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Oxidative dehydrogenation of C₃-C₄ paraffins in the presence of CO₂ over chromium catalysts

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The transformation of light alkanes into alkenes by catalytic oxidative dehydrogenation (ODH) might be an effective way, since cheap and natural starting materials are converted to valuable olefins. Use of mild oxidant, such as CO₂ instead of O₂ in ODH of light paraffins allows to increase the alkene selectivity. Besides, CO₂ can be a diluent in the process and remove reaction equilibrium to olefins formation. The enhancing the olefin selectivity and catalyst stability are main factors for making the process of light alkanes ODH commercially valuable. This can be achieved by the development of new catalytic systems and the optimization of reaction conditions.

Different Mo, Mn, Co, Cr and rare earth metal oxides were studied as catalysts for ODH of propane and isobutane. It was found that supported chromium catalysts are one of the best in these reactions (high activity and selectivity). We used different supports (for example SiO₂, Al₂O₃, and zeolites), adopted various methods of catalyst preparation, such as impregnation, equilibrium adsorption, and ion exchange (in the case of zeolites), stated the optimal chromium concentration, tested the influence of the reaction temperature and space velocity and studied catalysts deactivation and influence of added oxygen. ODH of propane and isobutane in presence of CO₂ is an endothermic process. The addition of a small amount of oxygen to the reaction mixture leads to the decrease of energetic inputs and depresses the residual coke formation thereby increasing catalyst stability.

Catalytic studies were carried out in a flow-reactor at 500–700°C and atmospheric pressure. The reaction products were analysed by GC methods using two columns – molecular sieves 5A and Porapak Q. It was found that SiO₂ is the optimal support and the impregnation is the best method of chromium supported catalyst preparation. The dependence of catalyst activity on Cr concentration indicates that propane and isobutene conversion grows nonlinear up to 5,0 % (wt.) of chromium. The further increase of active phase concentration results in significant decrease of catalyst activity. Propene and isobutene selectivity increases sharply with the increase of chromium concentration from 0,5 to 1,0 % (wt.) and then remains practically constant. It means that the change of active phase concentration affects in an identical way on the basic and side reactions. It was found that the addition up to 5,0 % of oxygen results in a significant increase of catalyst activity and stability at light decrease of catalyst selectivity. This can be used for optimization of reaction conditions.