

A study of the kinetics and mechanism of the adsorption and anaerobic partial oxidation of n-butane over a vanadyl pyrophosphate catalyst

ABSTRACT

The interaction of n-butane with a ((VO)₂P₂O₇) catalyst has been investigated by temperature-programmed desorption and anaerobic temperature-programmed reaction. n-Butane has been shown to adsorb on the (VO)₂P₂O₇ to as a butylóhydroxyl pair. When adsorption is carried out at 223 K, upon temperature programming some of the butyló hydroxyl species recombine resulting in butane desorption at 260 K. However, when adsorption is carried out at 423 K, the hydroxyl species of the butylóhydroxyl pair migrate away from the butyl species during the adsorption, forming water which is detected in the gas phase. Butane therefore is not observed to desorb at 260 K after we lowered the temperature to 223 K under the butane/helium from the adsorption temperature of 423 K prior to temperature programming from that temperature to 1100 K under a helium stream. Anaerobic temperature-programmed oxidation of n-butane produces butene and butadiene at a peak maximum temperature of 1000 K; this is exactly the temperature at which, upon temperature programming, oxygen evolves from the lattice and desorbs as O₂. This, and the fact that the amount of oxygen desorbing from the (VO)₂P₂O₇ at 1000 K is the same as that required for the oxidation of the n-butane to butene and butadiene, strongly suggests (i) that lattice oxygen as it emerges at the surface is the selective oxidant and (ii) that its appearance at the surface is the rate-determining step in the selective oxidation of n-butane. The surface of the (VO)₂P₂O₇ catalyst on which this selective oxidation takes place has had approximately two monolayers of oxygen removed from it by unselective oxidation of the n-butane to CO, CO₂, and H₂O between 550 and 950 K and has had approximately one monolayer of carbon deposited on it at 1000 K. It is apparent, therefore, that the original crystallography of the (VO)₂P₂O₇ catalyst will not exist during this selective oxidation and that theories that relate selectivity in partial oxidation to the (100) face of the (VO)₂P₂O₇ catalyst cannot apply in this case.

Keyword: Partial oxidation; Vanadyl pyrophosphate catalyst; n-butane; Kinetics; Mechanism; Adsorption