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Effect of Silver on the Photocatalytic Activity of TiO_2

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Silver was deposited on TiO_2 powders (Degussa P25) by the photodecomposition of two different silver salts, AgF and $AgNO_3$. The photocatalytic activity of TiO_2 powder samples was evaluated by the degradation of 1,4-dichlorobenzene (DCB). Photodecomposition of AgF on TiO_2 gave higher photocatalytic activity than that of $AgNO_3$. The optimum catalytic activity found by the deposition of Ag was comparable to that obtained from Au. It was also observed that the photocatalytic activity of Ag-loaded TiO_2 films was greater than that obtained for pure TiO_2 films. This result is consistent with the results obtained for Ag-deposited TiO_2 powders. © 1993 Academic Press, Inc.

Introduction

TiO_2 has been shown to be an excellent photocatalyst for the degradation of several environmental contaminants (*1*, *2*). Many organic compounds can be decomposed in aqueous solution in the presence of TiO_2 powders illuminated with near UV or sunlight (*3–5*).

In principle, a photocatalytic reaction may proceed on the surface of TiO_2 powders via several steps (*6*), namely:

(a) production of electron–hole pairs, photogenerated by exciting the semiconductor with light energy;

(b) separation of electrons and holes by traps available on the TiO_2 surface;

(c) a redox process induced by the separated electrons and holes with the adsorbates present on the surface; and

(d) desorption of the products and reconstruction of the surface.

It has been shown that the photocatalytic activity of TiO_2 is influenced by the crystal structure (anatase and/or rutile), surface area, size distribution, porosity, surface hydroxyl group density, etc. (7–9). These will have an influence on the production of electron–hole pairs, the surface adsorption and desorption process and the redox process.

Electron–hole recombination is in direct competition with the trapping process (step b). The rate of trapping and the photocatalytic activity of TiO_2 will be enhanced by retarding the electron–hole recombination. The principal method of slowing electron–hole recombination is thought to be through the loading of metals onto the surface of the TiO_2 particles. It is considered that the metal dispersed on the TiO_2 particles expedites the transportation of electrons produced by the photoexcitation to the outer system (*4*).

Previously, photochemical deposition of metal on semiconductor particles has been used as a means of noble metal recovery in waste solutions (*10*). Recently, this technique has been widely employed for the purpose of improving the photocatalytic activity of semiconductors. Pt, Pd, Au, Rh, RuO_2, etc. have been utilized in the improvement of photocatalytic activity (*11–15*). However, these metals may not be suitable for industrial applications since they are very rare and expensive. In this study, a less expensive Ag was used for the preparation of efficient photocatalysts.

Sclafani *et al.* reported that Ag can be

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used for the improvement of photocatalytic activity of TiO_2 by loading Ag on TiO_2 powders with the photodecomposition of $AgNO_3$ (*16*). He reported that Ag improves the photocatalytic activity of TiO_2 in the dehydrogenation of 2-propanol, even though the improvement is much lower than that of Pt. Kondo and Jardim have shown that thermally decomposed $AgNO_3$ on TiO_2 powders results in catalysts which can photodegrade chloroform to CO_2 and HCl (*17*). They also observed increased degradation of urea with Ag-loaded TiO_2.

In this present study, Ag was deposited on TiO_2 powders by the photodecomposition of two different silver salts, AgF and $AgNO_3$. The photocatalytic activities of these samples were compared by measuring the degradation efficiency toward 1,4-dichlorobenzene (DCB). Silver was also photochemically deposited on TiO_2 films and the effect of Ag on the photocatalytic activity of TiO_2 was evaluated. The activity of film samples was determined by the degradation of salicylic acid.

Experimental

Photochemical Decomposition of AgF on TiO_2 Powders

The TiO_2 used in these studies was Degussa P25 (47 m^2/g, 70% anatase). A reagent grade of AgF was obtained from Aldrich Chemical Co. and used as received. Ag was deposited onto TiO_2 by photochemical decomposition of AgF. A stock solution of AgF containing 4.2 mg AgF/ml was prepared in a polyethylene bottle. TiO_2 (Degussa P25), 0.3 g, was dispersed in solutions containing various amounts of the AgF. Distilled water was added to achieve a total volume of 30 ml. This mixture was transferred to the silica reaction vessel and inserted into the decomposition apparatus (Fig. 1). During the irradiation, nitrogen was bubbled vigorously through the samples. A Hg/Xe short-arc lamp (100 watts, 230–600 nm) was used to irradiate the samples. The irradiated solution was then centrifuged for 30 min. Finally, recovered precipitate was desiccated for 2 hr.

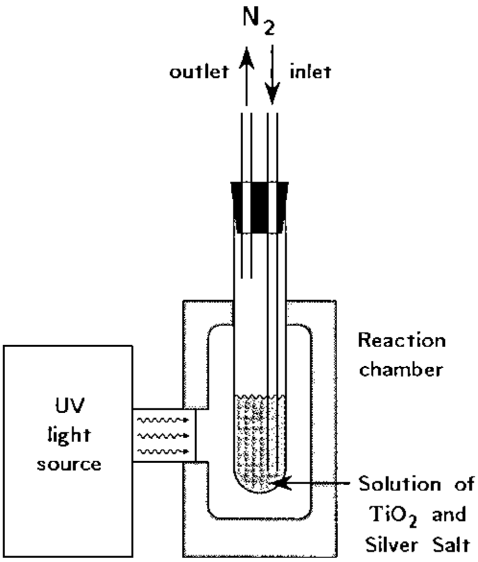

FIG. 1. Photodecomposition apparatus.

Photochemical Decomposition of $AgNO_3$ on TiO_2 Powders

Ag was deposited on TiO_2 (Degussa P25) by photochemical decomposition of $AgNO_3$. A reagent grade of $AgNO_3$ (Kodak, X491) was used as received. A stock solution of $AgNO_3$ containing 5.2 mg $AgNO_3$/ml was prepared. The procedure of the sample preparation was the same as that used for the photodecomposition of AgF.

Measurement of Photocatalytic Activity of TiO_2 Powders

The photocatalytic activities of various TiO_2 samples were evaluated by the degradation of 1,4-dichlorobenzene (DCB). A saturated DCB solution was prepared by adding an excess of DCB to distilled water and stirring for 8 hr. The solution was capped and preserved in darkness. A sample (0.0015 wt% of TiO_2) was ultrasonically dispersed in distilled water and 0.2 ml of a saturated aqueous solution of DCB was added to 3 ml of the TiO_2 suspension in a silica cuvette.

A sample containing 0.2 ml of distilled water and 3 ml of the TiO_2 suspension was used as a blank for the absorption measurement. The sample was then irradiated with a 150-watt xenon short-arc lamp whose output was passed through a pyrex filter. The differential absorption at 224 nm (maximum absorption peak of DCB) was measured using a Perkin-Elmer 552A spectrophotometer. The change in concentration of DCB of the irradiated sample as a function of time was compared to the blank.

Preparation of TiO_2 Films

TiO_2 thin films were deposited on pyrex glass substrates by a simple ultrasonic nebulization and pyrolysis technique (*18*, *19*). The schematic diagram of the deposition apparatus was reported in a previous publication (*18*). The reactor used in this investigation was heated by means of a two-zone mirror furnace (Transtemp Co., Chelsea, MA). Dipropoxy-titanium-bis(acetylacetonate) was used as a precursor for the preparation of these thin films. It was synthesized according to Yamamoto's method (*20*). An ethanol solution of dipropoxy-titanium-bis(acetylacetonate) was nebulized by a commercial ultrasonic humidifier (Holmes Air) and the mist was carried into the horizontal reactor by a stream of argon gas. The substrate was held perpendicular to the carrier gas flow in the furnace by means of a silica holder which was rotated by a low speed motor to achieve best uniformity of film deposition. Typical reaction parameters were: deposition temperature, 500°C; argon flow rate, 3.5 liter/min; distance between substrate and nozzle, 9.0 cm. Under such conditions, films of 0.3 μm in thickness were prepared on the pyrex glass substrates (1×1 cm^2, 1.5 mm thickness) in 10 min by consuming 7 ml of precursor solution. Pyrex glass substrates were cleaned with nitric acid, distilled water, and semiconductor grade acetone. The deposited films were postannealed in a flowing atmosphere of oxygen at 500°C for 20 min in order to eliminate the residual carbon.

Photochemical Decomposition of AgF on TiO_2 Films

AgF was reduced to silver on the TiO_2 films by photochemical decomposition. 30 ml of a 5×10^{-6} *M* AgF aqueous solution was added to a silica reaction vessel. A 1×1 cm^2 pyrex glass substrate, coated with TiO_2 on both sides, was immersed in the AgF solution with a pyrex holder which was rotated by a low-speed motor to stir the solution during the irradiation. The sample was then irradiated with a Hg/Xe short-arc lamp (100 watts, 230–600 nm). AgF was decomposed on the surface of the TiO_2 films. For the gradual deposition of Ag on the TiO_2 film, the used AgF solution was discarded and a fresh AgF solution was added every 5 min during the irradiation. The irradiated sample was then rinsed thoroughly with distilled water to remove any AgF residue on the film.

Characterization of TiO_2 Films

The thickness of the films on pyrex glass substrates was measured by interference fringes in their UV–visible transmission spectra (*21*). The positions of maxima and minima were used for the calculation. Since a TiO_2 film is a denser medium than the media on either side ($n_{air} = 1$ and $n_{pyrex} = 1.5$); transmission maxima occur at the wave numbers $\sigma_{max} = m/2nd$ and minima at $\sigma_{min} = (2m + 1)/4nd$, where m is an integer, n is the refractive index of TiO_2, and d is the thickness of the TiO_2 film. The interference spectra of TiO_2 films were obtained by using a Perkin-Elmer 552A spectrophotometer in the transmission mode.

X-ray diffraction patterns of these films were obtained using a Philips diffractometer and monochromated high intensity $CuK\alpha_1$ radiation ($\lambda = 1.5405$ Å). Diffraction patterns were taken with a scan rate of $1° \, 2\theta/$min over the range $20° < 2\theta < 72°$.

Measurement of Photocatalytic Activity of TiO_2 Films

The photocatalytic activities of TiO_2 films on 1×1 cm^2 pyrex glass substrates were evaluated by degradation of salicylic acid. Six ml of 60 μM salicylic acid aqueous solution were added to a pyrex test tube 18 × 150 mm. A 1 × 1 cm^2 substrate coated with TiO_2 on both sides was immersed in the salicylic acid solution with a pyrex holder which was rotated by a low-speed motor to stir the solution during the irradiation. The sample to be measured was then irradiated with a 150 watt xenon short arc lamp whose output was passed through a pyrex filter. The differential absorbance at 296 nm (absorption peak of salicylic acid) was measured using a Perkin-Elmer 552A spectrophotometer.

Results and Discussion

Silver was deposited on TiO_2 powder (P25 from the Degussa Corporation) by photodecomposing two different silver salts, AgF and $AgNO_3$. During the irradiation, the dispersed TiO_2 power turned violet in AgF solution and purple in $AgNO_3$.

The photocatalytic activity of Ag-deposited powder samples was evaluated by the degradation of 1,4-dichlorobenzene (DCB). All the samples were prepared by ultrasonically dispersing TiO_2 powders with the appropriate nominal concentration of AgF or $AgNO_3$. Nominal concentrations of silver are reported because the actual atomic percentage of silver on the TiO_2 particles could not readily be determined.

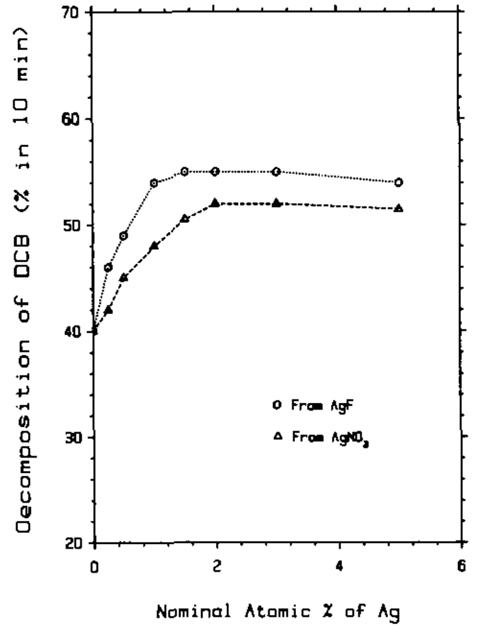

FIG. 2. Photocatalytic activity of TiO_2 powders as a function of nominal concentration of AgF and $AgNO_3$.

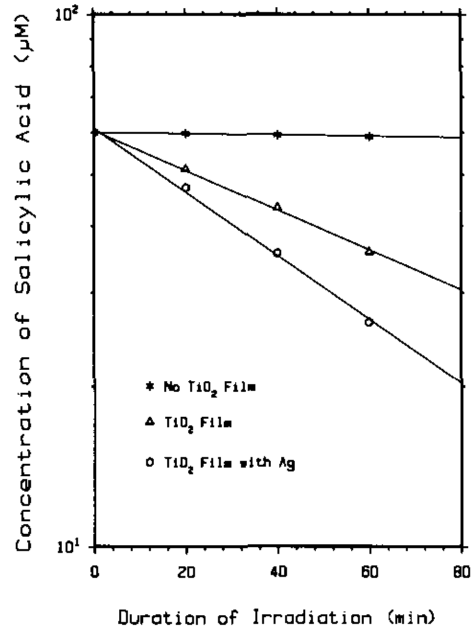

FIG. 3. Decomposition of salicylic acid vs irradiation time of a TiO_2 film and a TiO_2 film with Ag.

The duration of the irradiation used in decomposing the AgF or $AgNO_3$ affects the photocatalytic activity of the samples. Samples were prepared using 0.3 g of TiO_2 and a nominal atomic ratio of 99 : 1 TiO_2 : Ag in the reaction tube. The samples were irradiated with the UV light for varying amounts of time, 5, 10, 15, 30, 60, and 120 min. These samples were centrifuged and desiccated to dryness. The samples were evaluated by the relative degradation of DCB. For the evaluation of activity, TiO_2 samples deposited with Ag were redispersed as described above. The irradiation with the xenon lamp in the activity characterization totaled 10 min. The changes in concentration of DCB as a function of irradiation time in the photodecomposition process were compared.

For short periods of irradiation (5–30 min), the length of deposition time did not have much influence on the photocatalytic activity of the samples. However, the photocatalytic activity began to decrease for longer deposition times (>30 min). These results indicate that the optimum deposition time is approximately 15 min for both of the silver salts.

It was also shown that the nominal concentration of silver salts in the reaction tube affects the photocatalytic activity (see Fig. 2). Various concentrations of AgF or $AgNO_3$ were added to the dispersed TiO_2 solutions. The nominal atomic percent of the Ag concentration relative to TiO_2 before irradiation in the reaction tube was 0.25, 0.5, 1.0, 1.5, 2.0, 3.0, and 5.0 atomic percent. These suspensions were irradiated for a fixed amount of time, 15 min, in the photodecomposition apparatus shown in Fig. 1. The results of photocatalytic activity indicate that there is a critical loading of silver on the TiO_2 particles that corresponds to the optimum catalytic activity. This concentration of Ag on TiO_2 could not readily be determined. Hence, Fig. 2 indicates the variation in the nominal concentration of Ag relative to TiO_2 before irradiation. When the AgF was photodecomposed on TiO_2, the products from a solution containing 1.5 atomic percent of silver gave the optimum catalytic activity. The improvement of the photocatalytic activity of TiO_2 (P25) was approximately 35%. The optimum catalytic activity found by photodecomposition of AgF was comparable to that obtained from gold-deposited samples (*22*).

Nishimoto *et al.* reported that AgF was decomposed by photoirradiation at a much faster rate than $AgNO_3$ (*23*). Hermann *et al.* reported that a long period of illumination and a high concentration of silver salt increased the crystallite size of deposited Ag on TiO_2 (*24*). This is consistent with the results of this study where it was observed that the fast decomposition of AgF results in well-dispersed Ag on the surface of TiO_2 powders, and this influences the photocatalytic activity. The silver-deposited samples obtained from $AgNO_3$ solutions were less efficient.

Unlike the TiO_2 powders, a TiO_2 film can be used repeatedly for the measurement of photocatalytic activity, and unlike highly dispersed powders, films present no problem in terms of separating the catalyst from the solution after degradation of the organic impurities. Hence, thin films of TiO_2 on pyrex glass substrates were prepared and evaluated as photocatalysts. Nebulization of dipropoxy-titanium-bis(acetylacetonate) solution resulted in the production of films with good adherence to the substrate and uniform thickness. TiO_2 films of 0.3 μm thickness on 1 × 1 cm^2 pyrex glass substrates were prepared and studied in this investigation. The photocatalytic activities of TiO_2 films were evaluated by measuring the degradation of salicylic acid. Salicylic

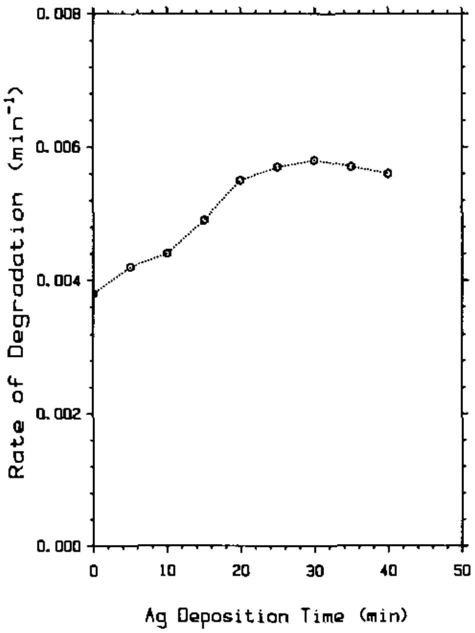

FIG. 4. The rate constant for degradation of salicylic acid vs the photodecomposition time of AgF (30 ml of 5 × 10^{-6} *M* AgF aqueous solution was used. Every 5 min, the used AgF solution was replaced by a fresh solution.)

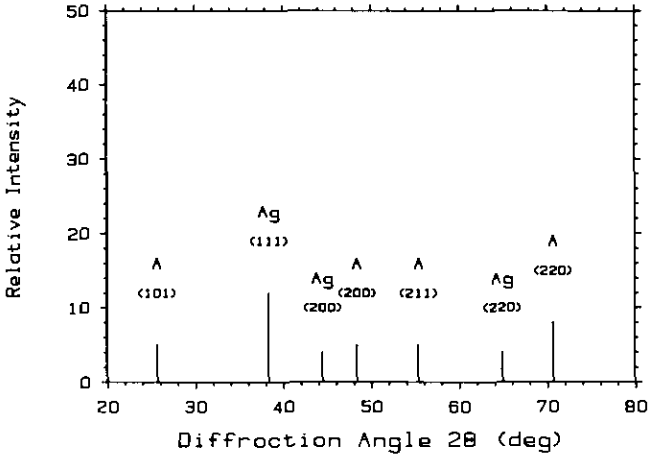

FIG. 5. X-ray diffraction spectrum of Ag-deposited TiO_2 film (A, anatase; 30 ml of 1.0×10^{-4} *M* AgF solution was photodecomposed on a TiO_2 film of 0.3 μm in thickness for 5 min.)

acid was chosen because it is not volatile and absorbs in the near UV.

Figure 3 shows the changes in the concentration of salicylic acid as a function of irradiation time. Matthews reported that photodecomposition of salicylic acid on TiO_2 films follows first order kinetics (*25*). It also can be seen that there is an approximately linear decrease in the logarithm of the concentration of salicylic acid with the duration of the irradiation (Fig. 3). Therefore, the slope, i.e., the rate of degradation of salicylic acid, was taken as the parameter for the evaluation of the photocatalytic activity of TiO_2 films (Fig. 4). The rate constant for TiO_2 films of 0.3 μm thickness on pyrex substrates prepared by the above method was 0.0037 min^{-1}.

AgF was reduced onto the TiO_2 films on pyrex glass substrates by the photochemical decomposition process described above. The amount of Ag deposit on a TiO_2 film affects its photocatalytic activity. For the gradual increase of Ag deposition on TiO_2 films, 30 ml of a very dilute AgF solution (5×10^{-6} M) was photodecomposed, and every 5 min the used AgF solution was replaced by a fresh solution. After 30 min, further deposition on Ag on the TiO_2 film decreased the photocatalytic activity. This result is in agreement with those obtained for TiO_2 powders.

The TiO_2 films deposited with Ag were analyzed by X-ray diffraction. The diffraction pattern shown in Fig. 5 indicates that the silver exists as metallic silver. This metallic silver dispersed on TiO_2 plays an important role in enhancing the photocatalytic activity of TiO_2.

Acknowledgments

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