Photodegradation of Sulforhodamine-B Dye in Platinized Titania Dispersions under Visible Light Irradiation: Influence of Platinum as a Functional Co-catalyst

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The photooxidative degradation of sulforhodamine-B dye (SRB) taking place in visible-light illuminated platinized titania dispersions is revisited to examine the influence of metallic platinum doped on TiO_2 particles (Degussa P25 titania) by photocatalytic deposition from a hexachloroplatinic acid solution. The various TiO_2/Pt specimens were characterized by transmission electron microscopy (TEM), UV–vis diffuse reflectance spectroscopy, and X-ray photoelectron spectroscopy (XPS). The self-photosensitized degradation of SRB mediated by TiO_2/Pt specimens is 3-fold faster than that occurring on TiO_2 alone under visible light irradiation and under otherwise identical conditions. That is, the TiO_2/Pt system exhibited greater catalytic activity than P25 TiO_2 alone, which earlier proved to be an effective photocatalyst in the degradation of dyes under visible illumination. A reaction mechanism is proposed on the basis of a series of experiments that included spin–trap electron spin resonance (ESR) spectral results, measurement of quantities of H_2O_2 formed, chemical oxygen demand (COD_{Cr}), and total organic carbon (TOC) data. The platinum dopant acts as an electron sink from which molecular oxygen scavenges the electrons to yield superoxide radical anions ($O_2^{-\bullet}$) first and then $^\bullet OH$ radicals, which are known to cause the ultimate self-destruction of the SRB dye.

Introduction

Titania particulates exhibit significant photocatalytic activity in the photodegradation of organic compounds.[1,2] As such, TiO_2 photocatalysis has become increasingly important in recent years for environmental remediation. UV light, which can excite TiO_2 particles at wavelengths shorter than 385 nm, is less than ca. 3–5% of sunlight. Artificial UV light sources tend to be expensive and consume large quantities of electrical power. The relatively large band gap of 3.2 eV for TiO_2 anatase limits its photoresponse to the ultraviolet region.

Textile and other industrial dyes have become major environmental contaminants in many countries.[3] Several of these dyes are stable and resist photodegradation by sunlight, oxidation by molecular oxygen O_2, and decomposition by common acids and bases. Effective utilization of visible light to degrade these dyes in the presence of TiO_2 provides an attractive approach with significant implications for energy resources and environmental remediation. In previous studies,[4–8] TiO_2 particulates were successfully employed to degrade dye pollutants efficiently with visible light radiation.

The mechanism of dye degradation under visible illumination is different from the pathway implicated when using UV light irradiation. Dyes, rather than catalyst, are excited by visible light to appropriate singlet and triplet states through intersystem crossing, followed by electron injection into the TiO_2 conduction band. The injected electrons, TiO_2 (e^-), reduce surface chemisorbed oxidants, typically O_2, to yield such oxidizing species as the superoxide radical anions $O_2^{-\bullet}$ and subsequently $^\bullet OH$ radicals that ultimately lead to the degradation and mineralization of dyes. Thus, TiO_2 plays the pivotal role of an electron carrier/mediator leading to separation of injected electrons and dye cation radicals, even though TiO_2 is itself not excited.
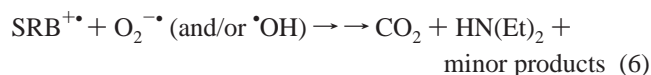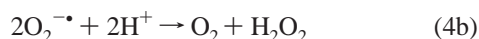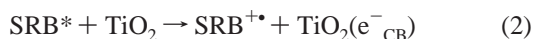
Methods to increase the activity of TiO_2 or to find a new type of more efficient catalytic systems to photodegrade dyes with visible light radiation remain an important issue. Investigations on new systems are also directed at a better understanding of the mechanism(s) of degradative processes under visible light irradiation. In this regard, the addition of group VIII metals as dopants on TiO_2 systems is effective in its ability to increase the photonic efficiency of reactions under UV irradiation.[9,10] Numerous reports[2,11] have shown that TiO_2/Pt can increase the photodecomposition rate of various organic compounds under ultraviolet light irradiation compared to that of TiO_2 alone.

To extend the wavelength range response of TiO_2 to the visible region, new types of TiO_2 systems have been reported. For example, Kisch and co-workers[12] noted that the photodegradation of 4-chlorophenol was significantly improved in the presence of an amorphous microporous titania system modified with platinum(IV) chloride ($Pt^{(IV)}/AMP–TiO_2$), a new type of

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catalyst, by extending the response of TiO_2 to visible light. Apparently, the photocatalytic activity of $Pt^{(IV)}/AMP-TiO_2$ under visible irradiation originated from photoexcitation of $PtCl_4$. Li and co-workers[13] also reported that modifying TiO_2 particles by doping with either gold or gold(III) ions (Au^o or Au^{3+}) extends the light absorption characteristics of titania into the visible region. A new energy level below the conduction band of TiO_2 generated in the $Au^{3+}/Au-TiO_2$ system made excitation by visible light ($E < 3.2$ eV) possible (extrinsic light absorption[14]). The photoinduced charge separation generated by light occurs on the doping metal salt[12] or between states localized on both the doping metal ion and TiO_2.[13] The above investigations focused mainly on *direct photocatalysis*, that is, excitation of the photocatalysts by visible light. This notwithstanding, however, only a few reports have appeared concerning the effect of metal dopants on the *self-photosensitized* degradation of dyes in a dye/TiO_2 dispersion under visible light irradiation, in which the dyes are excited by visible light and subsequently inject electrons into the conduction band and/or surface defect intragap levels of TiO_2. Note that no holes are generated under these conditions, unlike what occurs in UV-irradiated titania.

In a recent study,[8] we demonstrated that the self-photosensitized mineralization of SRB in a SRB/TiO_2 dispersion irradiated at all visible wavelengths greater than 420 nm yields carbon dioxide and diethylamine as the major oxidation products, along with small quantities of formic acid, acetaldehyde, diethyl and ethyl formamide, and diethyl and ethyl acetamide. The cationic SRB dye was adsorbed on the particle surface through the sulfonate group (see structure of SRB below). The pathway (reactions 1−6) was identified as involving formation of superoxide radical anions, $O_2^{-\bullet}$, and hydroxyl radicals, $^{\bullet}OH$.

$$SRB + h\nu \rightarrow SRB^* \tag{1}$$

$$SRB^* + TiO_2 \rightarrow SRB^{+\bullet} + TiO_2(e^-_{CB}) \tag{2}$$

$$TiO_2(e^-_{CB}) + O_2 \rightarrow TiO_2 + O_2^{-\bullet} \tag{3}$$

$$O_2^{-\bullet} + TiO_2(e^-_{CB}) + 2H^+ \rightarrow H_2O_2 \tag{4a}$$

$$2O_2^{-\bullet} + 2H^+ \rightarrow O_2 + H_2O_2 \tag{4b}$$

$$H_2O_2 + TiO_2(e^-_{CB}) \rightarrow OH^- + {}^{\bullet}OH + TiO_2 \tag{5}$$

$$SRB^{+\bullet} + O_2^{-\bullet} \text{ (and/or } {}^{\bullet}OH) \rightarrow \rightarrow CO_2 + HN(Et)_2 + \text{minor products} \tag{6}$$

In the presence of copper(II) and iron(III) ions, the self-photosensitized degradation of SRB is suppressed as these two ions interfere with reaction 3 competing with molecular oxygen for the TiO_2 (e^-_{CB}) electrons.[15]

Herein, we examine the influence of platinum in the TiO_2/Pt assisted photodegradation of dyes under visible light irradiation using sulforhodamine-B (SRB) as the test substrate. The results show that doping small amounts of platinum (0.2 wt %) on TiO_2 significantly enhances the degradation of the SRB dye. The mechanistic details of the process occurring in aqueous TiO_2/Pt dispersions exposed to visible light radiation were inferred from (a) measurements of chemical oxygen demand (COD_{Cr}), (b) total organic carbon (TOC) analyses, (c) quantitative determination of H_2O_2 formed, and (d) determination of active oxygen radicals ($O_2^{-\bullet}$ and $^{\bullet}OH$) formed during the photodegradative process by spin-trap (DMPO) electron spin resonance

spectroscopy (ESR). A variety of bulk and surface measurements (XPS, XRD, and TEM) were also performed to clarify the nature of platinized TiO_2 specimens.

Experimental Section

Materials. Titania P-25 (TiO_2; ca. 80% anatase, 20% rutile; BET area, ca. 50 m^2 g^{-1}) was kindly supplied by Degussa Co. The sulforhodamine-B dye (SRB) was of laser grade quality (Across Co.). The spin trap 5,5-dimethyl-1-pyrroline-*N*-oxide
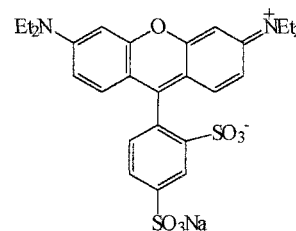

Sulforhodamine-B

(DMPO) was purchased from the Sigma Chemical Co. All other chemicals were of laboratory reagent grade quality and were used without further purification. Deionized and doubly distilled water was used throughout this study.

Platinized TiO₂ Catalyst. Platinized titanium dioxide samples (TiO_2/Pt) were prepared by a photocatalytic deposition method according to a published procedure.[16] Titanium dioxide (2.00 g) and 2-propanol (0.5 mL) were added to an aqueous solution (50 mL) of a calculated amount of hexachloroplatinic acid (H_2-$PtCl_6 \cdot 6H_2O$, 0.020 mmol). The suspension contained in a 100 mL Pyrex round-bottom flask was prepurged with pure N_2 and irradiated with a 100 Watt high-pressure mercury lamp for 30 h. The irradiation was performed with vigorous magnetic stirring at ambient temperature. After illumination, the particulates were separated by filtration and washed repeatedly with water until no Cl^- ions were detected in the supernatant liquid. The sample was dried overnight in a vacuum oven at about 100 °C. The dried samples were lightly ground with a mortar and pestle to break-up the larger aggregates; they were then stored in a desiccator. The amount of Pt loaded onto TiO_2 was determined by dissolving a given amount of the sample in a mixture of *aqua regia* and HF; the dissolved metal ions were then analyzed by atomic absorption spectroscopy using a nitrous oxide-acetylene flame.

X-ray photoelectron spectroscopic (XPS) examination of the samples was carried out on the 220I-XL multifunctional spectrometer (VG Scientific England) using Al Kα radiation. The results indicated that the deposited platinum on the TiO_2 surface was Pt^0. The size and shape of the catalyst particles were observed by transmission electron microscopy (TEM) using a JEM-100CX instrument. The average particle size of TiO_2/Pt was similar to that of TiO_2 (ca. 30 ± 5 nm). No diffraction peaks for the Pt^0 dopant were detected by XRD as the platinum was present only in trace quantities. The physical properties of both TiO_2/Pt and TiO_2 systems are very similar, despite the presence of Pt atoms in TiO_2/Pt. The UV−vis diffuse reflectance spectra of the catalyst were recorded using a Hitachi U-3010 spectrophotometer (Japan) equipped with an integrating sphere attachment. The analyzed range was 200 nm to 800 nm, and $BaSO_4$ was the reflectance standard.

Photoreactor and Light Source. A 500 Watt halogen lamp (Institute of Electric Light Source, Beijing) was positioned inside the cylindrical Pyrex glass reactor that was surrounded by a
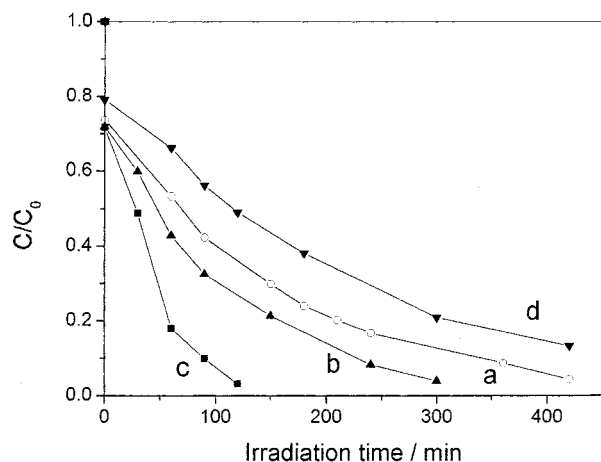
Figure 1. Temporal course of the photodegradation of SRB (2.0×10^{-5} M, 50 mL) at pH 3.5 in aqueous dispersions containing 25 mg of catalysts under visible light irradiation: (a) TiO_2, (b) TiO_2/Pt (0.1 wt %), (c) TiO_2/Pt (0.2 wt %), (d) TiO_2/Pt (0.5 wt %).

Figure 2. UV$-$Vis diffuse reflectance spectra of P25 TiO_2 (solid curve) and TiO_2/Pt (dotted curve).

circulating water jacket (Pyrex) to cool the lamp. An appropriate cutoff filter was placed outside the Pyrex jacket to ensure complete removal of radiation below 420 nm and to ensure that the irradiation of the dispersion was achieved only by visible light wavelengths.

Procedure and Analyses. Aqueous suspensions of SRB (usually 50 mL, 2×10^{-5} M) and 50 mg of catalyst powders (TiO_2 or TiO_2/Pt) were placed in the Pyrex vessel. Prior to irradiation, the suspensions were magnetically stirred in the dark for ca. 30 min to establish adsorption/desorption equilibrium between the dye and the surface of the catalyst under ambient air-equilibrated conditions. At given irradiation time intervals, 3 mL aliquots were collected, centrifuged, and then filtered through a Millipore filter (pore size 0.22 μm) to remove the catalyst particulates. The filtrates were analyzed by recording variations at the wavelength of maximal absorption ($\lambda = 565$ nm) in the UV$-$vis spectra of SRB using a Lambda Bio 20 spectrophotometer (Perkin-Elmer Co.). Assays of the chemical oxygen demand (COD_{Cr}) were carried out using the potassium dichromate titration method.[17] The COD_{Cr} value of the suspensions (25 mL, 5×10^{-5} M SRB; 25 mg of catalyst) was measured directly without removal of the catalyst particulates at the various irradiation time intervals. Total organic carbon (TOC) was also assayed in the SRB degradation process using an Apollo 9000 TOC analyzer (Tekmar Dohrmann Co.). The TOC analyses were carried out after removal of catalyst particulates by filtration with the Millipore filter, a procedure different from the measurement procedure of COD_{Cr}. ESR spectra were obtained using a Bruker model ESP 300 E electron paramagnetic resonance spectrometer equipped with a Quanta-Ray Nd:YAG laser system as the irradiation light source ($\lambda = 532$ nm). The settings were center field, 3480.00 G; microwave frequency, 9.79 GHz; power, 5.05 mW. Determination of the concentration of H_2O_2 formed in the degradation of the dye system has been described previously.[4]

Results and Discussion

Photodegradation of SRB under Visible Light Irradiation. The influence of Pt on the photooxidative activity of TiO_2 was determined by comparing the reaction rates of loss of SRB dye on TiO_2/Pt with those on pure TiO_2 under otherwise identical conditions (Figure 1). The photodegradation of SRB occurred in air-equilibrated TiO_2/Pt and TiO_2 dispersions under irradiation by visible light ($\lambda > 420$ nm). Figure 1 clearly indicates that
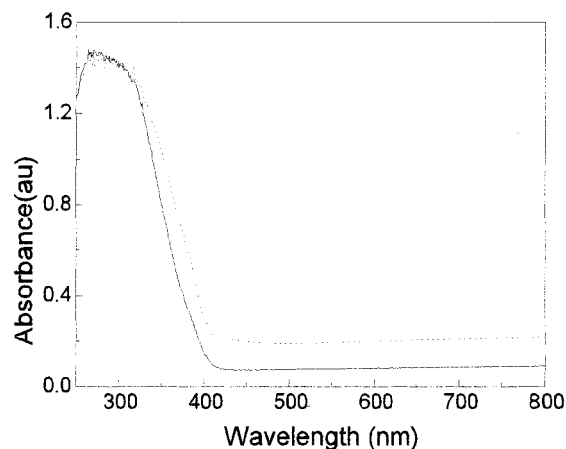
the TiO_2/Pt (0.2 wt %) exhibited greater activity than TiO_2 (P-25) alone; the latter proved to be an efficient catalyst in earlier studies.[4-8] Deposition of 0.5 wt % platinum on titania had a negative effect on the kinetics of degradation of the dye (compare curves a, b, and c with curve d). Accordingly, TiO_2/Pt (0.2 wt %) was chosen as the catalyst to be examined in some detail.

The disappearance of SRB followed approximate pseudo-first-order kinetics; the relevant rate constants are $(2.3 \pm 0.3) \times 10^{-2}$ min^{-1} for the $TiO_2/0.2$ wt % Pt system and $(0.61 \pm 0.01) \times 10^{-2}$ min^{-1} for the TiO_2 system alone. Clearly, the platinized titania system was nearly 4-fold more active than TiO_2 (P25), and the degradative process was significantly enhanced under the prevalent experimental conditions used.

Figure 2 displays the UV$-$vis diffuse reflectance spectra of TiO_2 and TiO_2/Pt. The TiO_2 displayed an absorption edge at 420 nm and strong absorption at wavelengths shorter than 350 nm. This absorption is attributed to transitions of electrons from the valence band to the conduction band of TiO_2. The onset of absorption at 390 nm correlates well with the band gap of TiO_2 (3.2 eV; ca. 385 nm). With platinum loading, the absorption of TiO_2/Pt is observed at slightly longer wavelengths ($\lambda \sim 350$ nm), with the intensity (likely because of scattering and absorption) increased somewhat compared to naked TiO_2; at wavelengths shorter than 350 nm, both systems display similar light attenuance. The platinized titania specimen exhibits a definite light attenuation throughout the visible wavelengths consistent with the slight brown color of the catalyst.

To test whether TiO_2/Pt can also be excited by visible light and whether it also displays catalytic activity toward the photooxidation of pollutants, 2,4-dichlorophenol (2,4-DCP) was chosen to be degraded under visible light irradiation ($\lambda > 420$ nm). Note that 2,4-DCP displays no absorption in the visible region and consequently cannot be photoexcited and undergo direct photolysis. The data were obtained by measuring the UV$-$vis spectral changes at regular intervals during 10 h of visible irradiation in the presence of either the TiO_2/Pt or TiO_2 system. In both cases, there was no degradation of 2,4-DCP as evidenced by the fact that the spectra of 2,4-dichlorophenol remained unchanged. The anionic sodium benzenesulfonate surfactant was also chosen as another test substrate to be degraded; results were similar to those observed for 2,4-dichlorophenol. That is, the surfactant was not affected by either catalytic system exposed to visible radiation. These results support the notion that both TiO_2 and TiO_2/Pt systems show no catalytic activity under these conditions. Accordingly, we deduce that the photodegradation of SRB in the presence of the TiO_2/Pt system under visible light

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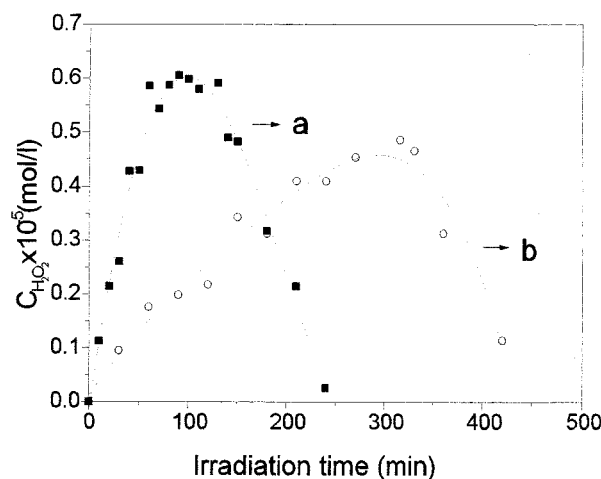
Figure 3. Plots showing the formation of H_2O_2 during the SRB degradation process: (a) in the SRB$-$ TiO$_2$/Pt system and (b) in the SRB$-$TiO$_2$ system

irradiation occurs by photoexcitation of the dye and not by excitation of TiO$_2$/Pt.

As suggested earlier,[4] the mechanism of dye degradation mediated by TiO$_2$ under visible light irradiation involves the generation of the intermediate H_2O_2 (eqs 1$-$6). The formation of H_2O_2 during the degradation process of SRB in aqueous TiO$_2$ and TiO$_2$/Pt dispersions, respectively, is displayed in Figure 3. In both systems (i.e., SRB$-$TiO$_2$/Pt and SRB$-$TiO$_2$), the quantities of H_2O_2 increased with irradiation time, reaching a maximal value (6 × 10^{-5} M for SRB$-$TiO$_2$/Pt and 4.5 × 10^{-5} M for SRB$-$TiO$_2$) at the point at which the dispersions became discolored. As evidenced by the results of Figure 3, whether the formation rate or the maximal quantity of H_2O_2 formed is chosen, it is clear that the SRB$-$TiO$_2$/Pt system is significantly more active than the SRB$-$TiO$_2$ system. The H_2O_2 formed under visible light irradiation originates principally from reactions 4a and 4b and involves the superoxide radical anion $O_2^{-\bullet}$ as the principal precursor of H_2O_2. In so far as the concentration of H_2O_2 is concerned, we suggest that production of $O_2^{-\bullet}$ during the degradative process with the SRB$-$TiO$_2$/Pt system is different from the manner in which it is produced in the SRB$-$TiO$_2$ system. To ascertain this conjecture, the ESR spin-trap technique (with DMPO) was used to detect both the $O_2^{-\bullet}$ and $^{\bullet}$OH radical species. This method has proven useful in the past to detect radical species and, hence, to examine the formation of $O_2^{-\bullet}$ and $^{\bullet}$OH radicals in the degradation of SRB.[18]

We reported earlier[19] that superoxide radical anions are produced first and remain stable in an organic solvent medium (at least in methanol). When the fraction of H_2O increased, such as occurred in a CH$_3$OH/H$_2$O mixed solvent system, the superoxide radical anion tended to be unstable, especially in H_2O alone; it readily converted to H_2O_2 and O_2. Consequently, we recorded the ESR spectra of the DMPO$-$O$_2^{-\bullet}$ spin adducts in both SRB$-$TiO$_2$/Pt and SRB$-$TiO$_2$ dispersions in methanolic media at different illumination times using a Nd:YAG laser (532 nm) as the irradiation source (see Figure 4A). The temporal changes in the signal intensity of the $O_2^{-\bullet}$ radical anions in the two systems are illustrated in Figure 4B. The six characteristic peaks of the DMPO$-$O$_2^{-\bullet}$ adducts were observed only under visible light irradiation. No such signals were detected in the dark; that is, generation of $O_2^{-\bullet}$ anions in these two systems inherently implicates irradiation. This confirms the formation of $O_2^{-\bullet}$ radicals via reaction 3 during the TiO$_2$-assisted photodegradation of SRB under visible light radiation. Compared to the ESR signals of $O_2^{-\bullet}$ in the SRB$-$TiO$_2$ dispersion,
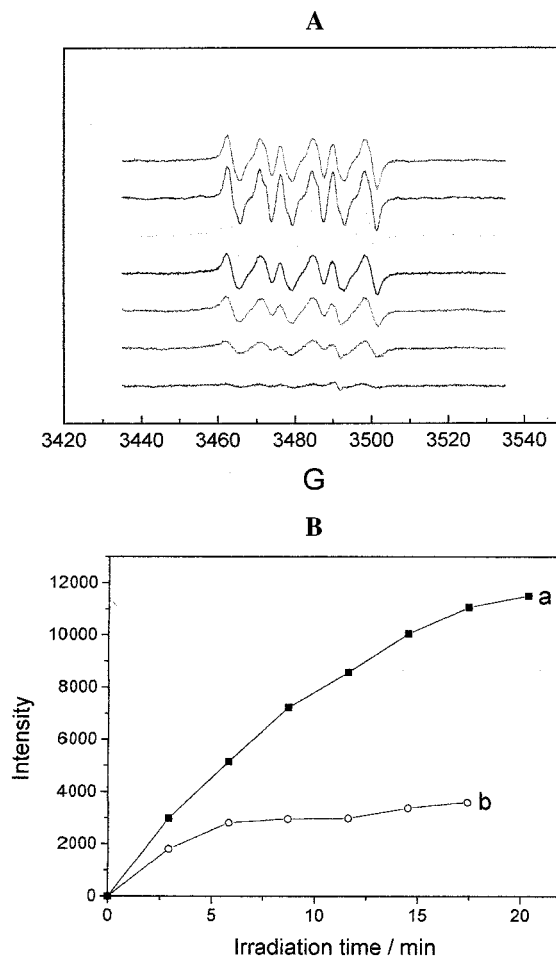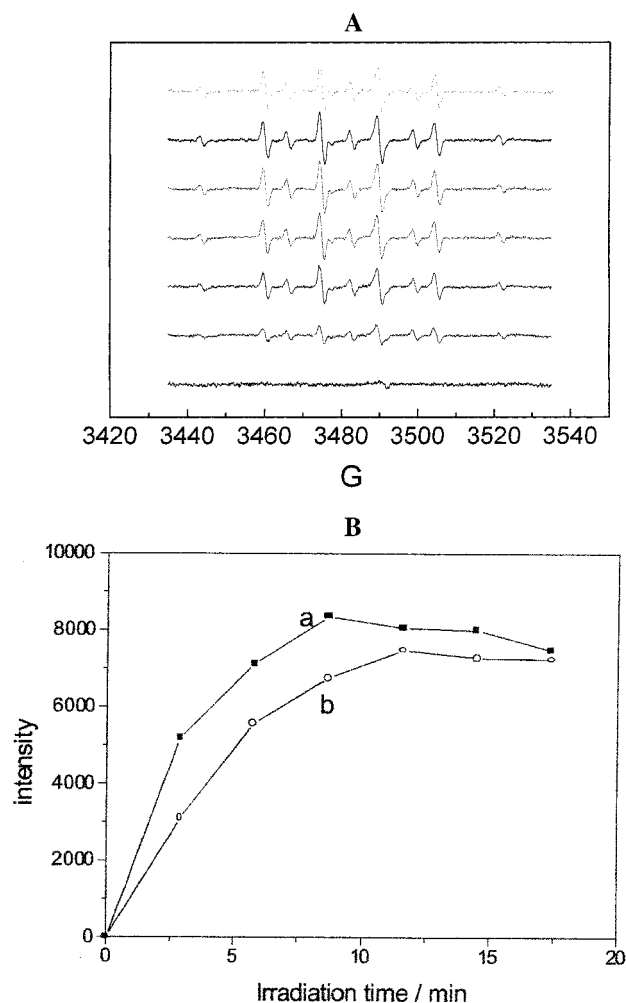

Figure 4. (A) ESR spectral changes of the DMPO$-$O$_2^{-\bullet}$. (B) Plots of ESR signal intensity changes of the DMPO$-$O$_2^{-\bullet}$ adducts with increasing irradiation time: (a) in the SRB (1 × 10^{-4} M)$-$TiO$_2$/Pt (1 g L^{-1}) dispersion and (b) in the SRB (1 × 10^{-4} M)$-$TiO$_2$ (1 g L^{-1}) dispersion.

the signals of $O_2^{-\bullet}$ were nearly 3-fold more intense in the SRB$-$TiO$_2$/Pt system. From Figure 4, it is evident (i) that the concentration of DMPO$-$O$_2^{-\bullet}$ spin-adducts formed in the SRB$-$TiO$_2$/Pt dispersion is much greater than that in the SRB$-$TiO$_2$ system and (ii) that in the former system the amount of DMPO$-$O$_2^{-\bullet}$ increased steadily with increasing irradiation time (Figure 4). By contrast, the signals for DMPO$-$O$_2^{-\bullet}$ produced in the SRB$-$TiO$_2$ system were less intense and remained unchanged after laser irradiation for ca. 6 min. This indicates that $O_2^{-\bullet}$ radicals are formed more efficiently in the presence of platinum on the TiO$_2$ particles than on naked TiO$_2$ alone. The details will be discussed below. Suffice it to note that the $O_2^{-\bullet}$ radicals yield H_2O_2 via reactions 4a and 4b. The ESR results are also consistent with the larger quantities of H_2O_2 produced in the SRB$-$TiO$_2$/Pt dispersion as a result of the generation of a greater quantity of $O_2^{-\bullet}$ radicals, compared to the SRB$-$TiO$_2$ system.

The DMPO$-$$^{\bullet}$OH spin-adducts with the characteristic 1:2: 2:1 quartet pattern $\{\alpha_N = \beta_H = 1.48$ mT $^{20}\}$ produced during the photodegradation processes were also observed in the ESR experiments (see Figure 5A). The intensities of the signals which are due to the hydroxyl radicals in the SRB$-$TiO$_2$/Pt dispersion are slightly greater than those in the SRB$-$TiO$_2$ system (Figure 5B). It is interesting to note that the quantities of $^{\bullet}$OH radicals do not correlate with those of H_2O_2 (see below).

We have already demonstrated in an earlier study[21] that the addition of DMPO had little, if any, effect on the rate of
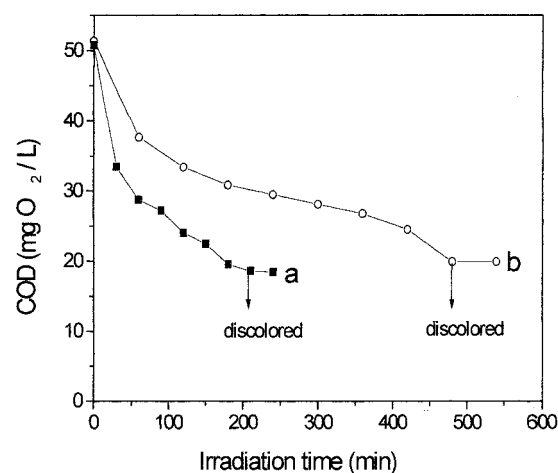
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A

B

Figure 5. (A) Temporal changes in the ESR spectra of the DMPO−•OH spin adducts with irradiation time in SRB−TiO$_2$/Pt system. (B) Plots of ESR signal intensity changes of the DMPO−•OH adducts with increasing irradiation time: (a) in the SRB−TiO$_2$/Pt system and (b) in the SRB−TiO$_2$ system. (SRB, 1×10^{-4} M; pH 3.5; catalyst, 1 g L^{-1}; DMPO, 0.025 M; irradiation laser source, $\lambda = 532$ nm).

Figure 6. Changes in COD$_{Cr}$ in the photodegradation of SRB (5×10^{-5} M, 25 mL, pH = 2.5) versus irradiation time in the presence of catalysts (25 mg): (a) TiO$_2$/Pt and (b) TiO$_2$.

photooxidation of SRB, at least in the first 30 min of irradiation. The TiO$_2$ surface is positively charged in acidic media (pH < 6.8), whereas it is negatively charged under alkaline conditions (pH > 6.8) as evidenced by ξ-potential measurements.[22] As a result, the anionic SRB dye can adsorb significantly on the surface of TiO$_2$ particles under the present conditions (pH = 2.5), whereas adsorption of the cationic DMPO spin trap is negligible. When the system is irradiated, •OH radicals generated on the surface of TiO$_2$ are very active, so much so that the SRB radical cations (or SRB molecules) adsorbed on the surface react easily with these reactive radicals to yield either intermediate products and/or completely mineralized products (see above).

Despite the greater quantities of •OH radicals generated in the SRB−TiO$_2$/Pt dispersions through reaction 5, most of these radicals react with the radical cations SRB$^+$ or SRB molecules, and only a few are scavenged by the DMPO spin trap to form the DMPO−•OH spin adducts detected by ESR. This inference suggests that the quantities of •OH radicals detected by the ESR method should not be expected to be proportional to those of H$_2$O$_2$. Note, however, that the amount of H$_2$O$_2$ formed accords well with the quantities of O$_2^{-}$• radicals produced.

Figure 6 shows the temporal changes of the COD in the photodegradation of SRB in the two systems. The COD results reflect the extent to which the organic SRB dye is mineralized[15]
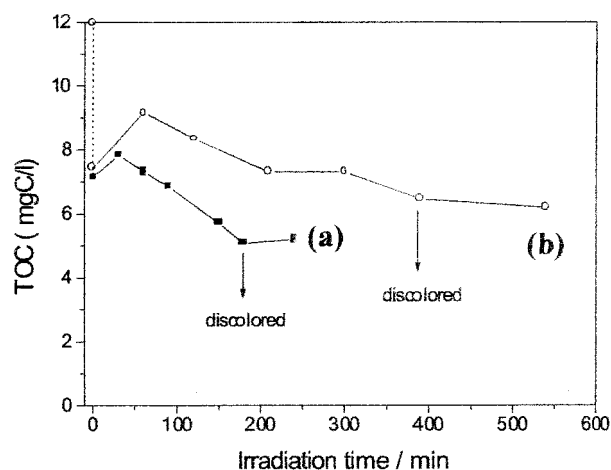
in the entire dispersion (i.e., in the bulk of the solution and on the surface of the catalysts as the measurements are done on the whole dispersion). The chemical oxygen demand in the SRB−TiO$_2$/Pt system was reduced by about 64% of total COD after 210 min of irradiation, whereas in the SRB−TiO$_2$ system, it required 480 min of visible irradiation to achieve a decrease of ca. 61% of total COD. In both systems, the COD no longer changed with further irradiation after the dispersions were totally discolored (see Figure 6). Of greater import is the observation that the final COD (18.4 mg O$_2$ l^{-1}) for the SRB−TiO$_2$/Pt dispersion is nearly identical to the COD (19.9 mg O$_2$ l^{-1}) for the SRB−TiO$_2$ dispersion at the times at which both dispersions were discolored.

In an earlier investigation,[23] we reported a comparative study between direct photocatalysis using UV irradiation and photosensitized catalysis under visible irradiation in the degradation of SRB in aqueous TiO$_2$ dispersions. In the direct photocatalysis in which the TiO$_2$ particles are photoexcited, the SRB dye was predominantly oxidized by the hydroxyl radicals (photogenerated holes) localized at the surface of irradiated TiO$_2$. This led to the destruction of the dye chromophore structure to yield such low molecular weight species as diethylamine, *N,N*-diethylacetamide, *N*-ethylformamide, *N,N*-diethylformamide, formic acid, and acetic acid. These intermediate products were further decomposed under UV irradiation to give the mineralized products SO$_4^{2-}$, NH$_4^+$, CO$_2$, and H$_2$O (among others). Parallel to this degradation, the COD of the dispersion was reduced to nearly 100%. By contrast, in the self-photosensitized catalysis using visible radiation to photoexcite the dye and not the TiO$_2$ particulates, diethylamine and 54% CO$_2$ (mineralization yield) were the major products that formed, together with ca. 14% SO$_4^{2-}$ ions and smaller quantities of the intermediates *N,N*-diethylacetamide, *N*-ethylacetamide, *N,N*-diethylformamide, *N*-ethylformamide, acetaldehyde, and formic acid.[8,23] These were mineralized no further once the dispersion was completely discolored. Accordingly, the COD in the self-photosensitization process no longer decreased to zero; it remained unchanged with irradiation time as observed herein (see Figure 6). On the contrary, for the direct photocatalytic route, mineralization of the SRB dye was nearly complete (97.5% yield of carbon dioxide) within 16 h of UV irradiation.[23]

The decays of total organic carbon (TOC) in the self-photosensitized degradation of SRB in the two systems are depicted in Figure 7. Because dye molecules are adsorbed on the titania surface, the TOC (7.3 mg L^{-1} for SRB−TiO$_2$ and

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Figure 7. Temporal changes in total organic carbon (TOC) of the degraded bulk solution during the photodegradation of SRB (5×10^{-5} M, pH = 2.5) process: (a) TiO_2/Pt and (b) TiO_2.
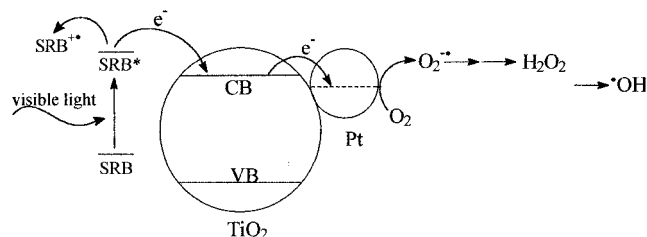
7.1 mg L^{-1} for SRB–TiO_2/Pt) of the solution bulk at t = 0 h was lower than of the initial solutions (12.0 mg l^{-1}) in the absence of catalyst particles; about 60% of the dye remained in solution. Upon visible light irradiation of the dispersions, the TOC of the bulk solution for both systems increased initially as a result of photodesorption of the dye and/or any intermediate formed within the first hour of illumination. TOC then decreased gradually to reach ultimately a steady state after ca. 3 h (ca. 31% of TOC remaining) and 8 h (ca. 35% TOC left) of irradiation of the SRB–TiO_2/Pt and SRB–TiO_2 dispersions, respectively. The TOCs remained unchanged after the dispersions were completely discolored, indicating that the degraded fragments were no longer decomposed upon further irradiation by visible light. Platinum loading on titania particulates appears to have little effect on the final mineralization yield, in keeping with the results of the COD measurements above.

To the extent that the presence of platinum caused no further mineralization of the intermediate products when the TiO_2/Pt dispersion was discolored further supports the inference that degradation of SRB occurs through a self-photosensitized process (excitation of the dye) and not through a photocatalytic process (excitation of the catalyst).

Role of Pt in the Self-Photosensitized Degradation of SRB in TiO₂/Pt Dispersions. The major results of this study are 4-fold. (i) The activity of the TiO_2/Pt particles in the degradation of SRB is greater than that of P25 TiO_2 alone when subjected to visible light radiation. (ii) There is rapid formation of relatively large quantities of H_2O_2 and $O_2^{-\bullet}$ species produced in the SRB–TiO_2/Pt system during the degradation process, in comparison to those formed in the SRB–TiO_2 system; the ESR signal intensities of the DMPO–$^\bullet$OH spin-adducts in the two systems are similar. (iii) The final mineralization yield of SRB on TiO_2/Pt is nearly the same as the yield on TiO_2 (see above). (iv) The degradation of SRB on TiO_2/Pt takes place through a self-photosensitization process.

A study by Schierbaum and co-workers[24] has shown that in the case of TiO_2 (110)/Pt there are newly derived electron states below the conduction band of TiO_2 because of the presence of Pt. The enhanced catalytic activity may be attributed to these Pt-derived states. Under visible light illumination, TiO_2 is not excited as its absorption threshold is 385 nm; only the SRB molecule is excited to produce the excited-state SRB*. Subsequently, the adsorbed SRB* species injects an electron into the conduction band of TiO_2 with SRB being converted to the radical cation SRB$^{+\bullet}$ (see Scheme 1). In the presence of Pt and

SCHEME 1: Proposed Mechanism of the Photodegradation of SRB on TiO₂/Pt Particles under Visible Light Irradiation

in keeping with the earlier work,[23] we suggest that the injected electrons are transferred to the Pt-derived states, yielding a relatively high density of electrons on the platinum islands. This electron transfer leads to efficient electron/hole separation and suppresses somewhat the recombination event (back electron transfer) between the SRB$^{+\bullet}$ radical cations and the injected electrons. In turn, the electrons react with adsorbed O_2 to produce superoxide $O_2^{-\bullet}$ radical anions (Figure 4A)[25−29] and then $^\bullet$OH radicals (Figure 5B)[15,23] as evidenced by ESR spectroscopy in accord with earlier studies. Clarkson and McClellan[30] have also reported similar formation of $O_2^{-\bullet}$ radical anions on gold, rhodium, and platinum supported on porous Vycor glass, whereas Bagghi and co-workers[31] reported its formation on electrochemically reduced platinum electrodes. Normally, direct ESR observations of superoxide radical anions produced on illuminated metal-oxide surfaces occur at low temperature (77 K).[32−34]

More germane to the present study, Einaga and co-workers[35] also report observing $O_2^{-\bullet}$ radical anions at 77 K on UV irradiation of TiO_2 and TiO_2/Pt dispersions. As well, these workers observed the $O_3^{-\bullet}$ radical anions at 77 K and subsequently at ambient temperature owing to its stabilization by platinum on the TiO_2 surface. Note that they found no direct evidence for the formation of O$^-$ species;[35] they alleged that formation of the $O_3^{-\bullet}$ anions occurs by reaction of molecular oxygen with a surface-trapped hole (O_s^-) through reactions 7 and 8 although they could find no direct ESR signature for the

$$h^+ + O_s^{2-} \rightarrow O_s^- \qquad (7)$$

$$O_s^- + O_2 \rightarrow O_3^{-\bullet} \qquad (8)$$
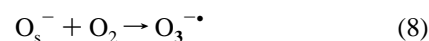
latter species. Formation of O$^-$ was presumed from oxidation of CO and from degassing (somewhat) the air-equilibrated dispersion (reverse of reaction 8[35]) upon noting a decreased intensity of the $O_3^{-\bullet}$ ESR signals under these conditions. In the present study, formation of the $O_2^{-\bullet}$ radical species was ascertained by DMPO spin-trapping at ambient temperature, albeit in methanolic media.

In the absence of Pt, recombination of the electron in the conduction band (or surface defect) of TiO_2 to the SRB$^{+\bullet}$ cation radical adsorbed on the surface of TiO_2 can comptete effectively with molecular O_2 so that the extent of scavenging the electrons by O_2 is lessened. By contrast, the higher density of electrons accumulated on the surface of TiO_2/Pt particulates and the diminished recombination increases the amount of $O_2^{-\bullet}$ formed on platinized titania relative to what is possible on the TiO_2 surface alone. Accordingly, the ESR difference in the quantity of $O_2^{-\bullet}$ radicals produced between the TiO_2/Pt and TiO_2 dispersions is understandable. To the extent that $O_2^{-\bullet}$ radicals continue to be converted to H_2O_2 (reactions 4 and Scheme 1) and then to $^\bullet$OH radicals through reaction 5, the SRB$^{+\bullet}$ and/or

SRB species can easily react with these active oxygen species to yield intermediate products and partial mineralization of the dye and intermediates,[8] at least as long as the dispersion remains colored.

Conclusions

When doped with small quantities of platinum, the TiO_2 semiconductor catalyst is an efficient system for the visible light photodegradation of the dye SRB. The improved activity is due to an enhanced ability to trap photogenerated electrons on the newly Pt-derived states that form on the TiO_2. The electrons that accumulate further react with molecular oxygen (O_2) to produce greater quantities of $O_2^{-\bullet}$ and $^\bullet OH$ than on naked TiO_2 alone, thereby leading to enhanced self-photosensitized degradation and (partial) mineralization of the dye. The inhibitory effect seen at a greater Pt^0 loading (0.5 wt%) on TiO_2 particulates (see curve d in Figure 1) in the self-photosensitized degradation of SRB is somewhat enigmatic, requiring further work which will be reported at a later date.[36]

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