

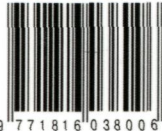
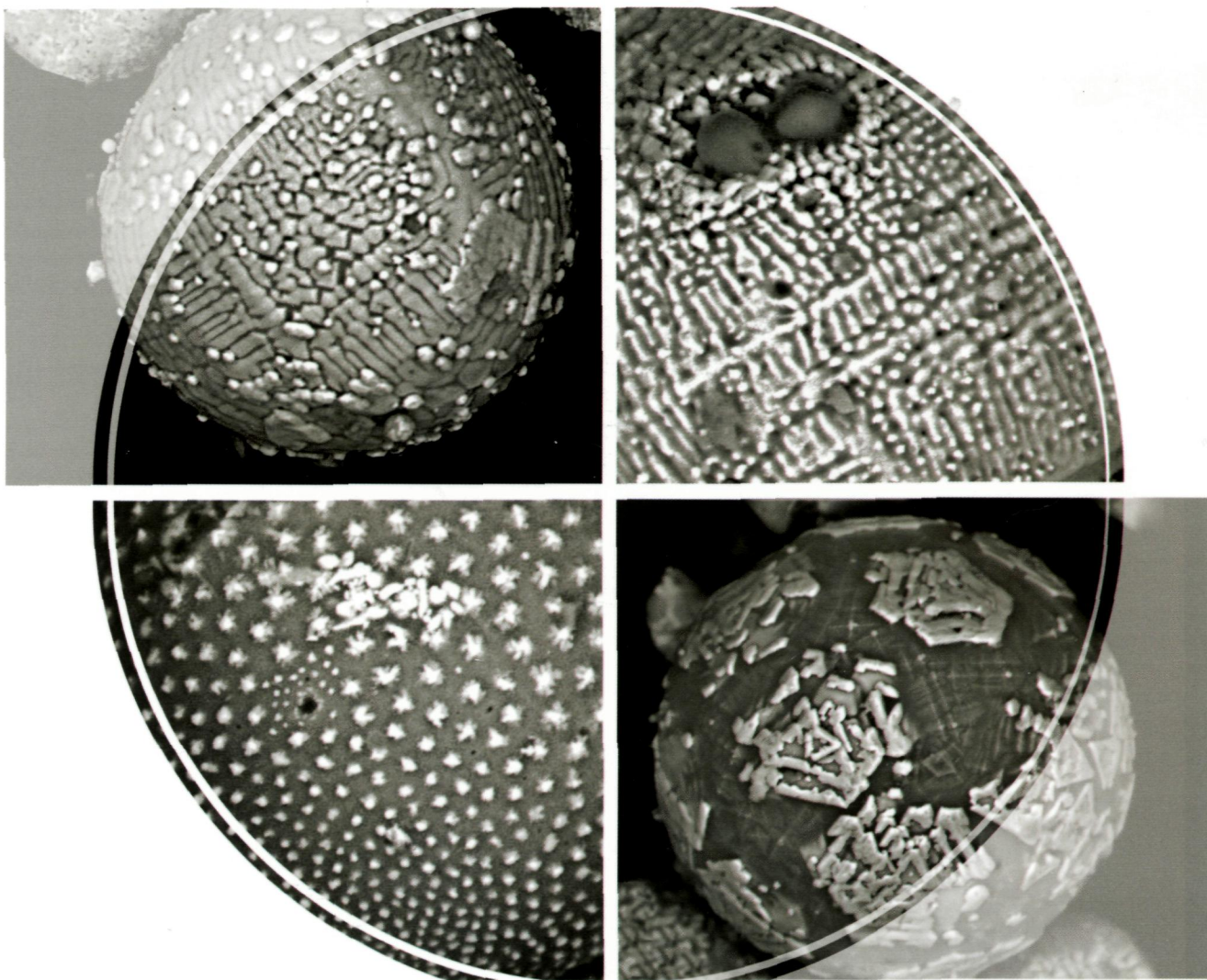
КАТАЛИЗ



В ПРОМЫШЛЕННОСТИ

CATALYSIS IN INDUSTRY

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Статьи на основе материалов устных докладов, представленных на II Российском конгрессе «РОСКАТАЛИЗ»
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(2–5 October 2014, Samara)

GENERAL PROBLEMS OF CATALYSIS

Role of Zeolite in the Preparation of Liquid Hydrocarbons from CO and H₂ on a Composite Co Catalyst 6

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It has been found that the major role of zeolites in the Fischer-Tropsch synthesis on composite Co catalysts is to reduce the average molecular weight of hydrocarbons produced from CO and H₂ on acid sites. Secondary transformations of hydrocarbons on zeolites presumably proceed by the carbocation mechanism. The total composition of the synthesis products depends on the properties of zeolite and on the interposition of active sites of the zeolite and cobalt. It is shown that in many cases the introduction of a zeolite in the H form into cobalt catalysts of the Fischer – Tropsch synthesis increases productivity and selectivity toward the synthetic oil and reduces the selectivity toward methane.

Keywords: Fischer – Tropsch synthesis, cobalt, zeolite, composite catalysts, synthetic crude oil.

Reactors with Membrane Catalysts: Operation Modes, Kinetic Experiment 14

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The paper reports on results of a kinetic study of two modes (contactor and distributor) of a membrane reactor with a porous membrane catalyst in the carbon dioxide reforming of methane. Material balances for the modes were found. The advantages of the modes are demonstrated in fast high-temperature reactions with strong diffusion resistance. An explanation of the observed effect is suggested. The distinction of the used membrane catalyst is that its active component is a bulk layer of molybdenum carbide placed on the outer surface of a tubular ceramic micro-filtration membrane. The application of the catalyst in the dry reforming of methane (at 850 °C) resulted in approximately a 10-fold increase in the reaction rate via the increasing the efficiency of using its internal surface.

Keywords: membrane reactor, membrane catalyst, contactor, distributor, kinetic experiment.

CATALYSIS AND NANOTECHNOLOGY

Silicate Fiberglass Catalysts: from Science to Technology 22

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Effective methods for stabilization of fine particles of Pd and Pt with the size 1,0–1,5 nm in the surface layers of silicate glass at a depth of 10–20 nm are developed. Despite the low metal content (0,01–0,02 wt %), fiberglass-based catalysts (FG) are highly active in the selective hydrogenation of acetylene and in the deep oxidation of hydrocarbons. For example, monometallic Pd/FG exhibits higher selectivity in the hydrogenation of C₂H₂ with the high conversion of acetylene (>99 %) than a commercial Pd-Ag catalyst does, and the activity of Pt/FG in the deep oxidation of organic and organochlorine compounds, including dioxins, is higher than that of the industrial catalyst AP-56 (Pt/Al₂O₃). The effectiveness of Pt/FG in the afterburning of exhaust gas was successfully demonstrated at the Monomer plant (PJSC Nizhnekamskneftekhim) for more than 4 years of continuous operation.

Keywords: fiberglass, palladium, platinum, selective hydrogenation of acetylene, deep oxidation of hydrocarbons, oxidative degradation of chlorinated organics.

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

Oxidation of Phenol with Nitrous Oxide. Role of Acidity of Zeolite Catalysts 30

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The gas-phase oxidation of phenol with nitrous oxide on zeolite catalysts may be of interest as an alternative method of obtaining dihydroxybenzenes (DHB). Previously, there were found catalysts that provide high selectivity of the reaction toward the sum of all three isomers of DHB (85–90 %). The present work is aimed at the optimization of the catalyst in terms of regulation of the regioselectivity of the reaction. The effect

of thermal-steam treatment (TST) of zeolites on their catalytic properties was studied. NMR and IR data showed that the increase in temperature of TST in the range 550–750 °C leads to a 5-fold decrease in the concentration of Bronsted acid sites of the zeolite and to a 2–3-fold increase in the number of α -sites that are responsible for the activity in the oxidation with nitrous oxide. It was found that the variation in the temperature of TST is a powerful instrument to influence the selectivity of the reaction toward individual isomers of DHB. The decrease in the acidity of a zeolite leads to a change in the ratio of isomers in favor of pyrocatechol. The paper discusses the causes of this phenomenon and its relation to the deactivation of the catalyst.

Keywords: dihydroxybenzenes, oxidation of phenol, nitrous oxide, zeolites, acidity of zeolites, hydroquinone, pyrocatechol, resorcinol.

One-Step Synthesis of Cumene from Benzene and Acetone on a Bifunctional Catalyst..... 37

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Hydroalkylation of benzene with acetone was studied on a bifunctional solid catalyst containing zeolite beta and copper supported on silica. The effect of temperature (100–230 °C), pressure (0,1–3,0 MPa), and the composition of the reaction mixture (benzene/acetone) on the process parameters was studied. It is shown that optimum reaction conditions are the temperature of 150–170 °C, pressure of 1–3 MPa and the molar ratio benzene/acetone = (4+9)/1. At 170 °C, 1 MPa, and a 9-fold dilution of acetone with benzene, the conversion of acetone achieves 98 % and the yield of the desired products — cumene and diisopropylbenzenes — is 94 %, which is comparable to the parameters of the industrial alkylation of benzene with propylene. The use of acetone instead of propylene as an alkylating agent makes the proposed method of hydroalkylation more attractive because of a surplus of inexpensive acetone.

Keywords: cumene, isopropylbenzene, acetone, hydroalkylation of benzene.

Zeolite Catalysts with Various Pore Structures in the Synthesis of Pyridines 42

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Development of catalysts based on modified zeolites with a micro- or micro-meso-porous structure and mesoporous metallosilicates is aimed at creating of highly selective methods for producing pyridine and alkylpyridines. A heterogeneous catalytic synthesis of pyridine and methylpyridines was first done via the reaction of ethanol with ammonia and formaldehyde in the presence of the following catalyst systems: microporous zeolites Y, Beta, ZSM-12 and ZSM-5 in the H form, and a granulated Y zeolite with a combined micro-, meso-, and macro-porous structure (HY-MMM). The last is the most effective for the synthesis of picolines: the selectivity toward their formation is 46–63 % at an ethanol conversion of 70–80 %. Among the microporous catalysts, the most active are the highly decationized zeolites H-Y and H-Beta. The main reaction products on the catalysts H-Beta and H-ZSM-5 are pyridine (up to 50 %) and picolines (up to 40 %), while on the catalysts H-Y and H-ZSM-12, the main product are picolines (45–52 %) and lutidines (19–25 %). For zeolite HY-MMM, the influence of reaction conditions on the conversion of ethanol and the composition of pyridines is studied.

Keywords: pyridine, picolines, lutidines, micro- and micro-meso-porous zeolites.

CATALYSIS IN PETROLEUM REFINING INDUSTRY

Hydrocracking of Vegetable Oil on Borate-Containing Catalysts. Effect of the Nature and Content of a Hydrogenating Component 49

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Catalysts based on metals (Pt, Pd) and metal oxides (NiO, Co₃O₄, MoO₃, WO₃) supported on the surface of borate-containing alumina (B₂O₃-Al₂O₃) were compared in hydrocracking of sunflower oil at temperature 400 °C, pressure 4,0 MPa, and mass hourly space velocity 5,0 h⁻¹. Methods TPR H₂, IR spectroscopy of adsorbed CO, and ESDR showed that the hydrogenating components of the catalysts are metals Pt and Pd, ions Ni²⁺, Co²⁺, metals Ni, Co, and higher and partially reduced oxides of Mo and W. Catalysts containing Pt, Pd, NiO, and Co₃O₄ were found to provide complete hydrodeoxygenation of the oil. The main reactions of oxygen removal in Pt- and Pd-systems are decarboxylation and hydrodecarbonylation. For catalysts with NiO and Co₃O₄, characteristic reactions are «reduction» and methanation. The highest yields of the diesel fraction were obtained on catalysts Pt/B₂O₃-Al₂O₃ with a metal content of 0,3–1,0 wt %. Along with n-alkanes, diesel fractions obtained with these catalysts include cycloalkanes and isoalkanes (up to about 40 wt %), while aromatic hydrocarbons are present in trace amounts. Hydrocracking with the Pt-system for 20 h at a mass hourly space velocity of 1,0 h⁻¹ provides a yield of the diesel fraction of at least 82,0 wt % with the content of isoalkanes at least 76,1 wt %.

Keywords: one-step hydrocracking, vegetable oil, supported catalysts, borated alumina, renewable diesel fuel.

Cracking of Heavy Oil Feedstock Using Catalytic Additives Based on Ferrospheres from Energy Ashes..... 65

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In processing a heavy oil feedstock, an urgent problem is to find new and less expensive, primarily cracking, catalysts. We have studied the activity of redox catalysts based on ferrospheres from energy ashes in the cracking of two types (paraffinic and asphaltenic) of heavy oil and paraffinic crude oil under autoclave conditions. It was found that at 450 °C and in the presence of 10 wt % of ferrospheres, the selectivity toward liquid products for paraffinic and asphaltenic feedstock achieves 95–96 % and 72 %, respectively. Compared with the thermal cracking, this catalytic system provides the composition of liquid products with the higher content of light products and higher percent of the gasoline fraction. The influence of ferrospheres is most pronounced in the cracking of paraffinic feedstock: compared with thermal cracking, the content of light fractions in the products of petroleum cracking increases by ~20 % and achieves 67 %, while in the products fuel oil cracking, the ratio of the gasoline fraction increases 14-fold. During the cracking, we detected changes in the phase composition and structural characteristics of ferrospheres, formation of surface carbonaceous deposits with different reactivity in the combustion, and accumulation of sulfur compounds from petroleum feedstock.

Keywords: heavy oil, fuel oil, ferrospheres, energy ashes, initiated cracking.

Co-Conversion of *n*-Hexane and *n*-Butane on Zirconium-Zeolite Catalysts 73

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To create a catalytic system for low-temperature isomerization of a mixture of normal and low-branched alkanes, conversion of *n*-butane, *n*-hexane and their mixture (mole ratio 1:1) was studied using a catalytic system Ni/MOR-SO₄²⁻/ZrO₂ and its components. It was shown that the combination of properties of Ni/MOR and SO₄²⁻/ZrO₂ can decrease the temperature of the isomerizing catalyst below 150 °C. The combined isomerization of *n*-butane and *n*-hexane provides an increase in the conversion of *n*-butane with the formation of isopentane and a decrease in the conversion of *n*-hexane as compared with the conversions obtained during their separate transformation. Thus, the combined isomerization can increase the octane number of straight-run gasoline fractions as a result of averaging their molecular weight because of the accumulation of isopentane.

Keywords: *n*-butane, *n*-hexane, isomerization, mordenite, sulfated zirconia, bimolecular mechanism.

Efficiency of Catalytic Dewaxing with the Use of Zeolite Catalyst with the Addition of Iron 79

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We have studied the possibility of production of diesel fuel for cold climates from middle distillates of different origins via the catalytic dewaxing on a zeolite catalyst with the addition of iron. The addition of iron into a zeolite provides the high stability of the catalyst. A technological scheme has been developed for catalytic dewaxing with the fractionation of hydrogenate, depending on characteristics of raw materials. The scheme involves subsequent dewaxing of the isolated heavy diesel fraction and compounding of the obtained product with a light fraction, which has desired low-temperature properties and does not require dewaxing. The technical result of the application of this method for any catalytic dewaxing process is the production of diesel fuels for the cold and arctic climate that satisfy the requirements of GOST 32511-2013 and/or GOST R 55475-2013 at minimized production costs.

Keywords: diesel fuel, low-temperature properties, catalytic dewaxing, catalyst, technological scheme, fractionation.

CHRONICLE

To 80th Anniversary of Yu.A. Treger 86