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ОБЩИЕ ВОПРОСЫ КАТАЛИЗА

КАТАЛИЗ В НЕФТЕПЕРЕРАБАТЫВАЮЩЕЙ ПРОМЫШЛЕННОСТИ

ИНЖЕНЕРНЫЕ ПРОБЛЕМЫ. ЭКСПЛУАТАЦИЯ И ПРОИЗВОДСТВО

ОТЕЧЕСТВЕННЫЕ КАТАЛИЗАТОРЫ

БИОКАТАЛИЗ

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GENERAL PROBLEMS OF CATALYSIS

Alumina desiccants prepared by extrusion of plastic pastes based on pseudoboehmite- and bayerite-containing hydroxides, including the ones modified with sodium and potassium ions, were studied. The hydroxides were synthesized via dehydration of the product of centrifugal thermal activation of hydrargillite under mild conditions. Physicochemical and structural-mechanical properties of the desiccants were characterized using fresh samples and the samples undergone 9 adsorption-regeneration cycles. The dynamic capacity was determined at 3 MPa under industrial-modeling conditions. A high dynamic capacity was characteristic of the sample prepared from bayerite-containing hydroxide against that of the sample prepared from pseudoboehmite-containing hydroxide, while close textural and strength parameters were determined for both adsorbents. After the sample prepared from pseudoboehmite-containing hydroxide was modified with sodium and potassium ions, the granules became less strong, volume and average size of pores increased, and dynamic capacity rose. At a low water content in the gas to be dried the dynamic capacity of the potassium modified sample was not inferior to that of the sample prepared from bayerite-containing hydroxide. The phase composition, content of alkali impurities, specific surface area and crashing strength did not change, within the measurement error, after cyclic testing of the samples. A high stability of the prepared desiccants and the possibility of achieving the minimal dew point (–80 °C) was established during repeated adsorption-desorption cycles.

Keywords: dehydration of natural gas, alumina, modification, dynamic capacity at high pressure.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

Main physicochemical and performance characteristics of Middle distillate fractions of hydrocatalytic and thermodestructive processes of one of Russian refineries – potential components of low-viscosity marine fuels (LMF) with improved ecological and low-temperature properties – were studied to characterize their physicochemical and operation parameters. A laboratory flow setup with the industrial nickel-molybdenum catalyst loaded in it was used for achieving hydrocracking of vacuum gasoils (Tebp ranged from 500 to 580 °C) at 340–380 °C and 15,0 MPa. The highest yield of the light hydrocracking gasoil (LHCG) was observed upon processing of the vacuum gasoil (Tebp 350–500 °C) at 360 °C, the highest cetane index (53) and the lowest sulfur content (7 ppm) being characteristic of the obtained LHCG. With heavier vacuum gasoil, the total yields of target distillates and, individually, of LHCG decrease. The physicochemical and operation parameters of obtained LHGC make then qualitative components of LMF. Comparative properties of the hydrotreated straight-run diesel fraction, light gasoils obtained by catalytic cracking, slow coking and the promising hydrocracking process were analyzed. Dependencies of physicochemical, ecological and main operation properties of the middle distillate fractions of secondary processes on the hydrocarbon and non-hydrocarbon composition and on the contents of key components were established. The obtained dependencies were used to make recommendations on the production of optimal low-viscous marine fuel with improved ecological and low-temperature properties.

Keywords: hydrocracking, light gasoil, diesel fuel, marine fuel, ecological and low-temperature properties.

A kinetic model was developed for reforming to describe chemical transformations of C_6–C_8 pseudocomponents over a Pt catalyst. The platformat composition was predicted upon taking into account activities of the «metal» and acid centers and the temperature profile through the reactors. Material and heat balance equations were used for calculations. Rate constants and activation energies of individual reactions were determined for the R-134 series catalyst. Stationary activity (as = 0,8), as well as deactivation constants of acid (0,0056±0,0004 min^{-1}) and «metal» (0,079±0,003 min^{-1}) centers at T = 490 °C were calculated. In modeling the platformat composition in respect of benzene, toluene and xylenes, the error was no more than 5 % (rel). The stability of the platformat composition was shown to achieve by stepwise elevation of the reactor temperatures during the service length. The developed model can be used for determining the operation temperature regimes in the production of aromatic compound to obtaine the desired platformat compositions.

Keywords: catalytic reforming, deactivation, reforming catalyst, modeling.

ENGINEERING PROBLEMS. OPERATION AND PRODUCTION

Results of pilot testing of the microspherical aluminochromium KDI-M catalyst mixed with IM-2201 in a large-scale unit (Nizhnekamskneftekhim) for isobutane dehydrogenation are discussed. Against the KDI catalyst, its modified analogue KDI-M is more active and selective; the optimized

grain-size composition and mechanical strength provides an improved isobutylene yield and a longer non-stop operation (up to 400 days) of the reactor unit.

Keywords: aluminochromium catalyst, fluidized bed, dehydrogenation, isobutylene, runlife.

DOMESTIC CATALYSTS

A new type catalyst based on a microfiber support is reported. The microfibers are twisted as looped threads (lemniscates) to form a geometrically regular flexible bulk bed which is stable and well penetrable for the reaction flow; there is no need in additional structuring elements. Experimental studies on deep oxidation of toluene showed that the suggested lemniscates fiberglass catalyst (LFGC) is much superior to the known geometrical type (including microfiber) catalysts; its observed activity per mass unit of the active component and the ratio of the observed activity to the specific pressure drop are as high as 8 to 10 times of those characteristic of the latter. The reason is the unique high efficiency of mass exchange at the outdiffusion region of the reaction. The potential application areas of the suggested systems are fast catalytic gas-phase reactions, as well as complex reactions where the selectivity and target product yields are sensitive to the diffusion.

Keywords: catalyst, microfibers, glass-fiber fabric, platinum, oxidation, mass exchange.

Results of the studies of a supercritical fluid CO_2-extraction regeneration of the industrial nickel-molybdenum catalyst DN-3531 for hydrotreatment at 323–383 K and pressure up to 30 MPa and of the basic extractant to be modified with polar compounds such as chloroform, methanol, ethanol, acetone and dimethylsulfoxide (DMSO) are reported. The said modifier sequence indicate an increase in the solubilizing ability of the modified supercritical carbon dioxide (SC-CO_2) with respect to the catalyst deactivating sediments. However, with DMSO as the most effective modifier, not only deactivating compounds but also nickel and molybdenum are removed that causes a considerable decrease in the final activity of the regenerated catalyst. The coke content in the catalyst decreases to one third while the specific surface area and pore volume increase during the extractive regeneration. After the catalyst deactivated during hydrodesulfurization of dibenzothiophene and hydrogenation of naphthaline was once subjected to the SC-CO_2 treatment, the catalyst activity increased several times to be as high as 2,5 times of that of the catalyst regenerated using the traditional oxidative method.

Keywords: Ni-Mo catalyst, hydrotreatment, extractive regeneration, supercritical carbon dioxide, dibenzothiophene, naphthalene.

The influence of the calcining temperature of the support WO_3/ZrO_2 at 700–1000 °C on the phase composition, acid and catalytic properties of catalysts $Pt/WO_3/ZrO_2$ was studied. The method of ammonia TPD was used to establish that strong acid centers formed at the calcining temperature between 850 and 950 °C favor an increase in the yields of target products of *n*-heptane isomerization – high-octane di- and trimethyl substituted isomers. IRS-DR studies revealed the role of the catalyst calcining in flowing air that is to form charged platinum atoms which contribute to improvement of the catalyst activity.

Keywords: isomerization of *n*-heptane, electron state of platinum, tungstenated zirconia, isomerizate.

Catalysts $Pt/BEA–Al_2O_3$ for hydroisomerization of benzene-containing gasoline fractions were studied using model feedstock (20 % benzene and 80 % *n*-heptane). The catalysts were prepared by varying the content of zeolite from 5 to 70 wt.% at the constant Pt loading equal to 0,3 wt.% in

all the samples; an aqueous solution of H_2PtCl_6 was used as the Pt precursor. Acid properties of the samples were studied by TPD. The influence of the zeolite/binder ratio in the support on the activity of the catalysts under study was demonstrated: an increase in the zeolite proportion resulted in an increase in the system acidity and in shifting of the reaction region towards lower temperature. The optimal zeolite/binder ratio was found to be 30 % BEA/70 % Al_2O_3. A change in the acid modulus SiO_2/Al_2O_3 of the zeolite from 25 to 40 was shown not to affect noticeable the catalyst activity. Catalysts supported on 30 % BEA/70 % Al_2O_3 used for hydroisomerization of benzene-containing gasoline fractions can be recommended for improvement of the environmental performance.

Keywords: BEA, beta zeolite, platinum catalysts, benzene hydroisomerization, n-heptane isomerization.

BIOCATALYSIS

Samoilova Yu.V.[1], Piligaev A.V.[1], Sorokina K.N.[1,2], Parmon V.N.[1,2]

[1] Boreskov Institute of Catalysis, Novosibirsk, Russia

[2] Novosibirsk State University, Novosibirsk, Russia

Properties of the biocatalyst based on recombinant lipase of bacterium Geobacillus stearothermophilus G3 immobilized on a porous silica gel were studied. The following was established for interesterification of a mixture of sunflower and soya bean (hydrogenated fat) oils in the static mode: sufficient reaction time 2 hours, biocatalyst concentration 10 wt.%, 70 °C, hydrogenated fat to sunflower oil ration 1 : 3. Physicochemical properties of the interesterification products were studied by HPLC-MC (triacylglyceride composition) and by measuring the oil melting points. A high stability of the biocatalyst was demonstrated: its lifetime in the feedstock mixture was calculated as 243 h that makes it promising for synthesis of modified fats including those based on oils with high melting points.

Keywords: immobilized lipase, Geobacillus stearothermophilus; oil interesterification.

Osipov D.O.[1], Bulakhov A.G.[1], Korotkova O.G.[1], Rozhkova A.M.[1], Duplyakin E.O.[2], Afonin A.V.[3], Sereda A.S.[4], Sinitsyn A.P.[1,5]

[1] FRC Biotechnologies, Moscow, Russia

[2] LLC KD Sistemy i Oborudovanie, St-Peterburg, Russia

[3] State Research Institute of Biosynthesis of Protein compounds, Moscow, Russia

[4] All-Russian Research Institute of Food Biotechnology, Moscow, Russia

[5] Moscow State University, Moscow, Russia

Potentialities of wheat bran as a feedstock for biocatalytic conversion to synthesize sugars were demonstrated. The relatively low reactivity of the feedstock can be 2–4 fold increased through its dry crushing using a planetary mill-activator. A complex enzymatic agent (EA) *Penicillium verruculosum* gaBG showing cellulolytic, hemicellulolytic and amylolytic activity was used to improve the yield of reducing sugars; the maximal yield equal to 68,8 mg/L at the initial substrate concentration of 100 g/L in the reaction mixture was reached through biocatalytic conversion of wheat bran milled for 7–10 min in the presence of 60 mg/g of EA gaBG (and additional EA β-glucosidase F10, 40 unit/g), glucose being predominant among the produced sugars (93–95 %). The content of polysaccharide components was 62,4 % of the dry basis of wheat bran; hence, the observed sugar yield was close to the theoretical yield (with regard to water added during the enzymatic hydrolysis), and the carbohydrate component of the broken wheat bran was practically completely converted. Lengthening of the crushing time to 7–10 min resulted in a considerable decrease in the bran particle size, in weakening of their ability to bind water (by 28 %), in doubling of the content of soluble sugars and in an increase (by 12,6 %) in the total content of soluble components against those in the initial feedstock.

Keywords: biocatalytic conversion, wheat bran, enzymatic agent, reactivity, pretreatment, *Penicillium verruculosum*.

Dotsenko A.S.[1,2], Rozhkova A.M.[1], Gusakov A.V.[1,2], Sinitsyn A.P.[1,2]

[1] FRC Biotechnologies, Moscow, Russia

[2] Moscow State University, Moscow, Russia

Plant biomasses are the predominant organic material on Earth. The efficiency of biocatalytic conversion of the plant materials is determined by the cost of their biotechnological processing to valuable commercial products (organic alcohols and acids, carbohydrates and hycrocarbons). The obtained recombinant strains *Penicillium canescens* produce, apart from their own enzymatic complex, heterological cellulases (mutant and non-mutant cellobiohydrolase I (CBHI) and endoglucanase II (EGII) *P. verruculosum*). Enzymatic agents (EA) prepared from recombinant strains *P. canescens* were more active to hydrolysis of crushed aspen wood. The yields of glucose and reducing sugars after 24–72 hour hydrolysis under the action of EA prepared from the recombinant strains were higher by на 48–52 % and 60–64 %, respectively, than under the action of EA prepared from the initial strain-recipient. Thus, introduction of site-specific mutations N45A and N194A for partial inhibition of the surface glycosilation led to a considerable increase in the yields of target CBHI and EGII.

Keywords: bioconversion, plant resources, enzymatic agents, cellulases, recombinant strains, *Penicillium*.