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Synthesis and properties of sulfur-containing multigrade additives for lubricants

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Sulfurized derivatives of hydrocarbons occupy a key segment in the field of lubricants owing to their excellent extreme pressure, antifriction properties on friction surfaces and ability to improve antioxidant properties. Despite the fact that sulfur carriers have been used for about 100 years, discussion about their structure and properties depending on the nature of feedstock and synthesis condition is still conducted. There are a lot of differences in the substantiation of reaction mechanisms, structure of by-products and their dark color, unfavorable eco-toxicological characteristics of substances with petrochemical origin.

The goal of this paper is synthesis of sulfur-containing surfactants based on renewable herbal raw materials, study of their structure and properties and creation of eco-friendly lubricants.

For this goal we have defined and addressed tasks as follows:

- We have developed new eco-friendly, energy and resource-saving methods of sulfurization of the oils and products of their chemical transformation.
- We have proved the structure and explored properties of synthesized products depending on the reagents correlation and conditions of the sulfurization. It was shown that dark color was a result of side reaction – hydrogen substitution in double bonds with formation of conjugated systems and chromophoric sulfur derivatives such as thioketones and thiophenes.
- We have proposed accelerants of sulfurization and chemical methods of synthesized products modification. It was shown that dithiacarbamates improve reaction conditions, and amides of guanidine protect copper against corrosion.
- We have created lubricants with improved eco-toxicological and operating abilities. It was proved that created lubricants surpass the national analogues and are not inferior to the international eco-friendly lubricants which have the ‘Blue Angel’ degree.

UDC 547.854.5+54.057

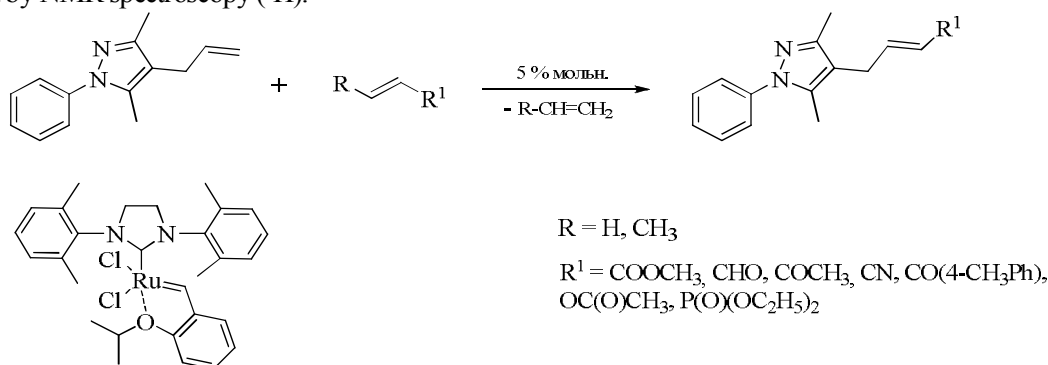
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The 1-phenyl-3,5-dimethyl-4-allylpyrazole functionalization via cross-metathesis reactions

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It was shown that 1-phenyl-3,5-dimethyl-4-allylpyrazole can be transformed via cross-metathesis to the new functionalized unsaturated pyrazole derivatives with different functional groups (ester, nitrile, carbonyl, phosphonate). It should be noted that these reactions were carried out using ruthenium containing Grubbs third generation catalyst (Grubbs-Hoveyda) (5 mol. %) in dry dichloromethane (0.5 N solution) at 41 °C for 12 hour. All new products were purified by column chromatography and the yields of obtained compounds ranged between 40–80 %. The structures of the new pyrazole derivatives were verified by NMR spectroscopy (¹H).



Grubbs-Hoveyda catalyst

According to prognosis of biological activity derived using Program “Prediction of Activity Spectra for Substances”, the cross-metathesis products obtained may be an anti-inflammatory agent, an insulysin inhibitor, a 5-O-(4-coumaroyl)-D-quinat 3'-monooxygenase inhibitor, a CYP2J substrate, a HMGCS2 expression enhancer.

UDK 628.38; 577.20

High temperature organic waste thermal decomposition under induction heating

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Today, it is extremely important for Ukraine to minimize its own energy dependence. The extensive use of renewable biological materials, or even better – organic waste, by means of creation of modern technologies of home processing is a promising way to provide consumers with high-energy fuel.

Fast thermal decomposition may form the basis of an effective way to obtain fuel from biomass, which according to the International Energy Agency is currently one of the cheapest methods. The main feature of rapid thermal decomposition, compared with the traditional, or slow decomposition, is a very high heating rate of particles of raw materials and rapid cooling of products.

The practical result of work has been the high temperature thermal decomposition of hydrocarbon wastes with receipt of combustible gases in a laboratory setup using induction heating reactor.

It was found that gases received as a result of high-temperature thermal decomposition of raw materials at temperature of 1100 °C exhibited a high content of hydrogen (30–50 %), carbon monoxide (24–42 %), methane (5–10 %) and carbon dioxide (16–28 %). Using recirculation mode of derived gases we can receive an additional amount of hydrogen and carbon monoxide, with the decrease of carbon dioxide concentration 2-3 fold.

The resulting ash after the process of high temperature thermal decomposition, which is represented by a number of inorganic oxides (a share of which varies depending on the type of raw materials from 0.5 to 50 %), is suitable for use in road construction; it is possible to fractionate the components and enable the soil to maintain mineral balance of plants.

Effective additives for pour point decreasing of biodiesel fuels

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The disadvantage of biodiesel fuel is its low temperature properties. The most undesirable components in the biodiesel fuel from this point of view are esters of stearic and oleic acids which have relatively high pour points (PP).

A range of methods can be used for low temperature property improvement of biodiesel fuel: mixing with oil diesel; adding low components (alcohols); adding esters of polyunsaturated fatty acids (FA); removing high temperature crystallizing components; etherification of unsaturated bonds molecules of FA; hydroisomerization of FA esters molecules; epoxidation of double bonds of FA esters molecules and, finally, use of cold flow additives.

Effective cold flow additive should have a branched structure and the same part of molecule as the high temperature crystallizing component molecules. Thus, the branched esters molecules of tristearate triethanolamine (TSTEA) and trioleate triethanolamine (TOTEA) were synthesized.

The efficiency of additives synthesized has been investigated over methylolate and ethyl and butyl esters of rapeseed oil in amounts from 0.05 to 1.0 wt. %. The best results obtained were: for methylolate PP decrease from -20 to -37 °C (TSTEA) and to -32 °C (TOTEA); for ethyl esters of rapeseed oil PP decrease from -15 to -33 °C (TSTEA) and to -29 °C (TOTEA); for butyl esters of rapeseed oil PP decrease from -19 to -23 °C (for both TSTEA and TOTEA). Low efficiency of the tested additives in mixture with FA butyl esters requires further investigations in search for different (polymer) nature additives or new combinations of additives.

Wasteless technology of waste processing – step to sustainable development

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Wasteless technology of waste processing is the only way to sustainable development of society. Thus, such technology should be integrated. It should allow full waste utilization in a variety of ways to produce a number of technical products.

The scheme of sludge processing aeration plants that are optimized for both organic and mineral components in marketable products was proposed. The scheme included such lines: 1. Preparation line; 2. Artificial organic soils and organo-mineral fertilizers manufacture line; 3. Briquette and/or pulverized fuels manufacture line; 4. Thermal recycling of sediments at fast heating conditions line; 5. Line for purification of gas obtained from different impurities in order to use it as a marketable product; 6. Electricity and thermal energies production line; 7. Line for mineral constituents (ash residue) recycling into marketable products; 8. Line for construction and road materials manufacture from ash residue (original ash residue and/or residue after fractionation); 9. Line for ash residues preparation such as cement addition; 10. Coagulant preparation line. The presence of one or another line in the scheme is determined primarily by the need to receive the appropriate final product.

We have scrutinized each stage of the proposed sludges processing scheme in the laboratory environment. The combination of these stages in one cycle or simultaneous utilization of organic and mineral components of the sludge indicate the proposed wastelessness of technology.

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The mechanism of conversion of aqueous suspension of brown coal under supercritical conditions

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Comprehensive experimental study was carried out for the conversion of an aqueous suspension of brown coal from Alexandria coalfield (Ukraine) under supercritical pressure. The reciprocal gaining interaction of the components of the system of “brown coal – water – mineral matter” owing to the formation of associates was shown. The latter ones corresponded to ion-dipole interaction “mineral cation – water” and the former – to dipole-induced and dispersion interactions “water – organic matter of coal”. The organic matter of coal was mainly gasified to carbon dioxide, hydrogen and methane. Mineral matter of coal reacts with supercritical water to deposition of the solid phase following the solution saturated with products of dissociation. It was established that the source of oxygen in the gaseous products of the supercritical conversion of lignite in the temperature range of 330–450 °C was chiefly ion-associative nanocluster water. The source of hydrogen for the subcritical temperatures is organic matter of lignite. The source of hydrogen for the supercritical region is water with ionic associates. Adding of acid catalysts to the reactive zone at supercritical temperature permits to involve organic oxygen to the transformation twice stronger. Alkaline catalysts improve the transition of hydrogen from water and mineral matter into the gas phase. The proposed mechanism of supercritical conversion of aqueous suspension of lignite is based just on the experimental results and requires further kinetic and quantum-mechanical calculations.

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Zeolites and Earnshaw's theorem

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Today zeolites are well-known and widely investigated adsorbents and catalysts. At the same time, the authors have not come across any papers that considered zeolites as a system of point charges and employed Earnshaw's theorem for the analysis. This theorem claims that the system of point charges in stable equilibrium on the final distance cannot get minimum of potential energy. Absence of such approach is a substantial omission in zeolite theory.

In the present work zeolites are considered as a system of point charges and Earnshaw's theorem is employed for the analysis of data on ammonia thermoprogrammed desorption (TPD) over acid forms of zeolites.

Significant data scattering was detected on two samples of zeolite X with different proportion of Brønsted and Lewis acid sites in experimental investigation of ammonia thermoprogrammed desorption. The fact that ammonia became associated with cations (low temperature maximum of TPD) and protons (high temperature maximum) suggested that cations were not strictly fixed in the definite positions of zeolite structure with minimum of potential energy. However, they demonstrated high mobility in the intervals between the experiments. At the same time, protons demonstrated considerably lower mobility. Thus cation migration was confirmed by ammonia TPD method over samples investigated. Such cations migration would provide the stability of zeolite structure according to Earnshaw's theorem.

Acid-base nanocatalysts for hydrolysis of fructose

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Acid-base nanocatalysts were synthesized by interaction of heteropolyacids ($H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$) with lysine. Transmission electron microscopy study has confirmed that $H_3PW_{12}O_{40}$ /Lysine formed separate particles with sizes of 3–5 nm, while $H_3PMo_{12}O_{40}$ /Lysine formed dendritic structure with primary particles about the same sizes. FTIR spectroscopy showed that there was deformation of Keggin ions both in the structure of acid-base nanocatalysts and in nanocatalysts included inside of hybrid nanocomposites. FTIR spectrum of lysine was absent in samples of nanocatalysts because of strong interaction with heteropolyacids.

Activity of synthesized nanocatalysts was tested in hydrolysis of fructose to 5-hydroxymethylfurfural (5-HMF) in an aqueous solution. Without any catalyst, the temperature dependence of fructose conversion to 5-HMF in the aqueous solution has extreme character with the maximum at 180 °C. With our synthesized acid-base nanocatalysts, both in initial forms and included inside of hybrid nanocomposites, hydrolysis of fructose to 5-HMF proceeded at the temperatures 105–120 °C. These results are very promising for practical application.

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Synthesis and biological testing of azoles and azines derivatives as furin inhibitors

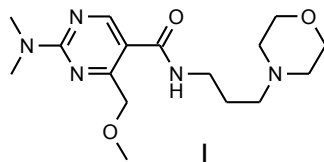
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Furin, as a multidomain calcium-dependent serine enzyme, belongs to the family of proprotein convertase subtilisin/kexins. In addition to normal physiological functions it plays an important role in the initiation and development of disorders such as cancer, cardiovascular pathologies, obesity, diabetes, neurological and cognitive dysfunctions, viral and bacterial infections, abnormalities in the reproductive and bone calcification processes. Therefore, furin is a promising target for development of new medication to combat various human illnesses. Discovery of the new effective and specific inhibitors of this enzyme helps to solve many biochemical, therapeutic and clinical problems.

In the present study we have searched for efficient non-peptide furin inhibitors in series of novel derivatives of azines and azoles which contained a positively charged group in the structure. The most active compound was found to be 2-(dimethylamino)-4-(methoxymethyl)-N-(3-morpholin-4-ylpropyl)pyrimidine-5-carboxamide (**I**) which reduced enzyme activity by mechanism of competitive inhibition ($K_i = 105 \mu\text{M}$).



We studied the influence of the nature of the substituent and structural modifications of azoles and azines on their efficacy as furin inhibitors. It was shown that the inhibitory activity of synthesized pyrimidines escalated with the increase in length and hydrophobicity of the substituent at 5-position. The similar effect was observed among the derivatives of azoles which contained the hydrophobic group at 2-position.

For higher inhibitor efficiency we are going to design structurally modified derivatives with two or more positively charged groups.

Key words: furin, inhibitors of furin, azines, azoles

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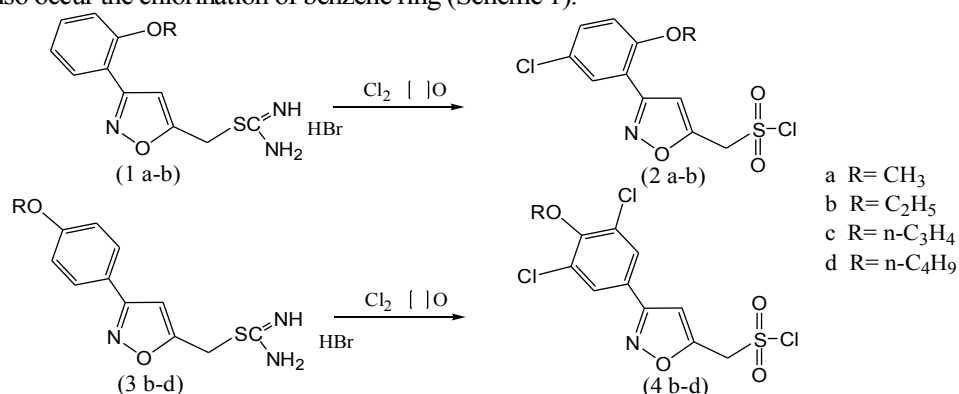
New pyroline containing 3-(chloroaryl) sulfonamides of isoxazoles by ring-closing metathesis reactions

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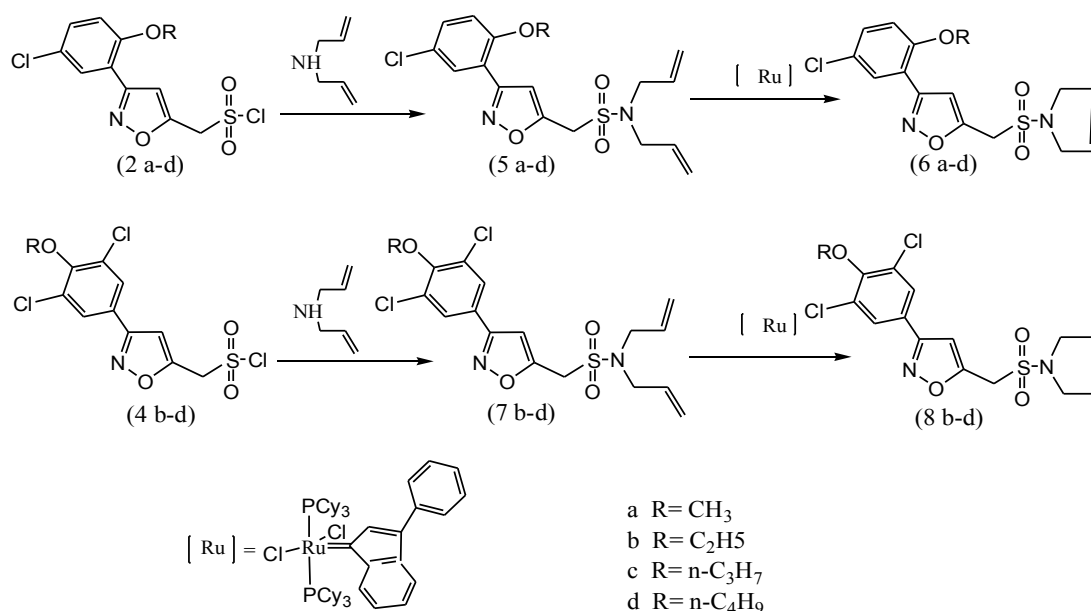
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Isoxazoles are a class of heterocyclic compounds with a wide range of pharmacological activities. Many of them found practical application as commercially available pharmaceutical drugs. Thus, the substances with high antiretroviral activity were discovered among 3-(chloroaryl), 5-sulfonamides of isoxazoles. The position of the incorporated halogen had a marked effect on the antiretroviral activity.

We found that under the oxidative chlorination of isotiuronium salts (1 a-d, 3 a-c) along with the formation of sulfonylchloride group, also occur the chlorination of benzene ring (Scheme 1).



The new 3-(chloroaryl) containing diallyl sulfonamides (5 a-d, 7 b-d) were obtained by the interaction of sulfonylchlorides (2 a-d, 4 b-d) with diallylamine in the presence of the base. They were subjected to the ring-closing metathesis reaction under influence of 1 mol % [Ru] catalyst (Scheme 2).



The new pyroline containing sulfonamides of isoxazole series (6 a-d, 8 b-d), with one or two chlorine atoms in benzene ring were obtained in high yields. The structure of all new substances was confirmed by elemental analysis and NMR ^1H spectroscopy.

Resolution of contradiction stemming from temperature-programmed desorption of ammonia experimental data generalization as base of creation of new knowledge

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The simplest models of electrostatic bonds in zeolites use ideas of point electrostatic charges [1]. In XIX century S. Earnshaw proved the theorem, which read that no system of charged particles can be in stable static equilibrium in the absence of external forces [2, 3]. But, the stability of zeolites during virtually unrestricted time period is well-known. Therefore, one has to find approaches that will agree with Earnshaw's theorem and will be able to interpret the stability of zeolite systems.

The first approach, which consists in assumption that the possibility of disappearance of distance between point charges, presented by negative charges of alumin-oxygen tetrahedra and positive charges of compensating cations, is unrealistic. The second approach involves the possibility of cations motion as factor, stabilizing the zeolite structure.

Two batches of drastically different dependences, interpreted as ones caused by cations motion, were obtained over the base catalyst using method of temperature-programmed desorption of ammonia. Such motion is just a factor, which according to Earnshaw's theorem stabilizes the zeolite structure as a system of point charges.

1. Rabo Jule A., *Zeolite chemistry and catalysis*, Washington, ACS Monograph, 1976.
2. Earnshaw S., *Trans. Cambr. Philos. Soc.*, 1842, V7, 97–112.
3. Jones W., *Eur. J. Phys.*, 1980, 1 (2), 85–88.

Conversion of the aqueous suspension of brown coal under supercritical conditions

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The conversion of aqueous suspension of lignite (Alexandria coalfield, Ukraine) in sub- and supercritical water fluid medium with acid-base and redox catalytic additives was investigated for energy-dense fuels used for heat and power generation, and synthesis gas used for the production of motor fuels and organic products. Oxidation of coal-water slurry in fluid medium in the temperature range of 200–450 °C and pressure of 23 MPa showed the possibility of conversion of lignite in flammable liquid (1.5–2.0 %) and gas (15–20 %) and non-combustible liquid phase containing hydrated ash and solid residues of non-convertible inorganic and organic materials. The addition of NaOH and Ca(OH)₂ of 5 and 10 % wt. to the 30 % of coal-water slurry allowed to increase the total conversion of coal. The highest yields of liquid (up 5.8 %) and gas (up to 40–48 %) of combustible products were obtained in the presence of Ca(OH)₂ (10 %) under the conditions of 450 °C. The total conversion of organic matter of coal increased to 52–55 %. Introduction of the coal-water slurry solid catalysts with acidic properties (industrial alumina-nickel-molibdenum and γ -alumina) for supercritical conditions reduced the overall conversion of organic matter to 25–30 %. The resulting combustible gases have composition (% vol.) H₂ – 45–76, CH₄ – 9–30, CO₂ – 16–25 and contain no sulfur compounds.

Antimicrobial polymeric films based on bacterial cellulose

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New promising antimicrobial material has been obtained by impregnation of bacterial cellulose (BC) hydrogel with low toxic polymeric biocide polyhexamethylene guanidine hydrochloride (PHMG-Cl). FT-IR analysis of BC/PHMG-Cl composites confirmed a sufficient saturation of the BC-matrix with PHMG-Cl and the formation of hydrogen bonds between chloride ions of the polymeric biocide and the hydroxyl groups of BC. AFM images revealed the formation of an interconnected network of fibre bundles within BC-based composite after the introduction of PHMG-Cl. The modified BC film specimens were challenged with multidrug resistant strains *Staphylococcus aureus* and *Klebsiella pneumonia* IMBG233, the phytopathogenic *Xanthomonas campestris* pv. *campestris* IMBG299 and *Pseudomonas syringae* pv. *tomato* DC3000, as well as yeast strains and showed excellent efficacy against these microbial species. The biocide release rate from BC matrix was shown to depend on the water content of the composite films and had the lowest value for dry films.

PHMG-Cl-embedded bacterial cellulose is promising low cost material for medical applications, particularly as dressing material for wounds healing.

Spectroelectrochemical behavior of 3-methylthiophene and 3,4-ethylenedioxythiophene copolymers

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Intrinsically conducting polymers (ICP) owing to their unique complex of chemical and physical properties are promising materials for usage in different high tech systems like batteries, supercapacitors [1], sensors [2], electrochromic devices [3], etc. Poly(3-methylthiophene) (P3MT) and poly(3,4-ethylenedioxy-thiophene) (PEDOT) are among the most perspective and studied ICP because of their stability, perfect spectral properties, high conductivity and charge mobility.

We used electrochemical copolymerization of 3-methylthiophene (3MT) and 3,4-ethylenedioxythiophene (EDOT) to synthesize ICP combining spectral properties of P3MT with charge transport properties of PEDOT.

The copolymerization was performed in a dry 0.1M LiClO₄ solution in acetonitrile with total concentration of both monomers 0.05 M at four feed 3MT:EDOT ratios 1:9999, 1:999, 1:99, 1:9 and with each monomer individually. The process was realized under cyclic voltammetry mode (CVA) in the potential range from -700 till 1400 mV vs. Ag/Ag⁺, with the reference electrode located on the transparent ITO electrode. It was found that a potential of the electrochemical copolymerization process decreased when the EDOT concentration in the reaction mixture increased.

The synthesized copolymers were studied by CVA, spectro-electrochemical measurements, UV-Vis and IR-spectroscopy. In particular, it was proved that the copolymer backbone contains both 3MT and EDOT units with the ratio which depends on the feed ratio of the monomers in the polymerization mixture and on the electrochemical conditions. Based on CVA measurements it was shown that the copolymers were highly stable even during 100 cycles in the range of -700 ÷ 850 mV.

Spectroelectrochemical behavior of the electrodeposited copolymer films was studied in the potential range of -500 ÷ 800. It was shown that the increase of the EDOT content in the feed ratio caused increase of the time of the spectroelectrochemical response under the films oxidation. At the same time, under the films oxidation, the response time was practically proportional to the EDOT content in the feed ratio that well agrees with the CVA data.

1. Arbizzani C., Mastragostino M., Meneghello L., *Electrochimica Acta*, 1996, (41), 21.
2. Janata J., Josowicz M., *Nature Materials*, 2003, (2), 19.
3. Yildirim A., Tarkuc S., Ak M., Toppare L., *Electrochimica Acta*, 2008, (53), 4875.

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Hydrothermal conversion of feldspar

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The disadvantage of lignite gasification for energy purposes is incidental formation of ash, which consists of products converted from a number of minerals: quartz, pyrite, zeolites, gypsum, feldspars, calcite, biotites, garnets and other. The formation of ash could be reduced due to the transformation of the mineral matter to soluble form followed by its separation. This way has been the subject of our research.

Potassium feldspar (orthoclase) was chosen as a model of mineral matter. Model reaction medium-solvent was water at supercritical fluid state ($T_{cr} = 374\text{ }^{\circ}\text{C}$, $P_{cr} = 22.1\text{ MPa}$). Orthoclase was loaded to the supercritical conversion reactor operated as dynamic autoclave under conditions: $t = 330$ and $425\text{ }^{\circ}\text{C}$, $P = 25\text{ MPa}$. Conversion of orthoclase was 11.84 % with dissolution rate of 248 mg/hr. Product of transformation was divided in the separator into liquid and solid phases. A material balance of 72 hours of operation showed the mass converted into solid product of 17.84 g. The permissible weight loss was 7.29 %. Elemental analysis, performed by non-destructive X-ray fluorescence (EXPERT 3L), indicated a decrease in K, Si and Fe compared with the raw feldspar. Thus minerals reacted with supercritical water with solids and planting saturated solution of dissociation products. In particular, at $300\text{ }^{\circ}\text{C}$ K^+ , AlO_2^- and silicon hydroxide penetrated the solution from orthoclase. For supercritical temperature of $425\text{ }^{\circ}\text{C}$ an ion exchange included iron cations to form a flaky precipitate. This suggests that the natural mineral matter of lignite can be exposed to transformation during hydrothermal gasification under supercritical conditions.

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Phenomenon of mechanochemical activation of CLM-U catalyst under condition of low temperature methanol synthesis

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Methanol is one of the main products of petrochemical synthesis. The current world industrial production of methanol is over 100 million tons per year. Modern ways of improving the process of methanol synthesis are aimed at eliminating deficiencies of used copper-containing catalysts (high catalytic sensitivity to poisons, overheating and gradual decontamination during the operation), increasing their activity, operating time, simplification of operating conditions and improved reactor designs and increase in efficiency of use of such catalysts.

One of the alternative ways to increase catalyst activity might be the use of force of mechanical effect. According to literature resources, catalyst mechanical activation *in situ* during the reaction assists the surface regeneration of catalyst and releases it from the hard deposits and coke.

In the submitted paper the influence of different methods of mechanical activation (stroke and offset) of industrial catalyst CNM-U on its performance and specific catalytic activity in the methanol synthesis at atmospheric pressure was studied. It was established that activity indicators of the catalyst which had been activated *in situ* by mechanical stroke subject to the availability of effective supplements, are significantly higher than the corresponding results obtained in the case of catalyst activation under mechanical offset. The use of mechanical methods of catalyst activation reduces the temperature of initiation and optimal temperature of synthesis reaction by 20–30 $^{\circ}\text{C}$. Catalyst productivity obtained by activating *in situ* at temperature of 220 $^{\circ}\text{C}$ and pressure of 0.1 MPa, are close to the results obtained under production-line conditions at a temperature of 220 $^{\circ}\text{C}$ and pressure of 9.0 MPa. Results of the study show that mechanical activation of the catalyst is a promising step towards simplification of the process of methanol synthesis.

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New nitrogen-containing thiacalix[4]arenes

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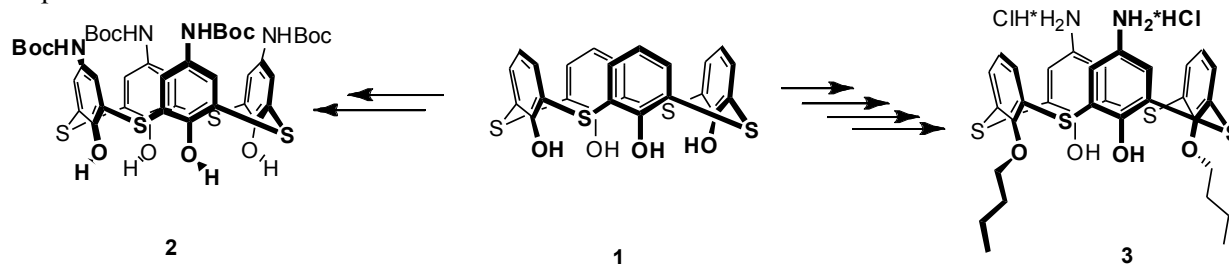
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Thiacalix[4]arenes, due to their unique spatial structure and functionalization possibilities of the upper and lower rims, are widely used in the synthesis of substances with practically useful properties [1, 2], especially complexants and extractants of radionuclides and rare earth metals.

In this paper we synthesized imidazolium and pyridinium task-specific ionic liquids containing metallocoordinating thiacalixarene groups in cationic or anionic part of the molecule.

Convenient methods of total or partial functionalization of the upper rim of thiacalixarene **1** by amino groups have been developed.



Diaminodibutoxythiacalixarene **3** and tetraaminotetrahydroxythiacalixarene **2** are promising building blocks for design of biologically active compounds and complexing metals.

1. Kumar R., Lee Y., Bhalla V., Kumar M., Kim J., *Chem. Soc. Rev.*, 2014, (43), 4824–4870.

2. Morohashi N., Narumi F., Iki N., Hattori T., Miyano S., *Thiacalixarenes. Chem. Rev.*, 2006, (106), 5291–5316.

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Nanostructured motor fuel – problems and prospects

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The reliability and efficiency of the machinery largely depend on the stability, as well as antiwear and anti-friction properties of the oil and lubricants being used. While doing the research of the exomodified fullerenes as additives to the motor fuels it was found out the simultaneous change in antioxidant capacity, tribological and other macrophysical characteristics depending on the concentration of the additive. We have examined physical-chemical model, in which a simultaneous change in these properties is stated by means of supramolecular solvated clusters (domains).

There are no published data on the effect of various additives on the nanocarbon lubricating properties of engine fuels. Apparently, wide practical use is limited because of the poor solubility of nanoparticles in low-viscosity liquids, as well as the high price of fullerenes.

We have synthesized and selected multilayer nanoscale carbon clusters with improved solubility in hydrocarbon fuels and future-proof ethanol based fuel. By means of chemical modification of the nanoparticles was created the additive, which is a solvatozol made of multilayer nanoscale carbon clusters – onions (CNOs), solvated by the solvent molecules.

Antiwear properties were tested with three types of fuel: I – high-octane oil petrol AI-95, II – biofuel E-85, III – biofuel E-85 with the nanoscale spherical clusters CNOs additives.

Assessment of the wear rate of the fuel pump was made basing on the change the operating pressure at the outlet of the fuel pump depending on the test duration. It has been found out that while operation on biofuel with the additive the fuel pump wear level is less than the wear level of pump with high-quality gasoline fuel AI-95 or with biofuel without the additive. The test of fuel pumps was performed during 80 hours in a specially designed bench thermostat.

Determination of antiwear properties of fuel was carried out in the Research Laboratory of nanotribotechnology of National Aviation University (Kyiv).

Thus, this additive made on the basis of spherical carbon nanoclusters, allows considerably improve stability and tribological characteristics of motor fuels and greatly reduce the wear of the fuel equipment.