Improved Photocatalytic Activity and Characterization of Mixed TiO2/SiO2 and TiO2/Al2O3 Materials

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Introduction

Heinz Gerischer recognized very early the importance of semiconductor electrodes.1 Following the introduction of TiO2 single-crystal electrodes for solar energy conversion by Honda and Fujishima,2 an enormous literature developed on the characterization and application of this material in photoelectrochemical applications. Photocatalysis at TiO2 particles, with possible applications to waste treatment,3,4 has been a particularly active area.5,6 For such applications, it is important to improve the efficiency of the TiO2-based photocatalysts. A strategy we have been investigating with such photocatalysts has been the combination of the photoactive TiO2 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.7 Moreover, this strategy allows the production of matrix-isolated quantum (Q-) particles of TiO2 with a different band gap than the bulk material.

In an earlier study,7 we demonstrated that a mixed oxide of TiO2 and SiO2 produced by a sol-gel method was a more efficient photocatalyst for the photocatalytic decomposition of rhodamine-6G (R-6G) than TiO2 alone. The increase in efficiency was attributed to the presence of an adsorbent (SiO2). The adsorbent phase increased the concentration of R-6G near the TiO2 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 TiO2 alone, but the dissolved form is photodecomposed by a TiO2 slurry.

The TiO2/SiO2 photocatalysts used in the earlier study7 are characterized here. The enhanced photocatalytic activity of TiO2 for the decomposition of salicylic acid in a mixed TiO2/Al2O3 photocatalyst relative to pure TiO2 is also demonstrated. The photocatalytic decomposition of phenol on TiO2/SiO2, TiO2/Al2O3, and TiO2 materials is also described. Further characterization of the TiO2/SiO2 materials was undertaken to understand better the increased efficiency of the materials. In 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 TiO2 domains in the materials aids in understanding their photocatalytic activity. Characteristics of the materials (TiO2/SiO2, TiO2/Al2O3, and TiO2), such as surface area, surface acidity, and their morphology (TiO2/SiO2 as a glass and TiO2/Al2O3 as particles), were studied.

A schematic model for the mixed phase system is given in Figure 1. The TiO2 and adsorbent (SiO2 or Al2O3) are prepared so they are intimately mixed (on a 10 nm scale or smaller). The TiO2 behaves as the photoactive center, e.g., generating hydroxyl radicals under irradiation, while the SiO2 and Al2O3 provide better adsorption sites in the vicinity of the TiO2. 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 TiO2/Al2O3 mixed catalysts were prepared by sol-gel methods to produce powders directly (as opposed to bulk glass materials for TiO2/SiO2 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...
The adsorption and decomposition of aqueous salicylic acid (SA) on TiO$_2$/Al$_2$O$_3$ materials as a function of TiO$_2$ content and the size of the particles for the desired application. We studied SA adsorbs to Al$_2$O$_3$. The TiO$_2$/SiO$_2$ materials were characterized by AFM and $^{29}$Si CP-MAS NMR, and both TiO$_2$/SiO$_2$ and TiO$_2$/Al$_2$O$_3$ materials were examined by XRD and UV–vis reflection spectroscopy.

**Experimental Section**

**Preparation of Photocatalysts.** The preparation method for the TiO$_2$/SiO$_2$ materials has been described previously. Solids of TiO$_2$/Al$_2$O$_3$ were prepared by the uncatalyzed hydrolysis of tetraisopropyl orthotitanate (TiOT, Fluka) and triisopropyl orthoaluminate (TIOA, 98%, Aldrich). A solution of 20 g TiO$_2$ 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 TiO$_2$ was prepared by the same procedure except no TiOT was added, and the TiO2/2-propanol solution was not cooled to 0 °C before the addition of water. Materials of 90/10 and 95/5 (TiO$_2$/Al$_2$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. Sols of TiO$_2$/Al$_2$O$_3$ were prepared by the uncatalyzed hydrolysis of tetraisopropyl orthotitanate (TiOT, Fluka) and triisopropyl orthoaluminate (TIOA, 98%, Aldrich). A solution of 20 g TiO$_2$ 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 TiO$_2$ was prepared by the same procedure except no TiOT was added, and the TiO2/2-propanol solution was not cooled to 0 °C before the addition of water. Materials of 90/10 and 95/5 (TiO$_2$/Al$_2$O$_3$ mole ratio) were prepared exactly as above, with the reaction scale reduced by a factor of 4.

The adsorption of SA on TiO$_2$/Al$_2$O$_3$ Materials. The adsorption of SA on TiO$_2$ and TiO$_2$/Al$_2$O$_3$ materials from the aqueous solutions was determined by a titration method. A 1 g/L slurry of the TiO$_2$/Al$_2$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$_{280}$nm = 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 (TiO$_2$/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 μM filters. The concentration was adjusted by addition of water until a satisfactory signal intensity was obtained. A solid state $^{29}$Si MAS NMR spectrum of the 30/70 TiO$_2$/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.

**Results and Discussion**

**Photodecomposition of Phenol.** When an aqueous solution of phenol, which does not adsorb on either SiO$_2$ or Al$_2$O$_3$, was exposed to light in the presence of TiO$_2$/SiO$_2$, TiO$_2$/Al$_2$O$_3$, or 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 TiO$_2$ present in the material compared to the widely used Degussa 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 SiO$_2$ or Al$_2$O$_3$. The measured rate for the photocatalytic decomposition of phenol was slower for all of the mixed materials than for pure TiO$_2$. This is consistent with the idea of the photocatalyst consisting of two independent domains. When the SiO$_2$ or Al$_2$O$_3$ phase does not adsorb the molecule being decomposed (phenol), it decreases the activity of the catalyst by reducing the quantity of TiO$_2$ available for photocatalysis relative to pure TiO$_2$. However, when the rates were normalized to the TiO$_2$ content of the material, the TiO$_2$/SiO$_2$ material demonstrated a more efficient use of the TiO$_2$ sites than TiO$_2$ alone or mixed TiO$_2$/Al$_2$O$_3$ materials. The normalized rate for the TiO$_2$/SiO$_2$ material was 6.7 × 10$^{-3}$ min$^{-1}$; the rate for pure TiO$_2$ was 4.0 × 10$^{-3}$ min$^{-1}$. The decreased reactivity of TiO$_2$ in TiO$_2$/Al$_2$O$_3$ materials was due to the decrease of...
Effect of TiO2/Al2O3 Ratio on Photocatalytic Decomposition of SA. The measured rate constants for the photocatalytic decomposition of SA (which adsorbs on Al2O3) are shown in Figure 5 as a function of TiO2 percentage. The region of %TiO2 = 75–90% gave the greatest activity, about twice the activity of Degussa TiO2. This increase in activity can be partially attributed to the increased surface area of the mixed

Characterization of TiO2/SiO2 Photocatalysts. The TiO2/SiO2 materials were characterized by AFM and 29Si CP-MAS NMR. An AFM image of a 25/75 material is shown in Figure 3. Images of the 30/70 TiO2/SiO2 material had similar features. The image indicates that the material consists of ∼200 nm spheres bonded together in a non-dense-packing arrangement. 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 TiO2/SiO2 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.

29Si NMR studies of TiO2/SiO2 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 29Si signal is a function of the environment and can distinguish neighboring −OSi groups from neighboring −Ti groups. Measurements were made with the 50/50, 75/25, and 30/70 materials and were compared to pure SiO2. 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 Q2 and Q3 regions (equivalent to two and three −OTi groups around a Si, with shifts of δ ≈ −90 and −100 ppm, respectively). The 30/70 material relative to materials with different TiO2/SiO2 ratios. The presence of −OTi in the SiO2 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 SiO2 ratios. The 30/70 material represented the optimum ratio for achieving the largest TiOSi interface area. As the fraction of TiO2 decreased, the Ti was incorporated into the SiO2 matrix, leaving little bulk TiO2 to form a TiOSi interface. At higher TiO2 ratios, the TiO2 and SiO2 phases tended to segregate again, producing mixed phases and a diminished interface region. TiO2/SiO2 materials with ratios close to 30/70 exhibit indications of a significant Ti−O−Si phase.

Effect of TiO2/Al2O3 Ratio on Photocatalytic Decomposition of SA. The measured rate constants for the photocatalytic decomposition of SA (which adsorbs on Al2O3) are shown in Figure 5 as a function of TiO2 percentage. The region of %TiO2 = 75–90% gave the greatest activity, about twice the activity of Degussa TiO2. This increase in activity can be partially attributed to the increased surface area of the mixed
materials (Figure 6). However, if these results were normalized for TiO₂ content of the material, we observed that the TiO₂/Al₂O₃ materials used the TiO₂ sites more effectively than did Degussa. This is thought to be the result of adsorption of SA on the Al₂O₃ near the TiO₂ 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 TiO₂/SiO₂.⁷ The increased activity for the 75/25 TiO₂/Al₂O₃ material is due to the favorable balance between enhanced reactivity of individual TiO₂ sites by adsorption of SA near those sites and the loss of catalyst activity by the replacement of the active TiO₂ sites with nonphotoactive Al₂O₃.

**Adsorption of SA on TiO₂/Al₂O₃.** The adsorption of SA on TiO₂/Al₂O₃ materials from a 0.144 mM SA solution indicates that the adsorption is a function of the Al₂O₃ content in the materials (Figure 7). The concentration used for the quantification of adsorption of SA on TiO₂/Al₂O₃ 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/m²). Unlike the adsorption of R-6G on TiO₂/SiO₂ experiments,⁷ this result indicates that the properties of the final material are simply a mixture of the individual properties of TiO₂ and Al₂O₃, because the adsorption is essentially proportional to the Al₂O₃ content of the material.

**Characterization of TiO₂/Al₂O₃.** The BET surface areas of the TiO₂/Al₂O₃ materials are shown as a function of TiO₂ content in Figure 6. The surface area of the material roughly correlates with the Al₂O₃ content in the material. This further supports the idea that the final TiO₂/Al₂O₃ materials are a mixture (with very little chemical interaction) of the TiO₂ and Al₂O₃ properties. Since the TiO₂ materials formed by these processes have lower surface areas than the Al₂O₃ materials, the surface area increases result from the Al₂O₃.

Dynamic light scattering measurements were performed on the TiO₂/Al₂O₃ powders to determine average particle sizes for the materials. These measurements indicated that particle size was not a function of the TiO₂/Al₂O₃ ratio and all had similar sizes of 1.3 ± 0.5 μm. This indicates that the Al₂O₃ controlled the final particle size, because the ratio of 2-propanol to TIOA was constant through all the reactions. Because both the TiO₂/SiO₂ and TiO₂/Al₂O₃ materials can be made as either bulk glassy solids (as the TiO₂/SiO₂ materials were) or powders (as the TiO₂/Al₂O₃ materials were), the sol–gel process conditions control the form of the final catalyst material.

**Analysis of TiO₂ in TiO₂/SiO₂ and TiO₂/Al₂O₃ Materials.** The physical form of TiO₂ in the mixed materials is important to the photocatalytic activity of the materials. And the size of the TiO₂ domains affects the distance between the TiO₂ centers and thus the distance an oxidizing intermediate (OH⁻) would have to travel before reacting with an adsorbed species on the SiO₂ or Al₂O₃ 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 TiO₂ and SiO₂ or Al₂O₃.

**XRD of TiO₂/SiO₂ and TiO₂/Al₂O₃ Materials.** XRD patterns of the materials studied gave the expected patterns for TiO₂ anatase or rutile phases when measured crystalline domains were greater than 5 nm. Powder XRD results are summarized in Figure 8. When the TiO₂/Al₂O₃ materials were heated to 1000 °C, the thermodynamically favored rutile phase of TiO₂ was formed. The TiO₂ domains were larger than 100 nm for the 75/25 TiO₂/Al₂O₃ and pure TiO₂ samples heated to 1000 °C. The growth of organized TiO₂ domains and the phase (anatase or rutile) of those domains was controlled by the fraction of TiO₂ in the material and the temperature to which it was heated. For pure TiO₂ samples, an anatase TiO₂ 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 TiO₂ was decreased in the TiO₂/Al₂O₃ material, the temper-
Characterization of TiO$_2$/SiO$_2$ and TiO$_2$/Al$_2$O$_3$

The interaction between TiO$_2$ and SiO$_2$ in the 30/70 TiO$_2$/SiO$_2$ material was demonstrated in the crystallization behavior of TiO$_2$ in that material (see Figure 8). The TiO$_2$ never formed a rutile phase as it did in the TiO$_2$/Al$_2$O$_3$ materials. This is due to the stabilization of the anatase phase by the surrounding SiO$_2$ phase through the TiOSi interface. At the interface, TiO$_2$ atoms are substituted into the tetrahedral SiO$_2$ 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. The SiO$_2$ lattice locks the Ti–O species at the interface with the TiO$_2$ domains preventing the nucleation that is necessary for the phase transformation to rutile.

**UV–Vis Reflectance of TiO$_2$/SiO$_2$ and TiO$_2$/Al$_2$O$_3$ Materials.** The TiO$_2$ 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 $F(R_m)$] vs the energy of irradiation was used to obtain the band gap $E_g$. This optical absorption behavior is consistent with a matrix-isolated Q-particles. At higher temperatures, the domains are very small (less than 3 nm), and the catalyst consists of isolated Q-particles. The ideal TiO$_2$/SiO$_2$ photocatalyst design would maximize the adsorption behavior and the proximity of the light absorbed to generate electron–hole pairs. When the TiO$_2$ 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$_2$ shows the existence of quantum effects and smaller organized TiO$_2$ domains. The trend observed here was that the lower the percentage of TiO$_2$, the smaller the TiO$_2$ particle size (larger $E_g$). Figure 9A shows the growth of the TiO$_2$ domains in TiO$_2$/SiO$_2$ materials as a function of temperature of photocatalyst preparation. For the TiO$_2$/SiO$_2$ materials prepared at 500–600 °C, the TiO$_2$ 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$_2$/Al$_2$O$_3$ was different. For ratios below 50/50, the TiO$_2$ 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$_2$/SiO$_2$ (Figure 8). The results suggest that the TiOSi interface stabilizes the TiO$_2$ domains, hindering the agglomeration of TiO$_2$ 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$_2$ domains were probably smaller and consequently were also isolated Q-particles. The ideal TiO$_2$/SiO$_2$ photocatalyst design would maximize the adsorption behavior and the proximity of the SiO$_2$ adsorption zones to TiO$_2$ photoactive ones (which are absorbing near 380 nm) allowing the verification of the similarity of the TiO$_2$ and SiO$_2$.

**Figure 8.** Crystalline phases determined by powder XRD for materials heated to different temperatures for 12 h. The crystal 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).

**Figure 9.** Band gap ($E_g$) of (A) TiO$_2$/SiO$_2$ and (B) TiO$_2$/Al$_2$O$_3$ materials measured by UV–vis reflectance as a function of (A) temperature and (B) percentage of TiO$_2$ in the material (at 200 °C).

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

\]

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^*

\]

where $m_e^*$ is the mass of the electron and $m_h^*$ is the mass of the hole. $\epsilon$ has been measured as 184,15 and $\mu$ has been calculated as 1.63$m_m$ (mass of electron at rest).16 For a 50/50 TiO$_2$/Al$_2$O$_3$ material heated to 500 °C, a $\Delta E_g = 0.25$ eV was measured, yielding 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$_2$ are valid for the nanocrystalline TiO$_2$.15–17

Knowledge of $E_g$ is also important in determining the energy of the light absorbed to generate electron–hole pairs. When the TiO$_2$ 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$_2$ shows the existence of quantum effects and smaller organized TiO$_2$ domains. The trend observed here was that the lower the percentage of TiO$_2$, the smaller the TiO$_2$ particle size (larger $E_g$). Figure 9A shows the growth of the TiO$_2$ domains in TiO$_2$/SiO$_2$ materials as a function of temperature of photocatalyst preparation. For the TiO$_2$/SiO$_2$ materials prepared at 500–600 °C, the TiO$_2$ 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$_2$/Al$_2$O$_3$ was different. For ratios below 50/50, the TiO$_2$ 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$_2$/SiO$_2$ (Figure 8). The results suggest that the TiOSi interface stabilizes the TiO$_2$ domains, hindering the agglomeration of TiO$_2$ 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$_2$ domains were probably smaller and consequently were also isolated Q-particles. The ideal TiO$_2$/SiO$_2$ photocatalyst design would maximize the adsorption behavior and the proximity of the SiO$_2$ adsorption zones to TiO$_2$ photoactive ones (which
would favor smaller domains) and minimize $E_p$. 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$_2$/Al$_2$O$_3$ materials demonstrated better activity when heated to a temperature sufficient to give bulk TiO$_2$ (anatase) behavior.

Conclusions

Improved photocatalysts can be prepared by fabricating composite materials through sol–gel processing. These materials combine the photocatalytic properties of TiO$_2$ and the adsorptive properties of SiO$_2$ or Al$_2$O$_3$. In the TiO$_2$/SiO$_2$ material the TiO$_2$ showed quantum particle effects characteristic of very small domains and a large amount of TiOSi structure. The more acidic SiO$_2$ sites promote the adsorption of rhodamine 6G and a higher decomposition rate than on pure TiO$_2$. The TiO$_2$/Al$_2$O$_3$ materials behave more as a composite of the two bulk phases. The basic Al$_2$O$_3$ adsorbed acidic species and showed improved photocatalytic decomposition of salicylic acid.

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References and Notes