

Implication of Electron Scavenging Character of Sulfated Titania in Photocatalysis

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Knowledge of the electronic structure of photocatalysts is of immense importance in understanding and enhancing photocatalytic reactions. Here, we used *in-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) during the reaction of TiO₂ with H₂ to reveal information about the electronic structure of TiO₂ as a function of crystal structure and chemical impurities. TiO₂ is n-doped upon H₂ dissociation [1] and the corresponding electrons can be detected with FTIR if they are in either the conduction band or shallow trap states. [2] However, electrons are not observed in the IR region when they occupy deep traps. Our results are consistent with sulfate impurities in anatase creating deep trap states that scavenge electrons. These results provide support for a model of improved photocatalyst activity in which trapping the electrons increases the hole lifetime and increases the efficiency of oxidation reactions. [3]

We present adsorption of H₂ and D₂ on pyrogenic titania (P90), rutile, several commercial anatase samples [Sigma Aldrich (SA), US Research Nanomaterials (USR), and Alfa Aesar (AA)] for which sulfate was detected, and our synthesized sulfate-free anatase. We observed the formation of surface hydroxyls and occupation of shallow traps by electrons for P90, rutile, and sulfate-free anatase. However, when sulfate is present on the TiO₂ surface, we continued to observe the formation of surface hydroxyls, but failed to observe electronic effects in the IR spectra. We ascribe the latter phenomenon to electrons being trapped in states deeper than the ~1eV range of mid-IR spectroscopy.

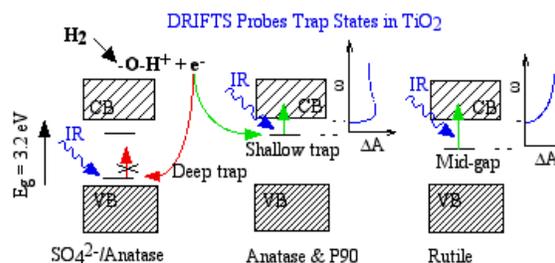


Figure 1. Schematic diagram of IR probe of electrons added to trap states of TiO₂ after H₂ dissociation to form surface hydroxyls.

References:

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