

КАТАЛИЗ В ПРОМЫШЛЕННОСТИ

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CATALYSIS IN INDUSTRY



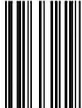
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A.N. Saliev¹, V.B. Il'in¹, M.A Timokhina¹, A.V. Dul'nev², A.P. Savost'yanov¹, R.E. Yakovenko¹

¹ Platov South-Russian State Polytechnic University (NPI), Novocherkassk, Russia

² OOO «NIAP-KATALIZATOR», Novomoskovsk, Russia

The applicability of some industrial catalysts for the process of carbon dioxide conversion into synthesis gas has been evaluated process of carbon dioxide conversion into synthesis gas. For the study were chosen catalysts on the basis of transition metals (Fe, Ni, Co) and Cu, used in large-tonnage hydrogenation processes and synthesis-gas technology: NIAP-03-01 (catalyst for steam conversion of hydrocarbon gases), NIAP-06-06 (catalyst for low-temperature conversion of CO), AmoMax 10 (catalyst for ammonia synthesis), Co-Al₂O₃/SiO₂ (catalyst for synthesis of hydrocarbons by Fischer-Tropsch method). The catalysts were tested in the process of catalytic reduction of CO₂ by reaction reverse gas-water shift (RGWS). It was shown that Cu-containing catalyst (NIAP 06-06) possesses the highest activity and selectivity in the process of catalytic reduction of CO₂. Under conditions of GHSV = 32 000 h⁻¹, H₂/CO₂ = 2, and temperatures of 500–800 °C, the equilibrium of the RGWS reaction is achieved by 97 %. Due to selection of technological parameters of CO₂ reduction (temperature, H₂/CO₂ ratio) it is possible to obtain synthesis gas of the required composition. Due to selection of technological parameters of CO₂ reduction (temperature, H₂/CO₂ ratio) it is possible to obtain synthesis gas of the required composition for the synthesis of hydrocarbons and methanol.

Keywords: carbon dioxide, catalyst, catalytic reduction, synthesis gas.

Dehydrogenation of *n*-butane to 1,3-butadiene on chromia-alumina catalyst:

1. Kinetics of dehydrogenation and coke formation 16

E.V. Ovchinnikova, R.V. Petrov, V.A. Chumachenko, A.S. Noskov

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

The kinetics of dehydrogenation of *n*-butane to butadiene was studied on K-CrO_x/γ-Al₂O₃ catalyst particles of 56–94 μm size by varying the temperature $T = 550\text{--}625$ °C, the time of catalytic step TOS = 5–30 min, and the space velocity GHSV = 4400–35 200 h⁻¹. The catalyst was similar to the commercial one. Prior to the studies, the catalyst granules were stabilized during the reduction-dehydrogenation-regeneration cycle at 593 °C, then the catalyst particles milled to a size of 56–94 μm were stabilized during the dehydrogenation-regeneration cycle at 650 °C. The highest butadiene selectivity of ~25 mol.% was obtained at *n*-butane conversion of 26–30 % (GHSV = 35 200 h⁻¹) at $T = 600$ °C and TOS = 5 min, and the highest butadiene yield of ~10 mol.% was obtained when the conversion was increased to ~50 % (GHSV = 8800 h⁻¹) under the same conditions. Increasing T to 625 °C, TOS to 30 min and decreasing GHSV to ~4400 h⁻¹ resulted in an increase in by-product selectivity to ~50 mol.%. It was found that the observed activation energy of product formation rates decreases in the series: by-products > butylene > > butadiene. A kinetic model is proposed that takes into account the formation of butadiene via butylene, the formation of by-products such as ethane/ethylene and methane/propylene in the butylene hydrocracking reactions, and the secondary conversion reactions of by-products. Inhibition of dehydrogenation reactions by components of the reaction mixture, coke formation and its effect on catalyst activity are also considered in the model. The adequacy of the kinetic model is confirmed by good agreement of the calculated results with the experimental data.

Keywords: kinetic model, *n*-butane, 1,3-butadiene, dehydrogenation, hydrocracking, coke formation.

Dehydrogenation of *n*-butane to 1,3-butadiene on chromia-alumina catalyst:

2. Mathematical model of the reactor 29

E.S. Borisova, V.M. Khanaev, E.V. Ovchinnikova, A.S. Noskov

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

The mathematical model of the adiabatic fixed-bed catalytic reactor for direct dehydrogenation of *n*-butane to butadiene operating under non-stationary conditions is formulated for the first time. The model includes kinetic equations that describe the formation of primary products, by-products, secondary products and coke on the K-CrO_x/γ-Al₂O₃ catalyst [Cat. Ind. 2024. V. 24(1). P. xx–xx]. The model allows predicting the yield of butadiene and other products depending on the process parameters, such as the catalyst activity, the feed gas composition, the cycle time of the dehydrogenation period, the ratio of the catalyst to inert material (for both uniform and non-uniform dilution). The model allows calculating the temperature regime of the catalyst operation and the degree of its coking along the bed length. The adequacy of the model to the industrial process in the description of *n*-butane conversion, butadiene and butylene formation, coke accumulation and loss of catalyst activity is shown on the example of test calculations of the main process parameters.

Keywords: dehydrogenation of *n*-butane into butadiene-1,3; mathematical model of the industrial process; verification of the model by industrial data.

Study of the kinetic regularities of the process of liquid phase oxidation of *sec*-butylbenzene in the presence of *N*-hydroxyphthalimide 39

V.S. Kabanova¹, A.S. Frolov¹, E.A. Kurganova¹, V.N. Sapunov², G.N. Koshelev¹, E.I. Baev¹

¹ Yaroslavl State Technical University, Yaroslavl, Russia

² Mendeleev University of Chemical Technology of Russia, Moscow, Russia

The kinetic patterns of liquid-phase aerobic oxidation of *sec*-butylbenzene to its tertiary hydroperoxide in the presence of *N*-hydroxyphthalimide as a catalyst have been studied. The influence of temperature, reaction duration and catalyst content on the rate of *sec*-butylbenzene oxidation was studied. Based on the experimental data obtained, a kinetic (mathematical) model of the process under study was compiled, which adequately describes the change in the concentration of the main components during the reaction. The numerical values of the rate constants of the main stages of the process are calculated. It was revealed that the oxidation of *sec*-butylbenzene in the presence of *N*-hydroxyphthalimide allows you to intensify the oxidation process of this hydrocarbon while maintaining high rates and selectivity of the formation of its hydroperoxide.

Keywords: liquid-phase aerobic oxidation, hydroperoxide, *N*-hydroxyphthalimide, phthalimide catalysts, *sec*-butylbenzene.

Perspectives for synthesis of linear alkylbenzenes via homogenous catalytic alkylation of benzene with olefin-containing complex mixtures: analysis of products composition using two-dimensional chromatography 50

F.S. Golub, V.A. Bolotov, A.Yu. Shabalin, P.A. Dolgushev, V.N. Parmon

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Multicomponent mixtures with wide fraction of olefins obtained from thermal pyrolysis of higher paraffins were used for catalytic alkylation of benzene. Reaction was carried out in the presence of methanesulfonic acid as a homogenous catalyst, which has low corrosive properties compared to common industrial catalytic systems. The use of two-dimensional gas chromatography to analyze the composition of both the initial multicomponent raw material and the alkylation products allowed us to tune the initial conditions of the reaction and correctly calculate important parameters of the process such as selectivity and conversion. Thus, depending on the feedstock, the selectivity of LAB formation was varied in the range of 82.4–88.3 %, while for the 2-LAB it was varied between 29.2–41.3 % at ~90 % olefin conversion.

Keywords: two-dimensional chromatography, benzene alkylation, linear alkylbenzenes, LAB, linear α -olefins, LAO, methanesulfonic acid.

Determination of the conditions of technologically optimized reduction of high-performance Fischer–Tropsch synthesis catalysts 60

I.G. Solomonik, V.Z. Mordkovich

Technological Institute for Superhard and Novel Carbon Materials (TISNCM), Moscow, Russia

The activation stage of high-performance cobalt catalysts for Fischer–Tropsch synthesis has been studied, taking into account the transformation of emerging structures and the presence of a percolation heat-conducting network of metallic aluminum. The influence of temperature, process duration, composition of the reducing gas, as well as its volumetric velocity on the degree of reduction and surface area of the active component of the catalyst was studied. These characteristics were determined by low- and high-temperature oxygen titration in a chromatographic-type sorption unit, as well as using temperature-programmed reduction. The possibility of reducing the temperature and concentration of hydrogen in the gas to achieve the required parameters during reduction to obtain a high-performance catalytic system has been experimentally demonstrated. Its performance in Fischer–Tropsch synthesis (CO conversion, liquid hydrocarbon productivity) is comparable or better than that achieved on a catalyst reduced under standard conditions.

Keywords: Fischer–Tropsch synthesis, Co catalyst, activation stage, degree of reduction.

Fabrication of SBA-15-supported nanoscale Co_3O_4 and its use in the catalytic hydrogenation of cinnamaldehyde 71

Ruhul Amin Bepari^{1,2}, Birinchi Kumar Das^{1,2}

¹ Department of Chemistry, Gauhati University, Assam, India

² Department of Chemistry, Bhattadev University, Assam, India

Nanoscale Co_3O_4 has successfully been supported onto the mesoporous SBA-15 following two methods viz. direct deposition (DD) and isonicotinate ligand assisted (INL) route. The later method (INL) involves the formation of cobalt isonicotinate tetrahydrate complex inside mesopore volumes of SBA-15 and subsequent calcination of the cobalt complex loaded SBA-15 composite. The present method is found to be

advantageous in reducing the formation of oxide particles outside mesopores. The synthesized materials are investigated by various physical tools such as XRD, SEM, TEM and H₂-TPR in combination with N₂ adsorption-desorption study. As a promoter, little amount of gold is also deposited in SBA-15 supported Co₃O₄ samples and all these materials are explored as catalysts in the hydrogenation of cinnamaldehyde. The composite material that is synthesized via DD method has shown promising results in the hydrogenation reaction giving 50 % CAL conversion with 66 % selectivity for H₂CAL at 170 °C under the hydrogen pressure of 20 bars.

Keywords: gold, Co₃O₄, isonicotinate, SBA-15, cinnamaldehyde, hydrogenation, hydrocinnamaldehyde.

Facile synthesis of nanoscale CuO and NiO via the PVA-assisted sol-gel method and their exploration in the catalytic epoxidation of styrene 72

Ruhul Amin Bepari^{1,2}, Nabajyoti Mochahari², Kibriya Siddique³, Birinchi Kumar Das^{1,2}

¹ Department of Chemistry, Gauhati University, Assam, India

² Department of Chemistry, Bhattadev University, Assam, India

³ Department of Instrumentation & USIC, Gauhati University, Assam, India

Both nanoscale copper oxide and nickel oxides, with diameter 17 and 25 nm respectively, have been synthesized via an easy sol-gel method using polyvinyl alcohol. The method involves the simple dispersion of metal ions (M²⁺ = Cu or Ni) into the PVA gel and subsequent calcination of the dried gel at 400 °C for 3 h. The synthesized oxide materials are characterized by different physical tools like TGA, powder XRD, SEM, TEM and DRS UV-visible spectroscopic technique. The oxides are found to be very efficient catalysts in the epoxidation of styrene. CuO gives 87 % styrene conversion and 88 % SO selectivity while, NiO gives 69 % styrene conversion and 80 % with TBHP as an oxidant at the end of 6 h. Both the catalysts can suitably be reused for several successive runs without appreciable loss in activity and selectivity. The cost-effective synthesis, excellent catalytic performance and reusability make these oxides promising catalysts for the industrial use.

Keywords: CuO, NiO, nanoparticles, sol-gel, calcination, styrene, epoxidation, TBHP.

BIOCATALYSIS

Comparative analysis of biotechnological and catalytic approaches to the production of organic acids 73

K.N. Sorokina, Y.V. Samoylova, V.N. Parmon

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

Using renewable resources to produce valuable chemical products is an alternative to traditional processes based on petrochemical synthesis. The review focuses on the main approaches associated with the production of organic acids from glucose and cellulose as the components of renewable biomass. It covers a comparison of biotechnological approaches for the production of glycolic, glutaric, mesaconic, muconic, isobutyric, lactic, 3-hydroxypropionic, succinic, itaconic and adipic acids with catalytic approaches. It was shown that the biotechnological production of succinic and lactic acids has been applied on an industrial scale, and that a number of other organic acids can be produced using fermentation if more productive strains will be used.

Keywords: biomass, fermentation, biotechnology, sugars, acids.

Biochar from microalgae: production and properties 83

Y.V. Samoylova, K.N. Sorokina, V.N. Parmon

Boreskov Institute of Catalysis SB RAS, Novosibirsk, Russia

This review examines approaches to producing biochar from microalgae biomass using pyrolysis, torrefaction, and hydrothermal treatment. Data on the textural characteristics of biochar obtained by different methods are presented, and the features of their production are also considered. It was revealed that the content of one or another component in the biomass, depending on the type of microalgae used, the conditions of its cultivation and the conditions of thermal treatment of the biomass (temperature, heating rate and duration) affects the textural characteristics of the resulting biochar.

Keywords: biomass, microalgae, biochar.