Photocatalytic oxidation of methanol and water on TiO_2(110) - A photochemical perspective

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Methanol and water on a single-crystal rutile TiO_2(110) surface are widely studied model systems for heterogeneous photocatalysis.[1] Using spin-polarized density functional theory with the HSE06functional we study the photocatalytic oxidation of these molecules as an excited-state process with triplet spin multiplicity.[2] The first O-H dissociation step follows excitonic interfacial proton-coupled electron transfer where the hole-electron (*h*-*e*) pair generated during the excitation is bound, and the *h* is transferred to the adsorbate. The O-H dissociation paths associated with other *h*-*e* pairs are unreactive. The CH_3O and HO radical intermediates can decay through different paths that involve intersections with the ground state. We will also discuss the differences in reactivity between water and methanol, which is more reactive in ultra-high vaccum. Our results highlight the importance of treating the excited state as a bound exciton rather than independent electrons and holes.

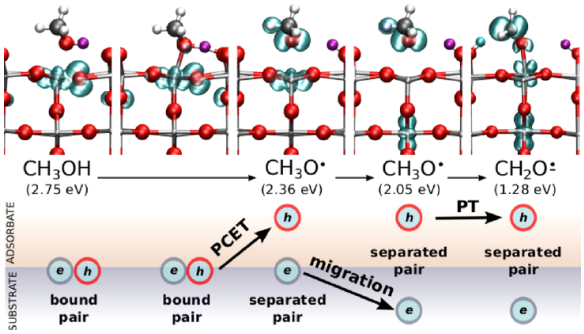

Figure 1. Scheme of Methanol photocatalytic oxidation showing the role of the bound exciton in the initial stage.

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