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CATALYSIS IN INDUSTRY



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- The Maximal «Content» of Reactive Hydrogen in Nickel Catalysts under Conditions of Liquid-phase Hydrogenation 6
Afineevskii A.V., Lukin M.V.

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A supplement to the procedure for determining the maximal «content» of hydrogen using the method of chemical dehydrogenation was developed to take into account processes of adsorption of the organic reactant used as the titrant. The supplement makes it possible to determine the quantity of reactive hydrogen on the catalyst surface, which is capable of entering the reaction with the organic reactant.

Keywords: porous nickel catalyst, liquid-phase hydrogenation, maximal «content» of hydrogen, catalyst activity, catalyst poison.

CATALYSIS IN CHEMICAL AND PETROCHEMICAL INDUSTRY

- Oxidation of Methanol to Formaldehyde in Microchannel Reactors: Prospects and Limitations 11
Chumachenko V.A., Ovchinnikova E.V., Gribovskii A.G., Makarshin L.L.

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Experimental studies of specific features of high-exothermic selective oxidation in a monolith microchannel reactor (MCR) were carried out with oxidation of methanol to formaldehyde over a Fe-Mo catalyst as an example. The intensive heat withdrawal from the reaction zone, a higher concentration of methanol (up to 12–12,5 %), fine catalyst particles (less than 0,25 mm in size) make it possible to intensify considerably the process and to increase the yield of the target product per catalyst unit volume to as large as 7–12 times of that in tube reactors. The temperature conditions in MCR are close to the theoretically optimal regime for this process family and provide a high selectivity to formaldehyde. While the activity of the Fe-Mo catalyst decreases in MCR, the problem of the catalyst stability should be solved in estimating potentials of MCR in this process. If catalytic processes in MCR can be intensified without noticeable decrease in the catalyst activity, the application of MCR will be rather promising and technologically useful.

Keywords: formaldehyde synthesis, iron–molybdenum oxide catalyst, tube reactor, microchannel reactor, productivity.

- Cobalt-aluminium Oxide Catalysts for Transformation of CO and H₂ in Fischer – Tropsch Syntheses 17
Simentsova I.I.¹, Khassin A.A.^{1,2}, Shtertser N.V.^{1,2}, Davydova L.P.¹, Minyukova T.P.¹, Yurieva T.M.¹

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Properties of cobalt-aluminium catalysts for the Fischer – Tropsch synthesis were studied to identify conditions for the catalyst preparation and activation that would allow the reduction temperature to be lowered and the catalyst performance to be improved. It was shown that an increase in the ratio of NO₃⁻/CO₃²⁻ anions to ca. 1,9–3,1 in the hydroxo-nitrate-carbonate precursors of the said catalysts favors a decrease in the temperature of reduction of cobalt cations in oxide precursors. Adsorption properties of the cobalt metal particles formed at different temperatures of the reduction of the oxide samples were studied to show that the catalyst activation at 500 °C is preferable for the formation of disperse particles of Co⁰. In the Fischer-Tropsch reactions with mixtures CO:H₂:N₂ = 30:60:10 vol.% at T = 210 °C and P = =2,1 MPa, the catalysts reduced at 500 °C demonstrate a high efficiency comparable with the efficiency of commercial Co-containing catalysts (ca. 0,34 g_{CH}/(g_{cat}·h)).

Keywords: Fischer – Tropsch synthesis, Co-Al hydroxo-nitrate-carbonate, reductive activation, dispersion of Co⁰ particles.

- Special Aspects of DME Production from Synthesis Gas over Mixed Catalysts 23
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The process of the production of dimethyl ether (DME) from synthesis gas over a mixture of catalysts for methanol synthesis (25,10 wt.% ZnO; 64,68 wt.% CuO; 10,04 wt.% Al₂O₃) and for methanol dehydration (γ-Al₂O₃) was studied at different modes of catalyst loading (one-, two-, three-bed). A common for all the modes regularity was established: The total conversion of CO decreases with temperature elevation, the conversion to methanol being decreased but to DME increased. The highest selectivities to DME and DME yields were observed in the case of the three-bed loading. The highest DME yields were obtained at 250–285 °C. It was shown that the use of a mechanical mixture of the catalyst for methanol synthesis and alumina allows effective production of DME from nitrogen-ballasted (20 vol.%) synthesis gas with a low ratio H₂/CO = 1, that is unfavorable for methanol synthesis, while DME yield per feed may reach ca. 10 wt.%.

Keywords: synthesis gas, DME, methanol, carbon dioxide, kinetics.

The Influence of Morphology of a Ti-Mg Catalyst for Propylene Polymerization in a Liquid Monomer Medium on the Polypropylene Properties 30

Salakhov I.I.¹, Batyrshin A.Z.¹, Sergeev S.A.², Bukatov G.D.², Barabanov A.A.², Matsko M.A.², Sakhabutdinov A.G.¹, Zakharov V.A.²

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The studies were focused on the influence of particle size of the Russian Ti-Mg catalyst IC-8-21 on the properties of polypropylene (PP) synthesized by polymerization of propylene in a liquid monomer medium. The catalysts with particles of 20 to 64 nm in size were shown to be highly active, identically sensitive to hydrogen and to provide synthesis of PP with a narrow particle size distribution, high isotacticity, close values of crystallinity, melting temperature and physicomechanical properties. A minor decrease in the activity and bulk density of PP powder was observed with an increase in the average size of catalyst particles from 20 to 43 nm. The activity and bulk density decreased more considerably over the catalyst with particles of 62–64 nm in size. The properties of polypropylene synthesized over IC-8-21 are not inferior to the properties provided by the known analogues.

Keywords: Zigler – Natt catalysts, Ti-Mg catalyst, propylene polymerization, polypropylene properties.

ENGINEERING PROBLEMS

Life Tests and Kinetic Experiment in a Displacement Reactor with a Fixed Catalyst Bed 34

Karalin E.A.¹, Oparin A.V.¹, Abramov A.G.², Pavlov S.B.¹, Murtazin N.F.¹, Appakova D.M.³, Ksenofontov D.V.¹, Miroshkin N.P.¹, Kharlampidi Kh.E.¹

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Alternative designs of a pilot reactor for long-term testing of heterogeneous fixed bed catalysts were discussed with liquid-phase hydrogenation of methylphenylketone to 1-phenylethanol as an example. The discussion is exemplified with the calculation of a reactor unit for hydrogenation over catalyst NTK-11. It was demonstrated that a cascade of three adiabatic reactors with a 4,5 m high catalyst bed in each of them is needed to provide the residual concentration of the reactant less than 1 wt.%.

Keywords: methylphenylketone, hydrogenation, heterogeneous catalysis, fixed catalyst bed reactor, mathematical model.

DOMESTIC CATALYSTS

Deliberate Synthesis of a Copper Catalyst with a Nanostructured Active Component 41

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The influence of hydrodynamic mode of mixing a copper-ammonium-carbonate slurry containing aluminosilica support on the chemical and phase composition of the active component (AC) precursor of the catalyst for dehydrogenation of cyclohexanol in the production of caprolactam was studied. XPS, DTA and adsorption techniques were used to establish that, under conditions of the advanced turbulent mode, the precursor is mainly deposited in the form of nanostructured hydroxocarbonates anchored tightly to the support. The lab-scale technology was scaled-up to industrial level. Properties of the new copper catalyst were studied to reveal that it is not inferior in the selectivity to the best known industrial (commercial) catalysts, but superior to them in the activity and thermostability.

Keywords: copper-containing catalyst, ammonium-carbonate technology, hydroxocarbonate structures, thermostability.

ELECTROCATALYSIS

Properties of Cathode Non-Platinum Catalysts for Oxyhydrogen Fuel Cell with Proton- and Anion-conducting Electrolytes 48

Korchagin O.V.¹, Bogdanovskaya V.A.¹, Tarasevich M.R.¹, Kuzov A.V.¹, Zhutaeva G.V.¹, Radina M.V.¹, Novikov V.T.², Zharikov V.V.²

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Pyrolysis of nitrogen-containing complexes of iron and cobalt on the surface of disperse carbon materials was used for synthesis of cathode catalysts for oxyhydrogen fuel cells (FC) with proton-conducting (acidic) and anion-conducting (alkaline) electrolytes. The catalysts were characterized by XPS and tested using a thin-film disc electrode and in oxyhydrogen FC under model conditions. Properties of the CoFe/C system prepared by pyrolysis of macroheterocyclic compounds of iron and cobalt on carbon materials (soot HS-72 and multilayer nanotubes (CNT))

were described for the first time. From XPS data, the surface of the catalytic CoFe/C systems is rich in carbon (95,5 at.%), contains nitrogen (2 at.%), oxygen (2 at.%) and metals (0,5 at.%). The data obtained by electrochemical measurements under model conditions revealed that the catalytic systems CoFe/CNT are close to the commercial platinum catalyst 60%Pt/C (HiSPEC9100) in their activity to oxygen reduction in an alkali medium (0,5 M KOH). Half-wave potentials are 0,85 and 0,88 V for catalysts CoFe/CNT and 60%Pt/C (HiSPEC9100), respectively. The maximal specific capacity of the oxyhydrogen FC with an anion-conducting electrolyte is 210 mW/cm² (a 60%Pt/C (HiSPEC9100) based cathode) and 180 mW/cm² (CoFe/CNT based cathode). In its characteristics, MEA with the non-platinum cathode compete well with the best analogues described in literature. The results obtained demonstrated the necessity of the further studies on scaling-up the technology for synthesis of the developed non-platinum cathode catalysts and on optimization of the MEA FC architecture based thereon.

Keywords: oxygen electroreduction, non-platinum catalysts, oxyhydrogen fuel cell, proton-conducting polymer electrolyte, anion-conducting polymer electrolyte.

BIOCATALYSIS

Pre-treatment of Rice Husk in a Semicommercial Mill for the Following Enzymatic Hydrolysis..... 57

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The influence of mechanical activation of rice husk on the reactivity of the comprised carbohydrates was studied. A semicommercial centrifugal roller mill was used for the activation. The mechanical activation of the raw material was established to result in improvement of the reactivity owing to enlargement of the surface area and amorphization of crystalline fragments of cellulose. Optimal technological regimes of the activation were determined to prepare the reactive product from rice husk: rotor speed of 1500 RPM, feed rate of 30 kg/h. Particles of rice husk of 45–50 mm are obtained under these conditions. As a result, the yield of low-molecular carbohydrates increases by a factor of 7 upon complete enzymatic hydrolysis.

Keywords: enzymatic hydrolysis, scaling, mechanical pretreatment, rice husk, biofuel, centrifugal roller mill.

CATALYSIS IN RUSSIA

Russian Patents on Catalysis 2000-2014: Bibliometric and Topical Analysis..... 62

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The database Chemical Abstracts Plus of the data retrieval system SciFinder was used for comparative bibliometric and topical analysis of patents on catalysis published in 2000–2014 in Russia and worldwide. Since the beginning of the century, the number of annually registered patent on catalysis has increased by a factor of 1,4 in Russia, but by a factor of 2,5 in the world and 22 in China. In the worldwide base of patents on catalysis, the current share of Russia is 2 % that corresponds to the sixth position. The topical distribution of the Russian patents on catalysis differs from that in the world: most of the Russian patents deal with processing of fossil fuel, while this topic is in the fourth position in the world, and the top position relates to high-molecular chemistry, air cleaning from contaminants and industrial hygiene.

Keywords: bibliometric analysis, patents, catalysis, Chemical Abstracts, SciFinder.