Probing the photocatalytic impact of interfacial titanium coordination in titania-silica materials

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Introduction
Identifying and quantifying active sites in heterogeneous catalytic systems is crucial to understanding and evaluating performance across different types of materials. This challenge is made more difficult for photocatalytic systems where the dynamics of light capture and charge separation are involved. It has previously been hypothesized that tetrahedral sites at the interface of anatase and rutile titania composites act as photocatalytic hotspots.[1] However, it is difficult to investigate this specific claim due to additional charge trapping and light absorption phenomena occurring in these materials.

Here we utilize the natural tetrahedral coordination of silica to template titania materials in different ways that allow us to tune the structure of the solid-solid titania-silica interface, and thus probe the effect of tetrahedral Ti on photocatalytic activity. We utilized newly-developed phosphorous-based titration techniques to quantify the number of accessible and tetrahedral Ti sites [2], and measure the rate of benzyl alcohol photo-oxidation as a reaction probe. Our work allows us to examine the effects of interfacial coordination, particle size, and synthesis method.

Materials and Methods
Silica spheres were synthesized as a support using a previously reported method.[2a]. Four sets of titania-based materials were examined: (1) As received anatase titania (Sigma-Aldrich, <25 nm nanoparticles); (2) As received anatase titania physically mixed with silica via sonication in 1 mL 18MΩ DI water, dried 12 to 15 hours at 150°C; (3) Material 2 subsequently calcined at 400°C to induce undercoordination at the titania-silica interface; (4) The same method as material 3 except using a sol-gel titania synthesized using a previously described method[3]. Crystallities sizes were estimated with the Scherrer formula for the anatase (101) reflection. The amount of fluid-accessible titanium was estimated using a previously reported method [2a], wherein phenylphosphonic acid (PPA) is selectively bound to the titanium oxide domains and quantified via elemental analysis. Photocatalytic activity was evaluated for the photocatalytic oxidation of benzyl alcohol to benzoic acid in acetonitrile, using ambient O2 as the oxidant and 365-nm UV light. Reported turnover frequencies (TOF) were calculated by dividing moles of benzoic acid per gram per hour by moles of fluid-accessible titanium per gram of material.

Results and Discussion
Figure 1 displays TOF versus titanium loading for the four sets of materials. After normalizing for the number of fluid-accessible reaction sites it becomes apparent that reactivity has not changed with synthesis method, suggesting that neither interfacial coordination nor crystallite size affect photocatalytic rates. However, it is possible that simply calcining the materials is not enough to induce coordination changes in already-condensed titanium oxides. Our near-future work will focus on growing titania crystals directly onto the silica support to examine whether tetrahedral sites at the interface change photocatalytic activity. Time permitting we will also discuss other combined thermo- and photocatalytic systems where tetrahedral Ti plays a critical role.

Figure 1. TOF vs. titanium loading for 1 (triangle, avg. crystal size = 15 nm), 2 (squares, avg. crystal size = 27 nm), 3 (triangles, avg. crystal size = 27 nm), and 4 (diamonds, avg. crystal size = 15 nm).

Significance
This work emphasizes that atomic-level details, such as fluid-accessibility and metal coordination, must be included when evaluating a photocatalyst’s performance along with more traditional features like surface area and crystallite size. It also highlights to usefulness of the PPA titration technique for understanding material structure.

References