

The oxidation of n-butane to maleic anhydride under hydrocarbon-rich conditions: contribution of homogeneous and mixed homogeneous-heterogeneous reactions

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The reactivity of vanadyl pyrophosphate, catalyst for the selective oxidation of n-butane to maleic anhydride, has been examined under n-butane-rich conditions, thus simulating a feed in which oxygen is the limiting reactant, and a process in which the unconverted n-butane is recycled. A lower selectivity to maleic anhydride was found with respect to the hydrocarbon-lean conditions, due to the higher formation of both carbon oxides, and of C₈ compounds: tetrahydrophthalic and phthalic anhydrides. The latter products formed by consecutive reaction upon maleic anhydride, which reacted with the unsaturated C₄ intermediate. This occurred under conditions of total oxygen depletion, due to the decreased catalyst property of giving O-insertion onto the unsaturated C₄ compounds. A relevant contribution of radicalic, homogeneous reactions was also observed, which mainly led to the formation of carbon oxides and olefins. This contribution decreased in the presence of the catalyst, which thus acted as a radical-scavenger. When conditions were used under which the conversion of oxygen was not total, olefins generated by means of homogeneous reactions reacted at the catalyst surface yielding maleic anhydride. This homogeneously-initiated heterogeneous process led to the unusual effect, of a relevant increase of maleic anhydride yield over 400°C.