ABSTRACT AND REFERENCES

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SYNERGISM OF STABLE NITROXYL RADICALS AND AMINES DURING THE OXIDATION PROCESS OF MOTOR FUELS AND OILS AT INCREASED TEMPERATURES (p. 4-9)

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The alkylphenol Mannich bases (N-(4-methylphenyl)-N,N-bis-(3,5-di-tert-butyl-4-hydroxybenzyl)amine, N,N-dibenzyl-N-(3,5-di-tert-butyl-4-hydroxybenzyl)amine and tris-(3,5-di-tert-butyl-4-hydroxybenzyl)amine), which are promising antioxidants for fuels and lubricants, were synthesized by condensation of 2,6-di-tert-Butylphenol with formaldehyde and amines (n-toluidine, dibenzylamine and ammonia). Mannich bases also were synthesized by condensation of alkylphenols with diethylenetriamine.

The induction periods of the fuels and lubricants oxidation on the example of the vaseline oil at a temperature of 200 °C were determined by the method of oxygen absorption for the obtained Mannich bases and stable nitroxyl radicals (in particular 2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl and di-(2,2,6,6-tetramethyl-1-oxyl-4-piperidyl)isophthalate). It was found that in the case of the inhibited oxidation of hydrocarbons of fuels and lubricants, even at high temperatures (~200 °C), there is also a synergetic effect of stable nitroxyl radicals with the nitrogen-containing compounds, including the alkylphenol Mannich bases, which have –NH or β-CH< groups in relation to Nitrogen. So, the obtained results confirm the perspectiveness of the alkylphenol Mannich bases usage as the high-temperature oxidation inhibitors for fuels and lubricants (motor fuels and oils).

Keywords: Mannich base, additive, additives to fuels and lubricants, antioxidant, stable nitroxyl radicals.

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RESEARCH INTO ESTERIFICATION OF MIXTURE OF LOWER DICARBOXYLIC ACIDS BY 2-ETHYLHEXAN-1-OL IN THE PRESENCE OF p-TOLUENSULFONIC ACID(p. 10-16)

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Regularities of esterification of the mixture of lower dicarboxylic acids (succinic, glutaric, adipic) by 2-ethylhexan-1-ol in the presence of catalysts – p-toluensulfonic and sulfuric acids under non-stationary conditions were studied. It was found that in the presence of mineral acid, the reaction flows at a lower rate. Application of benzene as a substance that facilitates separation of water, formed in the esterification reaction, makes it possible, due to a lower reaction temperature, to decrease energy consumption of the process at an increase in conversion of dicarboxylic acids from 95.8 to 99.5 %. It was shown that the use of activated carbon of different brands simultaneously with catalysis by p-toluensulfonic acid with virtually the same effectiveness can decrease chromaticity intensity of esterification products by more than three times. The use of finely dispersed activated carbon 208CP and DCL 200 compared with coarse-grained activated carbon BAU-A additionally provides higher intensity of esterification reaction due to improvement of removal of water from the reaction mixture. It was found that an increase in the content of activated carbon DLC 200 by more than 0.3 % by weight in the reaction mixture contributes to a sharp decrease in the process intensity. This influence is explained by neutralization of a part of the catalysts by alkaline components of activated carbon, which decreases its active concentration and inhibits the reaction. Optimum conditions of the esterification process were proposed. The authors determined dependences of density and kinematic viscosity of the mixture of diesters of succinic, glutaric and adipic acids, and 2-ethylhexan-1-ol, separated from the esterification reaction products, on temperature and described them with regression equations.

Keywords: esterification, lower dicarboxylic acids, 2-ethylhexan-1-ol, p-toluensulfonic acid, diesters.

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ESTABLISHING OPTIMAL CONDITIONS FOR CATALYTIC OBTAINING OF ALLYL-1,3,4-TRIMETHYLCYCLOHEX-3-ENCARBOXYLATE (p. 17-25)

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Kinetics of the reaction of the catalytic cyclic addition of 2,3-dimethylbuta-1,3-diene and allyl methacrylate by the Diels-Alder reaction was studied. Reaction rate constants $k=0.9\cdot10^{-3}$ l/(mol·s) at T=303 K; $k=1.6\cdot10^{-3}$ l/(mol·s) at T=313 K; $k=2.3\cdot1^{-3}$ l/(mol·s) at T=323 K; $k=2.9\cdot10^{-3}$ l/(mole·s at T=333 K and the activation parameters of the reaction E_{akt}=32.6 kJ/mol, ΔS=–203.7 J/(mol·K), ΔH=30.0 kJ/mol were determined. Influence of temperature, molar ratio of reagents and catalyst on the yield of the target product was investigated. At temperature increase from 303 to 333 K, ATMCGC yield increases from 58 % to 76 %. With further increase in temperature, DMB boils and AMA remains in a liquid state, accordingly it is not expected that the target product yield will materially increase. An increase in the excess of DMB:AMA=from 1.5:1 to 4:1 makes it possible to increase yield of ATMCGC from 54 % to 76 %. According to decreasing of the catalytic activity in the reactions of [4+2]-cyclic addition of DMB and esters of acrylic acids, the catalysts are placed in an order: $Ag_{n.p.}>Cu_2Cl_2>Pd_{n.p.}>Au_{n.p.}$.

At the established optimal conditions of catalytic production of allyl-1,3,4-trimethylcyclohex-3-enecarboxylate are: temperature of 323–333 K and molar ratio of reagents DMB:AMA=4:1 in the presence of $Ag_{n.p.}$ catalyst (0.25 % mol), the yield of ATMCGC reaches 72–76 % at productivity of 111–117 g/(l/h). Based on the obtained reaction rate constants and the activation parameters of the catalytic [4+2]-cyclic addition of 2,3-dimethylbuta-1,3-diene and allyl methacrylate, it was found that the reaction under study is subject to the kinetic law of the second order.

It was established that in the presence of Agn.p. catalyst, the reaction of [4+2]-cyclic addition of 2,3-dimethylbuta-1,3-diene and esters of acrylic acids proceeds through a two-stage mechanism with the initial stage of formation of a catalytic complex which activates the reaction by reducing its energy barrier by 44 kJ/mol.

The synthesized alkyl esters of alkylcyclohexenecarbonic acids have the ability of polymerization and can be used as a raw material for preparation of polymeric materials, compositions and hyper plasticizers for concrete mixtures. Polymer compositions made with allyl-1,3,4-trimethylcyclohex-3-enecarboxylate are recommended for manufacture of contact lenses and artificial crystalline lenses.

Keywords: 2,3-dimethylbuta-1,3-diene, allyl methacrylate, allyl-1,3,4-trimethylcyclohex-3-enecarboxylate, Diels-Alder reaction.

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INVESTIGATION OF COPPER ADSORPTION ON NATURAL AND MICROWAVE-TREATED BENTONITE (p. 26-32)

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The research studied the removal of copper ions from simulated wastewater by adsorption on natural and simulated with microwave electromagnetic radiation bentonite (EMR-stimulated bentonite). X-ray diffraction was employed to study the structure of the natural bentonite, which was proved to contain hydromica, montmorillonite, quartz, and chlorite. The maximal removal rates of Cu^{2+} were 20.5 % and 29.1 % for natural and EMR-stimulated bentonite, respectively.

The experimental data of copper adsorption were fitted with theoretical isotherms (Langmuir, Freundlich, Redlich-Peterson, Toth, and Langmuir-Freundlich) using non-linear modeling. The adsorption on natural bentonite followed the Langmuir model, while the Langmuir-Freundlich model fitted the adsorption on EMR-stimulated bentonite. The isotherms were used to calculate the maximal adsorption capacities, which were 11.82 and 25.74 mg/g for natural and EMR-stimulated adsorbents, respectively. The electromagnetic treatment stimulated the formation of the new adsorption sites, improved the pores structure, and influenced the surface charge. The specific adsorption and surface precipitation were involved in the adsorption on EMR-stimulated adsorbent.

Keywords: modified clays, microwave radiation, wastewater purification, adsorption modeling, non-linear modeling.

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DEVELOPMENT OF MATHEMATICAL MODEL OF METHANE OXIDATION ON FIBROUS CATALYST (p. 33-40)

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Using the experimental and numerical methods, the kinetics of deep methane oxidation on a fiber-like oxide catalyst with honeycomb structure is studied. ALSIFLEX-KT1600 fibers are used as a carrier, and spinel (% of mass) is used as a catalytic contact: $MgAl_2O_4$ – 22.07 %; NiO – 2.02 %; Cr_2O_3 – 3.49 %. Si+SiO2 adhesive – 18.97 % and organic glue – 1.72 are used to impart a stable honeycomb structure.

To complete the numerical analysis of kinetic data, a complete two-phase mathematical model is developed. The microchannel model is adopted as a basis. This model is characterized by the equality of the total area of the cross-sections of the microchannels and the area of the free section of the catalyst, and the total surface area of heat and mass transfer is equal to the specific surface area of the catalyst.

As a result of the work, the values of similarity, mass and heat transfer coefficients, the effective working surface of the catalyst, participating in the heterogeneously catalytic reaction of complete oxidation of methane S_w=7640±150 m^2/m^3 are calculated.

The experimental kinetic data of methane oxidation on the catalyst have been confirmed by mathematical calculations, a refined microkinetic equation has been derived, the flow areas of the process have been established, and the performance of the synthesized catalyst has been established.

Keywords: methane oxidation, specific surface, Runge-Kutta method, fibrous catalyst.

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RESEARCH INTO EFFECT OF PROPIONIC AND ACRYLIC ACIDS ON THE ELECTRODEPOSITION OF NICKEL (p. 41-46)

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Nickel coatings are widely used in machine-building, electronics, automotive and aerospace industries. High requirements for environmental safety and operational performance of contemporary processes of electrochemical nickel plating predetermine the search for the new electrolytes. Electrolytes based on carboxylic acids are characterized by high buffer properties, ecological safety, and enhanced values of limiting current. Heuristic approach when fabricating comprehensive electrolytes, based on empirical data, does not make it possible to conduct predictable optimization of the formulations of nickel plating electrolytes. Solving this problem seems possible when using a quantum-chemical simulation. In this work, we performed quantum-chemical calculations for the propionate and acrylate complexes of nickel. It was established that coordination numbers of the propionate and acrylate complexes of nickel are equal to five and six, respectively. It is shown that electroreduction of the propionate nickel complex proceeds with the formation of an intermediate particle. The negative charge of this particle is localized on the intrasphere molecules of water. This may lead to the electroreduction of the latter and to an increase in the pH of a near-electrode layer. In the intermediate particle of the acrylate complex, localization of the charge occurs on the vinyl fragment of acrylate-ion. Electrochemical reaction of reduction of the coordinated water molecules in such a particle is not energetically favorable. It was established that the isolation of nickel from the acrylate complex proceeds with lower kinetic difficulties than from the propionate complex. An assumption was made that fewer insoluble hydroxide nickel compounds, which block the cathode surface, form in the acrylate electrolyte.

Such an assumption is based on the fact that given close buffer properties of acids, electroreduction of the acrylate complexes does not imply the involvement of coordinated water molecules in the electrode process. The results obtained are very valuable for selecting the nature of carboxylic acid as a component for the complex nickel plating electrolyte.

Keywords: electrodeposition, quantum-chemical simulation, propionic acid, acrylic acid, monosubstituted nickel complexes.

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STUDY OF THE SORPTION AND DESORPTION PROCESSES OF SULFITES ON THE ANION-EXCHANGE REDOXITES (p. 47-52)

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At present, one of the promising methods for conditioning natural waters is the stabilization that employs redoxites based on the ion-exchange materials. This method of water treatment makes it possible to significantly reduce corrosion aggressiveness of water. The use of modified cationites and anionites enables a more efficient process of purification, helps reduce economic expenses in the operation of water treatment equipment.

We investigated dependence of sorption capacity of the high-base anionite in the salt form AB-17-8 for sulfites on the starting concentration of the latter in a solution. It is shown that sorption is determined by the concentration factor. Thus, at an increase in the concentration of sodium sulfite to 10 %, the anionite capacity increases to 4,200 mg-equiv./dm^3.

When using weakly-acidic anionites in the salt form and basic form (Dowex Marathon WBA and AMBERLITE IRA 96), the sorption capacity of ionites for sulfites increases with an increase in the concentration of solutions and reaches 5,000 mg-equiv./dm^3.

We estimated effect of the concentration of chlorides, sulfates in water, which is fed for deoxygenation, on desorption of sulfite-anions form the high-base anionite AB-17-8 and the low-base anionite Dowex Marathon WBA. It is demonstrated that during filtration of solutions of chlorides and sulphates with different concentration the washout of sulfites occurs through the given anionites. Therefore, to prolong the time of use of the obtained redoxites, modified with sulfites, it is recommended to utilize desalinated water or water with an insignificant content of anions.

Keywords: deoxygenation of water, redoxite, modification of ionites, water conditioning, anionite, sodium sulfite.

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OBTAINING SYNTHESIS-GAS BY THE STONE COAL STEAM CONVERSION USING TECHNOLOGY OF AEROSOL NANOCATALYSIS (p. 53-58)

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We investigated technology for converting coal into synthesis-gas under conditions of aerosol nanocatalysis and substantiated its expected benefits. They include a reduction in temperature, an increase in the rate of reactions as a result of mechanochemical activation of the catalyst and coal. The experiments were performed in a rotating reactor. A distinctive feature of a given reactor is that it rotates in the vertical plane (in contrast to reactors with a fluidized layer and a vibro liquefied layer). The increase in temperature increases the yield of hydrogen and carbon monoxide. We showed an increase in the ratio of CO:H$_2$ caused by temperature. If we compare the new process to the steam conversion of methane, which proceeds at 800–900 °C and at 2–2.5 bar, then the examined process of coal steam conversion using aerosol nanocatalysis proceeds stably at 600–700 °C and at 1 bar. The difference between yields of products at different load of coal and at varying water feed rate is due to the influence of change in the molar ratio of the utilized raw materials on a change in part of certain reactions in the total quantity of reactions that occur during this process. The process of stone coal steam conversion is typically conducted at temperatures 1,000–1,100 °C. In a given work, the temperature is much lower, by 350–450 °C. This particular pattern is the advantage of carrying out this process using the technology of aerosol nanocatalysis.

Keywords: aerosol nanocatalysis, mechanochemical activation, synthesis-gas, steam conversion, catalytic system.

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PLASMA-CHEMICAL FORMATION OF SILVER NANODISPERSION IN WATER SOLUTIONS (p. 59-65)

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The application of plasma discharges of different methods of generation is an innovative, environmentally safe and promising method of synthesizing silver nanodispersions. The efficiency of using the contact nonequilibrium low-temperature plasma in comparison with the conventional method of chemical reduction in solutions and photochemical deposition is investigated. Plasma-chemical synthesis of silver nanodispersions from water $AgNO_3$ solutions without the use of additional reducing reagents and in the presence of sodium alginate stabilizing reagent is carried out. It is found that the yield of silver nanoparticles in the plasma-chemical synthesis is 95.10–97.17 %. The obtained data are obtained by the chemical reduction method in solutions (93.9 %) and photochemical deposition (20.0 %). It is found that in the plasma-chemical synthesis of silver nanodispersions, the introduction of sodium alginate into the reaction mixture increases the yield of silver nanoparticles and allows synthesizing stable colloidal silver solutions. It is shown that the formation of silver nanodispersions under plasma discharge is characterized by the presence of the peak λ_{max}=400–420 nm. The formation of silver nanoparticles was confirmed by the X-ray diffraction analysis. Microscopic examination (SEM) indicates that the size of the formed silver particles is up to 100 nm. The mechanism of synthesizing silver nanoparticles in the sodium alginate solution under plasma discharge is proposed. The obtained data testify to the promising application of the nonequilibrium plasma for the controlled synthesis of silver nanodispersions and the need for further research in this direction.

Keywords: low-temperature plasma, conventional methods, chemical deposition, IR radiation, sodium alginate, aggregation, microphotographs.

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