Articles

Titanium(IV) Oxide Photocatalysts with Palladium

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Samples of palladium decomposed onto TiO_2 particles were prepared by two methods: the dispersion of a $PdCl_2$ solution followed by thermal decomposition, and the photodecomposition of $PdCl_2$. The addition of palladium to all samples increased their photocatalytic activity toward the degradation of 1,4-dichlorobenzene. This increase was optimized and compared for these two preparative methods. Palladium was also decomposed onto TiO_2 thin films by the photodecomposition of $PdCl_2$. The addition of palladium to the films increased their photocatalytic activity toward the degradation of salicylic acid.

Introduction

Photoassisted heterogeneous catalysis is currently of considerable interest as a means of removing harmful impurities from water. Many organic compounds can be decomposed in aqueous solution in the presence of titanium(IV) oxide powders and films illuminated with near UV or sunlight.[1-10]

It has been shown that the photocatalytic activity of titanium(IV) oxide is influenced by surface area, crystal structure (anatase and/or rutile) and density of surface hydroxyl groups.[11,12] Previous investigators have modified this density through the photodecomposition of the platinum group metals onto the surface of the titanium-(IV) oxide catalyst.[13-23] Early studies focused on the decomposition of metals and metal oxides on semiconductors such as TiO_2 in order to produce electrodes capable of photochemically splitting water. In addition, the photochemical decomposition of platinum metal and coinage metal compounds was a means of recovering precious metals from solution.

Although both anatase and rutile have been studied extensively as potential photocatalysts for the photodegradation of organic compounds, it has only been recently that photoassisted oxidation of chlorinated organic compounds has been studied using bifunctional catalysts. Wang, Heller, and Gerisher[24] have reported that the rate of photooxidation of organic compounds, on the surface of a catalyst, is limited by the rate of electron transfer to oxygen. Gerischer and Heller[6,25] predicted that modification of the TiO_2 surface by group VIII metals should increase the efficiency of electron transfer to oxygen and hence increase the efficiency of photoassisted oxidation in photocatalyst slurries. Wang et al.[24] measured the rate of oxygen reduction and found that it increased upon incorporation of palladium (Pd^0) onto the surface of the titanium(IV) oxide particles. Furthermore, the quantum efficiency of the photoassisted oxidation of sodium 2,2-dichloropropionate was increased compared to the undoped titanium(IV) oxide powder. The work at Brown University has focused on the photodecomposition of transition metals onto the surface of titanium(IV) oxide powder for the purpose of increasing its photocatalytic activity toward the degradation of 1,4-dichlorobenzene (DCB).[10]

In the first part of this study, photodecomposed palladium was utilized to improve the photocatalytic activity of titanium(IV) oxide powder toward the photoassisted oxidation of 1,4-dichlorobenzene (DCB). The photocatalytic activity was evaluated by measuring the change in absorption of DCB as a function of irradiation time. The results were compared with those of materials

(1) Gao, Y.-M.; Lee, W.; Trehan, R.; Kershaw, R.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1991**, *26*, 1247.
(2) D'Oliveira, J.-C.; Al-Sayyed, G.; Pichat, P. *Environ. Sci. Technol.* **1990**, *24*, 990.
(3) Matthews, R. W. *Wat. Res.* **1990**, *24*, 653.
(4) Matthews, R. W. *J. Catal.* **1988**, *111*, 264.
(5) Blake, D. M.; Webb, J.; Turchi, C.; Magrini, K. *Sol. Energy Mater.* **1991**, *24*, 584.
(6) Gerischer, H.; Heller, A. *J. Phys. Chem.* **1991**, *95*, 5261.
(7) Tunesi, S.; Anderson, M. *J. Phys. Chem.* **1991**, *95*, 3399.
(8) Matthews, R. W. *J. Phys. Chem.* **1987**, *91*, 3328.
(9) Sabate, J.; Anderson, M. A.; Kikkawa, H.; Xu, Q.; Cervera-March, S.; Hill, Jr., C. G. *J. Catal.*, **1992**, *134*, 36.
(10) Gao, Y.-M.; Shen, H.-S.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1992**, *27* (9) 1023.
(11) Kobayakawa, K.; Nakazawa, Y.; Ikeda, M.; Sato, Y. *Ber. Bunsenges. Phys. Chem.* **1990**, *94*, 1439.
(12) Oosawa, Y.; Grätzel, M. *J. Chem. Soc., Faraday Trans. 1*, **1988**, *84*, 197.
(13) Herrmann, J.-M.; Disdier, J.; Pichat, P. *J Phys. Chem.* **1986**, *90*, 6028.
(14) Izumi, I.; Dunn, W. W.; Wibourn, K. O.; Fan, F.-R. F.; Bard, A. J. *J. Phys. Chem.* **1980**, *84*, 3207.
(15) Borgarello, E.; Pelizzetti, E. *Inorg. Chim. Acta* **1984**, *91*, 295.
(16) Dunn, W.; Bard, A. *Nouv. J. Chem.*, **1981**, *5*, 651.
(17) Herrmann, J.-M.; Disdier, J.; Pichat, P.; Fernandez, A.; Gonzalez-Elipe, A.; Munuera, G.; Leclercq, C. *J. Catal.* **1991**, *132*, 490.
(18) Yoneyama, H.; Nishimura, N.; Tamura, H. *J. Phys. Chem.* **1981**, *85*, 268.
(19) Courbon, H.; Herrmann, J.-M.; Pichat, P. *J. Phys. Chem.* **1984**, *88*, 5210.
(20) Borgarello, E., Serpone, N.; Emo, G.; Harris, R.; Pelizzetti, E.; Minero, C. *Inorg. Chem.* **1986**, *25*, 4499.
(21) Goven, Z.; Willner, I.; Nelson, A. J.; Frank, A. J. *J. Phys. Chem.*, **1990**, *94*, 3784.
(22) Albert, M.; Gao, Y.-M.; Toft, D.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1992**, *27*, 961.
(23) Borgarello, E.; Harris, R.; Serpone, N. *Nouv. J. Chem.*, **1985**, *9*, 743.
(24) Wang, C.-M.; Heller, A.; Gerischer, H. *J. Am. Chem. Soc*, **1992**, *114*, 5230.
(25) Gerischer, H.; Heller, A. *J. Electrochem. Soc.*, **1992**, *139*, 113.

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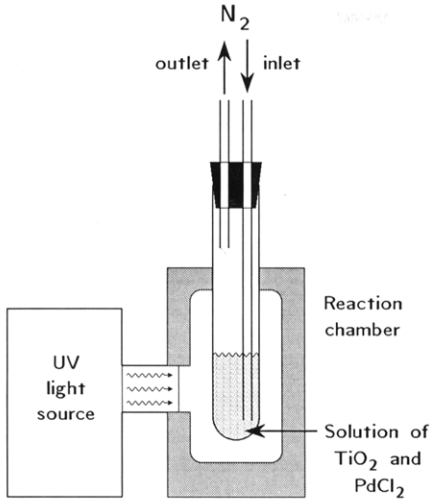

Figure 1. Photodecomposition apparatus.

prepared by thermally decomposing palladium(II) chloride onto titanium(IV) oxide.

When suspensions of titanium(IV) oxide powder are used to photodegrade organic contaminants in aqueous systems, the suspended catalyst must then be separated from the water. This separation problem can be avoided by replacing the titanium(IV) oxide suspension with a glass substrate coated with a titanium(IV) oxide film. While the rate of electron transfer from titanium(IV) oxide particles to adsorbed oxygen was shown to increase when palladium (Pd^0) was incorporated onto the surface[24] of the particles, this phenomenon has not yet been demonstrated for thin oxide films. Several publications have recently appeared which deal with the photodecomposition of organic compounds by titanium(IV) oxide films.[7-10] The second part of this study indicates how incorporating palladium onto the surface of titanium(IV) oxide thin films increases the photocatalytic activity of these films toward the photoassisted oxidation of salicylic acid.

Experimental Section

Photochemical Decomposition of Palladium(II) Chloride on TiO_2. The procedure for the photochemical decomposition of palladium(II) chloride onto titanium(IV) oxide sufaces is similar to that reported by Kraeutler and Bard.[26] Palladium(II) chloride (Matthey-Bishop, Inc.) was reduced onto TiO_2 by photochemical decomposition. A stock solution of palladium-(II) chloride containing 2 mg/mL was prepared. Various amounts of the $PdCl_2$ solution were added to 0.3 g of TiO_2 (Degussa P25). Distilled water was then added to achieve a final volume of 30 mL. The TiO_2 was dispersed in the diluted palladium(II) chloride solutions ultrasonically. By this procedure, solutions of known nominal composition, in terms of atomic percent Pd to Ti metal, were prepared. This mixture was transferred to a silica reaction vessel and inserted into a decomposition apparatus. The schematic diagram of the deposition apparatus is shown in Figure 1. During the reaction, nitrogen was bubbled vigorously through the sample and the silica vessel was rotated every 5 min. Samples were irradiated for 45 min with a Hg/Xe short arc lamp (100 W, 230–600 nm). The irradiated solution was then centrifuged for one h and the product was desiccated to dryness.

Thermal Decomposition of Palladium(II) Chloride on TiO_2. Palladium(II) chloride was reduced onto titanium(IV) oxide by thermal decomposition. An intimate mixture of palladium(II) chloride and titanium(IV) oxide (P25) was prepared containing 2 at. % of palladium. Various amounts of this mixture were diluted with an additional 0.3 g of titanium(IV) oxide, so that samples with varying concentrations of palladium were prepared. The samples were evacuated to 10 mTorr, sealed under vacuum, and then mechanically mixed for 5 min. The sealed samples were then transferred to a single zone furnace (Hevi-Duty MK-70) and annealed at 400 °C for 12 h. By this procedure, samples of known stoichiometry, in terms of atomic percent palladium to titanium metal, were prepared.

Measurement of Photocatalytic Activity. The photocatalytic activities of various TiO_2 samples were evaluated by degradation of 1,4-dichlorobenzene (DCB). This technique was suggested by Peterson and Gregg.[27] A saturated DCB solution was prepared by adding an excess of DCB to distilled water and stirring for 8 h. The solubility of DCB in water at room temperature is 76 ppm. The initial concentration of DCB used in this study was 5 ppm. Hence, all of the DCB was present in the aqueous phase. The solution was capped and preserved in darkness. TiO_2 (1.5 mg) was ultrasonically dispersed in 100 mL of distilled water. Three mL of the TiO_2 suspension were placed in a silica cuvette, and 0.2 mL of saturated aqueous solution of 1,4-dichlorobenzene was added. A second sample that contained 0.2 mL of distilled water and 3 mL of the TiO_2 suspension was used as a blank and maintained in the dark. The sample to be measured was then irradiated with a 150-W Xe 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 with that of the sample kept in darkness.

The procedure was corroborated in a separate experiment by direct analysis of the chloride ion concentration produced in solution by the photochemical degradation of DCB. At an initial DCB concentration of 14 ppm, after 1 h of irradiation analysis by both absorption decrease and direct chloride detection correlated to within 1 ppm. Hence, it can be concluded that the loss in absorption correlated reliably with the measured production of chloride.

Preparation of TiO_2 Films. Titanium(IV) oxide thin films were deposited on pyrex plate substrates (1 × 1 cm^2 × 1.5 mm) by a simple ultrasonic nebulization and pyrolysis technique.[10,28-30] The deposition apparatus was described in a previous publication.[31] The reactor used in this investigation was heated by means of a two-zone mirror furnace (Transtemp Co., Chelsea, MA). Dipropoxytitanium bis(acetylacetonate) was used as a precursor for the preparation of these thin films. It was synthesized according to Yamamoto's method.[32] An alcohol solution of 0.1 M dipropoxytitanium bis(acetylacetonate) was nebulized by a commerical 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. Both the efficiency of the deposition and the uniformity of the films were affected by the deposition parameters used. Typical reaction parameters were: deposition temperature, 490 °C; argon flow rate, 4 L/min; distance between substrate and nozzle, 9.0 cm. Under such conditions, a film of 350 nm in thickness could be coated on Pyrex glass in 10 min using 7.5 mL of precursor solution. Pyrex substrates were cleaned with nitric acid, distilled water, and semiconductor grade acetone. All deposited films were post annealed in a flowing oxygen atmosphere at 450 °C for 30 min in order to eliminate any residual carbon.

Photochemical Decomposition of Palladium(II) Chloride on TiO_2 Films. Palladium(II) chloride was reduced onto titanium(IV) oxide films by photochemical decomposition.

(26) Kraeutler, B.; Bard, A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4317.

(27) Peterson, M.; Gregg, B. NREL (Formerly SERI), Boulder, CO, private communication.

(28) Wu, P.; Gao, Y.-M.; Baglio, J.; Kershaw, R.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1989**, *24*, 905.

(29) Gao, Y.-M.; Wu, P.; Dwight, K.; Wold, A. *J. Solid State Chem.* **1991**, *90*, 228.

(30) Wu, P.; Gao, Y.-M.; Kershaw, R.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1990**, *25*, 357.

(31) Xu, W. W.; Kershaw, R.; Dwight, K.; Wold, A. *Mater. Res. Bull.* **1990**, *25*, 1385.

(32) Yamamoto, A.; Kambara, S. *J. Am. Chem. Soc.* **1957**, *79*, 4344.

Table I. Photocatalytic Activity as a Function of Decomposition Time: 0.5 At. % Pd (Relative to Ti) Photochemically Decomposed on Degussa P25

sample	duration of UV irradiation (min)	photocatalytic activity (relative)
1	30	45 (2)
2	45	52 (2)
3	60	51 (2)
4	75	44 (2)

Thirty mL of 3×10^{-5} M palladium(II) chloride aqueous solution was added to a silica reaction vessel. A 1×1 cm^2 Pyrex plate substrate coated with titanium(IV) oxide on both sides was immersed in the palladium(II) chloride solution with a Pyrex holder which was rotated by a low-speed motor in order to stir the solution during irradiation. The sample was then irradiated with a Hg/Xe short-arc lamp (100 W, 230–600 nm). Palladium(II) chloride was decomposed onto the titanium(IV) oxide film, and the thickness of the palladium layer was increased with increased time of irradiation. The sample was then rinsed with distilled water to remove any excess palladium(II) chloride remaining on the film.

Characterization of Films. The thickness of the titanium(IV) oxide films on Pyrex plate substrates was measured by interference fringes in the UV–visible transmission spectra.[33] X-ray diffraction patterns of these films were obtained using a Philips diffractometer and monochromated high intensity Cu $K\alpha_1$ radiation ($\lambda = 1.5405$ Å). Diffraction patterns were taken with a scan rate of 1° 2θ/min over the range $12° < 2\theta < 80°$. Optical measurements of titanium(IV) oxide films on pyrex plate substrates were performed using a Perkin-Elmer 552A spectrophotometer in the transmission mode.

The photocatalytic activities of titanium(IV) oxide films on pyrex plates were evaluated by the degradation of salicylic acid. Six mL of 6×10^{-5} M salicylic acid aqueous solution was added to a 18×150 mm Pyrex test tube. A 1×1 cm^2 substrate, coated with titanium(IV) oxide on both sides, was immersed in the salicylic acid solution with a pyrex holder which was rotated by a low-speed motor in order to stir the solution during irradiation. The sample to be measured was then irradiated with a 150-W 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. The change in concentration of salicylic acid of the irradiated sample as a function of time was compared with that of the sample kept in the dark.

All of the polycrystalline samples used in this study were prepared from Degussa P-25 (70% anatase, 30% rutile). The sizes of the particles were determined from the measured line broadening of the major peaks of both anatase and rutile. The average size of the anatase particles was 17 nm, and 25 nm for the rutile particles. The addition of Pd^0 on the surface of these particles did not alter their average sizes.

Results and Discussion

The two methods employed in the preparation of samples of palladium on TiO_2 powders were photochemical decomposition of $PdCl_2$ and the thermal decomposition of $PdCl_2$. The photochemical decomposition of $PdCl_2$ to load TiO_2 with Pd^0 has been reported by Krauetler and Bard[26] and the thermal decomposition of $PdCl_2$ has been used frequently in catalysis to prepare bifunctional palladium titania and palladium alumina. In all of the preparations, the catalysts were washed with distilled water to remove chloride ions. For the photochemical process, the duration of the irradiation used in photodecomposing the palladium(II) chloride affects the photocatalytic activity of samples (Table I). Samples were prepared using 0.3 g of TiO_2 (P25) dispersed in 30 mL of distilled water with a nominal atomic percent ratio of 0.5 Pd/99.5 Ti. The

(33) Heavens, O. S. *Phys. Thin Films* **1964**, *2*, 193.

Table II. Photocatalytic Activity as a Function of Nominal Concentration of $PdCl_2$ Photochemically Decomposed on Degussa P25

sample	at. % Pd rel to Ti (nominal concn)	photocatalytic activity (rel)
1	0.0	40 (2)
2	0.2	51 (2)
3	0.5	52 (2)
4	0.8	46 (2)

Table III. Photocatalytic Activity as a Function of Concentration of $PdCl_2$ Thermally Decomposed on Degussa P25

sample	at. % Pd rel to Ti	photocatalytic activity (rel)
1	0.0	40 (2)
2	0.08	44 (2)
3	0.1	48 (2)
4	0.15	53 (2)
5	0.2	47 (2)

nominal concentrations of $PdCl_2$ are reported because the precise amounts of palladium on the TiO_2 particles were not determined. The samples were irradiated with the UV light for varying amounts of time: 30, 45, 60, and 75 min. Increasing the time of irradiation increases the amount of palladium that is photodecomposed onto the titanium(IV) oxide powder. The results indicate that a critical deposition time was needed in order to give a photocatalyst with maximum activity. This study indicates the optimum activity is reached within 45 min. This was far less than the time needed to photochemically decompose all of the palladium from solution.

It was also shown that the nominal concentration of palladium(II) chloride in the reaction tube affects the photocatalytic activity (Table II). Samples were prepared by dispersing 0.3 g of TiO_2 (P25) in 30 mL of distilled water. Varying amounts of palladium(II) chloride were added to this solution. The concentration of palladium(II) chloride was chosen so that the nominal atomic percent of Pd relative to Ti in the reaction tube would be: 0.2, 0.5, and 0.8%. These suspensions were irradiated for a fixed amount of time, 45 min, in the photodecomposition apparatus (Figure 1). Again, nominal concentrations are reported because the precise amount of palladium which is photodecomposed onto the TiO_2 particles during this time is unknown. These results indicate that there is a critical loading of palladium on the TiO_2 particles that corresponds to the optimum catalytic activity. Catalysts showing maximum activity were obtained from irradiated solutions containing a nominal concentration of 0.2 at. % of palladium relative to titanium.

The concentration of palladium(II) chloride was also shown to affect the photocatalytic activity of samples prepared by thermally decomposing palladium(II) chloride on TiO_2 (P25) (Table III). In this case, the actual concentration of palladium on the sample is known. Samples were prepared by dispersing varying amounts of palladium(II) chloride onto TiO_2. The concentration of palladium(II) chloride was chosen so that the atomic percent of Pd relative to Ti in the reaction tube would be: 0.08, 0.1, 0.15, and 0.2 percent, respectively. These results indicate that there is a critical loading of palladium on the TiO_2 particles that corresponds to the optimum catalytic activity. This concentration of palladium on TiO_2 is 0.15 atomic percent of palladium relative to titanium.

As seen in Figure 2, the optimum catalytic activity found by photodecomposition of palladium(II) chloride was

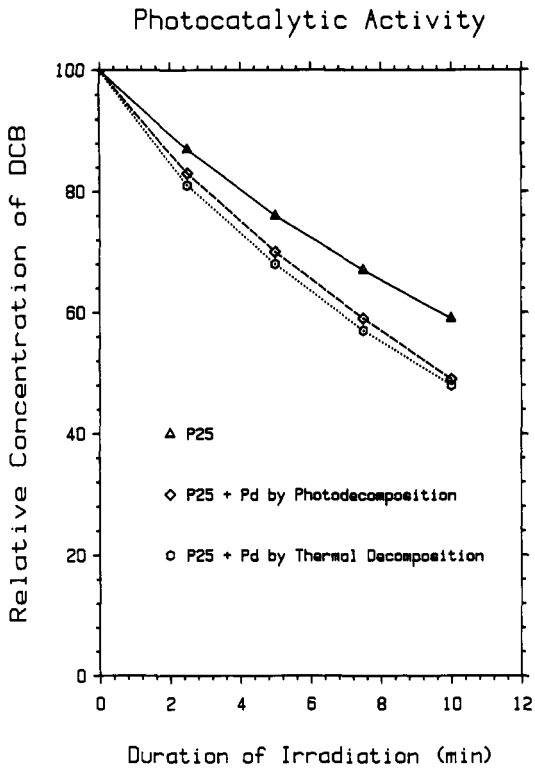

Figure 2. Decomposition of DCB vs irradiation time for uncoated TiO_2 powder (P25) and for P25 on which the optimum concentration of $PdCl_2$ was decomposed by two methods.

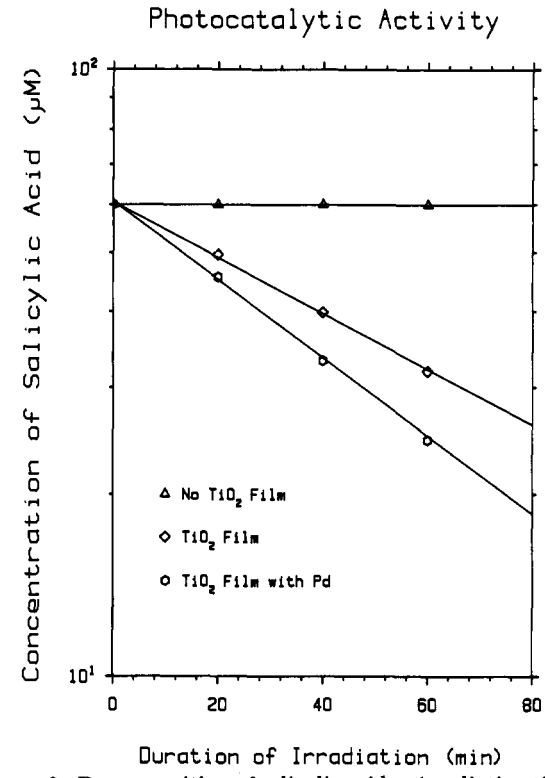

Figure 3. Decomposition of salicylic acid vs irradiation time of a bare TiO_2 film and a TiO_2 film with an optimum concentration of palladium.

shown to be similar to the optimum activity found by the thermal decomposition method. The palladium(II) chloride solution used for photochemical decomposition of palladium on TiO_2 corresponded to a nominal loading of 0.2 at. % of palladium relative to titanium. The thermal decomposition method required a concentration of 0.15 atomic percent of palladium relative to titanium, in order to obtain maximum activity. This indicates that the actual concentration of palladium on the sample prepared by photodecomposition of $PdCl_2$ approximates 0.15 atomic percent, which is far less palladium than would be present in a monolayer on the TiO_2 surface.

Smooth and homogeneous thin films of titanium(IV) oxide were coated by spray pyrolysis onto Pyrex plate substrates. Nebulization of dipropoxytitanium bis(acetylacetonate) solution resulted in the production of films with good adherence to the substrates. The bright and uniform color (due to interference fringes of the films on the Pyrex substrates) indicated that the films were of uniform thickness. Whereas titanium(IV) oxide films have been prepared by a number of elaborate methods, the simple procedure reported by Xu et al.[31] gave films of comparable quality.

The films prepared by the above method were analyzed by X-ray diffraction. In the diffraction pattern of an as-deposited film of 0.42 μm in thickness on a Pyrex substrate, four broad peaks at 25.3°, 48.2°, 55.3°, and 70.6° could be identified. They correspond to (101), (200), (211), and (220) reflections of the anatase phase of titanium(IV) oxide, respectively.[34] No impurity phase could be found in the X-ray diffraction pattern.

The transmission spectrum of the titanium(IV) oxide film on pyrex was used to calculate the thickness of the film.[33] Since the film is a denser media ($n_{film} \approx 2.5$) than the media on either side ($n_{air} = 1$ and $n_{Pyrex} \approx 1.5$), transmission maxima should occur at the wavenumbers $1/\lambda_{max} = m/2nd$ and minima at $1/\lambda_{min} = (2m + 1)/4nd$ where m is an integer. Film thicknesses were determined from the positions of the transmission maxima and minima.

The photocatalytic activities of titanium(IV) oxide films on 1 × 1 cm^2 plates of Pyrex were evaluated by measuring the degradation of salicylic acid. Figure 3 shows the change in concentration of salicylic acid as a function of irradiation time. It 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. It is clear that TiO_2 films containing Pd are more active than undoped films. The degradation of salicylic acid is a first-order reaction; therefore, the slope is taken as the rate of degradation and is a good parameter for the characterization of the photocatalytic activity of titanium(IV) oxide films. The rate constant of a 0.32 μm titanium(IV) oxide film on Pyrex prepared by the above method was 0.0045-(2) min^{-1}. The rate constant was increased to 0.0064 min^{-1} after depositing palladium for 10 min at which time the optimum activity is reached.

Palladium(II) chloride was reduced onto 0.32 μm titanium(IV) oxide films on pyrex substrates by the photochemical decomposition technique described above. X-ray diffraction of a film prepared with a sufficiently high concentration of palladium to be detected by X-ray analysis indicates that the palladium is deposited as elemental palladium[35] (Figure 4). The duration of the irradiation used in decomposing the palladium(II) chloride affects the photocatalytic activity of the samples. The change in photocatalytic activity for a 0.32 μm titanium-(IV) oxide film as a function of photodecomposition time of palladium(II) chloride is shown in Table IV. These

(34) X-Ray Powder Diffraction File (JCPDS), File No. 21-1272.

(35) X-Ray Powder Diffraction File (JCPDS), File No. 5-681.

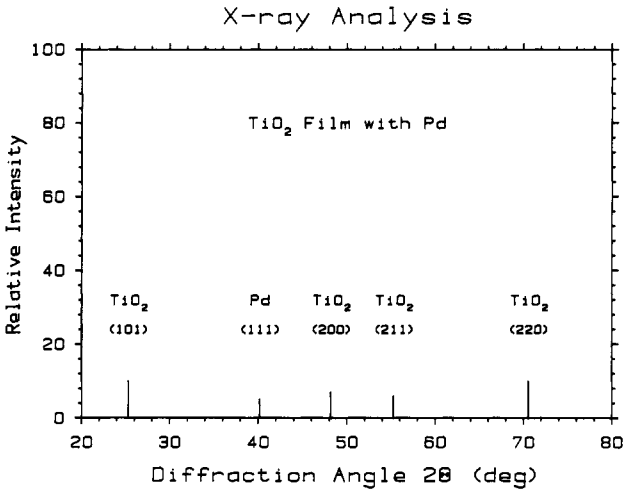

Figure 4. X-ray diffraction pattern of a 0.42-μm-thick TiO_2 film with photodecomposed $PdCl_2$. Only weak peaks of anatase and palladium metal are present.

Table IV. Photocatalytic Activity as a Function of Decomposition Time: 3×10^{-5} M $PdCl_2$ Decomposed on TiO_2 Thin Films

sample	duration of UV irradiation (min)	photocatalytic activity (rel)
1	0	44 (2)
2	5	51 (2)
3	10	57 (2)
4	15	53 (2)

results indicate a critical deposition time was needed in order to give a photocatalyst with maximum activity. Further deposition of palladium on the titanium(IV) oxide film decreased the photocatalytic activity.

It has been indicated by Gerischer and Heller[6] that the reduction of oxygen accompanying the photooxidation of organic compounds is the rate determining step. They proposed that a fast oxygen reduction rate is necessary for achieving a high quantum efficiency in the photoassisted oxidation of organic compounds. Wang et al. showed that the rate of oxygen reduction is increased when catalytic sites such as (Pd^0) are incorporated onto the surface of titanium(IV) oxide particles.[24] The results reported in Figure 2 are consistent with this model. The P25 samples with palladium particles on the surface show activities that are approximately 30% greater than that of P25 alone. The results reported in Figure 3 show that upon incorporation of palladium onto the surface of a titanium(IV) oxide thin film, the activity is improved approximately 30% over pure TiO_2 films. These results show that the rate of electron transfer from the titanium(IV) oxide thin film to adsorbed oxygen is increased when Pd^0 is incorporated onto the surface; therefore, the rate of the photooxidation of salicylic acid is increased. Thus, the titanium(IV) oxide thin film results are consistent with the model proposed for titanium(IV) oxide particles by Wang et al.[24]

Conclusions

The addition of palladium to TiO_2 powder by both photodecomposition and thermal decomposition increases its photocatalytic activity toward the degradation of DCB. The addition of palladium to a TiO_2 film by photodecomposition increases the photocatalytic activity toward the degradation of salicylic acid. In both cases, a critical amount of palladium was needed in order to give a photocatalyst with maximum activity. X-ray diffraction shows that the palladium on the surface of the catalysts is metallic palladium. Undoubtedly, the palladium particles are playing an important role in the transfer of electrons to the oxygen at the surface of the catalysts.

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