

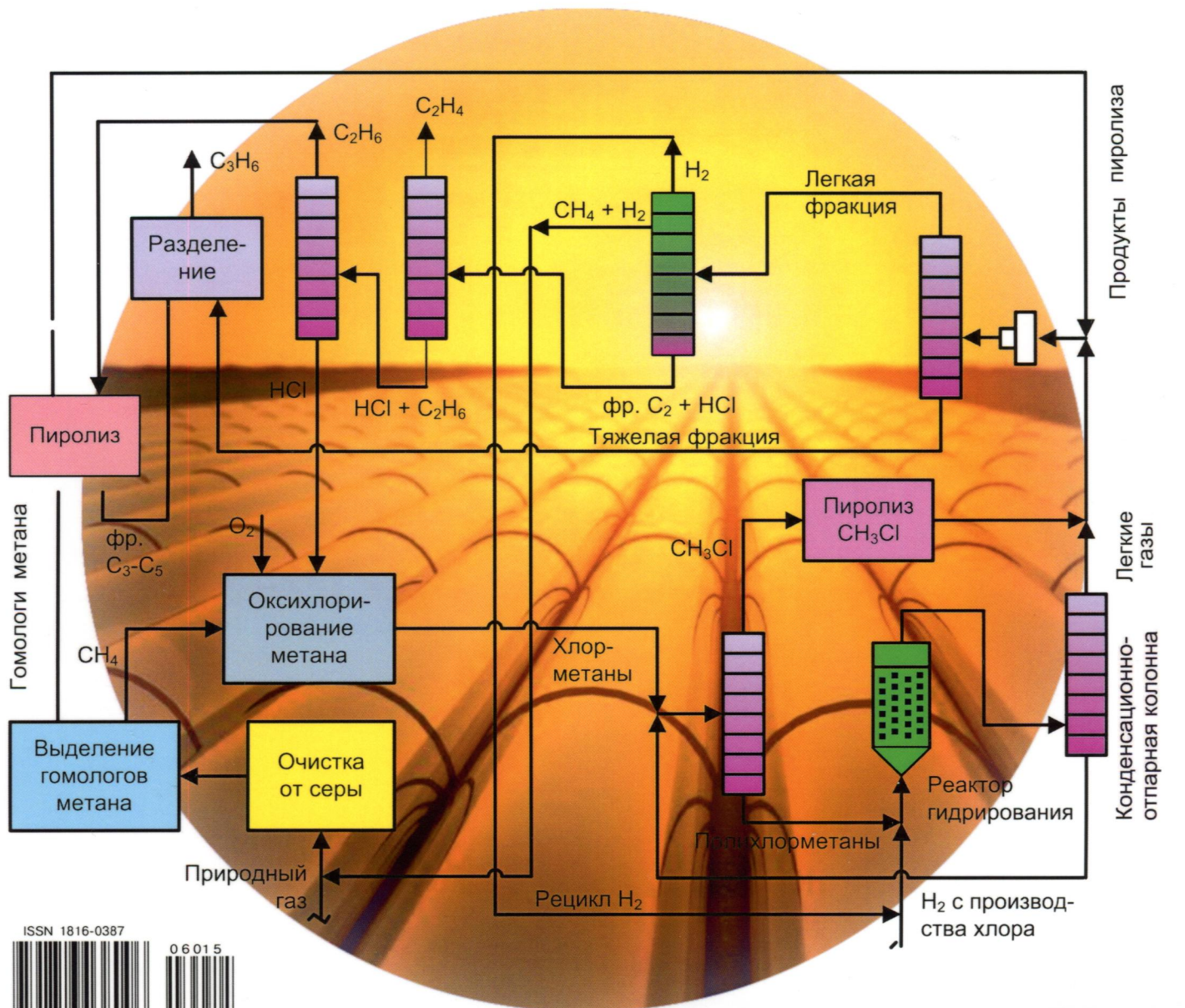
КАТАЛИЗ



В ПРОМЫШЛЕННОСТИ

CATALYSIS IN INDUSTRY

Том 15 № 6 2015



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An experimental setup was designed for studying the solubility of a catalyst-deactivating compound – polyisoprene – in pure supercritical carbon dioxide (SC-CO₂) and in SC-CO₂ with a co-solvent (3,5 wt % chloroform). In pure SC-CO₂, the crossover-type variations in the solubility was observed in isotherms $t = 70, 100$ and 120 °C at the pressure region between 15 and 34 MPa, and the pressure of ca. 19 MPa determined in the top crossover point. Addition of chloroform to SC-CO₂ was shown to result in an average 2 to 2,5 times increase in the solubility. The process of supercritical fluid CO₂-extraction regeneration of the aluminopalladium catalyst LD-265 for hydrogenation was studied. Dimethylsulfoxide and ethanol were used as co-solvents for SC-CO₂. The maximal efficiency of the regeneration was observed at the co-solvent concentration of 5,5–6,5 wt %, dimethylsulfoxide being more effective co-solvent than ethanol. With the catalysts subjected to the SC-CO₂ regeneration, the resulting diene and bromine numbers, as well as conversions of styrene and methylcyclopentadiene, meet the standards on catalytic systems for selective hydrogenation of diene hydrocarbons to benzene-toluene-xylene fractions.

Keywords: catalyst, regeneration, supercritical carbon dioxide.

- Activation of the Cement-containing Nickel Catalyst for Ammonia Dissociation 14
Efremov V.N.^{1,2}, Strekalov Yu.V.², Kashinskaya A.V.^{1,2}, Golosman E.Z.^{1,2}

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Dynamics of ammonia activation of the industrial cement-containing nickel catalyst KDA-10A (NIAP-13-02) at temperatures up to 750 °C was studied using methods of temperature-programmed reduction and high-temperature XRD. The activation dynamics was studied at 600, 650, 700 and 750 °C. The outlet ammonia concentration was observed to become constant at 700–750 °C after thermostating for 6 h that indicated practically complete activation of the catalyst. The high nickel dispersion and high catalytic activity at 700–750 °C was accounted for by the thermal stability of the catalyst under study. The shortened activation process was recommended for the industrial implementation.

Keywords: protective atmosphere, catalytic dissociation of ammonia, nickel-containing catalyst, activation dynamic, activation process.

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

- Studies of the Influence of the Process Parameters on Epoxidation of Propylene in the Methanol Medium
 in the Presence of Extruded Titanium Silicalite 21
Sulimov A.V.¹, Danov S.M.¹, Ovcharova A.V.¹, Ovcharov A.A.¹, Flid V.R.²

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² Moscow Lomonosov State University of Fine Chemical Technologies

Quantitative information was obtained on the effect of process parameters on main relationships of the liquidphase epoxidation of propylene with aqueous solution of hydrogen peroxide in the presence of extruded titanium silicalite in methanol. The influence of the solvent concentration (13,7–19,1 mol/l), reactant ratio of propylene: hydrogen peroxide ((2–5) : 1), and temperature (30–60 °C) on the yield – propylene oxide and byproducts – 1,2-propylene glycol, 1-methoxy-2-propanol and 2-methoxy-1-propanol was examined. Conditions of synthesis of propylene oxide in a lab-scale continuous setup were recommended based on the results obtained.

Keywords: propylene oxide, epoxidation, methanol, titan containing zeolite, optimal conditions.

- Production of Ethylene from Natural Gas via Synthesis of Methyl Chloride followed by its Pyrolysis:
 Improvement of the Selectivity by Adding the Stage of Hydrodechlorination of Methane Polychlorides 26
Treger Yu.A., Rozanov V.N., Averina E.A.

LLC Research and Engineering Center «Sintez», Moscow

An effective catalyst for synthesis of ethylene at the stage of hydrodechlorination of methylene chloride and chloroform was chosen through comparative studies of alumina-supported palladium, nickel-molybdenum and nickel-lanthanum-magnesium catalysts. A flow reactor with the fixed catalyst bed was used for the studies at 300 °C, 3,8 s contact time, molar ratio of hydrogen to methylene chloride equal to 3 : 1. The nickel-molybdenum catalyst was shown the best. The process flow sheet was improved in order to favor preferable synthesis of ethylene to be used for production of vinyl chloride: Ethylene was proposed to synthesize during an additional stage of pyrolysis of methane homologues which were extracted from natural gas and from reaction gas of methyl chloride pyrolysis, as well as at the stage of hydrodechlorination of methane polychlorides.

Keywords: hydrodechlorination of methylene chloride and chloroform, synthesis of ethylene by pyrolysis of methyl chloride.

- Activity of Industrial Alumina-based Catalysts to Dehydration of Ethanol to Ethylene 31
Chumachenko V.A., Ovchinnikova E.V.

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Commercial alumina – the support of hydrotreatment catalyst IC-GO-1 (AO_{IC-GO-1}), sorbents AN-2H and AOC-63-22, catalyst AOC-78-59 were tested for dehydration of ethanol to ethylene. The activities were measured using a flow reactor at the temperature range 375–400 °C, contact time 0,3 s. The influence of process temperature on the ethanol conversion and selectivities to the target and side products was determined. The specific activity was established

to correlate with the weight percentage of sodium in the phase-uniform samples: Na impurities cause a decrease in the activity of commercial alumina to dehydration of ethanol to ethylene. The activities of commercial alumina-based catalytic systems were found to change in the series: $AO_{IC-GO-1} > AN-2H > AOC-63-22 > AOC-78-59$.

Keywords: alumina, dehydration of ethanol, flow reactor, catalytic properties.

Oxidative Conversion of Ethane to Ethylene over VMoTeNb Oxide Catalyst.....	36
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Oxidative conversion of ethane to ethylene and CO_x over a multicomponent oxide catalyst $V_{0.3}Mo_{1.7}Te_{0.23}Nb_{0.12}$ was studied at 360–450 °C. No influence of temperature on the proportion of parallel and consecutive pathways towards the reaction products was established. Low temperature response of the selectivity to the reaction products will be taken into account in choosing the reactor type for scaling-up the process of oxidative conversion of ethane.

Keywords: ethane, ethylene, oxidative dehydrogenation, VMoTeNb oxide catalyst.

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<i>Nesterova T.N.¹, Chernyshov D.A.³, Shakun V.A.^{1,2}, Krymkin N.Yu.¹, Tarasov A.V.³, Voronin O.I.^{1,2}, Bilenchenko N.V.¹</i>	

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Kinetic parameters of transformations during alkylation of phenol with linear (C_9, C_{16}) alkenes over sulfocationites Amberlyst 15 Dry, Amberlyst 35 Dry, Amberlyst 36 Dry, Amberlyst 70, Amberlyst DT, Tulsion 66 MP, Lewatit K2640, Lewatit K 2431, Relite EXC8D were experimentally determined. Activities of the said catalysts to various type reactions were compared. The transition from 1-nonene to linear hexadecane was shown to be accompanied by a decrease in rate constants of all the transformations. It was established that the ortho-APh/para-APh ratio was statistically equal in phenol alkylation with linear alkenes over all the sulfocationites under study in their operation regions.

Keywords: phenol alkylation, high alkylphenols, isomerization, kinetics, sulfocationites.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

Prospects of Mo- and W-containing Catalysts for Hydroisomerization: Patent Survey. Part 1. Catalysts Based on Molybdenum and Tungsten Phosphides	47
<i>Urzhuntsev G.A., Toktarev A.V., Echevskiy G.V., Deliy I.V., Vlasova E.N., Bukhtiyarova G.A.</i>	

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Patent research was focused on methods for preparation and use of molybdenum and tungsten phosphide containing catalytic systems for hydroisomerization of paraffin hydrocarbons. Analysis of the patent data showed that modification of acidic supports with molybdenum and tungsten phosphides is promising for creating a stable catalyst for hydroisomerization of paraffin fractions, which would be stable to sulfur impurities in hydroisomerization feedstock.

Keywords: molybdenum, tungsten, phosphides, catalyst, hydrogenation, isomerization.

CATALYSIS AND ENVIRONMENTAL PROTECTION

Mesoporous Silica Based Catalysts for Oxidation of Azo Dyes in Wastewater	56
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Iron-containing catalysts were synthesized by supporting on mesoporous silica: commercial KCC silica, $\mu M-41$ silicalite and silica gels prepared under laboratory conditions using spray drying and drying in supercritical CO_2 . The support samples were prepared different ways. The porous structure of the catalysts was characterized by low temperature nitrogen adsorption. The catalytic activities and stabilities were compared during oxidation of an anionic dye – carmoisine – with 3 % H_2O_2 solution in water at 60 °C and pH 3. The initial contained 20 mg/l carmoisine, 3 g/l catalyst at the molar H_2O_2 /carmoisine ratio equal to 459/1. The KCC based catalyst was most active and stable to leaching of the active component to the solution: 99 % conversion of carmoisine was reached in 30 min of the reaction, while the concentration of iron ions was 0,27 mg/l, i.e. below its maximal admissible concentration. When the support was pre-impregnated with aluminium, the iron leaching decreased to a half. The synthesized catalysts seem promising for treatment of wastewater containing organic contaminants.

Keywords: mesoporous silica, heterogeneous Fenton catalysts, oxidative destruction of dyes, wastewater.

ENGINEERING PROBLEMS

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<i>Solov'ev S.A., Egorov A.G., Lamberov A.A., Egorova S.R., Kataev A.N.</i>	

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A mathematical model was developed for two units of industrial fluidized bed reactors equipped with different systems for feeding gaseous feedstock: three toroidal rings with nozzles in unit 1, and a false bottom with nozzles distributed through it in unit 2. Analysis of the efficiency (expressed as the yield of the target product – isobutylene) of the units during 4 month operation under industrial conditions demonstrated a higher efficiency of unit 2. The reasons for the differences in the product yields in two units were found using numerical solutions to obtain characteristic patterns of concentration fields of catalyst particles and temperature fields in the units; the results obtained demonstrated more uniform and dense catalyst distribution and more uniform reactor

heating characteristics of unit 2. The constructed patterns of main circulative flows of the catalyst accounted for the considerable differences in the catalyst concentration and gas temperature fields. The numerical solutions were used for comparative analysis of the operation efficiencies of the units to show good agreement with the analytic results on industrial reactors. The proposed approach can be used for the design of new and optimization of operating units.

Keywords: fluidized bed, dehydrogenation of isoparaffins, industrial reactor, mathematical model, numerical solution.

BIOCATALYSIS

Enzymatic Hydrolysis of Lignocellulosic Materials in Aqueous Media followed by Microbiological Synthesis of Bioethanol 70

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Enzymatic hydrolysis in aqueous media was studied using a lignocellulosic material (LCM) prepared from miscanthus and LCM prepared from oat covering (OC) as substrates to obtain bioethanol. LCM synthesis was a one-step processing of the feedstock with nitric acid (Pilot Plant of IPCET SB RAS). Commercially available enzymatic agents CelloLux-A and BrewZyme BGX were used for enzymatic hydrolysis in aqueous media at high initial concentrations (90 g/l) of the substrates. The yields of reducing substances (monosaccharides, mainly glucose) were established to equal 65,4 % and 73,3 % of the substrate weight for miscanthus LCM and OC, respectively. The composition of monosaccharides as products of biocatalytic decomposition of LCM was studied for the first time to show the predominant content of glucose. It was first time to synthesize bioethanol from LCM. The yield of bioethanol per unit of feedstock was 19,4 dal/t for miscanthus biomass and 16,2 dal/t for OC. A low methanol content (0,002–0,005 vol %) was characteristic of the experimental bioethanol samples.

Keywords: enzymatic hydrolysis, nitric acid process, miscanthus, oat covering, bioethanol.

Optimization of the Composition of Cellulase Enzymatic Complex *Penicillium verrucosum*:

Improvement of the Hydrolytic Ability Using Methods of Genetic Engineering 78

Sinitsyn A.P.^{1,2}, Korotkova O.G.², Sinitsyna O.A.^{1,2}, Rozhkova A.M.^{1,3}, Dotsenko G.S.³, Proskurina O.V.¹, Osipov D.O.², Kondrat'eva E.G.², Chekushina A.V.²

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Application of modern technologies of enzymatic hydrolysis of cellulose-containing raw materials makes it possible to obtain sugars that undergo microbiological conversion to synthesize alcohols (biofuels), organic and amino acids, biopolymers, food additives and other value-added products. Cellulolytic enzymes of three types – endoglucanase, cellobiohydrolase, beta-glucosidase – are required for the bioconversion of cellulose-containing raw material. The present work is aimed at studying a possibility of application of genetic engineering for improvement of the hydrolytic ability of secretory enzyme complex *Penicillium verrucosum* by adding homologous and the heterologous cellulases in different combinations and ratios – endoglucanase IV (EGIV) from *Trichoderma reesei*, endoglucanase II (EGII) and cellobiohydrolase I (CBHI) from *P. verrucosum*, and also beta-glucosidase (b-GLU) from *Aspergillus niger*. The optimal ratio of components is determined to double the catalytic activity of the new enzyme complexes.

Keywords: *Penicillium verrucosum*, enzymatic hydrolysis, optimal ratio, endoglucanase II, cellobiohydrolase I, beta-glucosidase.

Preparation of a Biocatalyst Based on Recombinant Cellulolytic Enzymatic Agents *Penicillium verrucosum*

and its Application for Pulp and Paper Industry 84

Sinitsyn A.P.^{1,2}, Rozhkova A.M.^{1,2}, Sinitsyna O.A.^{1,2}, Kholmova M.A.³, Terent'ev K.Yu.³, Kazakov Ya.V.³, Chuhchin D.G.³, Novozhilov E.V.³

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The studies dealt with the efficiency of a biocatalyst for modifying commercial bleached hardwood sulfate pulp. The biocatalyst was based on recombinant enzymatic agents prepared using *Penicillium verrucosum* fungus. The influence of the treatment with cellulase complex on the structure, morphology and surface state of cellulose fibers was estimated. It was shown that the biocatalytic treatment of cellulose led to improved beatability and bond-formation in paper sheets, to higher strength. Application of enzymatic modification of cellulose will help to solve some energy- and resource-saving problems in the paper industry.

Keywords: biocatalysts, cellulose, modification, cellulases, beating, properties of paper.

Properties of a Biocatalyst Based on Immobilized Recombinant Lipase *Geobacillus stearothermophilus* G3

in Synthesis of Methyl Esters of Fatty Acids 90

Samoilova Yu.V.¹, Piligaev A.S.¹, Sorokina K.N.^{1,2,3}, Rozanov A.S.², Pel'tek S.E.², Novikov A.A.⁴, Almyasheva N.R.⁴, Parmon V.N.^{1,3}

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A heterogeneous biocatalyst BCL based on recombinant extracellular lipase of thermophilic bacterium *Geobacillus stearothermophilus* G3 with the activity of 23,6 act.un./g was prepared by covalent immobilization on aminated silica gel. The influence of the solvent nature, temperature (30–60 °C), proportion of water (1–10 %) and catalyst (0,25–25 %) on the yield of methyl esters of fatty acids (MEFA) was studied in the reaction of methanolysis of sunflower oil over the BCL catalyst. The observed maximal MEFA yield was 43 %. A high operation stability of the catalyst under study was demonstrated: The catalyst kept more than 50 % of its initial activity after 480 h operation (20 cycles) that makes it promising for synthesis of fatty acid esters used for production of biodiesel fuel.

Keywords: immobilized lipase, *Geobacillus*, re-esterification, biodiesel fuel.

CHRONICLE

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