

# Improved Photocatalytic Activity and Characterization of Mixed $\text{TiO}_2/\text{SiO}_2$ and $\text{TiO}_2/\text{Al}_2\text{O}_3$ Materials

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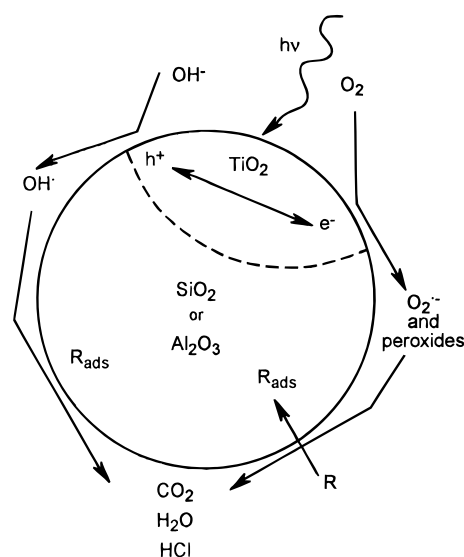
The characterization of mixed oxides of  $\text{TiO}_2/\text{SiO}_2$  and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  prepared by sol–gel methods is described. Application of the  $\text{TiO}_2/\text{Al}_2\text{O}_3$  material for the photocatalytic decomposition of salicylic acid gave improved activity relative to  $\text{TiO}_2$ -only materials. The photocatalytic activity of  $\text{TiO}_2/\text{SiO}_2$ ,  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  toward the photocatalytic decomposition of phenol demonstrated the enhancement of local  $\text{TiO}_2$  sites on  $\text{TiO}_2/\text{SiO}_2$  materials relative to the other materials. The characterization of the catalysts indicates that the  $\text{TiO}_2/\text{SiO}_2$  materials consist of matrix-isolated  $\text{TiO}_2$  quantum particles, while the  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials do not.

## Introduction

Heinz Gerischer recognized very early the importance of semiconductor electrodes.<sup>1</sup> Following the introduction of  $\text{TiO}_2$  single-crystal electrodes for solar energy conversion by Honda and Fujishima,<sup>2</sup> an enormous literature developed on the characterization and application of this material in photoelectrochemical applications. Photocatalysis at  $\text{TiO}_2$  particles, with possible applications to waste treatment,<sup>3,4</sup> has been a particularly active area.<sup>5,6</sup> For such applications, it is important to improve the efficiency of the  $\text{TiO}_2$ -based photocatalysts. A strategy we have been investigating with such photocatalysts has been the combination of the photoactive  $\text{TiO}_2$  material with an adsorbent. Not only does this provide preconcentration of the material near the photoactive sites, it also allows the possibility of adsorbing the material in the dark followed by later irradiation to decompose the material and restore the original photocatalyst. Studies of such materials also are of fundamental interest, because they allow one to probe such issues as the necessity of adsorption for decomposition in photocatalysis and whether photogenerated intermediates (like hydroxyl radical) escape the catalyst surface.<sup>7</sup> Moreover, this strategy allows the production of matrix-isolated quantum (Q-) particles of  $\text{TiO}_2$  with a different band gap than the bulk material.

In an earlier study,<sup>7</sup> we demonstrated that a mixed oxide of  $\text{TiO}_2$  and  $\text{SiO}_2$  produced by a sol–gel method was a more efficient photocatalyst for the photocatalytic decomposition of rhodamine-6G (R-6G) than  $\text{TiO}_2$  alone. The increase in efficiency was attributed to the presence of an adsorbent ( $\text{SiO}_2$ ). The adsorbent phase increased the concentration of R-6G near the  $\text{TiO}_2$  sites relative to the solution concentration. We also showed that while adsorption of R-6G was beneficial for photocatalytic activity of the catalysts, it was not a requirement. R-6G does not adsorb on  $\text{TiO}_2$  alone, but the dissolved form is photodecomposed by a  $\text{TiO}_2$  slurry.

The  $\text{TiO}_2/\text{SiO}_2$  photocatalysts used in the earlier study<sup>7</sup> are characterized here. The enhanced photocatalytic activity of  $\text{TiO}_2$  for the decomposition of salicylic acid in a mixed  $\text{TiO}_2/\text{Al}_2\text{O}_3$  photocatalyst relative to pure  $\text{TiO}_2$  is also demonstrated. The photocatalytic decomposition of phenol on  $\text{TiO}_2/\text{SiO}_2$ ,  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  materials is also described. Further characterization of the  $\text{TiO}_2/\text{SiO}_2$  materials was undertaken to understand better the increased efficiency of the materials. In



**Figure 1.** Schematic representation of the  $\text{TiO}_2/\text{SiO}_2$  or  $\text{TiO}_2/\text{Al}_2\text{O}_3$  photocatalyst with no interaction between the  $\text{TiO}_2$  and  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  phases.

particular, we want to explain the rapid rate of decomposition observed for R-6G adsorbed on the surface of the material. A better understanding of the size and phase of the  $\text{TiO}_2$  domains in the materials aids in understanding their photocatalytic activity. Characteristics of the materials ( $\text{TiO}_2/\text{SiO}_2$ ,  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$ ), such as surface area, surface acidity, and their morphology ( $\text{TiO}_2/\text{SiO}_2$  as a glass and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  as particles), were studied.

A schematic model for the mixed phase system is given in Figure 1. The  $\text{TiO}_2$  and adsorbent ( $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ ) are prepared so they are intimately mixed (on a 10 nm scale or smaller). The  $\text{TiO}_2$  behaves as the photoactive center, e.g., generating hydroxyl radicals under irradiation, while the  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  provide better adsorption sites in the vicinity of the  $\text{TiO}_2$ . In actual particles there are many such domains on a single particle. Of interest is whether the particles behave as simple mixtures of the bulk materials, as mixtures of much smaller (quantum particle) domains, or as completely random intermixed phases.

The  $\text{TiO}_2/\text{Al}_2\text{O}_3$  mixed catalysts were prepared by sol–gel methods to produce powders directly (as opposed to bulk glass materials for  $\text{TiO}_2/\text{SiO}_2$  catalysts, which are ground in a ball mill). These materials were prepared by the uncatalyzed hydrolysis of the Ti and Al monomers. Preparation of particles

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obviates the need for mechanical grinding and offers a means of controlling particle size within the sol-gel synthesis to tailor the size of the particles for the desired application. We studied the adsorption and decomposition of aqueous salicylic acid (SA) on  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials as a function of  $\text{TiO}_2$  content and the photocatalytic decomposition of phenol on  $\text{TiO}_2/\text{SiO}_2$ ,  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , and  $\text{TiO}_2$  materials. Both phenol and SA were stable to the reaction conditions when photocatalyst was not present. Phenol does not specifically adsorb to the materials used, but SA adsorbs to  $\text{Al}_2\text{O}_3$ . The  $\text{TiO}_2/\text{SiO}_2$  materials were characterized by AFM and  $^{29}\text{Si}$  CP-MAS NMR, and both  $\text{TiO}_2/\text{SiO}_2$  and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials were examined by XRD and UV-vis reflection spectroscopy.

## Experimental Section

**Preparation of Photocatalysts.** The preparation method for the  $\text{TiO}_2/\text{SiO}_2$  materials has been described previously.<sup>7</sup> Sols of  $\text{TiO}_2/\text{Al}_2\text{O}_3$  were prepared by the uncatalyzed hydrolysis of tetraisopropyl orthotitanate (TIOT, Fluka) and triisopropyl orthoaluminate (TIOA, 98%+, Aldrich). A solution of 20 g TIOA in 500 mL of 2-propanol (anhydrous, Baker) was prepared and stirred for 8 h. The solution was cooled to 0 °C and the quantity of TIOT necessary to give the desired Ti/Al ratio was added dropwise with stirring over the course of 1 h. While still at 0 °C, a molar quantity of water 4 times the total moles of TIOT and TIOA was added dropwise to the stirred solution. The resulting solution was slowly warmed to room temperature and stirred for 8 h. The mixture was allowed to age in the liquor for 7 days. After aging, the solvent was removed under vacuum at room temperature. The dry powder was stored for later heating and use. A material containing no  $\text{TiO}_2$  was prepared by the same procedure except no TIOT was added, and the TIOA/2-propanol solution was not cooled to 0 °C before the addition of water. Materials of 90/10 and 95/5 ( $\text{TiO}_2/\text{Al}_2\text{O}_3$  mole ratio) were prepared exactly as above, with the reaction scale reduced by a factor of 4.

The rates of photocatalytic decomposition of phenol (Aldrich) and salicylic acid (SA, Sigma) were determined directly with the molecule under study in an air-saturated aqueous solution. The conditions for the photocatalytic reactions were the same as previously reported:<sup>7</sup> 1 g/L of catalyst and initial concentrations of 3.7 mM phenol and 0.14 mM SA. The photoreactor was a Rayonet photochemical chamber reactor (RPR-100, Southern New England Ultraviolet Co., Harden, CT), the details of the reactor were given previously.<sup>7</sup>

**Adsorption of SA on  $\text{TiO}_2/\text{Al}_2\text{O}_3$  Materials.** The adsorption of SA on  $\text{TiO}_2$  and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials from the aqueous solutions was determined by a titration method. A 1 g/L slurry of the  $\text{TiO}_2/\text{Al}_2\text{O}_3$  material with a volume of 135 mL was prepared and warmed to 40 °C, and this temperature was maintained throughout the experiment. SA was titrated into the solution; the concentration of SA in solution was 0.144 mM (measured by UV-vis absorbance,  $A_{\lambda=308} = 0.600$ ). The slurry was stirred for 1 h to allow complete equilibration. The amount adsorbed was determined from the amount of SA added and the solution volume.

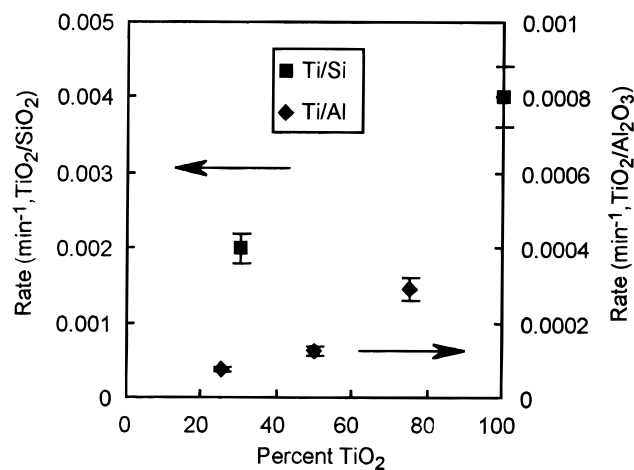
**Characterization of Materials.** An AFM image of a piece of 25/75 ( $\text{TiO}_2/\text{SiO}_2$ ) glass was taken after the material was dried and before it was crushed. Images were recorded with a Nanoscope II with an AFM "J" head (Digital Instruments, Santa Barbara, CA) using a SiN tip. Surface area measurements were made using an Autosorb 1 gas sorption system (Quantachrome, NY). Resident software for BET analysis of Ar sorption isotherms at 77 K was used to determine surface area. Light scattering measurements were performed on a light table using

a HeNe laser (638 nm) and a BI-2030 AT digital correlator (Brookhaven Instruments Corp., Holtsville, NY). The concentration of the sample started at ca. 0.1 g/L of catalyst in Millipore water filtered through Millipore Durapore 0.22  $\mu\text{M}$  filters. The concentration was adjusted by addition of water until a satisfactory signal intensity was obtained. A solid state  $^{29}\text{Si}$  MAS NMR spectrum of the 30/70  $\text{TiO}_2/\text{SiO}_2$  material heated to 200 °C was obtained using a cross-polarization (CP-MAS) pulse sequence. The spectrum was obtained with a Chemagnetics CMX-300 (Fort Collins, CO) operating at 60.0 MHz. The sample was spun at 3500 Hz. Powder X-ray diffraction measurements were made using a Philips Electronic Instruments X-ray diffractometer (Mount Vernon, NY) using a Cu (1.49 Å) anode. Samples were prepared by wet grinding catalysts with ethanol and casting a thin film from the slurry on a microscope slide of borosilicate glass by allowing the slurry to evaporate on the slide or by pressing the sample into a pellet (10 × 15 × 2.5 mm) in an aluminum frame. NaCl was used as the standard to determine instrumental peak broadening.

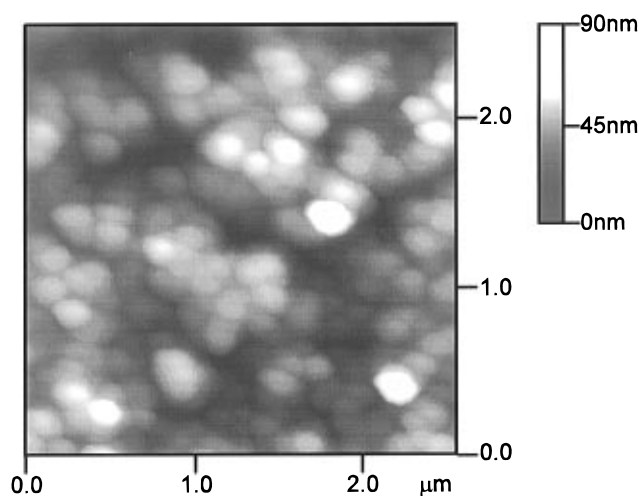
UV-vis reflectance measurements of powders were made using a RSA-MR-30 reflectance spectroscopy accessory (Lab-sphere Inc., North Sutton, NH) attached to a Milton Roy Spectronic 3000 diode array spectrophotometer (Milton Roy, San Leandro, CA). The samples were either bare (supported on filter paper) or placed in a sample holder with a quartz window. The thickness of the measured sample was such that no light passed through it. All spectra were obtained using an 8° sample positioning holder, giving total (diffuse and specular) reflectance relative to a calibrated standard SRS-010-99 (Lab-sphere Inc., North Sutton, NH). The reflectance data are reported as the  $F(R_\infty)$  value from Kubelka-Munk theory vs the wavelength (or energy).<sup>8</sup> Band gap determinations were made by plotting  $[F(R_\infty)hv]^2$  vs  $hv$  (eV) and calculating the  $x$  intercept of a line for  $0.1 < F(R_\infty) < 0.2$ . Band gap measurements were made only for  $\text{TiO}_2$ ,  $\text{TiO}_2/\text{SiO}_2$ , and  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials that were not discolored. Further experimental details and results are available.<sup>9</sup>

## Results and Discussion

**Photodecomposition of Phenol.** When an aqueous solution of phenol, which does not adsorb on either  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ , was exposed to light in the presence of  $\text{TiO}_2/\text{SiO}_2$ ,  $\text{TiO}_2/\text{Al}_2\text{O}_3$ , or  $\text{TiO}_2$ , the phenol concentration decreased exponentially with irradiation time. The rates are reported as pseudo-first-order rate constants for the purpose of comparing the relative efficiencies of the catalysts under identical reaction conditions. Figure 2 shows the measured rates of reaction as a function of the percentage of  $\text{TiO}_2$  present in the material compared to the widely used Degussa  $\text{TiO}_2$  powder. The concentration of phenol decreased negligibly over the time span of these experiments in the absence of a photocatalyst and in irradiated slurries of  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$ . The measured rate for the photocatalytic decomposition of phenol was slower for all of the mixed materials than for pure  $\text{TiO}_2$ . This is consistent with the idea of the photocatalyst consisting of two independent domains. When the  $\text{SiO}_2$  or  $\text{Al}_2\text{O}_3$  phase does not adsorb the molecule being decomposed (phenol), it decreases the activity of the catalyst by reducing the quantity of  $\text{TiO}_2$  available for photo-reactions relative to pure  $\text{TiO}_2$ . However, when the rates were normalized to the  $\text{TiO}_2$  content of the material, the  $\text{TiO}_2/\text{SiO}_2$  material demonstrated a more efficient use of the  $\text{TiO}_2$  sites than  $\text{TiO}_2$  alone or mixed  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials. The normalized rate for the  $\text{TiO}_2/\text{SiO}_2$  material was  $6.7 \times 10^{-3} \text{ min}^{-1}$ ; the rate for pure  $\text{TiO}_2$  was  $4.0 \times 10^{-3} \text{ min}^{-1}$ . The decreased reactivity of  $\text{TiO}_2$  in  $\text{TiO}_2/\text{Al}_2\text{O}_3$  materials was due to the decrease of



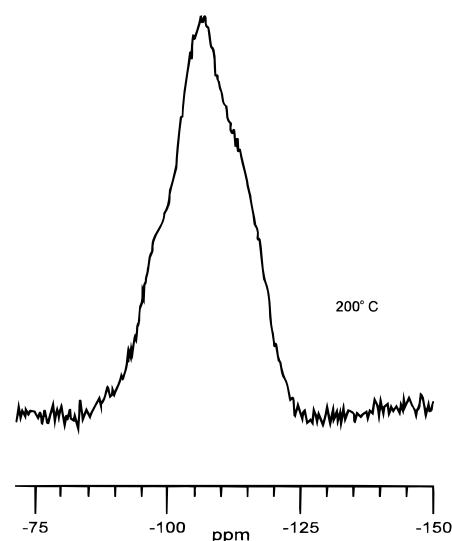
**Figure 2.** Rate constants for the photocatalytic decomposition of phenol on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>/SiO<sub>2</sub> materials, pure TiO<sub>2</sub>, and Degussa TiO<sub>2</sub> (square symbol at percent TiO<sub>2</sub> = 100). Initial phenol concentration =  $3.7 \times 10^{-9}$  M; catalyst concentration = 1 g/L.



**Figure 3.** AFM image of 30/70 TiO<sub>2</sub>/SiO<sub>2</sub> material (xerogel) prior to grinding.

available TiO<sub>2</sub> reactive sites on the catalysts without the benefit of adsorption to compensate for the lost activity. The normalized rate constants for 25/75, 50/50, and 75/25 TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials were  $3.0 \times 10^{-4}$ ,  $2.5 \times 10^{-4}$ , and  $3.9 \times 10^{-4}$  min<sup>-1</sup>, respectively. The increase in the photocatalytic activity of the TiO<sub>2</sub> on TiO<sub>2</sub>/SiO<sub>2</sub> materials is attributed to the presence of a mixed TiOSi phase at the TiO<sub>2</sub>/SiO<sub>2</sub> interface. An interface of this type has been described for systems containing TiO<sub>2</sub> and SiO<sub>2</sub> and has been shown to possess sites of high Bronsted acidity.<sup>10,11</sup> Materials possessing regions of mixed TiOSi have been shown to increase the rate of oxidation of phenol by peroxide in heated aqueous solutions relative to one component TiO<sub>2</sub> or SiO<sub>2</sub> catalysts.<sup>12</sup> The increased activity in our materials is also attributed to this interface region. The TiOSi region served to activate the oxidation of phenol (via strong Bronsted acid sites). These regions should be in very close proximity to the TiO<sub>2</sub> sites. Oxidizing intermediates (such as OH<sup>•</sup>) are produced at the TiO<sub>2</sub> sites. The photocatalytic activity of the TiO<sub>2</sub>/SiO<sub>2</sub> materials is enhanced by the chemical activation of phenol near the photoactive TiO<sub>2</sub> sites.

**Characterization of TiO<sub>2</sub>/SiO<sub>2</sub> Photocatalysts.** The TiO<sub>2</sub>/SiO<sub>2</sub> materials were characterized by AFM and <sup>29</sup>Si CP-MAS NMR. An AFM image of a 25/75 material is shown in Figure 3. Images of the 30/70 TiO<sub>2</sub>/SiO<sub>2</sub> material had similar features. The image indicates that the material consists of ~200 nm spheres bonded together in a non-dense-packing arrangement.

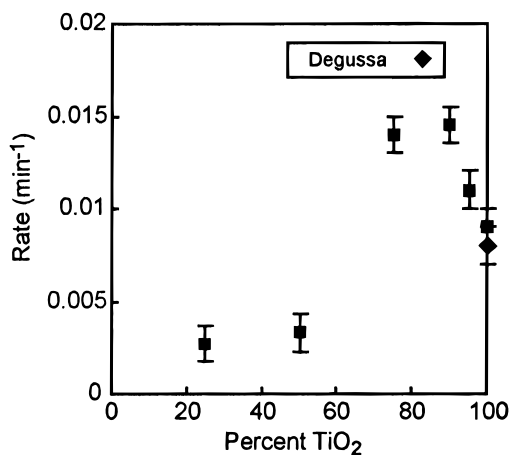


**Figure 4.** <sup>29</sup>Si CP-MAS NMR (60 MHz) spectra of a ground 30/70 TiO<sub>2</sub>/SiO<sub>2</sub> material heated to 200 °C.

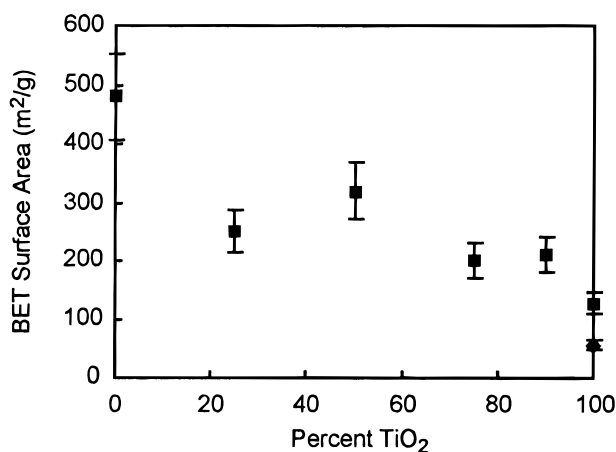
Note that these spheres are bonded together to form larger (5 μm) particles. The material, as it was used in photocatalytic reactions, consisted of ~5 μm particles (following mechanical grinding and sieving) made up of ~200 nm porous spheres bonded together. Thus, much of the reactive surface of the TiO<sub>2</sub>/SiO<sub>2</sub> materials is located within the particles. This indicates that the reactivity of these materials might be improved if the materials were prepared as dispersed 200 nm spheres. By not allowing the spheres to bond together, material transport to the spheres in the interior of the porous particles would no longer be a potential hindrance to photocatalysis.

<sup>29</sup>Si NMR studies of TiO<sub>2</sub>/SiO<sub>2</sub> materials were undertaken to understand the environment around the Si atoms and understand the degree of mixing of Si and Ti in the catalysts. The chemical shift of the <sup>29</sup>Si signal is a function of the environment and can distinguish neighboring -OSi groups from neighboring -Ti groups.<sup>13</sup> Measurements were made with the 50/50, 75/25, and 30/70 materials and were compared to pure SiO<sub>2</sub>. These measurements indicate that the average Si in the 30/70 material (Figure 4) had more -OTi groups around it than the other ratio materials. This is shown by the enhanced NMR signal in the Q<sub>2</sub> and Q<sub>3</sub> regions (equivalent to two and three -OTi groups around a Si, with shifts of  $\delta \approx -90$  and  $-100$  ppm, respectively)<sup>13</sup> for the 30/70 material relative to materials with different TiO<sub>2</sub>/SiO<sub>2</sub> ratios. The presence of -OTi in the SiO<sub>2</sub> phase supports the idea of a mixed phase in these materials. The presence of a TiOSi phase is thought to be responsible for the enhanced adsorption of R-6G on 30/70 materials relative to those with higher SiO<sub>2</sub> ratios.<sup>7</sup> The 30/70 material represented the optimum ratio for achieving the largest TiOSi interface area. As the fraction of TiO<sub>2</sub> decreased, the Ti was incorporated into the SiO<sub>2</sub> matrix,<sup>11</sup> leaving little bulk TiO<sub>2</sub> to form a TiOSi interface. At higher TiO<sub>2</sub> ratios, the TiO<sub>2</sub> and SiO<sub>2</sub> phases tended to segregate again, producing mixed phases and a diminished interface region. TiO<sub>2</sub>/SiO<sub>2</sub> materials with ratios close to 30/70 exhibit indications of a significant Ti-O-Si phase.<sup>10,11</sup>

**Effect of TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Ratio on Photocatalytic Decomposition of SA.** The measured rate constants for the photocatalytic decomposition of SA (which adsorbs on Al<sub>2</sub>O<sub>3</sub>) are shown in Figure 5 as a function of TiO<sub>2</sub> percentage. The region of % TiO<sub>2</sub> = 75–90% gave the greatest activity, about twice the activity of Degussa TiO<sub>2</sub>. This increase in activity can be partially attributed to the increased surface area of the mixed



**Figure 5.** Rate constants for the photocatalytic decomposition of salicylic acid on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials and pure TiO<sub>2</sub>. Initial SA concentration =  $1.4 \times 10^{-4}$  M; catalyst concentration = 1 g/L.

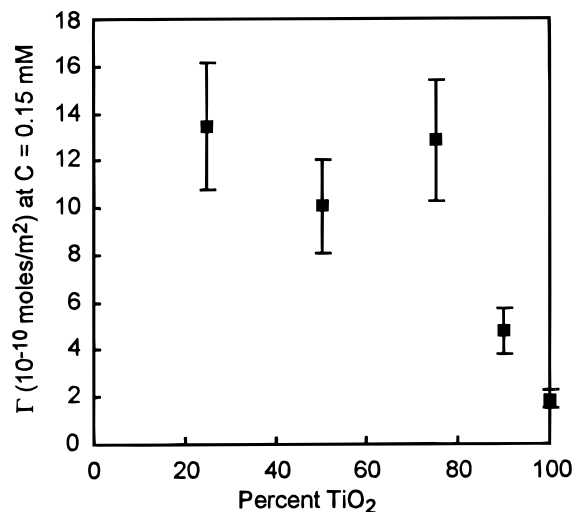


**Figure 6.** BET surface areas from Ar sorption isotherms at 77 K for TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials as a function of the percentage of TiO<sub>2</sub> in the material.

materials (Figure 6). However, if these results were normalized for TiO<sub>2</sub> content of the material, we observed that the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials used the TiO<sub>2</sub> sites more effectively than did Degussa. This is thought to be the result of adsorption of SA on the Al<sub>2</sub>O<sub>3</sub> near the TiO<sub>2</sub> sites, thereby increasing the concentration of SA at the surface relative to the solution concentration in a manner analogous to that previously discussed for R-6G on TiO<sub>2</sub>/SiO<sub>2</sub>.<sup>7</sup> The increased activity for the 75/25 TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> material is due to the favorable balance between enhanced reactivity of individual TiO<sub>2</sub> sites by adsorption of SA near those sites and the loss of catalyst activity by the replacement of the active TiO<sub>2</sub> sites with nonphotoactive Al<sub>2</sub>O<sub>3</sub>.

**Adsorption of SA on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.** The adsorption of SA on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials from a 0.144 mM SA solution indicates that the adsorption is a function of the Al<sub>2</sub>O<sub>3</sub> content in the materials (Figure 7). The concentration used for the quantification of adsorption of SA on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials was 0.144 mM, the starting concentration of the SA in photocatalytic reactions. The quantity of SA added (less the amount remaining in solution) was normalized to the surface area of catalyst present, and the results were reported as  $\Gamma_{SA}$  (mol/m<sup>2</sup>). Unlike the adsorption of R-6G on TiO<sub>2</sub>/SiO<sub>2</sub> experiments,<sup>7</sup> this result indicates that the properties of the final material are simply a mixture of the individual properties of TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>, because the adsorption is essentially proportional to the Al<sub>2</sub>O<sub>3</sub> content of the material.

**Characterization of TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.** The BET surface areas of the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials are shown as a function of TiO<sub>2</sub>



**Figure 7.** Single-point adsorption measurements for the adsorption of SA on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials as a function of the percentage of TiO<sub>2</sub> in the material. Final SA concentration =  $1.4 \times 10^{-4}$  M; catalyst concentration = 1 g/L.

content in Figure 6. The surface area of the material roughly correlates with the Al<sub>2</sub>O<sub>3</sub> content in the material. This further supports the idea that the final TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials are a mixture (with very little chemical interaction) of the TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> properties. Since the TiO<sub>2</sub> materials formed by these processes have lower surface areas than the Al<sub>2</sub>O<sub>3</sub> materials, the surface area increases result from the Al<sub>2</sub>O<sub>3</sub>.

Dynamic light scattering measurements were performed on the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> powders to determine average particle sizes for the materials. These measurements indicated that particle size was not a function of the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio and all had similar sizes of  $1.3 \pm 0.5$   $\mu$ m. This indicates that the Al<sub>2</sub>O<sub>3</sub> controlled the final particle size, because the ratio of 2-propanol to TIOA was constant through all the reactions. Because both the TiO<sub>2</sub>/SiO<sub>2</sub> and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials can be made as either bulk glassy solids (as the TiO<sub>2</sub>/SiO<sub>2</sub> materials were) or powders (as the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials were), the sol-gel process conditions control the form of the final catalyst material.

#### Analysis of TiO<sub>2</sub> in TiO<sub>2</sub>/SiO<sub>2</sub> and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Materials.

The physical form of TiO<sub>2</sub> in the mixed materials is important to the photocatalytic activity of the materials. And the size of the TiO<sub>2</sub> domains affects the distance between the TiO<sub>2</sub> centers and thus the distance an oxidizing intermediate (OH<sup>•</sup>) would have to travel before reacting with an adsorbed species on the SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub> phase. An ideal material would be one in which the particles were large enough to give bulk anatase behavior (e.g., no quantum effects that increase the band gap) and still achieve maximum mixing of the TiO<sub>2</sub> and SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>.

**XRD of TiO<sub>2</sub>/SiO<sub>2</sub> and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Materials.** XRD patterns of the materials studied gave the expected patterns for TiO<sub>2</sub> anatase or rutile phases when measured crystalline domains were greater than 5 nm. Powder XRD results are summarized in Figure 8. When the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials were heated to 1000 °C, the thermodynamically favored rutile phase of TiO<sub>2</sub> was formed. The TiO<sub>2</sub> domains were larger than 100 nm for the 75/25 TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and the pure TiO<sub>2</sub> samples heated to 1000 °C. The growth of organized TiO<sub>2</sub> domains and the phase (anatase or rutile) of those domains was controlled by the fraction of TiO<sub>2</sub> in the material and the temperature to which it was heated. For pure TiO<sub>2</sub> samples, an anatase TiO<sub>2</sub> phase was present at the outset and grew with increasing temperature. At 625 °C the rutile phase began to form, and the anatase was completely transformed to rutile by 1000 °C. As the fraction of TiO<sub>2</sub> was decreased in the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> material, the temper-

1000° C	A-11	R-48	R-43	R>100	R>100
750° C	A-5	R-13 A-14	R-15 A-16	R-35 A-18	R-67 A-62
625° C	N	N	A-13	A-13	R-26 A-32
500° C	N	N	N	A-13	A-30
200° C	N	N	N	N	A-11
	30/70 (Ti/Si)	25/75 (Ti/Al)	50/50 (Ti/Al)	75/25 (Ti/Al)	100/0 (TiO <sub>2</sub> )

**Figure 8.** Crystalline phases determined by powder XRD for materials heated to different temperatures for 12 h. The crystallite sizes were determined using the Scherrer equation for line width broadening. N, no crystalline phase was detected; A, anatase phase only (size of crystallites in nm); R, rutile phase only (size of crystallites in nm).

ature necessary for the crystallization of anatase, and the subsequent initial transformation to rutile increased. This is due to the increased separation of the TiO<sub>2</sub> domains as the fraction of TiO<sub>2</sub> decreases. At lower TiO<sub>2</sub> ratios, the initial TiO<sub>2</sub> domains are smaller, and hence greater heat is required to drive the crystallization.

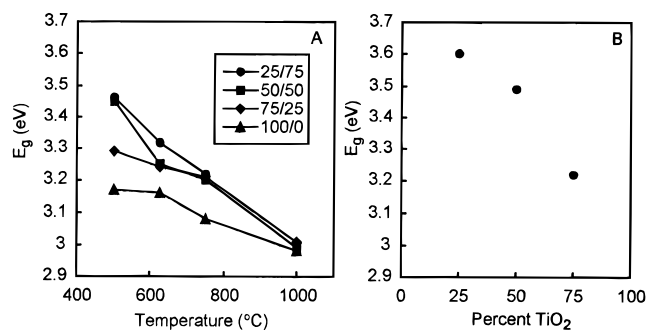
The interaction between TiO<sub>2</sub> and SiO<sub>2</sub> in the 30/70 TiO<sub>2</sub>/SiO<sub>2</sub> material was demonstrated in the crystallization behavior of TiO<sub>2</sub> in that material (see Figure 8). The TiO<sub>2</sub> never formed a rutile phase as it did in the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials. This is due to the stabilization of the anatase phase by the surrounding SiO<sub>2</sub> phase through the TiOSi interface. At the interface, TiO<sub>2</sub> atoms are substituted into the tetrahedral SiO<sub>2</sub> lattice forming tetrahedral Ti sites. The interaction between the tetrahedral Ti species and the octahedral Ti sites in the anatase is thought to prevent the transformation to rutile.<sup>14</sup> The SiO<sub>2</sub> lattice locks the Ti–O species at the interface with the TiO<sub>2</sub> domains preventing the nucleation that is necessary for the phase transformation to rutile.

**UV–Vis Reflectance of TiO<sub>2</sub>/SiO<sub>2</sub> and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> Materials.** The TiO<sub>2</sub> in the materials were studied by UV–vis reflectance, and a plot of the square of the absorbed light [proportional to the square of the Kubelka–Munk function  $F(R_{\infty})$ ] vs the energy of irradiation was used to obtain the band gap  $E_g$ . This optical absorption behavior is consistent with a direct band gap semiconductor. The Kubelka–Munk function is given by

$$F(R_{\infty}) = (1 - R_{\infty})^2 / 2R_{\infty} = K/S \quad (1)$$

where  $R_{\infty}$  is the measured reflectance ( $R_{\infty} = R_{\text{sample}}/R_{\text{standard}}$ ),  $K$  is the absorption coefficient, and  $S$  is the scattering coefficient.<sup>8</sup> The use of  $F(R_{\infty})$  as the equivalent of absorbance relies on the assumption that the scattering coefficients were consistent throughout the compared samples. This assumption was validated by the comparison of the reflectance spectra of the materials studied (TiO<sub>2</sub>/SiO<sub>2</sub> and TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) at wavelengths longer than the TiO<sub>2</sub> absorption (450–900 nm). The  $F(R_{\infty})$  value in nonadsorbing regions was a function of  $S$  only, thus allowing the verification of the similarity of  $S$  values.

TiO<sub>2</sub> domain sizes too small to estimate by XRD (~1 nm) were obtained from the blue shift in the absorption onset. The shift in  $E_g$  can be used to find the approximate organized domain size from the relationship derived by Brus<sup>15</sup> from a particle in



**Figure 9.** Band gap ( $E_g$ ) of (A) TiO<sub>2</sub>/SiO<sub>2</sub> and (B) TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials measured by UV–vis reflectance as a function of (A) temperature and (B) percentage of TiO<sub>2</sub> in the material (at 200 °C).

a sphere model for relating band gap shift ( $\Delta E_g$ ) to particle radius

$$\Delta E_g = \left( \frac{\hbar^2 \pi^2}{2r^2 \mu} \right) - \frac{1.8e^2}{r\epsilon} \quad (2)$$

where  $r$  is the radius of the particle,  $\epsilon$  is the dielectric constant of the materials, and  $\mu$  is the reduced mass of the excitation calculated from

$$\mu^{-1} = m_e^* + m_h^* \quad (3)$$

where  $m_e^*$  is the mass of the electron and  $m_h^*$  is the mass of the hole.  $\epsilon$  has been measured as 184,<sup>15</sup> and  $\mu$  has been calculated as  $1.63m_e$  (mass of electron at rest).<sup>16</sup> For a 50/50 TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> material heated to 500 °C, a  $\Delta E_g = 0.25$  eV was measured, yielding from eq 2 a particle radius of 9 Å. This estimated size is subject to substantial error because of the assumptions that  $\mu$  and  $\epsilon$  for the bulk TiO<sub>2</sub> are valid for the nanocrystalline TiO<sub>2</sub>.<sup>15–17</sup>

Knowledge of  $E_g$  is also important in determining the energy of the light absorbed to generate electron–hole pairs. When the TiO<sub>2</sub> domains are sufficiently large (> 3 nm), the  $E_g$  will be at or very near the bulk value (3.0 eV for rutile and 3.2 eV for anatase). An increase of  $E_g$  for the TiO<sub>2</sub> shows the existence of quantum effects and smaller organized TiO<sub>2</sub> domains. The trend observed here was that the lower the percentage of TiO<sub>2</sub>, the smaller the TiO<sub>2</sub> particle size (larger  $E_g$ ). Figure 9A shows the growth of the TiO<sub>2</sub> domains in TiO<sub>2</sub>/SiO<sub>2</sub> materials as a function of temperature of photocatalyst preparation. For the TiO<sub>2</sub>/SiO<sub>2</sub> materials prepared at 500–600 °C, the TiO<sub>2</sub> domains are very small (less than 3 nm), and the catalyst consists of matrix-isolated Q-particles. At higher temperatures, the domains grow to anatase material and finally to rutile at 1000 °C. However, the anatase to rutile conversion rate depends on composition, so that the 25/75 material remained in the anatase phase, even at 1000 °C. The behavior of the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> was different. For ratios below 50/50, the TiO<sub>2</sub> particle size was smaller (as indicated by the larger  $E_g$ ; Figure 9B); however, the bulk phases grew more rapidly with temperature compared to TiO<sub>2</sub>/SiO<sub>2</sub> (Figure 8). The results suggest that the TiOSi interface stabilizes the TiO<sub>2</sub> domains, hindering the agglomeration of TiO<sub>2</sub> and thus preventing their growth. The 30/70 material displayed quantum effects after being heated to 500 °C; when the material was heated to only 200 °C, the TiO<sub>2</sub> domains were probably smaller and consequently were also isolated Q-particles. The ideal TiO<sub>2</sub>/SiO<sub>2</sub> photocatalyst design would maximize the adsorption behavior and the proximity of the SiO<sub>2</sub> adsorption zones to TiO<sub>2</sub> photoactive ones (which

would favor smaller domains) and minimize  $E_g$ . The advantages of the TiOSi phase outweigh the potential loss of activity due to the loss of absorption of lower energy light due to quantum effects. The TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials demonstrated better activity when heated to a temperature sufficient to give bulk TiO<sub>2</sub> (anatase) behavior.

### Conclusions

Improved photocatalysts can be prepared by fabricating composite materials through sol-gel processing. These materials combine the photocatalytic properties of TiO<sub>2</sub> and the adsorptive properties of SiO<sub>2</sub> or Al<sub>2</sub>O<sub>3</sub>. In the TiO<sub>2</sub>/SiO<sub>2</sub> material the TiO<sub>2</sub> showed quantum particle effects characteristic of very small domains and a large amount of TiOSi structure. The more acidic SiO<sub>2</sub> sites promote the adsorption of rhodamine 6G and a higher decomposition rate than on pure TiO<sub>2</sub>. The TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> materials behave more as a composite of the two bulk phases. The basic Al<sub>2</sub>O<sub>3</sub> adsorbed acidic species and showed improved photocatalytic decomposition of salicylic acid.

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