Photocatalytic Properties of TiO_2

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This paper reviews the photocatalytic activity of TiO_2 toward the degradation of organic compounds in aqueous solutions at low concentrations. The photocatalytic activity of both polycrystalline samples and thin films can be related to the method of preparation of the catalyst. The increase in the catalytic activity of TiO_2 when certain metals such as silver, gold, and palladium are deposited on the surface is also discussed. These catalysts have potential use in removing harmful carcinogens from water as well as possible application in reducing the harmful effects of oil spills.

Introduction

The photocatalytic oxidation of organic compounds in an aqueous solution containing a suspension of titanium(IV) oxide is a comparatively new method for the removal of impurities from water. The photoactivating light required is sunlight or near-UV ($\lambda < 400$ nm). Many organic compounds have been shown to be oxidized to carbon dioxide by this method.[1-5] It has potential application in the treatment of both waste and drinking water. Heller and Brock have recently[6] indicated the potential of TiO_2 being used as a thin film coating on floating beads to photocatalyze the oxidation of organic compounds floating on water, such as those typically resulting from an oil spill.

In principle, a photocatalytic reaction may proceed on the surface of TiO_2 powders via several steps,[7] 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; (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.[8-10] These will have an influence on the production of electron–hole pairs, the surface adsorption and desorption process and the redox process.

In attempts to improve the efficiency of these processes, a number of catalyst properties, e.g., chemical nature of dispersed TiO_2, specific surface area, porosity, mean pore size, and presence of dopants have been studied. In addition, the reaction conditions such as pH, temperature, reactant and product concentration, and light intensity have been varied.[11-15]

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.[16]

Titanium(IV) oxide exists in nature in two tetragonal forms, rutile and anatase, and also in a rhombic form called brookite. Brookite is extremely difficult to synthesize in the laboratory but both anatase and rutile can be readily prepared. It is these two forms of TiO_2 which have been used in most photocatalytic studies.[15]

Anatase appears to be the more active of the two phases studied. This is probably due to differences in the extent and nature of the surface hydroxyl groups present in the low temperature anatase structure. Furthermore, the photoactivity enhancement can be related to the Fermi level of anatase which is about 0.1 eV higher than that of rutile.[17] One commercial form of TiO_2, namely Degussa P25, is commonly used in photocatalytic studies. This product is formed by the hydrolysis of $TiCl_4$ in a hot flame. The relatively short residence time necessary for the conversion of $TiCl_4$ to TiO_2 gives a product which has a high surface area ($\sim$50 m^2/g) and is a mixture of approximately 4:1 anatase to rutile.

Photoassisted Heterogeneous Catalysis of Organic Impurities in Water

Trace impurities of chlorinated hydrocarbons pose a potentially serious threat to our health since halocarbons

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such as trichlorethylene and chloroform are known to be toxic and/or carcinogenic.[18,19] Pruden and Ollis[20] have studied the complete conversion of trichloroethylene in dilute aqueous solutions to HCl and CO_2 by means of a heterogeneous photoassisted process using illuminated TiO_2. The presence of molecular oxygen is required for the complete conversion to CO_2 and HCl. Ollis and coworkers have shown that complete degradation of simple chlorinated hydrocarbons to CO_2 and HCl can occur in the concentration range of 10–1000 ppm.[20-22] Ollis also proposed[23] the existence of a surface species such as hydroxyl radicals which can act as reactive intermediate species between the photoexcited TiO_2 surface and the organic species to be degraded. The experimental evidence which supports this concept was the ESR detection of $OH^{\bullet}$ as the most abundant radical species in aqueous solutions of illuminated TiO_2.[24-26] Ollis was not able to distinguish between the reaction of an adsorbed radical and the reaction of a free radical close to the TiO_2 surface. Undoubtedly, because of its high reactivity, the radical is unable to diffuse very far from the surface before reacting with organic species. In a recent study, Chemseddine and Boehm[27] have shown that an important contribution to the photochemical degradation of monochloroacetic and dichloroacetic acids is the attack at the α-C–H position. The hydrogen abstraction takes place by the formation of intermediate photogenerated radicals such as $OH^{\bullet}$. In the presence of oxygen, Chemseddine and Boehm postulated the existence of superoxide ions or perhydroxyl radicals. The presence of dioxygen molecules contribute to the rate of degradation.

It has been observed by Tunesi and Anderson[28] that the efficiency of the photodegradation process for salicylic acid and related aromatics depends upon the chemistry of their adsorption. Hence, for studies of the photodegradation of organic molecules, the nature of the TiO_2, the concentration of adsorbed organic species, and the pH at which degradation studies are carried out, must be defined.

Thermodynamic Considerations

In a recent review paper, Blake et al.[29] have identified some bandgap and thermodynamic limitations which have to be considered in the use of TiO_2 as a viable photocatalyst for the oxidation of organic compounds.

The anatase form of TiO_2 requires photons having energies greater than 3.2 eV ($\lambda \sim 380$ nm) to excite an electron from the valence band to the conduction band. The separated electron–hole pairs can then be made available for oxidation–reduction reactions. The reduction potential for $OH^{\bullet}$ has been assigned a value of +2.85 V.[30] It is therefore thermodynamically favorable[30] for the hole site formed in the valence band of TiO_2 to oxidize water to $OH^{\bullet}$ and for the separated electron promoted to the conduction band to reduce oxygen at −0.13 V. The production of an OH radical from water, and the reduction of oxygen, requires a semiconductor with a band gap above 3 eV. Hence, anatase with a band gap of 3.2 eV is an ideal photocatalyst for use in aqueous solutions.

In the photocatalytic process, the absorption of a photon by anatase promotes an electron from the valence band to the empty conduction band and thus produces an electron–hole pair. The electron is probably removed by reaction with oxygen and the hole can react with OH^- to give the OH radical. The source of OH^- may be related to the nature of the surface-bound water associated with anatase. The hydroxyl radical is capable of oxidizing organic contaminants. This process finally results in the formation of carbon dioxide and water if the reaction proceeds to completion. The mechanism of the reactions leading to the formation of CO_2 and water is not known. Oxidation of the mixtures of organic compounds found in oil will proceed by a complex series of reactions. There are additional pathways which can result in a loss of the OH radical. They involve reaction with carbonate or hydrogen carbonate ions.[31] Furthermore, the radical can also oxidize metal ions which are in a reduced formal valence state, e.g., iron(II).

It is, therefore, clear that in heterogeneous photocatalysis the trapping of electrons and/or holes is in direct competition with electron–hole recombination. The trapping process in aqueous solution exposed to air involves absorbed species, either undissociated water or hydroxide ions:[9]

$$TiO_2 + h\nu \rightleftharpoons h^+_{v.b.} + e^-_{c.b.} \qquad (a)$$

$$e^-_{c.b.} + O_2 \rightarrow O_2^-$$

$$h^+_{v.b.} + H_2O_{ads} \rightleftharpoons H^+_{ads} + {}^{\bullet}OH_{ads} \qquad (b)$$

$$h^+_{v.b.} + OH^-_{ads} \rightleftharpoons {}^{\bullet}OH_{ads}$$

Any factor which slows the recombination process or aids in the transformation of electrons/holes to adsorbed species on the semiconductor will improve the photocatalytic activity of the solid.

One commercially available form of titanium(IV) oxide, Degussa P25, has an unusual microstructure[9] which results from the conversion of $TiCl_4$ vapor at high temperature but short residence time. It is a complex oxide with a coexistence of amorphous, anatase, and rutile phases of TiO_2. The intimate contact among these phases and the surface structure may account for its unusually high photocatalytic activity.

Modification of Photocatalyst

There have been a number of attempts to improve the performance of TiO_2 as a photocatalyst under UV illumination and to extend its light absorption and conversion capacity into the visible portion of the solar spectrum. These investigations have concentrated on the doping of

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TiO_2 with foreign ions. Kiwi and Morrison[32] report an increase in the rate of production of hydrogen when TiO_2 is promoted with 7 at. % Li^+ and the sample heated at 500 °C. A decrease in hydrogen production was observed when the sample was heated at higher temperature. The production of hydrogen was also increased under UV illumination when the TiO_2 was promoted with magnesium.[33] The introduction of Nb^{5+} into TiO_2 also increased the cleavage of water under visible light upon using $Ru(bipy)_3^{2+}$ as a sensitizer.[34] More complex systems were also studied by Borgarello et al.[35] For example, colloidal TiO_2 samples containing Cr to which Pt and RuO_2 were added were investigated in terms of their ability to cleave water with visible light. From these studies, it can be concluded that photocatalytic activity of TiO_2 is increased by either the doping of a foreign ion into the TiO_2 structure or the addition of a foreign species primarily onto the surface of TiO_2.

The characterization and properties of TiO_2 photocatalysts prepared by two fabrication techniques, i.e., flame hydrolysis and furnace pyrolysis, were also recently compared.[36] It was shown that the flame hydrolysis method is more efficient and gives products with higher photocatalytic activities.

Previously, photochemical deposition of metal on semiconductor particles has been used as a means of noble metal recovery in waste solutions.[13,16] 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.[14,15] Several studies[37,38] have shown that gold can be photodecomposed from aqueous solutions of $AuCl_3$ and the resulting photocatalyst has activities 30% higher than powders and films without the gold deposits. It was indicated by Gerischer and Heller[16] 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. This can be achieved when catalytic sites are incorporated in the TiO_2 surface. This is consistent with the observed increase in catalytic activity of TiO_2 samples having gold particles on the surface. Wang, Heller, and Gerischer[39] have reported that the incorporation of Pd^0 in the surface of TiO_2 particles increases the efficiency of photoassisted oxidation of an aqueous sodium 2,2-dichloropropionate solution. Papp et al.[40] have reported that P25 samples with palladium particles on the surface show activities toward photooxidation of 1,4-dichlorobenzene which is 30% greater than that of P25 alone.

Kondo and Jardim have reported that the photocatalytic activity of TiO_2 powder was also increased when silver was deposited by thermal decomposition of silver nitrate.[41] Oxidation was carried out on aqueous solutions of urea and chloroform to CO_2.

Sclafani et al. also reported that Ag can be used for the improvement of photocatalytic activity of TiO_2 by loading Ag on TiO_2 powders with the photodecomposition of $AgnO_3$.[42] 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.

Nishimoto et al. reported that AgF was decomposed by photo-irradiation at a much faster rate than $AgNO_3$.[43] Herrmann 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.[44] Lee et al.[36] deposited Ag 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). 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.[37]

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. TiO_2 films on pyrex glass substrates were prepared and evaluated as photocatalysts.[36,38] Nebulization of dipropoxytitanium bis(acetylacetonate) solution resulted in the production of films with good adherence to the substrate and uniform thickness. The photocatalytic activities of TiO_2 films were evaluated by measuring the degradation of salicylic acid. Salicylic acid was chosen because it is not volatile and absorbs in the near-UV.

Figure 1 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.[45] 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. 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.

AgF was reduced onto the TiO_2 films on pyrex glass substrates by photochemical decomposition. Figure 1 indicates higher photocatalytic activity for the film containing silver particles. The increase in the rate of degradation of salicylic acid on Ag/TiO_2 films was found to be the same as the increases observed for Au/TiO_2. The TiO_2 films deposited with Ag were analyzed by X-ray diffraction. The diffraction pattern shown in Figure 2 indicates that the silver exists as metallic silver. This

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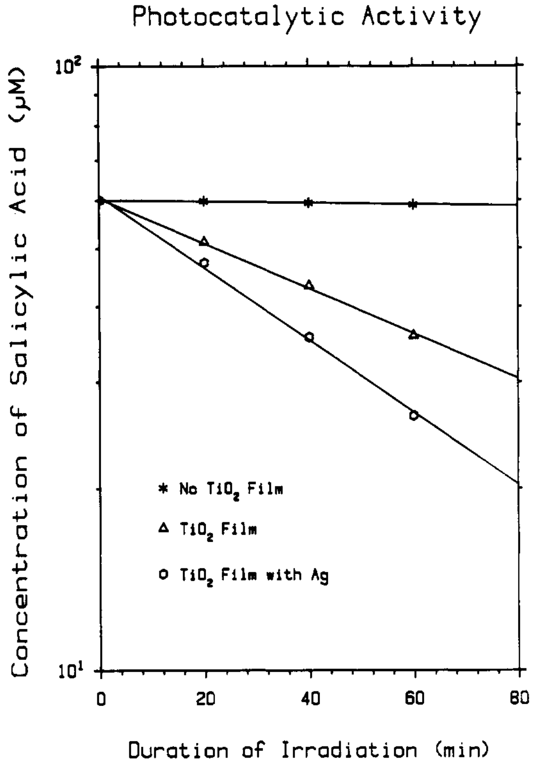

Figure 1. Decomposition of salicylic acid vs irradiation time of a TiO_2 film and a TiO_2 film with Ag.

metallic silver dispersed on TiO_2 plays an important role in enhancing the photocatalytic activity of TiO_2.

Papp also reported[40] that with the incorporation of palladium onto the surface of the titanium(IV) oxide thin film, the activity is improved approximately 30% over the TiO_2 films alone. 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.[39]

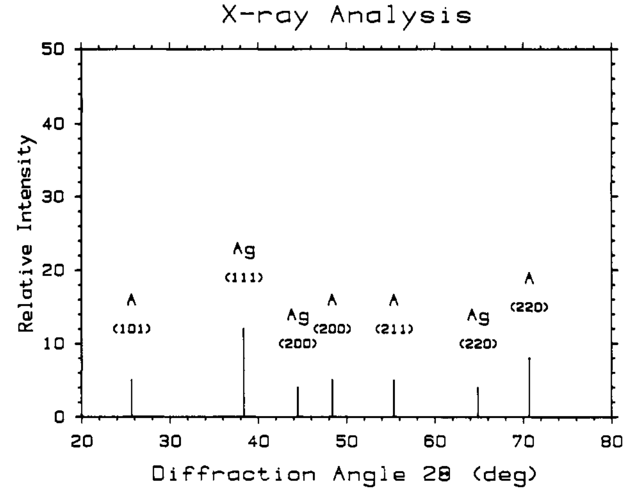

Figure 2. X-ray diffraction spectrum of Ag-deposited TiO_2 film (A ≡ Anatase; 30 mL of 1.0×10^{-4} M AgF solution was photodecomposed on a TiO_2 film of 0.3 μm in thickness for 5 min).

Conclusions

The addition of noble metal particles, e.g., Pd, Ag, Au to TiO_2 powder increases the observed photocatalytic activity toward the degradation of organic compounds such as dichlorobenzene. The addition of these metals to thin films of TiO_2 (thickness <2500 Å) also increases the observed photocatalytic activity toward the oxidation of organic compounds. In both cases, a critical amount of the metal added was needed in order to give a photocatalyst maximum activity. X-ray analysis shows that the metal on the surface of the catalyst is in the elemental state. The metal particles are undoubtedly playing an important role in the transfer of electrons to the oxygen at the surface of the catalysts.

There is a need for the development of an effective technique for the removal of trace organic contaminants in our water supply. The possible use of generated hydroxyl radicals has been reviewed in this paper and it appears that TiO_2 and perhaps other semiconductors can be used to develop a safe, cost-efficient solar water treatment process.