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CATALYSIS IN INDUSTRY

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The influence of addition of oxygen or hydrogen to the reaction mixture ($\text{CH}_4 + \text{N}_2$) on the pyrolysis of methane at temperatures from 700 to 1400 °C was studied with a pre-calcined fechral spiral heated by an electric current. It is shown that under conditions of both anoxic and oxidative pyrolysis, at the ratios of methane/oxygen 15/1 and 9/1, the reaction proceeds in two temperature areas that differ in the selectivities toward main products (C_2 hydrocarbons). After addition of hydrogen, the pyrolysis of methane proceeds only at high temperatures to form primarily acetylene. Addition of both hydrogen and oxygen leads to a shift of maximal conversions of methane and selectivities toward acetylene into a high temperature region, thus extending the temperature range of the catalytic operation.

Keywords: catalytic pyrolysis, methane, fechral, resistive catalysts, acetylene.

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A possible use of oxides of transition metals (cobalt, iron, copper, molybdenum, vanadium, zinc, cadmium, titanium, manganese, chromium, and tungsten) as catalysts for hydrolysis of borazane was studied. The hydrolysis was carried out at temperatures from 35 to 80 °C in an aqueous solution with a concentration of 0,24 wt.% of borazane. The weight of loaded oxides was 10–40 mg. The highest rate of hydrogen evolution was observed at 80 °C for oxides of cobalt (Co_3O_4) and iron ($\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$). From the data obtained for these oxides, the order of reaction with respect to borazane was found to be one. The activity of cobalt and iron oxides in the hydrolysis of borazane at operating temperatures (80 °C) of fuel cells based on proton-conducting membranes makes the oxides promising for the production of hydrogen in energy-autonomous devices, including vehicles.

Keywords: borazane, hydrolysis, kinetics, hydrogen, heterogeneous catalysis, transition metal oxides.

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The paper is devoted to the gas chromatographic retention of products of the catalytic synthesis of pentafluoroethane on a mixed stationary phase poly-(1-trimethylsilyl-1-propyne)/poly-(1-phenyl-1-propyne). The proposed phase is shown to be of a practical use for selective separation of a mixture of nitrogen, carbon dioxide, halocarbons, and water. It was found that the order of release of halocarbons is dependent on their boiling point.

Keywords: gas chromatography, mixed stationary phase, poly-(1-trimethylsilyl-1-propyne), poly-(1-phenyl-1-propyne), halocarbons, water.

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

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The main regularities of the side carbon oxides formation in the ethylene oxychlorination process in the fluidized bed catalyst are exa-

mined in the round-up article. On the basis of literature data conclusions about possible mechanism of oxidation are drawing. The oxidation of both initial ethylene and target dichloroethane is proceed at the oxychlorination process. The increase of the process temperature promotes of the rise of the part of dichloroethane oxidation. There is indicated that the catalyst should be active in the reaction of the carbon monoxide to the carbon dioxide oxidation for the process stabilization and increase of selectivity of 1,2-dichloroethane formation. In the industrial conditions the lowering of the side carbon oxides yield is reached at the minimum excess of the ethylene and oxygen related to hydrogen chloride. The use of the catalysts with the not high copper content at the external surface of the granule is required for that. The availability of the promotion additives of alkali or alkali-earth metals chlorides is important. The iron penetration to the catalyst due to the erosion of the industrial reactor walls leads side by side with the decrease of the oxychlorination process rate to the increase of the deep oxidation products yield.

Keywords: oxychlorination, selectivity, ethylene, oxygen, hydrogen chloride, catalyst, cupric chloride, carbon monooxide, carbon dioxide, promoting additives, alkali metals, iron.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

Hydroisomerization of Long-Chain Paraffins: Mechanism and Catalysts. Part II..... 30

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The paper provides an overview of publications devoted to catalysts for the hydroisomerization of long-chain paraffins. Part I described the reaction mechanism and analyzed data pertaining to the catalysts based on zeolites of different types. Part II is devoted to the catalysts that are based on mesoporous structured materials, on partially reduced oxides and oxycarbides of molybdenum, and on mixed oxides of tungsten and zirconium. Industrial catalysts, which have found their use in the isodewaxing of diesel fuels and oils, are described.

Keywords: hydroisomerization, catalysts, long-chain paraffins, zeolites, isodewaxing.

A Catalyst for Production of Diesel Fuels with Improved Low Temperature Performance 46

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The purpose of research was to develop a catalyst for hydroisomerization of a hydrotreated straight-run diesel fraction, which allows one to obtain diesel fuels with improved low-temperature characteristics. The synthesized catalysts contained zirconia modified with tungstate anions, high silica zeolite, noble (Pt, Pd) or transient (Ni, Mo) metals, binding agents (alumina), and promoters. The samples were tested in the hydroisomerization at temperatures 250–360 °C, at a pressure of 3,0 MPa, feed space velocity of 1,5–3,0 h⁻¹, and the ratio H₂/feedstock of 1000 nm³/m³. The yield of the target product over samples GIC-1 (with Ni, Mo) and GIC-2 (with Pt, Pd) was 84,6 and 91,0 wt.%, respectively. The depression of the cloud point and of the cold filter plugging point in comparison with the feed was 20 °C for both samples. A possibility of producing the diesel fuel for cold climate zones according to GOST R 52368–2005 or the winter diesel fuel in accordance with TR CU 013/2011 is shown.

Keywords: bifunctional catalyst, hydroisomerization, isodewaxing, diesel fuels for cold climatic zones, cold flow properties, high-silica zeolite, zirconia, hydrogenating metal.

DOMESTIC CATALYSTS

Industrial Nickel-Kieselguhr Catalyst for Dehydrogenation of Isopropyl Alcohol: Morphology, Catalytic and Electronic Properties 53

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Conversion of isopropyl alcohol is first studied in the presence of an industrial nickel-kieselguhr catalyst. It has been established that this catalyst provides the synthesis of acetone in a one-step process (in contrast to usual two-step technologies) at moderate temperatures with a 97 % conversion of the feedstock and with a yield of 82,4 %. Scanning electron microscopy, thermal analysis, X-ray diffraction, and

conductometry were used to study the changes in the phase composition, surface structure and electronic properties of the nickel catalyst that proceed under the action of the reaction mixture. It is shown that the dehydrogenation of isopropyl alcohol to acetone is accompanied by loosening of the initial homogeneous globular structure of the catalysts with the formation of nickel nanoclusters. Active centers in the conversion of alcohols are nickel ions in different oxidation states, cationic and anionic vacancies.

Keywords: nickel-kieselguhr catalyst; dehydrogenation of isopropyl alcohol; surface morphology; electronic state; nickel clusters.

Iron-containing Catalysts for Deep Oxidation in the Fluidized Bed 61

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Iron-containing catalysts for the deep oxidation were prepared by impregnation of a support (γ -Al₂O₃) with a solution of (NH₄)₃[Fe(C₂O₄)₃] (sample Fe_{OX} Fe_{OX}/γ-Al₂O₃) or a solution of Fe(NO₃)₃ (sample Fe_{NO} Fe_{OX}/γ-Al₂O₃). The samples were studied by the BET method, XRD, XPS, and HREM. The catalyst activities were determined in the oxidation of CO: it was shown that the sample Fe_{OX} Fe_{OX}/γ-Al₂O₃ is more active than the sample Fe_{NO} Fe_{OX}/γ-Al₂O₃. It is shown that the active component of the catalyst obtained with Fe(NO₃)₃ is α-Fe₂O₃, while the active component of the catalyst obtained with the solution of (NH₄)₃[Fe(C₂O₄)₃] is a solid solution of Fe³⁺ in Fe_{OX}/γ-Al₂O₃. The sample Fe_{OX} Fe_{OX}/γ-Al₂O₃ and industrial catalysts SHKZ-1 and IC-12-73 were tested in the combustion of brown Kansk-Achinsk coal in the fluidized bed. It is shown that the use of the sample Fe_{OX} Fe_{OX}/γ-Al₂O₃ provides the high degree (95 %) of the lignite burning and reduces the CO emission as compared with the level obtained with an inert material.

Keywords: heterogeneous catalysts, fluidized bed, deep oxidation of CO.

Synthesis of palladium nanocatalysts on the base of silica gel for selective hydrogenation of phenyl acetylene 68

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Pd/SiO₂ catalysts containing 4,0 and 9,1 wt.% were synthesized. Their characterization by electron microscopy revealed nano-size of Pd particles (1,70±0,72 and 1,30±0,64, respectively). The effect of Pd content and conditions of precursor (Pd acetate) reduction on the catalytic properties of Pd/SiO₂ samples in the reaction of selective hydrogenation of phenyl acetylene (PA) to sterol (S) at 25 °C was studied. Increase of both Pd content (from 4,0 to 9,1 wt.%) and temperature (from 50 to 120 °C) was shown not to lead to substantial enlargement of Pd particles and, as a consequence, on the rate and selectivity of PA hydrogenation. It was found that nano-sized Pd/SiO₂ systems are the efficient catalysts for industrially important process of PA hydrogenation demonstrating high selectivity to S (96,75 and 90,3 % at conversion values of 50 and 100 %, respectively), which exceed substantially the reported values (75 % at complete conversion).

Keywords: palladium nanocatalysts, synthesis, silica, hydrogenation, phenylacetylene, conversion, selectivity.

BIOCATALYSIS

Enzymatic Synthesis of Esters of Polyethylene Glycol-400 73

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Esters of fatty acids (FA) and polyethylene glycol-400 (PEG) are valuable surface-active compounds usually produced by chemical methods. This study shows the possibility of replacing the chemical synthesis of polyethylene glycol esters by the enzymatic synthesis, which is implemented under milder conditions and via a simpler and more environmentally friendly technology. The main obstacles for the enzymatic synthesis of PEG and higher fatty acids are the high viscosity of PEG and a low solubility of FA in water. These problems were solved by the selection of an organic solvent and by the choice of other conditions of the process carried out by pancreatic lipase. The optimal conditions for the synthesis of esters of PEG and FA were determined as follows: the reaction medium was benzene/hexane in the ratio of 2/3; a temperature was 25 °C; the water content was not above 0,2 %; the molar ratio of FA/PEG was equal 1/1,8; and the reaction time was 48 h. The product yield under these conditions was: 80 % for the synthesis of PEG ester and capric acid, 78 % for the synthesis of PEG ester and lauric acid, and 44 % for the synthesis of PEG ester and palmitic acid.

Keywords: polyethyleneglycol-400, fatty acid, biocatalyst in organic solvents, pancreatic lipase.