The Single-Site Vanadyl Activation, Functionalization, and Re-oxidation Reaction Mechanism for Propane Oxidative Dehydrogenation on the Cubic $V_4O_{10}$ Cluster

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Abstract

Vanadyl oxide ($V=O$) sites are thought to play a role in a number of industrially important catalysts for activating saturated alkanes, but in no system is the mechanism for the activation, product formation, and re-oxidation steps established. In this paper we use quantum mechanical methods (B3LYP flavor of density functional theory) to examine the detailed mechanism for propane reacting with a $V_4O_{10}$ cluster to model the catalytic oxidative dehydrogenation (ODH) of propane on the $V_2O_5(001)$ surface.

We here report the mechanism of the complete catalytic cycle, including the regeneration of the reduced catalyst using gaseous $O_2$. The rate-determining step is hydrogen abstraction by the vanadyl ($V=O$) group (in agreement with experiment) to form an $iso$-propyl radical that binds to an adjacent V-O-V site. Subsequently, this bound $iso$-propyl forms propene product by $\alpha$-hydride elimination to form bound $H_2O$. We find that this $H_2O$ (bound to a $V^{III}$ site) is too stable to desorb unimolecularly. Instead, the desorption is induced by binding of gaseous $O_2$ to the $V^{III}$ site, which dramatically decreases the coordination energy of $H_2O$ from 37.8 to 12.9 kcal/mol. Further rearrangement of the $O_2$ molecule leads to formation of a cyclic $VO_2$ peroxide,
that activates the C-H bond of a second propane to form a second propene (with a lower reaction barrier). Desorption of this propene regenerates the original $V_4O_{10}$ cluster.

We find that all reactions involve the single vanadyl oxygen ($V=O$), with the bridging oxygens ($V-O-V$) serving to stabilize the iso-propyl radical intermediate. We refer to this mechanism as the Single-Site Vanadyl Activation, Functionalization, and Re-oxidation mechanism (SS-VAFR). This SS-VAFR mechanism should be applicable to propane ODH on the supported vanadium oxide catalysts where only monovanadate ($VO_4$) species are present.