

Mechanism of butane skeletal isomerization on sulfated zirconia (SPP 1091)

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Due to its unique activity for skeletal isomerization of short alkanes at low temperature, sulfated zirconia (SZ) is generally recognized as the most promising alternative for the zeolite based hydroisomerization catalysts. However, despite the large amount of investigations, several important topics related to SZ are still discussed controversially. Here we report on our detailed investigation of the mechanism of butane skeletal isomerization on SZ. Typically, SZ had an induction period followed by a period of virtually constant activity. The selectivity to isobutene was higher than 96%, the byproducts being propane and pentanes. The induction period can be related to the formation and accumulation of reactive intermediates on the catalyst surface. We show that the alkane activation is initiated via stoichiometric oxidative dehydrogenation of butane by sulphate species to butane, water and SO₂. For the first time, direct experimental evidence is given for all reaction products formed by oxidative dehydrogenation. In situ IR spectroscopy and density functional calculations indicate that pyrosulfate or re-adsorbed SO₃ species are the active species for the oxidation. Butene formed interacts with Bronsted acid sites and forms sec-butoxy groups which isomerize mono-molecularly to tert-butoxy groups, as deduced from the 100% selectivity to isobutane at zero conversion. The tert-butoxy group undergoes hydride transfer from n-butane, forming a new sec-butoxy group and isobutane. The lower selectivity to isobutane with increasing conversion is explained by the higher isobutene concentration which triggers a

bimolecular pathway. Note that isobutane is kinetically a primary product, while propane and pentanes are secondary products formed in sequential reactions. The larger amount of propane with respect to pentanes for conversion above 40% is attributed to multiple alkylation reactions followed by cracking. Transient experiments showed conclusively that the isomerization of the carbenium ion is the rate-determining step in the chain sequence and that hydride transfer is in quasi equilibrium. A kinetic model for butane isomerization under differential conditions is presented showing that the overall rate of butane conversion is proportional to the rate constant of the monomolecular isomerization of the carbenium ion, the concentration of Bronsted acid sites, the partial pressure of the alkane and the concentration of the labile sulfate-based redox sites. We show here that the key to successful catalysts for skeletal isomerization does not lie in high acid strength, but that a subtle balance between redox and acid sites is necessary.