Influence of oxidants and promoters on propane dehydrogenation over chromium-oxide catalysts

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Abstract

Dehydrogenation of low paraffins in the presence of oxidants is a promising method for olefins production. Oxidants shift the equilibrium of the dehydrogenation reaction interacting with hydrogen and oxidize the coke, forming during the reaction. The use of O_2 results in an oxidation of the produced olefin, what leads to a decrease of the process selectivity. The use of an oxidant with less oxidizing power than molecular oxygen, such as CO_2 allows to increase the selectivity but the amount of formed coke during the process is rather high. The introduction of small amount of O_2 in the reaction mixture could decrease coke formation. Early [1] we have found that the introduction of 5.0 % (vol.) in the reaction mixture of propane and carbon dioxide resulted in some increase of the activity and stability of chromium-oxide catalysts but the yield of propene is decreased in comparison with the experiment without O_2. Another way to increase the activity and selectivity of chromium-oxide catalysts could be the addition of alkaline or alkaline earth promoters in chromium catalysts. In this work we tried to find optimal concentrations of O_2 and CO_2 for separate and simultaneous presence at which the yield of propene is kept on high level during long time. The contents of oxidants in the reaction mixtures are changed in the following limits (%, vol.): O_2 (0-7.5), CO_2 (0-60.0). The catalysts of CrO_x/SiO_2 (KSKG) contained 1.0; 2.0 and 5.0 Cr (wt.). Long-time studies were carried out in a flow reactor at 600^{o}C, volume space velocity *200* h^{-1}. It was found that the yield of propene at contents of O_2 and CO_2 at the simultaneous presence equal 2.0 and 30.0 %, respectively, is higher than the propene yield at the separate presence of such amounts of these oxidants. High yield of propene is kept during more long time than at the use of the reaction mixture without O_2. The increase of O_2 concentration results in the enhancement of the stability and the decrease of propene yield. Thus, at low O_2 concentration formed coke is oxidized more actively than adsorbed propene. It was stated that introduction of Li, Na, K and Ca results in the decrease of the stability of catalysts. The stability is decreased over Li-Cr-catalysts in the most extent. The share of irreversible deactivation of all promoted catalysts was more than for unpromoted catalysts, especially after repeated regenerations. The yield of propene over promoted catalysts is higher than one over unpromoted catalysts only at initial period (200-300 min.), but after this time the propene yield is fallen very quickly and it becomes below than one over unpromoted catalysts. So, increase of activity and selectivity chromium-oxide catalysts in propane dehydrogenation can be reached rather by the finding the optimal concentrations of oxidants than by the introduction of such promoters as Li, Na, K, Ca.

1. Lapidus A.L., Botavina M.A., Agafonov Yu.A., Trushin D.V., Makashov A.A., Nekrasov N.V., Gaidai N.A. Proceeding of DGMK/SCI-Conference. Milan, 2005, p.187.