Ethanol Dehydrogenation on γ-Al_2O_3: Site Requirements and Mechanism of Acetaldehyde Synthesis

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Steady state kinetic measurements of ethanol dehydrogenation on γ-alumina confirm acetaldehyde synthesis to be independent of water partial pressure and inhibited only by reactive precursors at temperatures between 623 K and 673 K. Measured kinetic isotope effects for ethanol dehydrogenation demonstrate that either C_α-H bond cleavage or the removal of surface hydrogen species is rate limiting in acetaldehyde synthesis. Ethane is produced at a rate equivalent to that of acetaldehyde synthesis at all measured temperatures (623 – 673 K) and ethanol pressures (0.9 – 8.0 kPa) and independent of co-fed ethylene pressure (0- to 1.5 kPa) at ethylene pressures up to 1.5 kPa, indicating that acetaldehyde and ethane are co-products of the reaction. Pyridine was observed to inhibit the syntheses of ethylene, acetaldehyde, and ethane to the same extent, demonstrating that the synthesis routes to form these molecules require acidic surface sites and share at least one common reactive intermediate. An indirect hydrogen transfer mechanism for the synthesis of acetaldehyde from the dehydrogenation of ethanol on γ-alumina consistent with the steady state kinetic measurements, formation of ethane, observed pyridine inhibition, and determined kinetic isotope effects is presented.

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