Transient Study of 1-Butene Conversion over TiO_2/VO_x Catalysts

Cornelia Breitkopf, Wladimir Suprun, Helmut Papp
Institut für Technische Chemie, Universität Leipzig, Linnéstr. 3, 04103 Leipzig

Supported transition metal oxides are known to catalyze the partial oxidation, oxidative dehydrogenation of hydrocarbons as well as isomerization of olefins. V/TiO oxides are in general used for the production of oxygen-containing compounds (carboxylic acids, ketone) by catalytic oxidation of C_3-C_4 alkanes and alkenes. The selective oxydation of C_4 hydrocarbons for the production of C_1 to C_4 carboxylic acids by catalytic oxidation is of industrial interest.
TAP single pulse experiments were done to characterize the sorption properties of the catalyst systems. In addition pump probe experiments were used to investigate the formation of intermediate and product species of 1-butene conversion. Several desactivation states of the catalyst were addressed via repeatedly pulsing reactant.

The VO_x-TiO_2-catalyst are prepared by spray-drying of TiO_2 and vanadium oxides. All samples (0.02 –0.1 mg) were activated in situ in O_2 (50 ml/min) at 180 °C for two hours. Single and pump probe experiments were carried out under high vacuum conditions; O_2 and 1-butene were pulsed over the catalyst samples. Desactivation of the samples were achieved by continiuos flow of 1-butene (5 ml/min) for definite time intervalls. Subsequent pulses of either O_2 or 1-butene were applied then. Pulse response intensities were detected with QMS.

First the interaction of 1-butene over fresh catalysts was investigated. Main products observed were CO (m/e=28), CO_2 and HCOOH (m/e=44). On fresh catalyst samples oxygen was pulsed to investigate the role of lattice oxygen species. Additionally pump probe experiments showed that lattice oxygen is mainly responsible for the formation of products. With increasing number of pulses the shape of the response curves changes dramatically showing first of all the subsequent formation of acetic aldehyde, propione aldehyde and acetic acid which could be observed in transient experiments for the first time.