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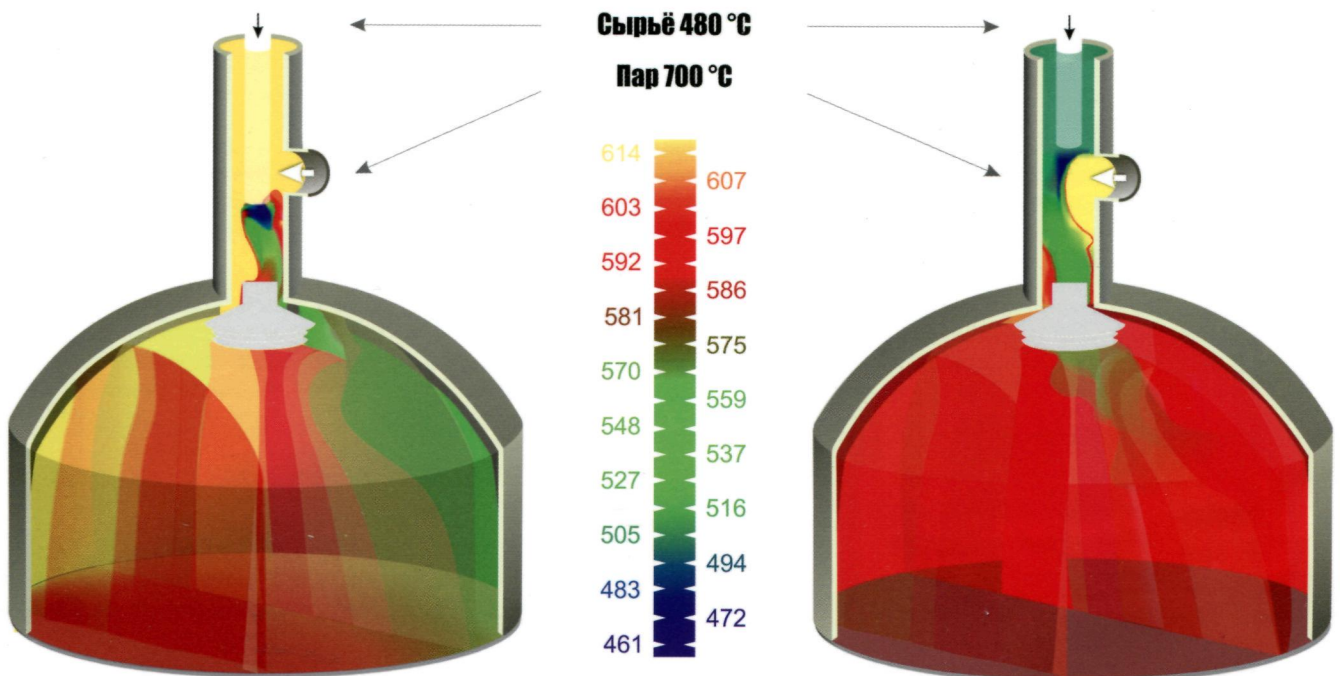
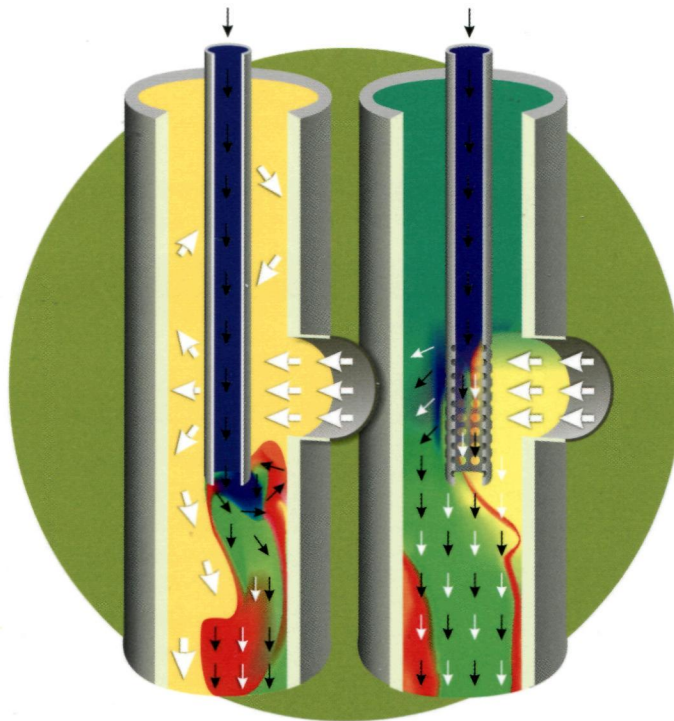
КАТАЛИЗ



В ПРОМЫШЛЕННОСТИ

CATALYSIS IN INDUSTRY

Том 15 № 3 2015



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Lavrenov E.N.¹, Saifulina L.F.¹, Buluchevskii E.A.^{1,2}, Bogdanets E.N.¹

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The paper is a review of both contemporary and promising industrial technologies for producing propylene from raw gas and oil. The review includes combined processes and processes based on raw materials of biological origin. A particular attention is paid to Russian projects in this area.

Keywords: propylene, ethylene, pyrolysis, catalytic cracking, dehydrogenation, metathesis, raw biological materials, catalysts.

Efficient Homogeneous and Supported Ionic Liquid Catalysts for Production of Linear Alkylbenzenes 20

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AlCl₃ based homogeneous ionic liquids such as 1-butyl 3-methyl imidazolium chloroaluminate ([BMIm]⁺Al₂Cl₇⁻), 1-butyl 3-methylpyridinium chloroaluminate ([BMPy]⁺Al₂Cl₇⁻) and triethylamine hydrochloride chloroaluminate (Et₃NHCl-AlCl₃) were prepared to study the benzene alkylation with 1-dodecene. All homogeneous ionic liquid catalysts have shown higher selectivity (~ 40 %) for desired 2-LAB (2-linear alkylbenzene), than the conventional AlCl₃ catalyst (~ 32 %). Apart from the homogeneous catalysts, one supported ionic liquid catalyst (SG-N⁺(C₂H₅)₃-Al₂Cl₇⁻), was also synthesized. The supported ionic liquid catalyst showed further increased selectivity of the 2-LAB (~ 45 %). Moreover, the reusability of SG-N⁺(C₂H₅)₃-Al₂Cl₇⁻ catalyst was much higher than the homogeneous ionic liquid catalysts. The supported ionic liquid catalyst was characterized by various techniques such as FT-IR, MAS-NMR and Scanning Electron Microscopy (SEM). Hammett acidity function (H₀) was used to determine the acidity of supported ionic liquid catalyst. The pyridine adsorbed FT-IR spectra of (SG-N⁺(C₂H₅)₃-Al₂Cl₇⁻) catalyst showed presence of common Brønsted-Lewis acidic sites. The ²⁷Al MAS-NMR of (SG-N⁺(C₂H₅)₃-Al₂Cl₇⁻) catalyst showed a band at ~ 6,987 ppm, which is attributed to 6-coordinated Al species. A nonlinear optimization algorithm was developed in MATLAB 7.4.0 to determine the kinetic parameters of the benzene alkylation with 1-dodecene in presence of (SG-N⁺(C₂H₅)₃-Al₂Cl₇⁻) catalyst. The concentrations of the products predicted by model were found in good agreement with experiments (relative error ~ 1,5 %).

Keywords: homogeneous ionic liquid catalyst, supported ionic liquid catalyst, production of linear alkylbenzenes, kinetic of the benzene alkylation with 1-dodecene.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

A New Method for Reactivation of Supported CoMo/Al₂O₃ and NiMo/Al₂O₃ Catalysts of Deep Hydrotreating after Oxidative Regeneration 29

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A new method for reactivation of CoMo/Al₂O₃ and NiMo/Al₂O₃ catalysts for deep hydrotreating of diesel fuel after their oxidative regeneration consists in the impregnation of regenerated catalysts with an aqueous solution of chelating compounds (e.g. citric or oxalic acids, ethylene glycol or diethylene glycol) followed by drying. After such treatment, the activity of reactivated catalysts can exceed the activity of fresh samples. The activity of the catalyst IK-GO-1 in the hydrotreating of straight-run diesel fuel was studied in dependence on the nature and amount of an added chelate. The best results were obtained by treating the oxidized sample with a solution containing both citric acid and a glycol at an optimum molar ratio (0,5–1,0) of the sum of chelating compounds to the sum of metals. The catalysts reactivated in this way give diesel fuels with ultra low (10 ppm) sulfur content. At that, with the use of the reactivated catalysts, the starting temperature of hydrotreatment is 10–15 °C lower than the temperature provided by the catalysts after oxidative regeneration and is 3–4 °C lower than the temperature provided by the fresh catalysts.

Keywords: hydrotreating, regeneration, rejuvenation, complex agents, catalysts, diesel fuel.

Hydrotreating of Raw Oil Materials over $\text{Ni}_6\text{-PMo}_n\text{W}_{(12-n)}(\text{S})/\text{Al}_2\text{O}_3$ Catalysts 36*Tomina N.N., Solmanov P.S., Maksimov N.M., Pimerzin A.A.*

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To develop an effective catalyst for hydrotreating of petroleum feedstock, the activity of Ni-Mo-W sulfide catalysts was studied in dependence on the molar ratio Mo/W. Trimetallic catalysts with the composition $\text{Ni}_6\text{-PMo}_n\text{W}_{12-n}/\text{Al}_2\text{O}_3$ ($\text{Ni}_6\text{-PMo}_n\text{W}_{12-n}(\text{S})/\text{Al}_2\text{O}_3$ after sulfiding), where $n = 0\text{-}12$, were synthesized. The morphology of the particles of the active phase of sulfide samples was studied by high-resolution transmission electron microscopy. The following parameters were calculated: the mean length of layers of the phase NiMo(W)S, the average number of layers in the crystallite, the number of atoms Mo(W) in the layer, and the portion of atoms Mo(W) in edge and corner positions. The influence of the molar ratio Mo/W on the catalytic activity of the prepared samples was studied in the following processes: the hydrogenolysis of dibenzothiophene, hydrodesulfurization (HDS) and hydrogenation of olefins and aromatic compounds during hydrotreating of a mixture of diesel fractions and vacuum gasoil. It was found that in the HDS and hydrogenation, the most active sample is the sample with the molar ratio Mo/W = 1/1.

Keywords: hydrotreating, catalysts, heteropolyacids, molybdenum, tungsten, dibenzothiophene, diesel fractions, vacuum gasoil.**CATALYSIS AND ENVIRONMENT PROTECTION**

Combustion of Sour Crude Oil in a Fluidized Catalyst Bed 43

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A possibility of environmentally friendly combustion of sulfur crude oil in a fluidized catalyst bed has been studied in an attempt to use this method in energotechnological systems for the local heating. Two types of oil were chosen for the experiments: sour and heavy sour. The oils were combusted in a layer of an Al-Cu-Cr catalyst for deep oxidation of organic substances. For comparison, the oil was combusted in a layer of inert material. The combustion efficiency was determined according to the degree of burning of organic components of sour crude oil and according to the amount of toxic products (CO , SO_2 and NO_x) in the flue gas. To remove SO_2 from the flue gas, calcite was added into the fluidized bed. It was shown that the combustion of the oil in the presence of calcite provides complete combustion of the oil at relatively low temperatures (700 °C) and prevents the presence of CO and SO_2 in the flue gas. At that, the concentration of nitrogen oxides is minimal and does not exceed sanitary standards.

Keywords: catalytic combustion, fluidized bed, oil, sour crude oil.**ENGINEERING PROBLEMS**

A Single-Stage Adiabatic Catalytic Reactor for Oxychlorination of Methane 49

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To simplify a design of reactors for oxychlorination of methane, a number of adiabatic catalytic reactors have been studied and pilot tested. As a result, a single-stage adiabatic reactor with an internal recycle was designed, which allows one to replace traditional 6- or 4-stage reactors. The new reactor design reduces the number of points for monitoring and control over the oxychlorination process. A recycle of waste hydrochloric acid, which was applied to remove the heat of the reaction, provides the full use of hydrogen chloride during the oxychlorination and simplifies both the evolution of the outlet water and the oxygen supply system. On the basis of results of the pilot testing, an industrial reactor was designed.

Keywords: oxychlorination, methane, adiabatic reactor.

Catalytic Membrane Reactor. Kinetic Modeling of Carbon Dioxide Conversion of Methane 54

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A reactor (contactor) with a membrane catalyst is considered as one of the types of heterogeneous catalytic apparatuses. A kinetic model is developed to describe the carbon dioxide reforming of methane in the presence of molybdenum carbide both in the contactor and in a reactor with a fixed bed catalyst. It is shown that such modeling is possible on the basis of a common system of differential equations, and parameters of the model allow one to estimate the acceleration of the reaction due to the membrane effect. On the basis of the activation energies of the reaction experimentally estimated for both reactors, it is concluded that in the contactor, the pore-diffusion resistance plays an important role. In contrast, in a traditional heterogeneous catalytic reactor, the process is controlled by the mass transfer to the external surface of the catalyst while the inner surface of pores stays virtually inaccessible.

Keywords: membrane catalysis, carbon dioxide conversion of methane, kinetic modeling.

Mathematical Modeling of Changes in Particle Size Distribution of Dehydrogenation Catalysts in a Fluidized Bed Reactor	60
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A mathematical model was suggested for the destruction of catalyst particles in an industrial fluidized bed reactor with taking into account the crushing and abrasion of the particles. The differences between the mechanical properties of catalysts IM-2201 and KDI, which are used at the PJSC «Nizhnekamskneftekhim» for the dehydrogenation of isobutane to isobutylene, were determined. It was shown that the use of the KDI catalyst after the modification of the cyclone groups and maintaining the equilibrium particle size distribution can reduce the consumption of the catalyst more than two and a half times.

Keywords: mathematical modeling, chromia-alumina catalyst, dehydrogenation, granule, particle size distribution, crushing, abrasion.

DOMESTIC CATALYSTS

Structured Fiberglass Catalyst IC-12-C111 for Deep Oxidation of Organic Compounds	67
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The paper is devoted to the development of a platinum catalyst supported on the fiberglass IC-12-C111. The method of preparation of the catalysts is based on a pulsed surface thermosynthesis. The catalyst IC12-C111 contains a small amount (0,05–0,10 wt.%) of platinum and is produced using inexpensive types of commercially available fiberglass. Technology of its production has the advantage of a small number of process steps and of the absence of wastes and production losses of platinum. The activity of the designed catalyst in the deep oxidation of hydrocarbons exceeds the activity of conventional platinum and oxide catalysts. In addition, the catalyst is highly stable and heat resistant. Catalytic cartridges with a regular structure of channels based the catalyst IC-12-C111 have a low flow resistance and provide minimal deposition of solids in the catalyst bed during operation in contaminated streams. With the use of the cartridges, it is possible to form catalyst layers of any size and configuration. The designed catalyst can be used in the post-combustion of hydrocarbons and organic compounds from the exhaust gases, in the flameless oxidation of flare gases, and in the catalytic combustion of hydrocarbon fuels in the systems of local power supply.

Keywords: catalyst, fiberglass, platinum, deep oxidation, hydrocarbons, catalytic cartridge.

ACTIVE CATALYTIC CENTERS IN RUSSIA

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The article represents a systematized summary of the practical experience of the Laboratory of Sorption and Catalytic Processes (the Department of Physical Chemistry, the Butlerov Institute of Chemistry, the Kazan (Volga region) Federal University) in the development and implementation of catalysts at the PJSC Nizhnekamskneftekhim in 2000–2015. A specific attention is paid to the importance of studying the conditions of the catalyst usage and to equipment upgrades.

Keywords: petrochemistry, catalysts, implementation.

CHRONICLE

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