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One-pot synthesis of granulated alumina-chromia catalysts for fixed-bed isobutane dehydrogenation

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The demand for olefins continues to grow rapidly that is associated with a growing manufacturing of polymers and other chemicals. In the Russian petrochemical industry, the microspherical alumina-chromia fluidized-bed catalysts are mainly used for the dehydrogenation of paraffinic hydrocarbons into the corresponding olefins [1]. The processes of dehydrogenation of paraffins with a fixed catalyst bed (Catofin and Catadiene processes are practically not implemented in Russia because of the lack of Russian-made fixed-bed catalysts.

High requirements are imposed to fixed-bed catalysts: they should feature high activity and selectivity, be resistant to catalytic poisons, withstand short-term overheating, have high stability, including maintaining high catalytic activity and pellet strength for a long operation time (more than 1 year [2]. Particular attention is paid to the porous structure of the catalyst since it determines the catalytic properties of the catalyst granules. For high-temperature processes such as the dehydrogenation of paraffins, which proceed with an increase in the number of moles of a substance and are limited by thermodynamic equilibrium, the porous structure significantly affects the process performance since it determines the mass transfer inside the catalyst granule [3,4]. The development of supports and catalysts with a biporous structure, including meso- and macropores, is a promising solution. One-stage wet mixing method of catalyst preparation may be an alternative to the impregnation method for the industrial implementation of the synthesis of alumina-chromia catalysts. This method is based on the preparation of catalysts directly from the precursors of support, active component, and modifiers, followed by extrusion and heat treatment. This approach can significantly reduce the number of stages and, accordingly, energy costs. The development of methods to control the structure of alumina-chromia catalysts, in particular, the creation of a biporous (hierarchical pore structure, is an important challenge to create catalysts that meet the requirements of industrial application in dehydrogenation in a fixed-bed reactor.

A series of chromium-containing catalysts was synthesized by wet mixing. Alumina precursor (thermally activated aluminum trihydroxide was mixed with an aqueous solution containing dissolved precursors of chromium oxide (CrO_3, chemically pure and modifier (KNO_3, chemically pure. Wood flour was used as a porogen agent in an amount of 2 to 8 wt.%. Then, the resulting mass was molded by extrusion to obtain cylindrical granules with a diameter of about 3 mm. The catalyst was dried at a temperature of 100°C for 4 h and calcined in air at 750°C for 4 h. It was shown that the addition of a wood additive made it possible to obtain catalyst granules with the biporous structure (the presence of meso- and macropores. Wood flour did not affect the phase composition and distribution of chromium in the catalyst. The catalytic properties of the composites obtained by the one-stage wet mixing method were close to those of the catalysts obtained by the impregnation method. The isobutane conversion of 60–68% with the selectivity towards isobutylene of above 93% were achieved at 570-610 °C over alumina-chromia catalysts synthesized by the one-pot wet mixing method.

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