A.L.Lapidus*, N.A.Gaidai
N.D.Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences
119991 Moscow, Leninsky Pr., 47, Fax: 1355328, E-mail: albert@ioc.ac.ru

Dehydrogenation of C_4-C_5-Paraffins over platinum catalysts

The dehydrogenation of C_4-C_5 paraffins is important process in the petrochemical industry because of olefins and dienes production. Platinum systems are highly effective catalysts for dehydrogenation of paraffins. We studied the dehydrogenation of iso- and n-butanes and isopentane over platinum-alumina catalysts without of promoter and added K, Se, Pb, Cu, Ge, In and Sn in the presence of hydrogen and hydrogen and steam. We used both bimetallic and threemetallic catalytic systems. The optimal concentrations of promoters were found. Kinetic methods were used to investigate promotion effects of platinum catalysts with optimal concentrations of additives. Besides, isotopic and nonstationary methods were applied for the study of process mechanism.

The kinetics of main (olefin production) and side reactions (diene production, cracking, isomerization and coke formation) as well as the kinetics of catalyst deactivation were studied in a circulating flow system at atmospheric pressure in the presence of hydrogen and steam. A reactor having a McBain type spring balance was used in studying coke formation. Reaction mixtures were analyzed with an chromatograph and mass-spectrometer.

The kinetics equations on all directions were found. The introduction of promoters does not change the form of kinetic equations on dehydrogenation, cracking, isomerization and coke formation, respectively, while the kinetic constants do vary widely. The changes reflect the increase in constants in numerators of kinetic equations for dehydrogenation of paraffins and the decrease in adsorption constants for the olefins and dienes in the denominators of these equations over promoted catalysts. It was found that the most effective promoters are Sn and In.

The formation of dienes in n-butane and isoamilene dehydrogenation proceeds by parallel-consecutive scheme. The mechanism of the processes does not depend on promoters introduction too. The step-schemes for all reactions proceeding in the systems are proposed. Dissosiative adsorption of paraffins with removal of first hydrogen atom is the slow step in the olefin formation.

The promotion effects in platinum-alumina catalysts of paraffins dehydrogenation can be summarized as follows: 1) the slow step rate is increased, 2) olefins and dienes formed are bound with the surface less tightly and the retardation of the reaction by olefins and dienes is reduced, 3) the selectivity in olefins is increased due to decreasing the contribution of side reactions, 4) the stability of the catalysts is raised owing to the increase in critical quantity of coke at which the activity of catalysts began to fall, 5) the initial rate of coke accumulation decreases, 6) the hydrogen content in coke rises and the coke removal from catalysts is facilitated, 7) preventing a decrease of Pt dispersity, 8) creation of optimal concentration of reactants over catalyst surfaces.