechanochemical method showed that in both cases the distribution of homogeneous nanoparticles in the structure of the macromolecular matrix is well manifested. It was found that the Fe_3O_4, $CoFe_2O_4$ nanoparticles have a spherical shape, at that the diameter of the particles reaches 7-10 nm. There is no sharp difference between the size and shape of nanoparticles obtained by different methods.

It was found that the central paramagnetic component of the spectrum increases with the relaxation frequency increase. As a result, a similarity of a wide quadrupole spectrum occurs at first, which then narrows into one component. Some magnetic characteristics for hybrid nanocomposite Fe_3O_4–microspherical aluminosilicate (MAS) are presented in Table 1. It is revealed that single-domain particles have the maximum coercive force. Larger particles consist of several domains, and its magnetization can be changed by a weak magnetic field by displacement of the domain walls. In the case of small particles, the exchange forces are significantly weakened by thermal forces and the matter transits into a superparamagnetic state.

Table 1. Magnetic properties of the original magnetite and nanocomposite on the base of MAS

Sample	Maximum magnetization, emu/g	Residual magnetization, emu/g	Coercive force, Oe	Rectangularity of hysteresis loop
Fe_3O_4	33.6	4.14	86	0.12
Fe_3O_4/MAS (mech)	4.99	0.8	91.5	0.16
Fe_3O_4/MAS *(in situ)*	6.81	1.1	89	0.16

PP-24

THE USE OF CHP FLY ASH TO OBTAIN OF MULTIFUNCTIONAL POROUS MAGNETOCONTROLLABLE NANOSCALE MATERIALS

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The ash content of coal of Ekibastuz coal basin arriving at the energetics enterprises amounts up to 40-50 %. The chemical composition of ash and slag waste is identical in large part to natural mineral raw materials, and in some cases, has unique and useful properties. The most original and, perhaps, the most valuable components of fly ash at coal combustion on CHP – aluminosilicate microspheres, which are hollow, almost perfectly shaped silicate balls with a smooth surface, with a diameter from 10 to several hundred micrometers, about 100 microns at an average. Wall thickness is from 2 to 10 microns, melting point 1400-1500 °C, density 580-690 kg/m^3. The presence in the ASM structure of paramagnetic (oxides of rare earth metals) and supramagnetic (iron oxides) particles with a spinel structure and with a size of 30-50 Å and dispersed in the aluminosilicate glass makes them magnetocontrollable materials, the properties of which depend on external and internal magnetic fields.

The use of the technology of fly ash fractional separation in the upward flow of the separating medium with the imposition of the magnetic field of a certain intensity and multiple pulsation allows to obtain cenospheres of stabilized chemical, mineral-phase and magnetic compositions.

The nanoscale magnetic composites elaborated by us on the basis of aluminosilicate microspheres of fly ash of CHP not only have a large specific surface area (>50 m^2/g) necessary for high efficiency of sorbents, but also are effective catalysts of spin-forbidden processes (cracking, dehydrogenation, oxidation of organic compounds). We have shown that the magnetic interactions are only interactions that can change the spin of pre-reaction intermediates and transform non-reaction, spin-forbidden states into reactionary, spin-allowed states. Its input to the total energy is negligible, but it control the behavior of spin in chemical particles, modify their chemical reactivity and determine a new, magnetic scenario of chemical reactions. In the case of a radical pair the non-reactive triplet pairs can be transformed into reaction singlet pairs (triplet-singlet conversion) either at the cost of native, intrinsic magnetic interactions inherent in the reaction itself, or under the action of external radio frequency or microwave fields. These effects are of kinetic origin. It should be emphasized that magnetic interactions do not affect the chemical reaction itself, i.e. it do not affect the movement of a chemically reacting atomic system on the surface of potential energy. In reality, these interactions lead to the following: it switch the reaction from spin-forbidden channels to spin-allowed ones, regulating the spin behavior of reagents and replacing non-reaction channels with reaction ones (or vice versa). This applies to both magnetic interactions inherent in the reaction itself (Zeeman, Fermi, dipole, spin-orbital) and external electromagnetic fields and their effects on spin-containing reaction precursors (in particular, radical pairs).

On the basis of microspheres separated from fly ashes from the combustion of brown or stone coal on CHP we have developed the technology of preparation of modified catalysts for:

- cracking of masout or heavy oil, which allows to obtain up to 64 % wt of light fractions from masout;
- oxidative transformation of methane using microwave radiation, which allows to increase the selectivity of the formation of C_2-products up to 67.4 % at 23.8 % conversion of methane, what corresponds to the best known catalysts of the oxidative condensation of methane;
- production of olefins by thermocatalytic treatment of liquid or gaseous hydrocarbon raw materials using microwave radiation as an energy source and microspherical modified catalyst from the ash of CHP, allowing to obtain up to 95 % α-olefin from hexadecane.

PP-25

BIODIESEL PRODUCTION BY MAGNETIC CATALYST IN REACTOR ASSISTED BY MAGNETIC FIELD

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In this study, the biodiesel synthesis from sunflower oil and ethanol was evaluated in a reactor assisted by magnetic field, using K_2CO_3/Sepiolite/Fe_3O_4. To prepare the catalyst, firstly the magnetite (Fe_3O_4) was synthetized by co-precipitation [1] and finally the active phase (K_2CO_3) and the support (sepiolite and magnetite) was extruded. Then, the mechanical, magnetic and textural properties of the prepared catalyst were assessed by dynamometry, vibrational magnetometer (VSM) and BET analysis (Table 1). The Fig.1a shows the experimental system, the axial lines distribution of magnetic field in the reactor was verified and can be seen in the Fig. 1b. The transesterification reaction was carried out in the reactor assisted by magnetic field at batch regime, the best result, i.e. 99.9 % of biodiesel conversion (Fig. 2), was obtained with 5 wt % of the catalyst, reaction temperature at 70 °C, molar ratio of 1:9 (oil: ethanol) , reaction flux at 0.5 L/min (200 rpm) and magnetic induction of the 12.5 mT. In addition, the transesterification reaction was carried out in the conventional process, i.e. stirring system (200 rpm) without magnetic field application, in the same parameters of reaction to comparative purpose. The attained results are attractive because the magnetic induction was important for establization of the magnetic catalyst in the reactor, which contributed to the improved performance of the magnetic catalyst in the reaction, and, in addition, retain/separate the magnetic catalysts after reaction for further reuse.

Table 1. Physicochemical characterization of K_2CO_3/Sepiolite/Fe_3O_4

Physicochemical characterization	**Values**
Mechanical strength (kgf/cm)	1.81
Magnetization (emu/g)	12.93
Specific area (m^2/g)	8.3
Pore size (nm)	23
Pore volume (cm^3/g)	0.06

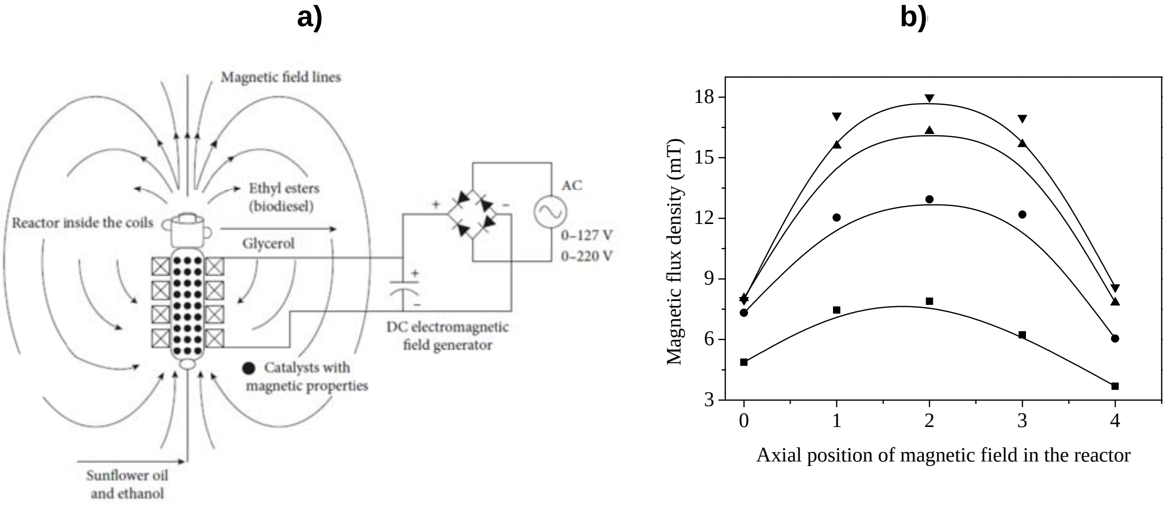

Fig 1. a) Experimental setup of the chemical reactor assisted by magnetic field for biodiesel synthesis [1,2]; b) Magnetic field axial lines distribution in center of reactor

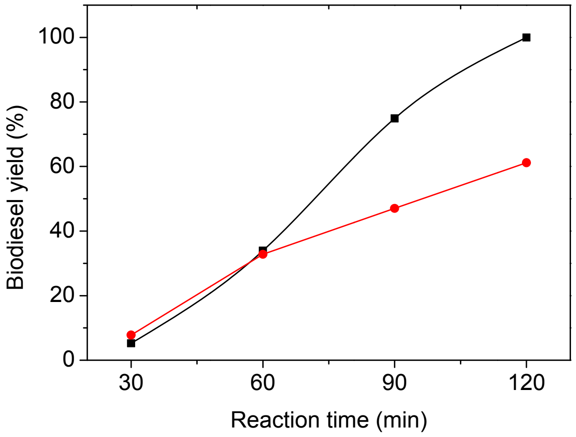

Fig. 2. Biodiesel yield from reaction catalyzed by K_2CO_3/Sepiolite/Fe_3O_4 in:
● conventional process and ■ reactor assisted by magnetic field

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PP-26

$Rh/Ce_{0.75}Zr_{0.25}O_{2-\delta}$-η-$Al_2O_3$/FeCrAl STRUCTURED CATALYST IN REFORMING OF FOSSIL AND RENEWABLE FUELS

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Catalytic reforming is considered as one of the most effective methods of producing hydrogen from hydrocarbon fuels for solid oxide fuel cells (SOFC). Diesel and gasoline are attractive fuels because of high energy density, wide applications and well developed infrastructure. In addition, biodiesel, which is produced from renewable sources, is of particular interest as a source of hydrogen. The catalysts supported on structured carriers (FeCrAl blocks) provide controlled reaction conditions throughout the reactor volume that favorably competes, for example, fixed bed reactors. The use of the structured catalysts provides efficient heat and mass transfer, low gas dynamic resistance, and high catalyst performance that allows reducing the catalyst quantity per unit volume of the reactor. The opportunity to perform the process under controlled optimum conditions allows to increase the selectivity and minimize undesirable side reactions, such as coke formation.

In the present work, active component Rh/CZ was supported on FeCrAl metal meshes using Al_2O_3 as a binding structural component. The obtained catalyst Rh/CZ-η-Al_2O_3/FeCrAl was tested in the n-hexadecane (used as model diesel), isooctane (used as model benzine), commercial diesel and biodiesel reforming. Winter grade diesel used in the experiments contained up to 30 % of aromatics, in contrast to biodiesel, in which the aromatics content is minimized. And the lower aromatics content in the fuel the higher catalyst performance was achieved. Operating conditions were found to provide a near 100 % conversion of hydrocarbon fuels and stable catalyst activity for a long time-on-stream exposure.

It was shown that 0.24 wt. % Rh/(12 wt. % $Zr_{0.25}Ce_{0.75}O_{2-\delta}$-η-$Al_2O_3$)/FeCrAl catalyst provided high efficiency of fuels conversions into syngas. The produced syngas can be supplied as a fuel for power generation units based on high-temperature solid oxide fuel cells.

PROPERTIES OF BIOFUELS - METHYL-ESTERS AND BIO-OILS (HYDROCARBONS) - FROM *PACHIRA AQUATIC* AUBL AND *MAGONIA PUBESCENS* A ST-HIL

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Two perennial tree species *Pachira aquatica* Aubl (PA) and *Magonia pubescens* A St-Hil (MP), both being endemic to Brazil, were studied as potential sources for biofuels production [1]. The main benefit of those sources is the lack of competition with the food market and the preservation of native vegetation. The chemical composition and the physical-chemical properties of the oils extracted from both species were evaluated. Furthermore, their oils were processed to produce biofuels using two approaches: obtaining mixtures of methyl fatty acid esters (biodiesel) and mixtures of hydrocarbons (bio-oil). The physical-chemical properties of the biodiesels obtained from PA and MP are compatible with diesel engines. The bio-oils obtained from both sources, despite not being completely deoxygenated, displayed physical-chemical properties acceptable for diesel engines fuel. The possibility of obtaining two kinds of fuels with suitable properties is a good sign for the exploration of those trees [2,3].

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PP-28

INFLUENCE OF ALUMINOSILICATES ON THE PROCESS OF THERMAL DESTRUCTION OF HEAVY HYDROCARBONS OF OIL AND BIOMASS

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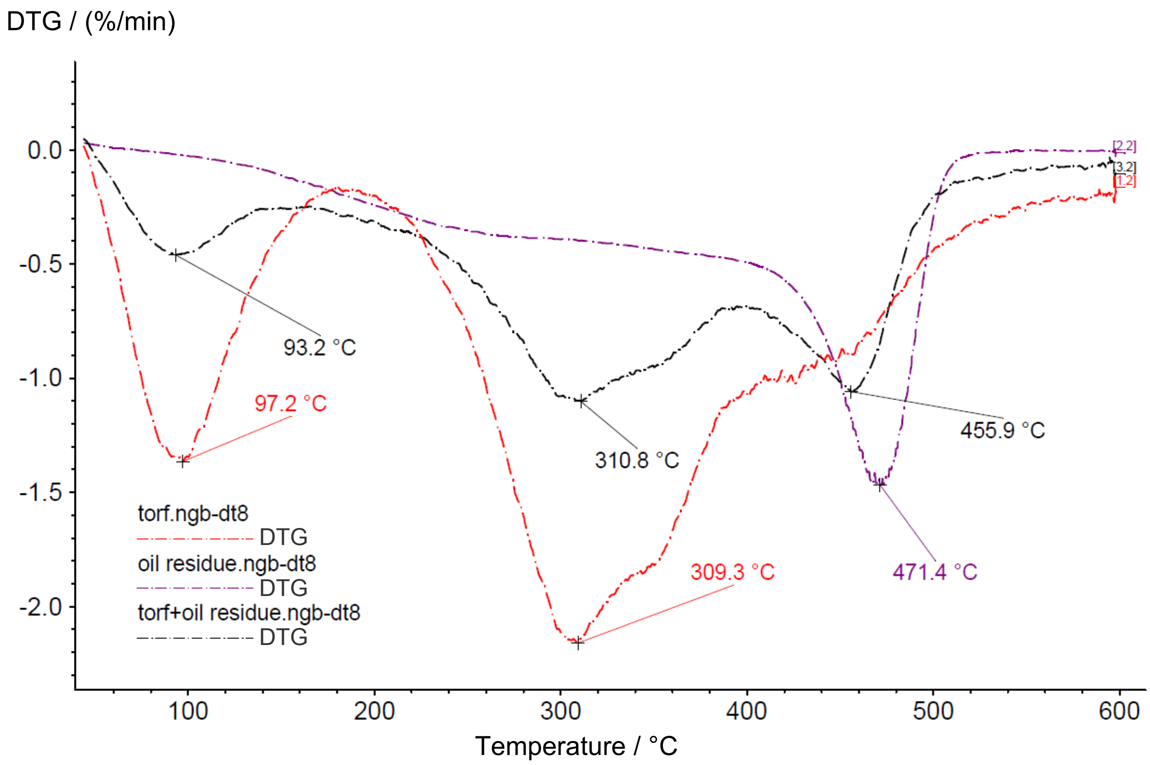
In this paper, the process of thermal catalytic destruction of heavy petroleum and peat hydrocarbons was investigated. Model oil-sludge (a mixture of heavy oil and quartz sand), peat, and a mixture of peat and sludge were used as a feedstock. Natural aluminosilicates (kaolin clay, bentonite clay, clay marl) were used as catalysts.

Disposal of oil production and refining is an important environmental issue. The amount of oil waste can reach 7 % of the volume of oil produced [1]. Emergency spills of oil and oil products pose the greatest threat to the environment, they require the most prompt response. Various sorbents are used for the effective collection of spilled oil. The use of peat is economically justified [2]. It has good sorption properties for oil and is an affordable and cheap raw material.

Processing of the impregnated sorbent is the most energy-intensive and time-consuming stage. Among the existing methods (chemical, thermal, biological, etc.), thermal destruction has several advantages: the ability to process a wide range of organic raw materials; complete disposal of waste; production of combustible gaseous and liquid products; obtaining a solid residue used as a sorbent; does not require the use of solvents and complex biological systems.

Studies were carried out in a fixed bed reactor in a nitrogen atmosphere (pyrolysis). The experimental set-up of pyrolysis includes reactor, electric furnace with a thermostat, cylinder with nitrogen, gas sampler, a collection of liquid products, eudiometer for collecting gas and measuring cylinder. The range of temperatures studied was 450-600 °C. Analysis of gaseous products was carried out by gas chromatography (Gazokhrom 2000 and Crystallux 4000M).

The kinetics of the degradation process was investigated by thermogravimetry using TG 209 F1 (NETZSCH). The analysis was carried out in argon medium (carrier gas rate 30 mL/min). Samples were heated to a temperature of 600 °C at a rate of 10 K/min.



Pyrolysis of a mixture of oil residue and peat led to an increase in the yield of the liquid fraction by 10 % (mass.) compared with the predicted calculated value. The use of peat in the pyrolysis of oil residue contributed to the intensification of the process.

When using aluminosilicates, an increase in the content of C_1-C_3 hydrocarbons in the composition of gaseous products was observed by 10-20 %. Bentonite clay showed the greatest catalytic activity.

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PP-29

CATALYTIC REFINING OF VOLATILE PRODUCTS OF PLANT BIOMASS PYROLYSIS

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Thermocatalytic refining of gaseous products of pyrolysis is one of the technological methods focused on the decrease of the content of high-boiling fractions and tars. The gaseous products of the pyrolysis flow through the catalyst layer that result in the thermal destruction of high-boiling components and tars. The significant amount of gaseous hydrocarbons form in the thermocatalytic destruction of pyrolysis gases tars. They increase the “working” combustion heat of the pyrolysis gaseous products. The biomass waste processing is rather complex because of the physical-chemical characteristics of this type of raw material: low temperature of ash melting, high ash content etc., so their conversion is an important applied problem. It is noteworthy that the complexity and variability of the composition of one type of biomass do not allow solving the problems of effective complex processing of biomass. The use of catalysts in the organic source conversion process allows increasing of liquid and gaseous products yield as well as increasing of concentration of aromatic compounds and branched hydrocarbons in liquid pyrolysis fraction. For this reason, catalytic pyrolysis causes a significant interest all over the world because the use of catalysts promotes the growth of the effectiveness of organic compounds processing. Catalytic pyrolysis causes a significant interest all over the world because the use of catalysts promotes the growth of the effectiveness of organic compounds processing [1, 2].

The use of catalysts in the organic source conversion process allows increasing of liquid and gaseous products yield as well as increasing of concentration of aromatic compounds and branched hydrocarbons in liquid pyrolysis fraction. Products obtained by catalytic pyrolysis have a much more narrow range of the molecular mass distribution in comparison with the non-catalytic process. So these products carry the higher quality and can be used as transportation fuels, it is an important benefit of catalysts application in the waste pyrolysis process [3, 4].

The total time of the experiment was 30 min. To estimate the rate of thermodestruction of the initial source in the presence of the catalysts the rate of gaseous products evolution was controlled during the experiment.

The gaseous products analysis was performed by the gas chromatography method. The use of metal-containing alumosilicate catalyst in the pyrolysis gas refining from the tars results in the change of the gas volume and heat value. The use of the studied zeolite catalysts containing the iron subgroup metals leads to the change in the concentration of hydrogen, C_1-C_4 hydrocarbons and carbon oxides.

The concentration of metal on the surface of the alumosilicate catalyst strongly affects the catalyst activity in the thermodestruction process of a pyrolysis gas tars. The gaseous product composition depends on the type and concentration of the metal on the catalyst surface. In comparison with a non-catalytic process the volume concentration of C_1-C_4 hydrocarbons increases by 1.39; 1.66 and 1.52 times using Fe-containing, Co-containing, and Ni-containing alumosilicate catalysts respectively.

The use of the catalysts also results in the increase in hydrogen concentration; moreover, the growth of hydrogen concentration in a gaseous product increases from Fe to Ni. The increase in alumosilicate catalyst metal content also leads to an increase in hydrogen concentration that is caused by the dehydration reaction of pyrolysis organic products in the presence of iron subgroup metals. The growth of hydrogen concentration in a pyrolysis gas is accompanied by the increase in coke-formation on the catalyst surface, so the use of the catalysts with higher metal content is economically unfavorable.

The considerable effect of the studied catalysts on the pyrolysis gas composition can be explained both by the catalyst high activity in the thermodestruction process and thermal decomposition of high-boiling fractions of pyrolysis liquid products. According to the data on the gaseous product composition, the optimal Co content in the zeolite catalyst is 2 % (wt.). Such metal content in the catalyst allows increasing C_1-C_4 hydrocarbons concentration and removing the tars from the combustible gas of the fast pyrolysis of the studied types of biomass.

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HYDROLYSIS-OXIDATION OF STARCH TO FORMIC ACID WITH SOLUBLE AND SOLID HETEROPOLYACID CATALYSTS

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The gradual depletion of fossil hydrocarbon sources has made it necessary to intensify a search for alternative renewable feedstocks for industry and energetic all over the world. Plant polysaccharides (starch etc.) are among the most promising alternative carbon-containing feedstock for production of chemicals. Formic acid (FA) is a value-added commodity which is applied for production of medicaments, solvents, fragrances, and fibers, in pulp and leather industries and for conservation of food products and forage. Formic acid seems to be a very promising for hydrogenation processes as a reducing agent or as a source of molecular hydrogen. Thus, the development of a one-pot way for direct transformations of plan polysaccharides to FA via hydrolysis-oxidation appeared to be an important scientific topic. Previously we developed the one-pot hydrolysis-oxidation process to transform robust cellulose to FA in the presence of bifunctional heteropoly acids (HPA) which are promising catalysts for green chemistry [1]. In this work our efforts were focused on creating the hydrothermal one-pot method of processing available polysaccharide (potato and microbial starch) to FA in the presence of soluble and solid Mo-V-P, W-V-Si and W-V-P HPA catalysts.

Two types of HPA catalysts which differed from each other by acidity and vanadium content were prepared: 1) soluble HPA catalysts $H_5PV_2Mo_{10}O_{40}$, $H_7PV_4Mo_8O_{40}$ and there soluble salts $Co_{0.6}H_{3.8}PV_2Mo_{10}O_{40}$, $Na_2H_5V_4Mo_8O_{40}$; 2) solid catalysts of tetraamine butilates and cesium salts of Mo-V-P, W-V-P and W-V-Si heteropoly acids ($[(C_4H_8)_4N]_{3.6}H_{0.6}PMo_{11}VO_{40}$, $[(C_4H_8)_4N]_{3.6}H_{0.6}SiW_{11}VO_{40}$, $Cs_{3.6}H_{0.6}PW_{11}VO_{40}$, $Cs_{4.6}H_{0.6}SiW_{11}VO_{40}$, $Cs_{3.6}H_{0.6}PMo_{11}VO_{40}$ ((Bu_4N)HPA and CsHPA)). The catalysts were characterized by NMR (for soluble HPAs) and low-temperature N_2 absorption, IR spectroscopy and pH of solution (for solid catalysts). The stability of solid catalysts under hydrothermal reaction conditions was also investigated.

All the catalysts were tested in the hydrothermal one-pot hydrolysis-oxidation of starch under 20 bar air pressure. The following main results were obtained The optimal reaction temperatures equal to 120 and 150 °C, respectivelly, for soluble and solid HPA catalysts were revield. The dependence of the yields of formic acid on the content of active centers in the reaction medium was found. Thus, for soluble HPAs at constant pH, the reaction rate and FA yield incresed when the concentration of vanadium atoms in the solution rised to [V] = 80 mmol/L. At a constant concentration of vanadium atoms (80 mmol/L), an increase of the acidity of the HPA catalyst solutions raised initial rate of the target product formation, but did not affected it's yield. It has been established that solid catalysts based on Mo-V-P HPA is the most active among the solid catalytic systems due to the highest content of acid groups on the surface.

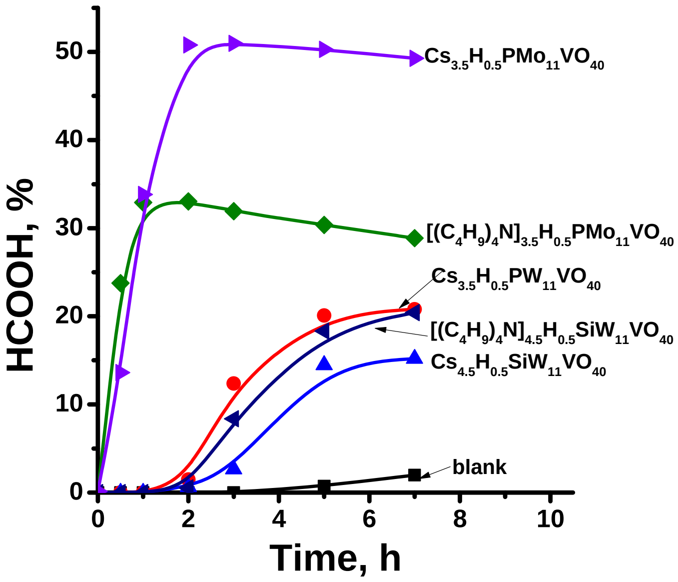

Fig. 1. The yield of FA over solid HPA catalysts

The most active soluble and solid HPA catalysts were selected. Catalytic systemes based on Mo-V-P heteropoly acid provided the highest yield of the FA compared to W-V-P and W-V-Si HPAs (Fig. 1). Thus, 66 % FA yield % with 100 % were achieved in the presence of $Co_{0.6}H_{3.8}PV_2Mo_{10}O_{40}$ soluble catalyst under the optimal conditions (120 °C, a concentration of vanadium atoms in the solution [V] = 80 mmol/L). On the other hand, the solid catalyst of the composition $Cs_{3.6}H_{0.6}PMo_{11}VO_{40}$ provided 51 % FA yield at 150 °C. Solid CsPHAs were more active that (Bu_4N)HPAs due to high stability, low solubility and significant acidity of the surface (Fig. 1).

Comparison of soluble and solid catalysts allows us to conclude that soluble systems are more selective at milder reaction conditions.

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Acknowledgments

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PP-31

FLARE GASES UTILIZATION VIA LOW-TEMPERATURE STEAM REFORMING REACTION

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Nowadays, there is an urgent problem of gas flaring all over the world. Billions of cubic meters of gas are wasted in flare installations due to the lack of required transportation or refinery infrastructure or economical inefficiency. This includes associated petroleum gas (APG), separation gas from gas conditioning units at off-shore fields, shale gas and plant gas. These multi-component gas mixtures predominantly consist of methane and its homologues with some inert components such as CO_2, N_2 and can neither be pumped to pipelines due to high dew point temperature, nor directly used as a fuel for internal combustion engines (ICE) due to high calorific effect (NCV) and detonation risk. Thus, an alternative way of APG utilization is necessary.

Low temperature steam reforming (LTSR) of flare gases (FG) represents a promising method of FG utilization. The process occurs at 250-350 °C and low steam to carbon molar ratio H_2O/C_{C2+} 0.5-1 and therefore differs from conventional pre-reforming. Overall process converts C_{2+}-hydrocarbons into CH_4, CO_2 and H_2, which results in lowering net calorific value, Wobbe index and dew point temperature of the gas obtained.

However, complete conversion of C_{2+}-hydrocarbons leads to excessive dilution of methane by CO_2 and H_2 according to equilibrium product distribution and to insufficient energy content of gas for fuel applications. In this case, kinetically controlled partial conversion of ethane and propane provides a way to obtain methane-rich mixtures with desired calorific properties for various applications. This idea was verified experimentally. The reactivity of hydrocarbons under low-temperature steam conversion conditions was shown to increase in the order: $C_2H_6 < C_3H_8 < n\text{-}C_4H_{10} < n\text{-}C_5H_{12}$, making background for preferable conversion of butanes and pentanes and production of methane-rich mixtures with low dew point temperature and sufficient energy content.

Kinetic study of C_2H_6-C_5H_{12} low-temperature steam conversion was performed. A simple macrokinetic model, which included irreversible first-order kinetics for C_2H_6-C_5H_{12} steam conversion and quasi-equilibrium mode for CO_2 methanation, was suggested. The model adequately described the experimental data on the conversion of model flare gas mixtures at various temperatures and flow rates and was applied to predict reaction conditions which would allow obtaining methane-rich mixtures with the desired properties for various applications from APG of different fraction C_{2+}-hydrocarbons. Fig. 1 represents an example of such calculation for "light APG".

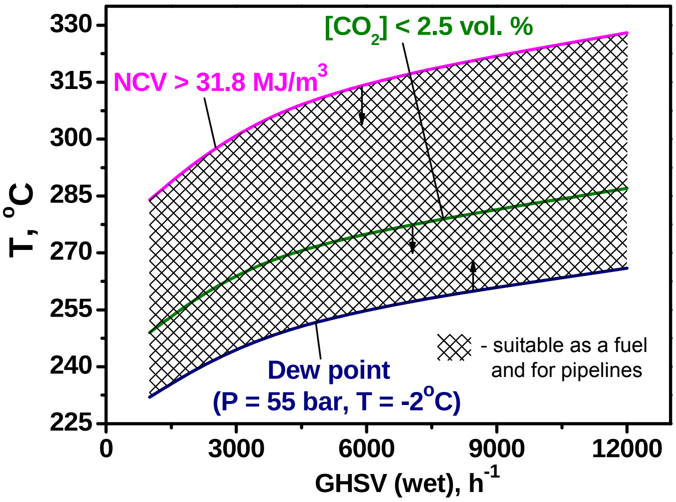

Fig. 1. Calculated area of reaction conditions that allow obtaining product gas mixtures which meet the requirements on natural gas according to the standard of "Gazprom" company (Russian Federation). Only dry gas is taken into account. H_2O/C_{C2+} = 0.7, P = 1 bar. Inlet gas mixture (vol. %): (vol. %): 86.5 CH_4, 5.6 C_2H_6, 4.9 C_3H_8, 1.2 C_4H_{10}, 0.50 Σ-C_{5+}, 0.6 CO_2, 0.8 N_2

LTSR could be applied for conversion of various flare gas mixtures into fuel gases with desired and preset properties: suitable for pipeline transportation, for internal combustion engines, for turbines.

Acknowledgements

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SELECTIVE Mo-BASED CATALYSTS TO CONTROL THE CARBON OXIDES PRODUCTION IN THE HDO OF ALIPHATIC OXYGENATES

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Triglyceride-based feedstock attracts much attention as a renewable source for the production of normal alkanes – valuable diesel components, so-called green diesel or renewable diesel. The hydrodeoxygenation (HDO) of triglycerides can proceed via H_2O removal (direct HDO pathway – HDO) or through the hydrodecarbonylation-hydrodecarboxylation ($HDeCo_x$) route, accompanied by CO/CO_2 formation. The main drawbacks of DeCOx route are carbon oxides emissions, which can lead to the additional hydrogen consumption in methanation reaction and demands separation of carbon oxides. Using a selective catalytic system is an effective way to avoid the above problems and prevent carbon loss that decreases the yield of liquid hydrocarbons. The non-promoted MoS_2/Al_2O_3 catalysts provide conversion of aliphatic ester without considerable CO_x formation [1], but sulfiding agent should be fed in the reactor to prevent deactivation. We assumed that MoP catalysts may be a promising alternative to sulfide systems in the HDO of renewable feedstocks in the stand-alone units.

The scope of the present work is the comparison of Al_2O_3-supported MoP and MoS_2 catalysts in the HDO of rapeseed oil (RSO) and methyl palmitate (MP) as the model compound. The aspects of phosphide- and sulfide-based systems using in the HDO reactions will be discussed.

Experimental

The γ-Al_2O_3-supported MoS_2 catalyst was prepared by impregnation of alumina with an aqueous solution of MoO_3, citric acid, and H_3PO_4 as described elsewhere [2]. Before the catalytic experiments, the catalyst precursor was sulfided *in situ* [2]. The γ-Al_2O_3-supported MoP catalyst was prepared by the impregnation of the support with an aqueous solution of $(NH_4)_6Mo_7O_{24}$ and H_3PO_3 (molar Mo/P = 1/2) followed by drying at 80 °C during 24 hours. Before the catalytic experiments, the catalyst precursor was reduced *in situ* in H_2 flow at 650 °C for 1 hour.

Chemical analysis (ICP-AES), N_2 physisorption, H_2-TPR, XRD, XPS, and TEM have been employed for the catalysts characterization. The HDO of MP was carried out in the trickle-bed reactor at hydrogen pressure of 3.0 MPa, H_2/feed – 600 Nm^3/m^3, T – 230-330 °C, LHSV-60 h^{-1} using GC analysis of liquid and gas phases, and oxygen elemental analysis of liquid products by Vario EL Cube. The RSO hydroprocessing was performed at conditions close to commercial hydrotreating process: hydrogen pressure of 3.0 MPa, H_2/feed – 600 Nm^3/m^3, T – 300-340 °C.

Results and discussion

The formation of nickel phosphide particles on alumina surface after temperature-programmed reduction (TPR) was proved by XRD and TEM methods. Characterization of the sulfide MoS_2/Al_2O_3 catalyst by means of XRD and HRTEM confirmed that the applied preparation and sulfidation procedures provide the formation of highly dispersed MoS_2 nanoparticles on the alumina surface.

We observed that the MP conversion over MoP/Al_2O_3 at whole temperature range (230-330 °C) was higher than one over MoS_2/Al_2O_3 catalyst. Complete oxygen conversion was achieved at temperature 310-330 °C and HDO selectivity to C_{16} hydrocarbons was lower over MoS_2/Al_2O_3 and equaled to 94-91 % instead of 99-96 % for MoP/Al_2O_3. It should be noted that the temperature increase leads to lower HDO route selectivity of MP conversion.

It was shown that the conversion of RSO mostly occurred through the direct HDO route at temperature range 300-340 °C over MoP/Al_2O_3 and MoS_2/Al_2O_3 catalysts. It was obtained that the increase of the reaction temperature from 300 to 340 °C resulted in the decrease of the HDO route selectivity from 97 % to 92 % for MoP/Al_2O_3 and from 96 % to 88 % for MoS_2/Al_2O_3 catalyst.

Conclusion

Our result allowed us to conclude, that MoP and MoS_2 catalysts control the formation of carbon oxides in MP and RSO hydrodeoxygenation and maximize the yield of liquid motor fuels components. Phosphide-type catalysts can be used in the stand-alone unit, while the MoS_2/Al_2O_3 is a promising candidate for the hydrotreating of renewable feed stocks in the mixture with petroleum distillates.

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PP-33

SYNTHESIS OF 1-BUTANOL FROM ETHANOL OVER CALCIUM ETHOXIDE: EXPERIMENTAL AND DFT SIMULATION

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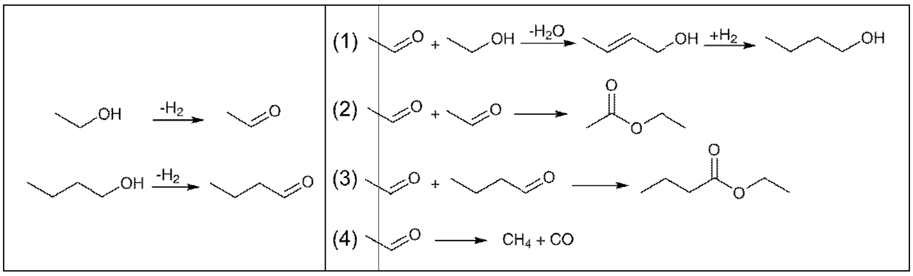
1-Butanol is a bulk platform chemical and a promising gasoline additive [1,2]. Conversion of ethanol to 1-butanol is an important route for ethanol-upgrading reaction. Guerbet reaction is the main pathway of ethanol conversion to 1-butanol [3]. Another pathway of ethanol-upgrading is self-condensation of ethanol [4]. The catalysts for condensation of ethanol include homogeneous Ru and Ir catalysts [5,6] and heterogeneous catalysts, such as hydroxyapatites (HAP) [7,8] and Mg-Al mixed oxides [9,10]. As a kind of metal alkoxide, calcium ethoxide may accelerate the adsorption and reaction of organic matter by the lattice oxygen active sites (base sites). Although there are two pathways for the condensation of ethanol to 1-butanol, the reaction mechanism is still controversial even for the same catalyst. DFT simulations help to understand the microscopic reaction mechanism.

The ethanol reaction was carried out in an autoclave reactor. The liquid and gas products were analyzed by gas chromatography (GC) and GC-mass spectrometry (GC-MS). The solid residuals were analyzed by X-ray diffraction (XRD) and total organic carbon (TOC). DFT simulations were performed using the Gaussian 09.

The main alcohol products are 1-butanol, 2-butanol, 2-pentanol, 2-methyl-3-hexanol and 2-butenol, and other products are 2-pentanone, ethyl acetate, ethyl butyrate and ethyl 2-ethylbutyrate. The maximum ethanol conversion is about 25% with 1-butanol and total alcohols yields of 11 % and 22 %, respectively, at 275-300 °C for 8-10 h. Calcium ethoxide is gradually converted to calcium hydroxide and calcium carbonate during the reaction. The gas product is predominantly H_2, and lower amounts of CH_4, CO and C_2H_4 are also observed. H_2 is derived from the dehydrogenation of alcohol to aldehyde [8,9]. CH_4 and CO indicate decomposition of acetaldehyde [3], C_2H_4 indicates dehydration of ethanol [9]. According to the above analysis, acetaldehyde that generated by dehydrogenation of ethanol may participate in four reactions as shown in Scheme 1. (1) condensation of acetaldehyde and ethanol to 2-butenol, followed by hydrogenation to 1-butanol; (2) disproportionation of acetaldehydes to ethyl acetate; (3) disproportionation of acetaldehyde and 1-butyraldehyde to ethyl butyrate; (4) decomposition of acetaldehyde to CH_4 and CO.



Scheme 1. Ethanol reaction network speculated according to liquid products

DFT simulations show that Ca atom in calcium ethoxide as the Lewis acid sites adsorbs O atom of ethanol to promote dehydrogenation of ethanol to acetaldehyde, and adsorbed state H is easier to be formed than H_2 in the dehydrogenation. For the condensation of acetaldehyde and ethanol to 2-butenol, ethanol and acetaldehyde may adsorb on the same calcium ethoxide or on associated calcium ethoxides. The highest energy barrier of the former route lies on ethanol dehydrogenation and is 288 kJ mol^{-1} (Fig. 1,(a)). The highest energy barrier of the latter route lies on the formation of 2-butenol and is 319 kJ mol^{-1} (Fig. 1,(b)). In addition, the hydrogen source for the hydrogenation of 2-butenol is mainly derived from activated H instead of H_2.

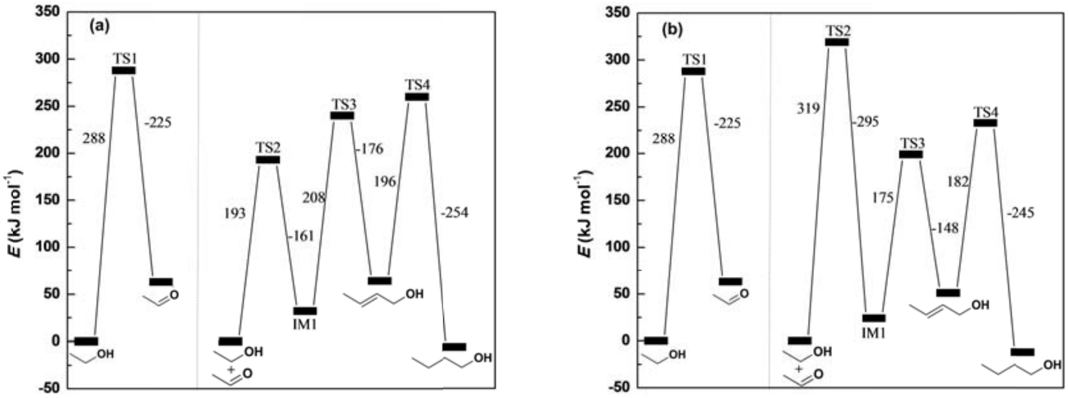


Fig. 1. Potential energy curves of ethanol condensate to 1-butanol. (a) ethanol condensation on one calcium ethoxide; (b) ethanol condensation on associated calcium ethoxides

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PP-34

PALLADIUM-CATALYZED AEROBIC OXIDATIVE CARBONYLATION OF ALKYNES WITH AMINES: A GENERAL ACCESS TO SUBSTITUTED MALEIMIDES

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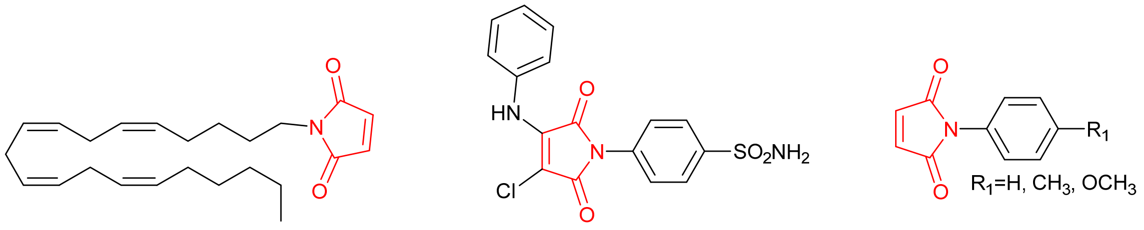
Substituted maleimides represent interesting building blocks which are widely found in bioactive natural products and drug molecules (Figure 1).[1] In addition, this class of compounds are also applied in engineering, natural rubbers, resins, and the aerospace industry.In general, the traditional industrial process for manufacturing maleimides is the reaction of amines with maleic and related anhydrides. However, this methodology is mainly used for the preparation of non- or symmetrically substituted maleimides. Consequently, there is still a need for new procedures to access polysubstituted maleimides.



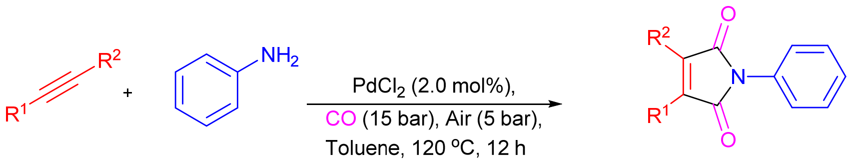
2-Arachidonoyl glycerol (2-AG)

Anti-inflammatory

Inhibited tumor growth

Figure 1. Selective examples of bioactive maleimides

Recently, we and other groups became interested in the oxidative carbonylation of olefins and alkynes.Herein, we report the first general Pd-catalyzed oxidative carbonylation of alkynes with amines in the presence of air for the synthesis of various maleimides in high yields^1.



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PP-35

OXIDATIVE DIMERIZATION OF METHANE TO C_2-HYDROCARBONS

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Global oil reserves are decreasing every day due to the continuous processing of raw materials and the production of valuable chemical materials based on modern technologies. In this regard, much attention is drawn to natural gas as an alternative source of raw materials for petrochemical industries. Ethylene is the main industrial raw material of petrochemical synthesis from which it is possible to receive many products such as polyethylene, polyvinyl chloride and etc. This is primarily due to the low cost of methane compared to other hydrocarbons [1].

La-Ce-Mg catalyst was synthesized by solution combustion method to produce ethylene from methane. Activity of the 20 % $La(NO_3)_3$ + 10 % $Ce(NO_3)_2$ + 20 % $Mg(NO_3)_2$ catalyst was tested in an automated flow installation. Activity of the developed catalyst was investigated by varying the ratio of the initial CH_4/O_2 gaseous mixtures (2/1; 2,5/1; 3/1; 4/1; 5/1), space velocity from 2500 to 7500 h^{-1} at the temperature range from 600 °C to 900 °C.

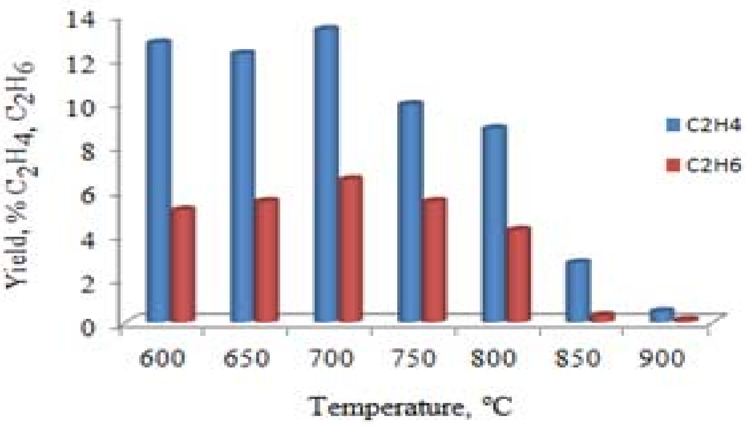

Figure 1. Effect of varying the process temperature on dimerization of CH_4 over the La-Ce-Mg catalyst

It was experimentally found that the optimal ratio of the initial gases for ethylene production is 43 % CH_4 + 17 % O_2 + 40 % Ar at 5000 h^{-1}. Hydrogen and carbon monoxide are formed in addition to ethylene during the reaction at high temperatures (850-900 °C).

Thus, the optimal yield of ethylene and ethane is 13.3 % and 6.2 %, respectively, at a temperature of 700 °C.

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Acknowledgements

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BIOGAS REFORMING OVER Mg-Mn-Ai-Co CATALYST PREPARED BY SOLUTION COMBUSTION SYNTHESIS METHOD

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Around the world, the development of alternative energy in the form of renewable energy sources is very relevant today. It is known that the use of fossil energy emits a large amount of greenhouse gases and it pollutes the environment. Therefore, the need to develop environmentally friendly renewable energy in the form of the use and processing of biogas to synthesis gas is an important step towards improving the environmental situation and the utilization of greenhouse gases to useful chemical products. Reforming methane with carbon dioxide is a modern and promising method of producing synthesis gas from biogas.

The study of the activity of catalysts based on multi-component Mg-Mn-Al-Co system obtained by solution combustion synthesis (SCS). The catalysts were synthesized from nitrates of cobalt, aluminum, magnesium, manganese and urea at the preheating temperature of the muffle furnace to 500 °C. The activity of the developed catalysts was investigated in the process of carbon dioxide methane conversion in an automated flow installation. To study the carbon dioxide conversion of methane into synthesis gas, a mixture of 33 % CH_4 + 33 % CO_2 + 34 % Ar (CH_4:CO_2 = 1:1) gases was used in the temperature range 750-900 °C.

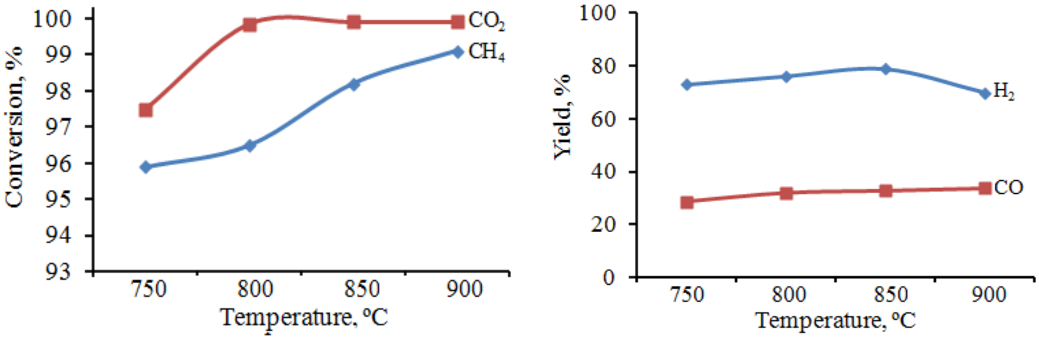

Figure 1. Effect of varying the process temperature on CH_4 and CO_2 conversion and yield of H_2 and CO on the Mg-Mn-Al-Co catalyst

As a result of temperature variation, it was found that the process at 900 °C allows to achieve the highest values of both yield and selectivity for H_2 and CO. Thus, at $W = 860\ h^{-1}$, up to 69.4-70 % H_2, 33.6-33.7 % CO were obtained with selectivity up to 100 % for hydrogen and 97 % for CO, the ratio $H_2/CO = 2$. Under the found optimal reaction conditions, the conversion of CH_4 and CO_2 was 99.1 % and 99.9 %, respectively.

Acknowledgements

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SYNTHESIS OF ACETYLENIC ALCOHOLS IN THE PRESENCE OF DIFFERENT CATALYTICAL SYSTEMS

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For synthesis of acetylenic alcohols selective nanocatalysts of type Et_2O + PhMe + Hex, $TiCl_4/Me_2S$, $Et_3N/Zn(OTf)_2$ and $Cl_2Ti(OPh)_2$ have been used. Synthesis of acetylenic alcohols and their derivatives on the base of secondary raw materials of oil-gas and chemical industries, elaboration of technology of their production, obtain of vitamins, antibiotics, antibactericidic biocides, polymers for high temperatures, cross-linking agents for obtain nanomaterials and their application are very important scientifical trend.

In this investigation synthesis of acetylenic alcohols: 1-(2-phenylethynil)cyclohexanol, 2-methyl-1-(2-phenylethynil) cyclohexanol, 2-izopropil-5-methyl-1-(2-phenylethynil)cyclohexanol and 1,7,7-treemethyl-2-(phenylethynil)-biciclo-[2,2,1]-heptanol-2 on the base off cyclic ketones: cyclohexanon, 2-methylcyclohexanon, mentone and camphor by reaction enantioselective alkynilation by phenylacetylene has been investigated. Influence of nature and quantity of catalysts on yield of products was determined. At synthesis of above-mentioned acetylenic alcohols systems: $Zn(OTf)_2/NEt_3$; 3,3'-Ph_2BINOL-2Li/THF; $MeOH/NH_3/KOH$; $Cs_2CO_3/DMSO\cdot H_2O$; BuLi/KO^{t}Bu/THF were used as catalysts.

By carbonylic group of ketones reactions of addition of different compounds can be carried out in practically nucleophylic addition owing to breaking of connection C=O in carbonylic group of ketones. Electronic density in carbonylic group is mixed to oxygen atom that is on atome of carbon the positive charge has increased and on atome of oxygen-negative harge that is polyarization of carbonylic group has carried out.

Carbon atom of carbonylic group owing to polyarization has acquired electrophilic properties and participates in reaction with nucleophyl reagents. At this negatively charged part of molecule has addited to carbon of carbonilic group and positiv by charged part-to oxygen atom.

It is known that chemical properties of alkynes are determined by nature of triple bond and sp-hybridizations of atoms of carbon. Acid properties alkynes are expressed in higher degree than in alkenes or alkanes, what is coused by strong polyarization of ≡C–H bond. By this reason owing to substitution of hydrogen atom at triple bond alkynes participate in reactions Ad_N and Ad_E. In molecule of phenylacetylene electronical density is mixed from phenyl radical to triple bond and carbon atoms in groups C≡CH and C_6H_5- are in sp and sp^2 hybridisation. Electronic density of π-bond is mobile and induction effect of compounds with π-bond is stronger than in compounds only with δ-bonds. By this reason between choosed ketones camphor easier introduced in reaction with phenylacetylene in presense of above-mentioned ketones. On the base of experimental results it was determined that with increasing of molecular mass, Gibbs energy, quantity of radicals and their branching in cyclical ketones yield of forming acetylenic alcohols has been decreased. Their formation has depended on nature and structure of radicals which are at carbon atom of carbonylic group and at this investigated ketones by their activity can be presented by following raw: camphora < mentone < 2-methylcyclohexanon < cyclohexanon.

Used catalytical systems by their activity in synthesis of acetylenic alcohols can be presented by following raw: $Cs_2CO_3/DMSO{\cdot}H_2O$ < $MeOH/NH_3/KOH$ < 3,3'-Ph_2BINOL-2Li/THF < BuLi/KO^{t}Bu/THF < $Zn(OTf)_2/NEt_3$.

Practical importance of investigation is consisted in that what synthesized acetylenic alcohols have high bacteriostatical and bactericidal properties against microorganisms and also they are inhibitors of corrosion of equipment using in oil-gas industry what is the alternative way of solving environmental problems.

Acknowledgements

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VIRTUAL PRESENTATIONS

CONVERSION OF POLYETHYLENE WASTE TO MOTOR FUELS AND BASIC OIL OVER ZEOLITE CATALYSTS

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During last decades, the population growth together with improving of living standart led to an increase in polymers (mainly plastic) waste. The recycling of polymer waste helps to conserve natural resource because the most of polymer materials are made from oil and gas. A significant part of plastic waste is polyethylene goods with a short lifetime such as variuos packing material, household items, medical accessories, etc. There are two ways to recycle polyethylene waste: mechanical and chemical recycling. In the first case, the polyethylene waste is ground and then reprocessed and compaunded to produce a new component. But this method of recycling usually lead to decrease of product strenght by 15-20 % [1]. In our work we used the most preferred method of chemical recycling.

In the Boreskov Institute of Catalysis has developed a technique of production of fuels and basic oil from polyethylene waste [2]. According this method polyethylene wastes are decomposed by pyrosis over zeolite catalyst at constant pressure. As a result of this decomposition, an unbranched hydrocarbon mixture with boiling point up to 450 °C is formed. In our work we use various kind of polyethylene such as LDPE, HDPE and UMWPE. We found that nature of polyethylene does not affect the ratio between fuel fraction. This ratio depends only on pressure as shown on figure 1.

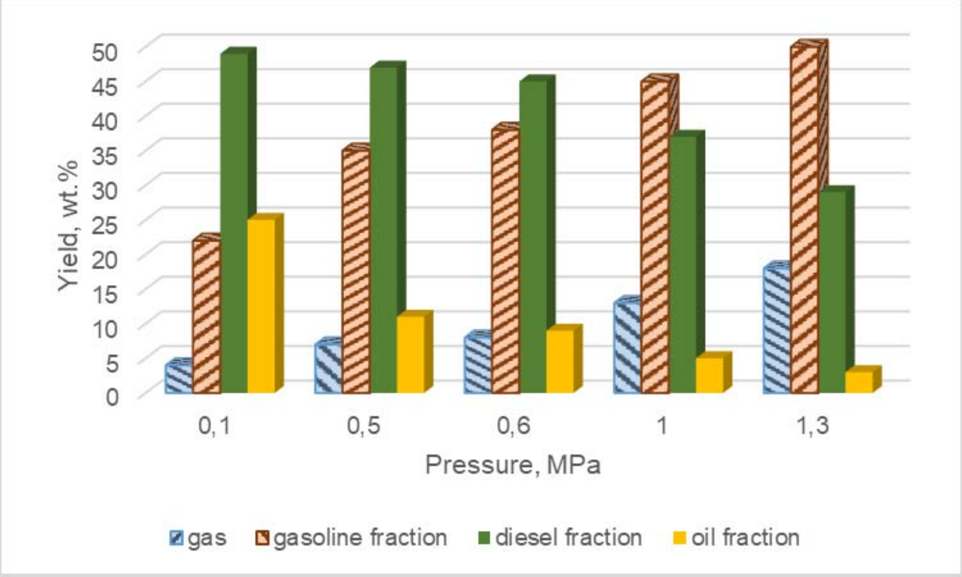

Figure 1. Yields of hydrocarbon fractions as function of pressure

VP-1

We can see that an increase in a pressure decreases of the yield of diesel and oil fractions and increases yield of gas and gasoline. In all cases, the yield of liquid fractions is above 80 % by weight. The obtained fractions cannot be used as a fuels and lubricant due to the high alkenes content up to 45 %.

Gasoline fraction alone or with diesel fraction can be used as a compound of feedstock for production of liquefied petroleum gases, highoctane gasoline and wintergrade diesel fuel by BIMF technology. This one-stage process is performed over MFI structure zeolite catalist not containig noble metals. We found that using the products of polyethylene decomposition in the BIMF process without diluting with gas condensate or crude-oil condensate leads to a significant reduction in time-on-stream of catalyst. The main reason for rapid deactivation of the catalyst is coke deposit due to the high alkenes content. Our research have shown that the most optimal content of polyethylene decomposition products in raw materials of BIMF process is 15-20 % by weight.

Diesel and oil fractions obtained from polyethylene waste are converted into wintergrade diesel fuel and basic oil by hydroisomerization process. Pt or MoC [3] supported on silicoaluminophosphate with SAPO–31 structure is used as catalyst.

As a result, we can produce motor fuel and basic oil components from polyethylene waste and regulate ratio between obtained products by pressure.

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THE CALCIUM HYDROXYAPATITE CATALYTIC ACTIVITY IN THE DEHYDRATION REACTION OF METHYL LACTATE

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Introduction

Acrylic acid (AA) is an important monomer for the production of polymers, the request on polymers based on AA increases annually. In connection with unstable prices for fossil hydrocarbons, the biggest companies form requests for alternative AA technologies in order to be able to diversify production facilities and react in a timely manner to the changing economic situation in the world. The alternative technologies for production of "basic" organic substances, combining a catalytic chemical processes and the fermentation of plant renewable raw materials - is also of interest for countries with limited volumes or access to hydrocarbon raw materials. One of such technologies is the production of lactic acid and its esters by fermentation of plant materials and its subsequent catalytic dehydration in AA or its esters.

In scope of this study was studied the effect of the pH of the solution in the synthesis of calcium hydroxyapatite and the following influence on the activity in the process of dehydration of methyl lactate. The catalytic activity of the following samples was investigated [1]: $Ca_{10}(PO_4)_6(OH)_2$ (CaHAP) - pH = 7, pH = 9, pH = 11, for control, pH was used 35 % w ammonia water solution.

Experimental part

Investigation of the catalyst systems were carried out in a vertical cylindrical reactor with a fixed catalyst bed 10 cm^3 at atmospheric pressure in a nitrogen stream, at temperatures ranging 360-410 °C and a contact time of 0.5 to 1.5 second, ML mixture was fed to the reactor with water in a weight ratio of input 20/80.

Experiment duration was 4 hours, with an interval analysis of the reaction mixture in 1 hour. The product composition was determined using GC and HPLC. Activity of catalysts were evaluated for ML conversion (X_{ML}, wt. %) and the selectivity to AA (S_{AA}, wt. %), which was determined by the amount of acrylic acid formed by the dehydration reaction.

After each experiment, the catalyst was regenerated by feeding air at 480 °C temperature for 40 min. During regeneration, all samples recovery their initial catalytic properties.

Results

The data are presented in the table below for samples synthesized in the range of pH = 6-11, show a strict relationship between the pH of the solution and the conversion of ML, with increasing pH there is an increase in the conversion of ML. The dependence of the AA selectivity of on the pH of the solution has a maximum in the region of pH = 8–9, and the maximum selectivity for AA is achieved (S_{AA} = 37 %).

Samples	Contact time, s	Temperature, °C	X_{ML}, wt. %	S_{AA}, wt. %
CaHAP-6	1	370	42.0	18.0
CaHAP-7			78.0	34.0
CaHAP-9			77.0	37.0
CaHAP-11			94.0	21.0

Additionally, all synthesized samples (CaHAP) show stable activity (ML conversion and AA selectivity) throughout the experiments without loss of activity.

Conclusions

The study of the catalytic activity of calcium hydroxyapatite in the reaction of dehydration of ML to AA, showed that the optimum pH of the synthesis of this salt is in the range of 8-9. Additionally, calcium hydroxyapatite did not lose its catalytic activity throughout all experiments. In future need try to use different cation combination like in our previously theses [2] with pyrophosphates, for increase AA selectivity.

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DRY REFORMING OF METHANE OVER Co-CONTAINING CATALYSTS

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In the twenty-first century, humanity is faced with the global problem - climate change of the Earth as a result of growth of greenhouse gas concentrations in the atmosphere [1]. Humanity feels action of greenhouse effect now. Currently, seven of the ten disasters are climate-related. According to estimates by the Intergovernmental Panel on Climate Change (IPCC), by the year 2050 relocation will affect 200 million people as a result of climate impacts. Seriousness of the problem has forced representatives of practically all governments of the world, including Kazakhstan, sign the Kyoto Protocol on limiting and partial reduction of greenhouse gas emissions. Progress in gas chemical technologies can play a crucial role in solving the problem. Huge contribution to reducing greenhouse gas emissions can give catalytic conversion of associated and refinery gases. The catalytic processing of carbonaceous feedstock into valuable end products to produce synthesis gas which is further used for the production of hydrocarbons and oxygenated compounds, according to a process known as GTL is the most promising method for processing [2]. Synthesis gas is generally recognized alternative of oil energy source and raw material for basic organic and petrochemical synthesis. There are several catalytic technologies for producing synthesis gas of different compositions, such as steam methane reforming (SMR), partial methane oxidation (POM), autothermal reforming (ATR) and dry reforming of methane (DRM). DRM is of particular interest because it allows you to simultaneously dispose of two greenhouse gases - methane and carbon dioxide. The main problems of DRM are the low activity of catalysts and their instability to carbonization [3], as a result of which they lose their effectivity. Nickel catalysts are the most widely studied for these reactions, their main advantage is low cost [4]. However, the main problem with nickel catalysts is the rapid deactivation due to the formation of coke. Therefore, there is still an open question on the development of an active and resistant to carbonization catalyst for the carbon dioxide conversion of methane.

In this work, we studied the influence of the nature of carriers, oxides of transition elements, and the method of catalyst preparation on the direction of dry reforming of methane. The comparative influence of methods for the preparation of cobalt catalyst on its effectivity in the studied reaction was investigated. Catalyst 15 wt. % Co_2O_3/ γ-Al_2O_3 catalyst was prepared by the method of solution combustion. The "solution combustion" method is one of the variants of self-propagating high-temperature synthesis [5]. The synthesized catalysts were dried at 300 °C (2 hours) and calcined at 500 °C for three hours. Testing the activity of the carriers and the synthesized catalysts in the dry reforming of methane was carried out on a flow-type laboratory unit. Process conditions: 0.1 MPa, the temperature was set in the range of 650-900 °C, the ratio of $CH_4 : CO_2 = 1:1$, the volume of catalyst in the reactor was 2 ml. The physicochemical properties of the cobalt containing catalyst were investigated by the methods, X-ray analysis, SEM and BET.

Carriers of various nature (θ-Al_2O_3, γ-Al_2O_3 and 4A, 13X, HY, HZSM-5) are investigated in the DRM reaction. The most effective in the reaction of DRM was γ-Al_2O_3, methane conversion of 20 %. The getting results show that the activity of carriers in the process of DRM depends on their specific surface. The effect of the preparation method on the activity of 15 wt. % Co_2O_3/γ-Al_2O_3 in the DRM to synthesis gas has been investigated. It has been shown that the preparation of a cobalt catalyst by the “solution combustion” method increases the efficiency of the catalyst in the conversion of methane and carbon dioxide by increasing the dispersion of the catalyst. Under the reaction conditions: $CH_4 : CO_2 = 1 : 1$, GHSV = 1500 h^{-1}, $T_r = 700$ °C on a 15 % Co_2O_3/Al_2O_3 catalyst, synthesized by the “solution combustion” method, methane conversion is 95 %, carbon dioxide conversion is 98 %, H_2 / CO ratio = 1.1.

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THE DEVELOPMENT OF BIFUNCTIONAL CATALYSTS BASED ON SAPO MOLECULAR SIEVES FOR SINGLE-STAGE PRODUCTION OF LOW POUR POINT DIESEL FUELS FROM VEGETABLE OILS

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One-dimensional medium-porous materials with SAPO-11, SAPO-31 and SAPO-41 structures proved to be good catalysts for the conversion of hydrocarbons due to the combination of their crystal lattice properties and moderate acidity [1-5]. The purpose of the given work was to develop a catalyst based on SAPO for single-stage production of low pour point diesel fuels from vegetable raw materials.

The effect of silicon on the size and morphology of crystals silico aluminophosphates, their chemical composition, adsorption and acidic properties is shown with the use of the complex of physico-chemical methods. The influence of the degree of SAPO-31 crystallinity and of the properties of the binding material on the adsorption and acid characteristics of the samples is demonstrated. The effect of the nature of the metal, the method of its application to the acid component, and the conditions for thermal pretreatment of the catalyst on its activity and stability is determined. The method of optimal and effective distribution of the modifying hydro-dehydrogenating component with the necessary dispersion of particles is found. The optimal conditions for the process of hydroconversion of vegetable oil into low-setting diesel fractions (T = 340 °C, and P = 2.0 MPa, WHSV = 1.3 h^{-1}) are determined.

It is shown that the crystal structure of the silicalyminophosphate has a significant effect on the catalytic properties of the bifunctional catalyst for the conversion of plant raw materials. Catalysts based on silicalyminophosphate with SAPO-11 structure, modified with Pd or Pt have very low activity in the conversion of sunflower oil and soybean oil. As a result of the reaction, a mixture of carboxylic acids is formed. Bifunctional catalysts based on silicalyminophosphate with the structure of SAPO-41 modified with Pd or Pt, allow obtaining a mixture of diesel fraction hydrocarbons at the initial moment of the reaction; however, after 6 hours only a mixture of carboxylic acids is formed.

The most effective catalyst for the hydroconversion of vegetable oil into a low pour point diesel fraction is the bifunctional catalyst based on SAPO-31 with

$SiO_2/Al_2O_3 = 1$ and crystal size of 500-800 x 30-100 nanometers, with a metal component deposited on their surface (preferably Pt), with a dispersion of >40 % and with particle size of 2-2.5 nm, which demonstrated very stable catalytic properties (Fig. 1). The average output of the diesel fuel fraction in terms of the missed raw materials during the development of the diesel fuel fraction sample, according to the results of the 48-hour test run of the catalyst, was 76.5 % by weight, which is 94 % of the theoretically possible yield of hydrocarbons. The pour point of the accumulated diesel fuel fraction was <-58 °C, and the turbidity temperature was -17 °C.

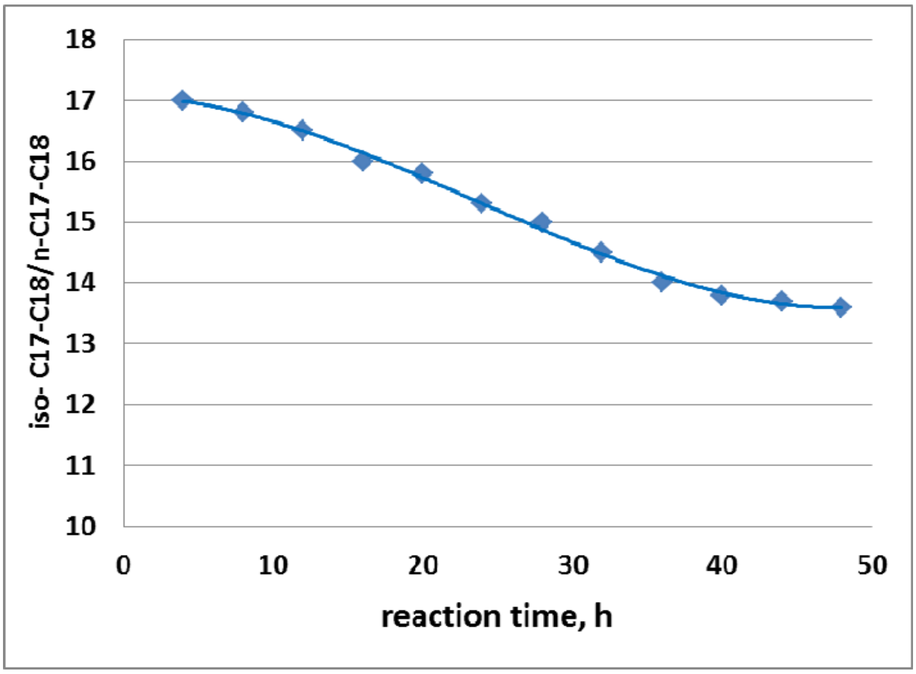

Fig. 1. Change in the ratio of iso-C17+C18/n-C17+C18 in the products of vegetable oil conversion depending on the time of the experiment

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NANOPHASE Co-CONTAINING CATALYSTS, SYNTHESIZED BY THE SOLUTION COMBUSTION METHOD

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The rapid growth of deep refining of oil and gas, as well as coal gasification, which we are now observing, would not have been possible without the development and emergence of new catalytic processes. The widespread use of catalysts contributes to progress to a greater extent, it is they who help turn low-grade raw materials into high-quality products. The main consumers of the catalyst are the oil refining industry, petrochemical, chemical, ecology and environmental protection, etc.

Currently, one of the most important problems of petrochemical and gas chemistry is the production of liquid hydrocarbons by the method of Fischer-Tropsch. Upon receipt of a liquid fuel based on Fischer-Tropsch synthesis (FTS), various carbon compounds are converted into synthesis gas, and then it is converted into synthetic "crude oil". This is a mixture of hydrocarbons, which during subsequent processing is divided into various types of practically environmentally friendly fuel, free from impurities of sulfur and nitrogen compounds. It is enough to add 10 % of artificial fuel to conventional diesel, so that the combustion products of diesel fuel become compliant with environmental standards [1]. Currently, as catalysts for the FTS, depending on the tasks, both highly dispersed iron catalysts supported on oxides of aluminum, silicon and magnesium, and cobalt catalysts are used. According to the latest data, the specific activity of cobalt catalysts is higher than that of iron [2]. Despite the large number of works, there is no single point of view on the nature of the influence of the carrier, the active phase, the preparation method, and the conditions for activating the catalyst for FTS. In the development of effective catalysts for the FTS, the determination of the mild conditions of the preliminary activation of catalysts is of great importance [3]. Therefore, research in this direction remains relevant. The purpose of this work was to study cobalt-containing catalysts in the FTS with the definition of favorable conditions for the preparation and activation of cobalt catalysts. Testing of the activity of cobalt-containing catalysts in the conversion of synthesis gas was carried out in a flow-through installation under the conditions: P = 6 atm, Tr = 200-300 °C, the ratio $H_2/CO = 2/1$. The analysis of the products and the source gases was carried out on a chromatograph "Chromos 1000". Cobalt containing catalysts were prepared by the method of "solution combustion". The "solution combustion" method is one of the variants of self-propagating high-temperature synthesis [4]. The physicochemical characteristics of the catalysts were studied by the methods H_2-TPR, SEM and BET. The study of cobalt containing catalysts in the FTS made it possible to establish optimal conditions for the activation of cobalt containing catalysts. The most favorable modes of activation of cobalt catalysts are: the activation temperature in a stream of hydrogen is 300 °C, the reduction time is 30 minutes. When a mixture of $H_2/CO = 2/1$ is converted on a cobalt-containing catalyst with REE additives, at a reaction temperature of 300 °C and a pressure of 6 atm, methanol, ethanol, and dimethyl ether are formed as liquid products (10-15 vol. %). The results of H_2-TPR showed that the synthesis of cobalt-containing catalysts using the “solution combustion” method leads to a decrease in the catalyst reduction temperature, as compared with the impregnation method. According to the results of SEM and BET, the preparation of a cobalt catalyst by the “solution combustion” method leads to an increase in the dispersity of the catalyst; in the composition of the catalyst, nanophases with sizes of 10-50 nm are observed. The specific surface of the catalyst rises from 166 to 171 m^2/g.

The obtained data can be used in the development of new promising catalysts for the FTS, which do not require a special stage of high-temperature reduction with hydrogen.

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BIFUNCTIONAL ZEOLITIC CATALYST FOR BUTANOL PRODUCTION FROM BIOETHANOL

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In recent years, there is a growing trend towards replacement of fossil fuel renewable biofuel both in fundamental and applied science. Since global bioethanol production by fermentation constantly increse it is often used as an additive to conventional fuel. Unfortunately, ethanol has several significant drawbacks that limit its further use as a fuel: low energy density, hydrophilicity, corrosion and equipment damage. Butanol, in contrast to ethanol, has significant advantages and can be a potential biofuel. In this case, the problem lies in the requirment for a simple and effective method of butanol production from renewable ethanol. This transformation could be accomplished through well-known Guerbet dimerization of ethanol in presence of heterogeneous and homogeneous catalysts. Over solid catalysts this reaction is rather complex and involves several consequitive stages: 1) ethanol dehydrogenation to ethanal, 2) condensation of ethanal to crotonal, 3) hydrogenation of crotonal to butanol with H2 or by transfer hydrogenation with ethanol itself. A set of heterogeneous catalysts described in the literature have significant drawbacks such as low activity and selectivity, so the development of the optimal catalyst continues.

Bifunction catalysts containing both metal hydrogenation/dehydrogenation component and acid component shows high selectivity towards butanol [1]. The aim of the present study was to elucidate the bifunctional metal-doped zeolite catalysts in ethanol-to-butanol transformation and to highlight key reaction parameters.

Zirconium-containing aluminium-free BEA zeolite (Zr-BEA) was prepared by direct hydrothermal synthesis in fluoride media. Palladium was introduced as metal component by incipient impregnation. Ethanol conversion was studied in fix-bed reactor at 235 °C in WHSV range 0.5-2 h^{-1}. Ethanol undergoes two primary reactions over Pd/Zr-BEA: bimolecular dehydration to diethylether and dehydrogenation to acetaldehyde. Optimal Pd content coresponds to ca. 1 % wt.

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VP-7

STUDIES OF THE EFFECT OF THE ACTIVE PHASE STATE OF Cu-CONTAINING Zr-Al OXIDES CATALYSTS IN ETHANOL DEHYDROGENATION REACTION

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The use of ethanol seems to be the most promising long-term solution of some ecological problems since ethanol is can be transformed in to fuel or chemical value products, is absolutely harmless and is easily obtained from bio-organic masses. However, existing catalytic systems show unsatisfactory reaction yields or are too expensive for production [1-3].

Copper catalysts that extensively used in environmental catalysis reactions seem to be promising for ethanol conversion. Among wide variety of materials that has been developed as catalyst supports mixed oxide of ceria, zirconia and alumina should be paid attention as they have good structural characteristics and thermal stability and have several applications in heterogeneous catalysts [4-7]. In this study we investigate the effect of the amount of copper and supports composition on catalytic performances of 5 % $Cu/ZrCeO_2–Al_2O_3$ in ethanol dehydrogenation.

The systems of mixed oxides supports (20 % Al_2O_3–80 % $ZrCeO_2$, 50 % Al_2O_3–50 % $ZrCeO_2$, 75 % Al_2O_3–25 % $ZrCeO_2$) were undergone with surface modification of 7-20 wt % Cu. Oxide supports were obtained by the sol-gel method at final synthesis temperature T = 950 °C with the following Cu impregnation from an aqueous solution. Catalytic activity of the systems was studied in a model reaction of the conversion of ethanol in the temperature range of 240-400 °C in a flow-through catalytic installation with gas chromatographic analysis of the products. The physical and chemical properties of the catalysts were further studied by XRD, low-temperature adsorption of N_2 and electron microscopy. To describe the state of copper EXAFS and XANES-spectroscopy were also used.

Catalytic systems demonstrated ethanol dehydrogenation up to 85 % with 100 % selectivity in acetaldehyde. The experiments revealed that the composition of oxide supports and the amount of copper strongly effects on the structural characteristics. Thus, a change in the physic-chemical and structural characteristics of the $Cu/ZrCeO_2–Al_2O_3$ systems depending on the composition and changes of the structure of copper particles formed depending on copper amount and supports composition lead to the formation of catalytic centers with different nature and changes of their number. Additionally, correlation of copper particles characteristic and the number of active site provide with opportunity to predict the structure of active site and the reaction mechanism.

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MODELING OF BIO-OIL CATALYTIC CRACKING REACTIONS IN HYDROCARBON MEDIUM

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A steady decrease in raw hydrocarbon reserves and industrial carbon dioxide accumulation in the atmosphere forces researches to develop alternative ways to obtain energy and petrochemical feedstock. Nowadays the most promising replacement for conventional oil is biomass. Herewith with biomass refining a new task rises to develop an approach to process byproducts of such process: technical grade glycerol, acetone etc. As shown in [1] one of the perspective methods to convert oxygen containing compounds to value added products is their mutual catalytic cracking with hydrocarbons. However today for authors' knowledge systematic studies concerning this approach are still lacking in scientific literature.

The goal of the present research is a systematic study of mutual catalytic cracking of model compounds: acetone, representing one of the classes of bio-derived compounds, and C_6 hydrocarbons representing each of the classes of organic hydrocarbon compounds – n-hexane, hexane-1, cyclohexane, benzene. Conversion of reagents was conducted as pure substrates and as hydrocarbon-acetone mixtures (95:5 mass ratio) in the presence of Y and ZSM-5 containing catalysts. Catalytic experiments were carried out on laboratory unit with stationary catalyst bed at 500 °C. Different conversion levels were achieved via catalyst to feed variation. Detailed study of occurring substrate reactions was carried out via *in situ* FTIR spectroscopy at temperature of 400 °C.

Resulting data from catalytic experiments indicated mutual effect of acetone and hydrocarbon medium on their cracking reactions. A change in molar selectivity to gaseous products derived from acetone is observed: carbon dioxide selectivity is decreased from 32 to 13 % mol., whereas C_3 hydrocarbon products selectivity is increased nearly three times from 20 to 56 % mol. In turn, addition of acetone changes the composition of primary and secondary products of hydrocarbon cracking. This effect is indicated by a change of conversion curves extrapolated to zero conversion: the ratio of saturated to unsaturated products is decreased nearly two times in the presence of acetone. According to data obtained by *in situ* FTIR spectroscopy (Fig. 1) in hydrocarbon medium absorption lines of acetone dimers (1705, 1600-1640, 1355 cm^{-1}) typical to pure acetone conversion disappear instead, a dramatic increase in intensity of alkenes absorption lines (1170, 1290, 900 cm^{-1}) is observed. Also a change in structure of acetone intermediates is observed: in case of pure acetone conversion R_3O^+ cations are detected (lines 1190-1230 cm^{-1}) which are referred to acetone molecules protonated by zeolite acid centers. Addition of hydrocarbon medium leads to shift of mentioned lines to higher frequencies (1300 cm^{-1}) which indicates a change of substitutes in R_3O^+ cations.

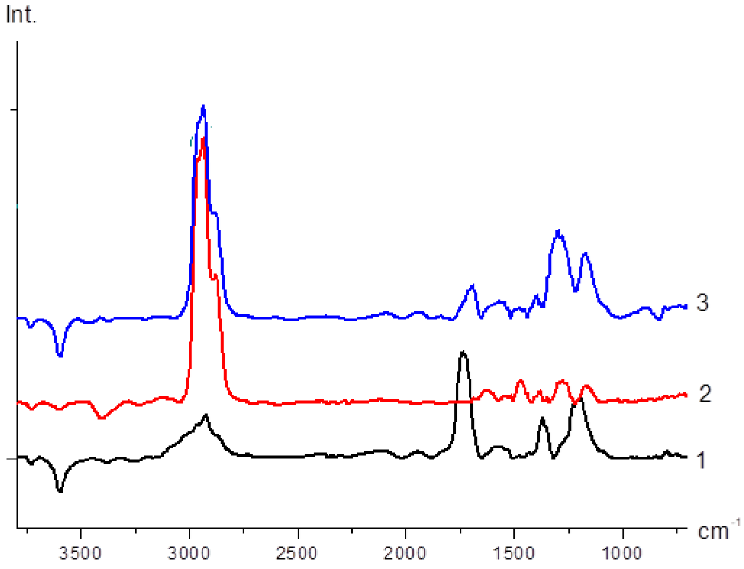

Fig. 1. Spectra obtained by *in situ* FTIR spectroscopy during conversion of model compounds in the presence of zeolites: 1 – acetone; 2 – hydrocarbon; 3 – acetone-hydrocarbon mixture

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VP-9

PHOTOACTIVE COTTON FABRIC MODIFIED WITH TiO_2 FOR EFFICIENT DEGRADATION OF VOC AND DNA CONTAMINANTS

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Currently, the self-cleaning materials in forms of coatings, paints, cements, fabrics, filters and other products are actively being used in many areas of human activity. The self-cleaning effect is related to the removal of impurities or to the degradation of adverse chemical and biological agents on the surface of material and can provide an enhancement in the operational characteristics of the product made from this material. In the former case, this effect can be attributed to easy removal of mechanical and chemical impurities (e.g., dirt, spot, dust) due to (super)hydrophilic or, oppositely, (super)hydrophobic properties of the material surface.

Another appearance of self-cleaning effect is the degradation of biological and chemical agents. Well-known materials in this field are the antimicrobial fabrics modified with special additives (e.g., Ag and Cu ions), which promote the death of microorganisms and provide permanent protection against bacteria and molds. This effect can also be achieved via the modification of fabrics with a photocatalyst, which can provide the oxidative destruction both biological and chemical agents. Under irradiation, the photocatalyst is capable to decompose molecular and supramolecular micropollutants by their oxidation in oxygen-containing mediums. In the field of photocatalytic oxidation, TiO_2 with the crystal structure of anatase is regarded as the most active and stable photocatalyst.

The self-cleaning fabrics produced from natural or synthetic fibers are in focus of research interest, because they can clean own surface from impurities and pollutants, possess filtering and adsorption properties, and can be used as textiles to produce personal protective clothing (e.g., suites, coats, overalls). The development of active and stable textile materials modified with a photocatalyst is an important task in this field.

In this study, we synthesized the textile materials via the fixation of TiO_2 nanoparticles on the surface of cotton fibers using two compounds, titanyl sulfate and titanium isopropoxide, which are also the precursors of TiO_2. In contrast to titanium alkoxides, titanyl sulfate is much cheaper and can be easily dissolved and hydrolyzed in water mediums without organic solvents, but a little information on the application of titanium inorganic precursors for the preparation of photocatalytic textiles can be found in the papers. The effect of titanyl sulfate and titanium isopropoxide precursors on the activity and stability of cotton fabric modified with TiO_2 was investigated. Additionally, TiO_2 doped with nitrogen was used as a photocatalyst to extend the photocatalytic activity of the materials to the visible region. As a result, the strategy to produce high-active phototextiles was formulated.

The synthesized materials were tested in the degradation of harmful volatile organic compounds and human genomic DNA under UV and Vis irradiations. The results showed the potential of photoactive fabrics to produce personal protective clothing for working with harmful heteroatomic compounds, because the materials can be neutralized during long-term treatment with UV or Vis light followed by washing with water. Another potential area for the application of photoactive textiles is self-cleaning materials for the medical and biochemical labs. Here, we present for the first time the results on the degradation of DNA contaminants, which was studied using a PCR technique. For the evaluation of DNA degradation, the initial cotton and synthesized materials were polluted with a model DNA object and irradiated using UV and Vis light. No substantial effect of the irradiation on the threshold cycle value during the PCR analysis was observed for the initial cotton that indicates the stability of DNA object, which was selected for these experiments. For the cotton fabric modified with TiO_2, the threshold cycle value was increased as the irradiation time was increased that confirms the degradation of DNA over photoactive textiles under irradiation. The level of DNA concentration on the surface of cotton sample modified with TiO_2 after the irradiation for 180 min was reduced by 510 times compared to the level for cotton fabric. Therefore, the synthesized textile materials may be used for the degradation of DNA contaminants in the biochemical labs to reduce to probability of false-positive responses during the PCR analysis.

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VP-10

QUANTITATIVE ANALYSIS OF LIQUID-PHASE ADSORPTION OVER METAL-ORGANIC FRAMEWORKS Cr-MIL-100 AND Cr-MIL-101

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Introduction

Metal-organic frameworks (MOFs) are a class of crystalline porous hybrid materials assembled by bonding of metal ions or clusters linked with polydentate organic molecules. Well-ordered tunable porous structures with a wide range of pore size and exceptional textural properties make MOFs perspective candidates for a variety of practical applications, including separation, catalysis and gas adsorption/storage.

Cr-MIL-101 and Cr-MIL-100 consist of Cr_3O-carboxylate trimers bridged by anions of trimesic and terephalic acid, respectively [1, 2]. These MOFs show fairly good resistance to moisture, air, thermal treatment, common solvents, and possess promising catalytic properties. For example, Cr-MIL-101 was found to catalyze allylic oxidation of with molecular oxygen under mild conditions [3], and both Cr-MIL-100 and Cr-MIL-101 were able to catalyze hydrocarbon [4] and alcohol oxidation [5] with *tert*-butyl hydroperoxide, an environmentally benign oxidant. These are important chemical processes that are usually carried out in industry using hazardous oxidants and homogeneous catalysts. Developing a clean catalytic process with recoverable heterogeneous catalysts is an important challenge.

Adsorption of reagents and products on the catalyst surface is an essential part of heterogeneous catalytic reactions. Since most reactions catalyzed by MOFs are liquid-phase processes, characterization of liquid-phase adsorption over MOFs is necessary for understanding their catalytic properties.

Results

Both Cr-MIL-100 and Cr-MIL-101 were synthesized according to published protocols [1, 2]. Their structure was supported by X-ray diffraction and N_2 adsorption measurement. Excessive adsorption of cyclohexanone, cyclohexanol, *tert*-butanol and styrene over Cr-MIL-100 (101) from *n*-hexane was measured at room temperature. Under the assumption of monolayer adsorption, observed adsorption equilibrium constants were calculated. One for styrene does not depend on its concentration in the liquid phase. In contrast, observed adsorption equilibrium constants for oxygen-containing compounds strongly depend on their concentration. It was assumed that oxygen-containing compounds possess a different affinity to the metal centers and organic linkers within MIL framework. Indeed, while oxygen-containing compounds may form relatively strong coordinative bonds with chromium centers, their interaction with the organic framework of Cr-MIL *via* Van-der-Waals forces is relatively weak. On the other hand, styrene is not supposed to form coordinative bonds with metal centers which make MIL surface energetically homogeneous toward it.

A statistical model developed using assumptions above allows good fitting of the experimental data. It was found that the equilibrium constant of adsorption of oxygen-containing compounds over chromium centers is $1\text{-}2\cdot10^3$ and one for organic linkers is 2-9. These values support the hypothesis that the interaction of oxygen-containing compounds with metal centers is stronger than one with linkers. Additionally, the equilibrium constant of styrene adsorption is 4, which is close to values obtained for adsorption of oxygen-containing compounds over the organic part of MIL framework.

Finally, competitive adsorption of *tert*-butanol and cyclohexanone over Cr-MIL-101 was measured and the observed equilibrium constant was calculated. The obtained value of *tert*-butanol – cyclohexanone exchange equilibrium constant, 0.7, is close to one obtained from the individual adsorption data (0.8) and to one calculated *via* DFT (0.6) for adsorption on the metal centers. All these facts also support the proposed adsorption model.

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