An Improved Photocatalyst of TiO_2/SiO_2 Prepared by a Sol–Gel Synthesis

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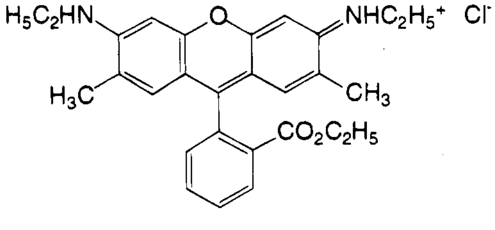
The effect of incorporation of SiO_2 on the behavior of a TiO_2-based photocatalyst prepared by a sol–gel technique from organometallic precursors is described. Application of photocatalysts with different TiO_2/SiO_2 ratios to the photodecomposition of rhodamine-6G (R-6G) demonstrates that a ratio of 30/70 produces a catalyst about 3 times more active than Degussa P-25 TiO_2. Larger amounts of SiO_2 decrease the activity. The adsorption of R-6G on the different materials and the photodecomposition of preadsorbed R-6G is also described. The studies suggest that photogenerated intermediates are sufficiently mobile to react with R-6G adsorbed on SiO_2 sites but that adsorption of R-6G on TiO_2 is not a prerequisite for reaction.

Introduction

We describe improvement in the photocatalytic behavior of particulate TiO_2 by the intimate incorporation of SiO_2 and describe how the adsorptive properties of this material may also find application. Since the initial studies suggesting the use of irradiated TiO_2 for destruction of pollutants[1,2] and the deposition of metals,[3] there have been many studies on the application and modification of this material.[4,5] Although its large bandgap, 3.2 eV for the anatase form, necessitates ultraviolet irradiation and thus the use of lamps or only a small portion of the solar spectrum, the good stability of TiO_2 and the strong oxidizing potential of the photogenerated holes (~+2.9 V vs NHE at pH 0) have made it the material of choice in most practical photocatalytic systems.[4,5] One approach to improve the efficiency of TiO_2 is the prevention of recombination of the photogenerated electron (e^-) and hole (h^+) by increasing the rate of transfer of e^- and h^+ to solution species. This can be accomplished, for example, by the use of charge-transfer catalysts on the TiO_2 surface. Rapid scavenging of holes can also be promoted by adsorption of the reductant and any oxidized intermediates from the solution by incorporation of more effective adsorption sites than TiO_2 on the catalyst surface. These sites must be near the TiO_2 sites, so that hole-generated oxidants (e.g., hydroxyl radicals) can reach them before these intermediates are lost through a reaction such as recombination with e^-. This has been accomplished in the present study by the preparation of TiO_2/SiO_2 composites with different Ti/Si ratios using a sol–gel process.[6]

The sol–gel process is also advantageous in that it is capable of producing photocatalysts with high surface areas.[7] For example, TiO_2 and SiO_2 aerogels with surface areas near 600 and 1000 m^2/g, respectively, have been reported.[6,8] High surface area TiO_2 materials prepared by a sol–gel method have recently been shown to be more efficient in the degradation of salicylic acid than the conventional (~55 m^2/g) material.[8]

There have been a number of preparations of mixed silica-titania glasses described[6,9–11] as well as studies of photocatalysts produced by mixing SiO_2 and TiO_2 particles[12] or forming TiO_2 layers on a SiO_2 substrate.[13] In this paper, we describe the photodecomposition of rhodamine-6G (R-6G), a species that adsorbs on SiO_2 but not on TiO_2. R-6G was also used because it does not undergo photodecomposition in aqueous solutions or SiO_2 slurries under UV irradiation in the absence of photocatalyst. R-6G's high molar absorptivity (87 000 M^{-1} cm^{-1}) permits easy spectrophotometric analysis of test solutions even at low (~0.5 μM) concentrations.



Rhodamine-6G (R-6G)

Experimental Section

Gels were prepared by the acid-catalyzed hydrolysis of tetraisopropyl orthotitanate (TIOT, Fluka) and tetraethoxysilane (TEOS, Fluka). A TIOT/TEOS mixture with the desired Ti/Si ratio was prepared in a drybox, sealed, and then removed from the drybox. This solution was added dropwise to a solution of 250 mL of anhydrous 2-propanol and 1 mL of concentrated HCl at 0 °C. The resulting solution was stirred in an ice bath. While still at 0 °C, a molar quantity of water 4 times the total moles of Ti and Si was added dropwise with vigorous stirring. The mixture was allowed to age at room temperature in a covered beaker for 1 week after gelling. Solvent was then removed under vacuum, and while still under vacuum, the catalysts were heated to 200 °C for 12 h. The resulting glassy material was ground in a mixer mill for 1 h.

Rates of photocatalytic decomposition of R-6G were determined directly with R-6G in solution or with R-6G that was preadsorbed on the TiO_2/SiO_2 material. A slurry of 120 mL of water (air saturated) and 0.125 g of catalyst was prepared in a 3-cm-diameter, 32-cm-long Pyrex tube. The catalyst/water slurry was preirradiated in a Rayonette photochemical chamber reactor (RPR-100, Southern New England Ultraviolet Co., Harden, CT) for 12–18 h to decompose any organic material left on the catalyst after synthesis. The reactor was fitted with 16 RPR 350 nm lamps arranged within a reflecting cylinder 23 cm in diameter and 32 cm high, and the reaction vessel was placed in the center of this. The intensity at the center of the reactor was ca 9.2 μW/cm^2 (Figure 1). A 5-mL portion of 1 mM R-6G was added to the slurry in the reactor, after which 5-mL aliquots were removed periodically and centrifuged. The solution was then analyzed by UV–visible

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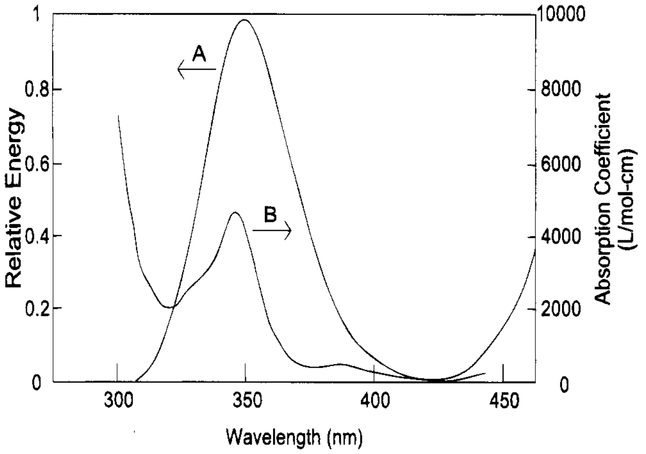

Figure 1. (A) Relative intensity (data from Southern New England UV Co.) of the RPR 3500 Å lamp. (B) Absorption coefficient for R-6G, 1.0×10^{-5} M, 1-cm cell.

absorbence on a Spectronic 3000 array spectrophotometer (Milton Roy, Urbana, IL).

In experiments with preadsorbed R-6G, 0.125 g of 25/75 (TiO_2/SiO_2) catalyst was preirradiated as above then filtered and placed in a 1 mM R-6G solution and allowed to adsorb the R-6G for 5 h. The catalyst with adsorbed R-6G was filtered, rinsed with water, and suspended in 125 mL of aerated water. This slurry was irradiated, and aliquots were removed over time. The aliquots were filtered and any unreacted R-6G stripped off of the catalyst with 1:1 acetonitrile (Spectrum Chemical Co., UV grade)/aqueous 1 M KNO_3. The resulting solution was analyzed by UV–visible spectrophotometry. Adsorption isotherms were obtained in a similar way by exposing the catalyst to solutions with different concentrations of R-6G in the absence of irradiation followed by centrifugation and spectrophotometric determination of R-6G remaining in solution.

Powder XRD data were obtained with a Philips Electronic Instruments X-ray diffractometer (Mount Vernon, NY) using a Cu (1.54 Å) anode. Surface areas were determined by BET analysis of Ar sorption data obtained with an Autosorb 1 gas sorption system (Quantachrome, Syosset, NY).

Results and Discussion

Effect of TiO_2/SiO_2 Ratio. When preirradiated catalyst was employed with an initially 1 mM R-6G solution, the concentration of R-6G decreased exponentially with irradiation time. The kinetics of this reaction can be approximated as a pseudo-first-order process, and the rate constants can be used to compare the relative efficiency of the different materials under essentially identical conditions. Rate constants obtained from these data as a function of percent SiO_2 and BET surface areas of the catalysts are shown in Figures 2 and 3. The rate of reaction of the widely used material Degussa P-25 TiO_2 is also shown for comparison. R-6G in the absence of particles or in slurries of pure SiO_2 shows negligible photodecomposition. As shown, the rate of decomposition of R-6G depends on the TiO_2/SiO_2 ratio and was largest at 30/70, which showed an activity about 3 times that of pure TiO_2. Although this increase in reactivity can partly be attributed to an increased surface area,[8] the beneficial effect of SiO_2, which shows no photoactivity, probably relates to the preferential adsorption of R-6G on SiO_2. This effectively increases the surface concentration of R-6G at or near the TiO_2 sites promoting more efficient oxidation by photogenerated species. In addition to the TiO_2/SiO_2 ratio, the reaction conditions used to prepare the materials (i.e., pH of the solution, aging time, nature of organometallic precursor concentration) can affect the physical and chemical properties of the materials and hence relative efficiency. Properties such as TiO_2 crystallite size, surface area, pore distribution, and surface conditions are all affected by the reaction conditions, producing different rates of R-6G oxidation at a given TiO_2/SiO_2 ratio.

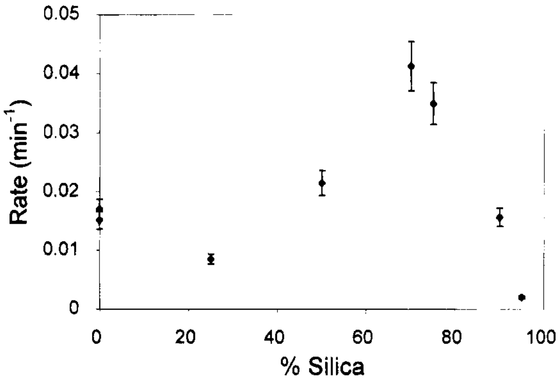

Figure 2. Pseudo-first-order rate constants for the destruction of R-6G in air-saturated water vs percentage of silica in the material. Initial R-6G concentration = 4×10^{-5} M; catalyst concentration = 1 g/L.

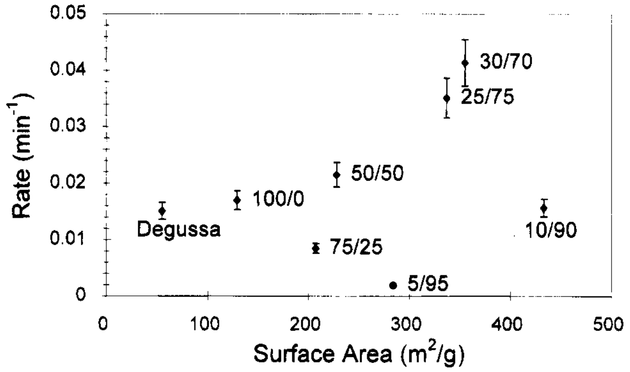

Figure 3. Pseudo-first-order rate constants for the destruction of R-6G in air-saturated water vs BET surface area of the material. Data points are labeled with their corresponding TiO_2/SiO_2 ratio. Initial R-6G concentration = 4×10^{-5} M; catalyst concentration = 1 g/L.

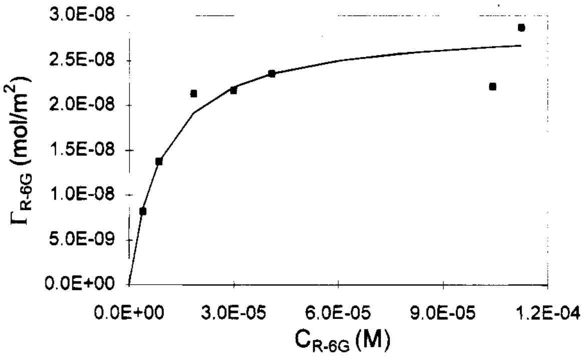

Figure 4. Adsorption isotherm for R-6G on 5/95 TiO_2/SiO_2. Concentration, c, was measured after 2 h. Catalyst concentration = 1 g/L. The solid line is the Langmuir isotherm $\Gamma = [\Gamma_s\beta c/(1 + \beta c)]$ with $\beta = 1.07 \times 10^5$ and $\Gamma_s = 2.89 \times 10^{-8}$ mol/m^2.

Adsorption of R-6G. Isotherms of R-6G adsorption in different aqueous solutions on the catalysts demonstrated Langmuir-like behavior; a typical curve is shown in Figure 4. In these systems, the TiO_2 alone (e.g., 100/0 and Degussa) did not adsorb R-6G, while the materials containing SiO_2 did adsorb R-6G. The saturation coverage of R-6G, Γ_s, did not directly correlate with the surface area of SiO_2 in the catalyst as one might expect. If one assumes the percentage of SiO_2 on the surface is the same as that in the bulk and that R-6G is adsorbed

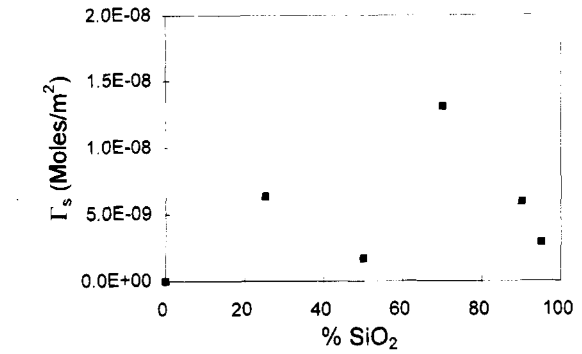

Figure 5. Saturated surface coverage (Γ_s in Figure 4) of R-6G on TiO_2/SiO_2 vs the percentage of silica in the material.

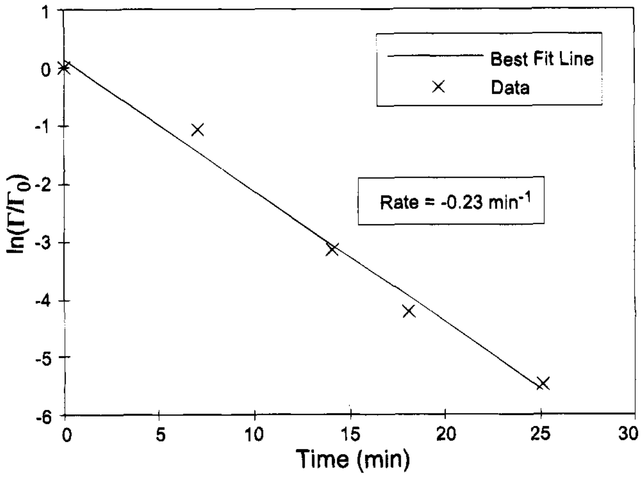

Figure 6. Rate of decomposition of adsorbed R-6G, $\ln(\Gamma/\Gamma_0)$ vs time, on 25/75 TiO_2/SiO_2. The pseudo-first-order rate constant was determined by a linear least-squares fit to the data (solid line).

as a monolayer with each molecule occupying about 120 Å^2, then one would calculate that only about 5 (±3)% of surface SiO_2 is occupied by R-6G. This very small number suggests that either a large fraction of the SiO_2 in a particle is not on the surface or that a large part of the surface SiO_2 area is in micropores that are inaccessible to the R-6G. However, Γ_s (see Figure 5) followed the rates of reaction shown in Figure 2 for samples containing both TiO_2 and SiO_2. The 30/70 material, which showed the largest Γ_s, was the most effective for photodecomposition of R-6G. This supports the idea that an adsorption step is important in the enhancement of this type of reaction scheme. The explanation for the lack of correlation between SiO_2 area and R-6G adsorption must lie with physical and chemical surface properties that have yet to be measured.

Photodecomposition of Adsorbed R-6G. It is possible to use this approach not only to increase the activity of the photocatalyst but also to provide for preadsorption of a species followed by separation and later irradiation. This is illustrated with an experiment with preirradiated 25/75 TiO_2/SiO_2. Following adsorption of R-6G onto the material, it was rinsed with water and irradiated in an aerated aqueous slurry; a typical decomposition curve is shown in Figure 6 . The destruction of adsorbed R-6G is very efficient, with a rate of removal of 0.23 min^{-1}. Note that this type of experiment could not be performed with pure TiO_2, since it does not adsorb R-6G.

These experiments also provide information about the mechanism of the surface photoreaction on TiO_2. The R-6G is adsorbed on the SiO_2 sites but not on TiO_2. Therefore, a photogenerated oxidant must move from the TiO_2 to the SiO_2 to reach molecules adsorbed on SiO_2 sites. Photogenerated holes in the TiO_2 are energetically incapable of entering the SiO_2 lattice. Hence, photogenerated oxidants, such as hydroxyl radical or species resulting from reduction of O_2 (e.g., $HO_2^\bullet$), must diffuse on the surface, or in solution near the surface, to the adsorbed R-6G. This process was observed to be faster than the destruction of R-6G in solution (0.23 min^{-1} compared to 0.04 min^{-1} for the solution reaction). However, the observed photooxidation of dissolved R-6G on TiO_2 alone demonstrates that adsorption of reactant on the surface of the photocatalyst is not a requirement for reaction.

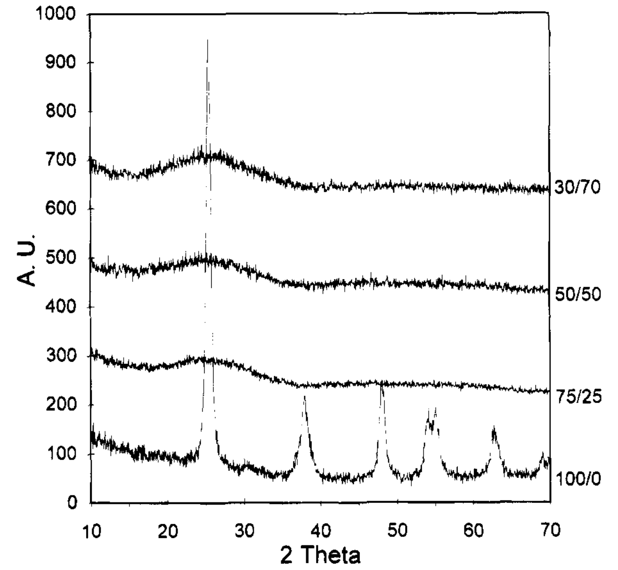

Figure 7. X-ray diffraction spectra of 100/0, 75/25, 50/50, and 30/70 TiO_2/SiO_2. Materials with a TiO_2 content less than 30% showed signals difficult to distinguish from background. The Scherrer equation indicates a TiO_2 crystallite size of 16 ± 9 Å (calculated from the peak width at half the peak height of each spectrum) for the 30/70, 50/50, and 75/25 samples.

An important factor in the design and behavior of such mixed photocatalysts is the size of the individual SiO_2 and TiO_2 units or crystallites. The TiO_2 crystallite should be large enough that its bandgap approaches that of bulk material. On the other hand, if the SiO_2 domains are too large, longer distance transport of unstable oxidizing intermediates would be required. For example, transmission electron microscope studies of mixed silica/titania glasses, with titania percentages above 9% show that the titania aggregates into crystallites of 20–100 nm after annealing at 1200 °C.[14] However, the nature of SiO_2/TiO_2 mixed oxides is a function of the preparation conditions.[15] The powder XRD spectra shown in Figure 7 indicate that the pure TiO_2 sample shows the pattern expected for anatase TiO_2. The 75/25, 50/50, and 30/70% samples show a broad peak at $2\theta = 25.3°$ where the most intense line of the anatase pattern lies. From the width of these peaks and the Scherrer equation,[16] we calculate a TiO_2 crystallite size of the order of 16 ± 9 Å. Characterization of the photocatalysts described here by microscopy, X-ray spectroscopy, surface UV–vis spectroscopy, sorption methods, and infrared methods, as well as studies of surface treatments to improve their performance are currently underway.

Conclusion. A mixed oxide of SiO_2 and TiO_2 produced by sol–gel methods is a more efficient photocatalyst for the destruction of R-6G than TiO_2 alone. The presence of an adsorbent (SiO_2) promotes efficiency by increasing the quantity of R-6G near the TiO_2 sites relative to the solution concentration of R-6G. Photogenerated oxidants from TiO_2 have been shown to be mobile either in solution or on the surface of SiO_2.

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