

Deactivation of Sulfated Zirconia Catalysts with n-Butane Studied by Transient Experiments

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Sulfated zirconia (SZ) catalysts deactivate rapidly during n-butane isomerization. To investigate the sorption ability of the SZ surface for reactant and product molecules with time we employed a TAP reactor. Single pulse and pump-probe experiments were performed to characterize adsorption, desorption and reaction processes. Additionally to the pulsing of reactants we simulated deactivation by switching from flow conditions at atmospheric pressure comparable to catalysis conditions for different times to TAP pulse conditions.

Single and multipulse experiments were done under vacuum conditions at 10⁻⁹ mbar. For the deactivation experiments the TAP reactor was used as fixed bed flow reactor (0.1-0.4 g SZ, 423 K, 5 % n-butane in He) with on-line GC. After distinct time intervals the reaction was stopped and the reactor was evacuated. Pulsing of probe molecules followed immediately. Detection of the outlet pulses was obtained by QMS.

In general the time scales addressed in catalytic and TAP pulse experiments are different. Single pulses may not modify the catalyst surface sufficiently enough to follow the change in catalytic activity with time. To introduce improved transients into the system we pulsed reactant and product molecules over fresh and partly deactivated SZ. Intensities for n-butane pulses showed a significant change depending on the deactivation status after flow of n-butane for distinct time intervalls. Increased intensities of m/e 43 were observed in pulse experiments thus indicating a decreased interaction of the reactant with the surface of SZ. Additional pump-probe experiments were done to check for reaction intermediates.