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Oxidative dehydrogenation of isobutane over molybdenum and chromium catalysts

The oxidative dehydrogenation (ODH) of isobutane is attractive way for isobutene production owing to the absence of thermodynamic limitations and catalyst deactivation. Different catalysts can apply for this process. In our investigation we were prepared and tested various molybdenum and chromium catalysts which are effective ones for ODH of paraffins. SiO₂, TiO₂, MgO, Al₂O₃ are used for preparing various supported catalysts. Besides such catalysts as CoCrO₄, NiCrO₄, MnCrO₄, CoMoO₄, NiMoO₄ with different relation Me (Co, Ni, Mn) and Cr (Mo) and additives (K, Ba) were tested to choose the optimal catalysts in the presence of oxygen. Co_{0,95}MoO₄ was the most active and selective catalyst in ODH of isobutane. The selectivity in olefins was 44,5% at conversion 62,0% for 550°C. The kinetics and mechanism of isobutane ODH were investigated in order to determine the factors controlling the activity and selectivity of this catalyst.

The kinetic experiments under steady-state conditions were carried out using a circulating flow system at atmospheric pressure in wide interval of process parameters. There were found the kinetic equations describing different routes of the process: formation of olefins, carbon oxides and cracking products.

The experiments under nonstationary conditions were conducted in a special reactor of small volume connected with a flight of time mass-spectrometer. The relaxation curves describing a transition of the system to a new steady-state were obtained after a jump change of corresponding concentrations. The study of transient processes of the attainment of a steady state under different conditions allowed to obtain the detailed information for the process mechanism.

The data obtained in stationary and nonstationary regions showed that isobutene and carbon oxides are primary reaction products. Lattice oxygen takes part in dehydrogenation reactions. Carbon oxides formation proceeds by the interaction with adsorbed oxygen. Cracking products are formed from paraffins. The optimal conditions were found. Cobalt molybdate can work with high selectivity for a long time because of oxygen vacancies is quickly reduced and coke formation is insignificant over it. Its performance does not take much excess of oxygen that can provide the large productivity.

The step-schemes for all reactions proceeding in the system were proposed.