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CATALYSIS IN INDUSTRY



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ФОТО- И ЭЛЕКТРОКАТАЛИЗ

Фотокаталитическое окисление модельных органических красителей в присутствии

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Oxidative chlorination of hydrocarbons. Part 1. The Deacon reaction. Oxidative chlorination of saturated hydrocarbons C_1 and C_2 5

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The review paper considers main regularities of the hydrogen chloride oxidation (the Deacon reaction) and oxidative chlorination of methane and ethane. The most efficient catalysts for these processes were shown to be the copper chloride systems on various supports, which contain also chlorides of alkaline and rare-earth metals that decrease the carry-over of the active phase from the catalyst surface and increase the activity. The main kinetic and technological regularities of the oxychlorination processes were considered. The conditions that promote an increase in the yield of target products – lower chloromethanes at oxychlorination of methane and vinyl chloride at oxychlorination of ethane – were revealed. Variants of technological schemes for the oxychlorination processes were proposed.

Keywords: oxychlorination, hydrocarbons, methane, ethane, catalyst, copper chloride.

A bifunctional cobalt catalyst for the synthesis of waxy diesel fuel by the Fischer–Tropsch method – from the development to implementation. Part 3. The experience of industrial implementation of the preparation technology 34

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The work summarizes the results of testing the technology for preparing a bifunctional cobalt catalyst for the synthesis of hydrocarbons from CO and H₂, obtained by extruding a mixture of Co-Al₂O₃/SiO₂ catalyst powders and HZSM-5 zeolite with a binder – boehmite in industrial conditions (2 batches of 50 kg each were prepared). The catalyst technology was implemented on the equipment of Ishimbay Specialized Chemical Catalyst Plant LLC. The obtained industrial samples of the catalyst were characterized by XRF, TPR H₂, DTG, and tested in the synthesis of hydrocarbons from CO and H₂ at a temperature of 250 °C, a pressure of 2.0 MPa, GHSV 1000 h⁻¹. It has been shown that the implementation of the technology of a bifunctional cobalt catalyst for the production of low pour point diesel fuel in industrial conditions makes it possible to reproduce the characteristics of the catalyst obtained in laboratory conditions. The technology for producing the catalyst can be recommended for the production of industrial batches. It was determined that changes in the heat treatment conditions of the catalyst, as well as the presence/absence of a peptizer and pore former do not lead to a significant decrease in the productivity of C₅₊ hydrocarbons. The content of the diesel fraction in C₅₊ products obtained from industrial samples of the catalyst remains at the level of the value obtained from the laboratory sample of the catalyst. At the same time, the low-temperature properties of diesel fuel obtained using all catalyst samples have similar values. Using an industrial sample synthesized without the use of a peptizing agent and a pore-forming component, the best low-temperature properties of diesel fuel were achieved – the cloud point and fluid loss point were minus 16 and minus 24, respectively.

Keywords: Fischer–Tropsch synthesis, bifunctional cobalt catalyst, technology, HZSM-5 zeolite, catalytic performance.

Synthesis of hydroxylamine sulfate via NO hydrogenation over Pt/Graphite catalysts. Part 3: Functionalization of the support surface and formation of the active component during the catalyst synthesis 44

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The peculiarities of formation of platinum nanoparticles and chemical coating of carbon support surface during preparation of model (0.5%Pt/Sibunit) as well as industrial (0.5%Pt/Graphite) catalysts for hydroxylamine sulfate synthesis by NO hydrogenation in H₂SO₄ solution have been disclosed. It is shown that functionalization of the support surface with nitrogen-containing groups in the course of platinum deposition promotes not only metal dispersion but also a significant increase in its selectivity towards hydroxylamine sulfate. Based on

experimental data, it is suggested that the maximal selectivity is inherent in the active centers representing single atoms or small clusters of platinum bound to nitrogen-containing ligands at the carbon surface.

Keywords: Pt catalyst, preparation, NO, hydrogenation.

Microwave-assisted synthesis of solketal from glycerol and acetone 60

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Herein, microwave-assisted synthesis of solketal from glycerol and acetone in the presence of montmorillonite modified with aqueous solution of 0.25 mol/l HCl (0.25M HCl/MM) was demonstrated. The reaction was studied in a methanol solution at an acetone/glycerol molar ratio of 2.45–7.53, a catalyst concentration of 1.2–2.8 wt.% (based on the mass of loaded glycerol), and 30–56 °C. Solketal was shown to be the major product with 96.1–99.2 % selectivity. The maximum solketal yield of 91.3 % with 98.6 % selectivity was obtained in 15 min of the reaction at an acetone/glycerol molar ratio of 7.53, a catalyst loading of 2.3 wt.% and 56 °C. The catalytic properties of 0.25M HCl/MM in the reaction under MW heating and thermal conventional heating were compared. It was found that the yield of solketal in the MW-assisted synthesis is 2 times higher compared to the process with conventional heating.

Keywords: Microwave-assisted synthesis, solketal, glycerol, acetone, montmorillonite, modification with acid.

PHOTO- AND ELECTROCATALYSIS

Photocatalytic oxidation of model organic dyes in the presence of Na⁺, NO₂⁻, NO₃⁻ ions:
theoretical and applied aspects 69

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The influence of the concentration of Na⁺, NO₂⁻, NO₃⁻ ions on the rate of photocatalytic oxidation of model organic dyes was studied in the article: cationic – methylene blue (MB); anionic – methyl orange (MO). Based on studies of hydrochemical indicators of polluted rivers in urban areas (Khabarovsk, Russia) in the period from 1999 to 2019, it was shown that the concentration of ions varies in the ranges: 0.005–0.7 mg/l for NO₂⁻; 0.05–15 mg/l for NO₃⁻; 13–180 mg/l for Na⁺. Optical spectrophotometry was used to study the kinetics of photooxidation of MC and MO in the concentration ranges of the studied ions: 0–1–10–100–1000–10000 mg/l using P25 titanium oxide as a photocatalyst. The photooxidation time (*t*) was estimated at various values of the degree of transformation (α) of dyes at: initial – 10%*t*; medium – 50%*t*; final – 90%*t* stages of the photocatalytic process. The effect of absorption of light quanta with wavelengths of 200–350 nm by Na⁺/NO₂⁻ and Na⁺/NO₃⁻ ions is shown depending on the concentrations of these ions in the photocatalytic solution. Recommendations for practical applications of the method of photocatalytic water purification of real polluted waters are given, showing the need to take into account the concentration of the studied ions. A description of the observed effect of ions on the rate of photocatalytic oxidation of model organic dyes is proposed from the point of view of the band structure of semiconductors, elements of the theory of electrolytic dissociation and recombination of free radicals in photocatalytic processes.

Keywords: photocatalysis, photodecomposition of organic dyes, ionic composition.