

Electronic structure and catalytic reactivity of model oxide catalysts

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Understanding the mechanistic details of heterogeneous catalytic reactions will provide a way to tune the selectivity between various competing reaction channels. In this regard, catalytic decomposition of alcohols over the rutile $\text{TiO}_2(110)$ surface as a model oxide catalyst has been studied to understand the reaction mechanism employing the temperature-programmed desorption (TPD) technique. The $\text{TiO}_2(110)$ model catalyst is found to be active toward alcohol dehydration. We find that the active sites are bridge-bonded oxygen vacancies where RO-H heterolytically dissociates and binds to the vacancy to produce alkoxy (RO-) and hydroxyl (HO-). Two protons adsorbed onto the bridge-bonded oxygen atoms (-OH) readily react with each other to form a water molecule at ~ 500 K and desorb from the surface. The alkoxy (RO-) undergoes decomposition at higher temperatures into the corresponding alkene. Here, the overall desorption kinetics is limited by a first-order decomposition of intermediate alkoxy (RO-) species bound to the vacancy. We show that detailed analysis on the yield and the desorption temperatures as a function of the alkyl substituents provides valuable insights into the reaction mechanism. After the catalytic role of the oxygen vacancies has been established, we employed x-ray photoelectron spectroscopy to further study the surface electronic structure related to the catalytically active defective sites. The defect-related state in valence band has been related to the chemically reduced Ti^{3+} defects near the surface region and are found to be closely related to the catalytic activity of the $\text{TiO}_2(110)$ surface.