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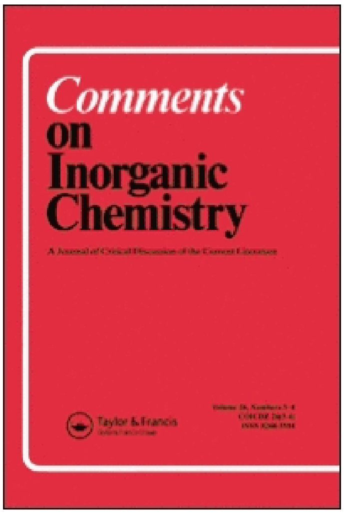

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Metal Oxides as Photocatalysts for Environmental Detoxification

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Metal Oxides as Photocatalysts for Environmental Detoxification

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Heterogeneous photocatalysis occurs over semiconductor particulates irradiated with light of proper wavelengths, which generates charge carriers (electrons and holes). These e^-/h^+ pairs are ultimately positioned at the particle surface to undergo a variety of events (recombination, trapping) in competition with other processes (redox chemistry). These charge carriers may be implicated in photocatalytic transformations of inorganic anions (cyanides, sulfides) and reduction of precious and/or toxic metals. When organic compounds are present in aerated suspensions, the photocatalytic oxidation leads to total mineralization to carbon dioxide and inorganic anions (for example, chloride from chlorinated organics). The present Comment focuses on the fundamental and primary events occurring in the heterogeneous photocatalysis on semiconductor metal oxides, with particular reference to TiO_2, and reports on the mechanism of some redox transformations concerning inorganic and organic species. Actual research on photocatalytic materials and on solar detoxification is outlined.

Key Words: *heterogeneous photocatalysis, semiconductor metal oxides, titanium dioxide, hydrogen sulfide, cyanide, metal recovery, lead(II), mercury(II), mineralization, doping, supported catalyst, solar detoxification*

Abbreviations Used: *ads* = *adsorbed*, *app* = *apparent*, *bg* = *band gap*, *org* =

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organic substrate or molecule, ox = oxidized, rec = recombination, red = reduced, trap = trapped

I. INTRODUCTION

Most primary light absorbers used in photocatalysis are semiconductors.[1-3] Semiconductors are characterized by two separated energy bands: a filled low-energy valence band and an empty high-energy conduction band (Fig. 1). A forbidden region of energy, called the band gap, is present between the conduction and the valence band. Light excitation of a semiconductor promotes electrons from the valence band to the conduction band. The empty level in the valence band is called a hole. Electrons and holes are called carriers. The existence of the band gap prevents rapid deactivation of the excited electron–hole pairs, which can disappear only by recombination.

The favorable combination of electronic structure, light absorption properties, charge transport, carrier lifetimes and carrier recombination rates are crucial for obtaining materials suitable to photocatalytic processes.

The present Comment will discuss the metal oxide semiconductors and their use as photocatalysts with particular attention to processes of environmental interest.

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II. PRINCIPLES OF PHOTOCATALYSIS

The term photocatalysis implies the combination of photochemistry with catalysis. The light and the catalyst are both necessary to achieve or accelerate a chemical reaction. A detailed attempt to formulate a definition of photocatalysis may be found in Ref. 4. For the present purpose, the term is related to the use under irradiation of a stable and solid semiconductor for stimulating a reaction at the solid/solution interface. By definition, the solid can be recovered unchanged after many turnovers of the redox systems.

The basic theory of semiconductors, with emphasis on their optical and electronic properties, is reported in numerous texts.[5] The

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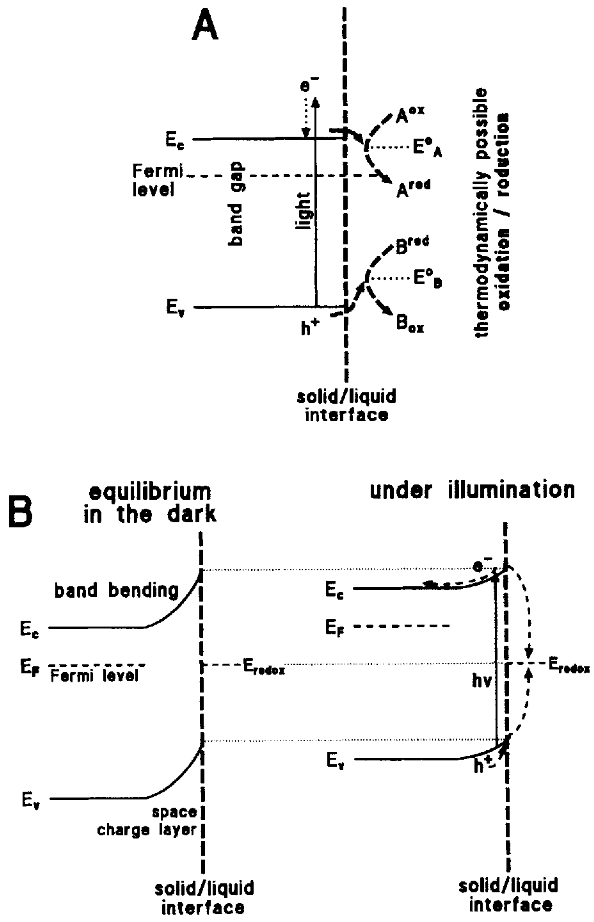

FIGURE 1 (a) Band structure in an n-type semiconductor and thermodynamic constraints for redox processes at the illuminated semiconductor/electrolyte interface. (b) Typical charge distribution at the n-type semiconductor/electrolyte contact in the dark and under illumination.

basic concepts relevant to photocatalysis have been concisely and clearly described in Ref. 6. It is noteworthy that differences in the properties exist when colloidal particles are considered with respect to bulk crystalline samples.[6,7]

When a semiconductor is in contact with a liquid electrolyte solution containing a redox couple, charge transfer occurs across the interface to equilibrate the potentials of the two phases. An electric field is formed at the surface of the semiconductor and the bands bend as the field forms from the bulk of the semiconductor toward the interface (see Fig. 1). During the photoexcitation (exemplified by an n-type semiconductor, rendered electron-rich by doping with effective electron donors), band bending provides the conditions for the carrier separation and the inhibition of the recombination. It is a method for electron/hole separation.

In the case of semiconductor particles with magnitude of the order of 1 μm, that we specifically consider in this Comment, the difference with a semiconductor electrode is the absence of the ohmic contact. With particles there is no ohmic contact to extract the majority carriers and to transfer them by an external conductor to a second electrode. This means that the two charge carriers should react at the semiconductor/electrolyte interface with species in solution. Under steady state conditions the amount of charge transferred to the electrolyte must be equal and opposite for the two types of carriers. When particles are concerned, charges reach the surface more easily than with electrodes and active centers are much more numerous. This leads to a higher rate for the photocatalytic process.

The semiconductor mediated redox processes involve the electron transfer across the interface. When electron/hole pairs are formed in the space charge region, the electron will move away from the surface to the bulk of the semiconductor (in the case depicted in Fig. 1) as the hole migrates toward the interface. This picture predicts that oxidation will occur at the interface for any species that has an oxidation potential less positive than the semiconductor valence band. Similar considerations should apply to photosensitized reductions.

In the case of photoelectrochemical cells, as the oxidation of adsorbed species occurs, charge accumulation in the bulk of the semiconductor is discharged at the connected electrode. In powders sufficient charge can build up to render the particle electrophoretically mobile. Ultimately, such a charged aggregate can act as a reducing center and affect solution-phase reductions. The photoredox events occurring at the interface between the excited

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semiconductor and the redox species in solution are unidirectional and generally nonreversible for organic substrates.[8]

The above principles have found extensive applications in the field of light-induced generation of fuels,[9] in organic phototransformations,[10] and only recently in the area of environmental chemistry and pollution abatement.[11]

Metal oxides represent a large class of semiconductor materials

TABLE I

Selected properties of metal oxide semiconductors

Material	Band Gap [V]	Wavelength Corresponding to Band Gap [nm]	p.z.c.	Stability
p-CuO	1.7	730	–	unstable
n-CdO	2.1	590	12	in NaOH
n-Fe_2O_3	2.2	565	8.6	pH > 4.5
n,p-Bi_2O_3	2.8	440	–	unstable
n-TiO_2	3.0–3.2	390–410	5.8	stable
n-ZnO	3.2	390	8.8	fairly stable
n-$BaTiO_3$	3.3	375	–	stable
n-$SrTiO_3$	3.4	365	–	stable
n-SnO_2	3.7	335	4.3	stable

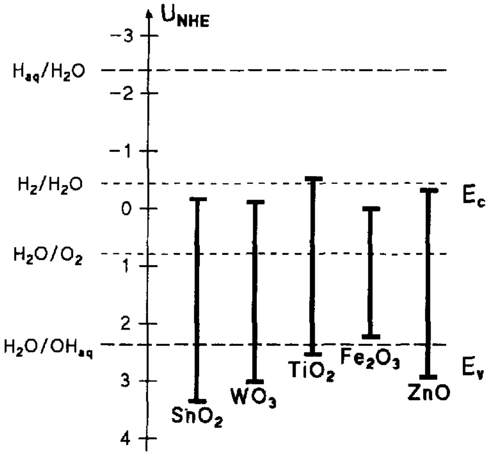

FIGURE 2 Energy levels of conduction and valence bands for metal oxide semiconductors.

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suitable for photocatalytic purposes. Table I lists some selected semiconductor oxides together with some of their relevant properties for photocatalytic applications.[12] Figure 2 reports the energy of valence and conduction bands. It is noteworthy that some semiconductor oxides are widespread in nature (MnO_2, Fe_2O_3, TiO_2, CdS, PbO_2). Only recently their impact on environmental transformations has been considered.[13]

III. PHOTOCATALYTIC OXIDATIONS IN AQUEOUS SOLUTION

Band gap irradiation renders the semiconductor an effective oxidant. The hole with proper redox potential (see Fig. 1) can be filled by electron transfer from an adsorbed species like a solute or a solvent molecule. Photocatalytic reactions of environmental interest take place in water as a solvent and consequently oxygen derived radicals can be generated. On the other side, the photogenerated electrons can be captured by molecular oxygen adsorbed onto the surface of the semiconductor. This completes the first step, in which the charge separation and subsequent modification of the overall chemical system take place (see below). Most frequently TiO_2 has been used in environmental decontamination studies. The reason will be discussed later together with other semiconductors suitable for this application. The main features of the photocatalytic process using almost exclusively TiO_2 particles will be described here.

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A. Primary Events and Reactive Species at Irradiated TiO_2 Particles

In the case of particles whose dimensions are small compared to the typical width of space charge layers for the low doping levels within the particle, it is unlikely that electric fields within the particle play a role in promoting electron–hole separation. However, fields may exist because of specific ionic adsorption on the particle surface or charges can be trapped at the surface. After charge generation (Eq. (1)), other reactions can compete with electron/hole recombination (Eq. (2)).

$$\mathrm{TiO_2} + h\nu_{(>E_{bg})} \xrightarrow{\phi I_a^n} \mathrm{e^-} + \mathrm{h^+}, \tag{1}$$

$$\mathrm{e^-} + \mathrm{h^+} \xrightarrow{k_{rec}} \mathrm{TiO_2} + \text{heat and/or } h\nu'. \tag{2}$$

When the carriers reach the surface, they can be ultimately trapped by intrinsic sub-surface energy traps $[\mathrm{Ti^{IV}{-}O^{2-}{-}Ti^{IV}}]$ for the hole and by surface traps $(-\mathrm{Ti^{IV}}-)$ for the electrons (Eqs. (3) and (4))[14] and/or by extrinsic surface traps via interfacial electron transfer with adsorbed electron donors $(\mathrm{Red_2})_{ads}$ and acceptors $(\mathrm{Ox_1})_{ads}$, respectively (Eqs. (5) and (6)).

$$(\mathrm{Ti^{IV}{-}O^{2-}{-}Ti^{IV}})_{sub\text{-}surface} + \mathrm{h^+_{VB}} \xrightarrow{k_{trap}} (\mathrm{Ti^{IV}{-}O^{-\bullet}{-}Ti^{IV}})_{sub\text{-}surface}, \tag{3}$$

$$(-\mathrm{Ti^{IV}}-)_{surface} + \mathrm{e^-_{CB}} \rightarrow (-\mathrm{Ti^{III}}-)_{surface}, \tag{4}$$

$$\mathrm{h^+_{VB}} + (\mathrm{Red_2})_{ads} \rightarrow (\mathrm{Ox_2})_{ads}, \tag{5}$$

$$\mathrm{e^-_{CB}} + (\mathrm{Ox_1})_{ads} \rightarrow (\mathrm{Red_1})_{ads}. \tag{6}$$

Since electron/hole recombination (Eq. (2)) is rapid, for efficient charge carrier trapping $\mathrm{Red_2}$ and $\mathrm{Ox_1}$ have to be pre-adsorbed prior to light excitation of the $\mathrm{TiO_2}$ photocatalyst. Adsorbed redox-active solvents can act as electron donors and acceptors. For a hydrated and hydroxylated $\mathrm{TiO_2}$ anatase surface, hole trapping by interfacial electron transfer yields surface-bound $^\bullet\mathrm{OH}$ radicals.[15]

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This is a major route of formation of $^{\bullet}OH$ radicals (Eq. (7)). They can also be formed from H_2O_2 via the superoxide $O_2^{-\bullet}$ radical anion (Eqs. (8) and (9))[16] and by photolysis of H_2O_2 (Eq. (10)).

$$(Ti^{IV}\text{–}O^{2-}\text{–}Ti^{IV})\text{–}OH^- + h^+_{VB} \rightleftharpoons (Ti^{IV}\text{–}O^{2-}\text{–}Ti^{IV})\text{–}OH^{\bullet}, \quad (7a)$$

$$(Ti^{IV}\text{–}O^{2-}\text{–}Ti^{IV})\text{–}OH_2 + h^+_{VB} \rightleftharpoons (Ti^{IV}\text{–}O^{2-}\text{–}Ti^{IV})\text{–}OH^{\bullet} + H^+, \quad (7b)$$

$$O_{2(ads)} + e^- \rightarrow O^{-\bullet}_{2(ads)}, \quad (8)$$

$$H_2O_2 + O_2^{-\bullet} \rightarrow OH^{\bullet} + OH^- + O_2, \quad (9)$$

$$H_2O_2 + h\nu \rightarrow 2\ OH^{\bullet}. \quad (10)$$

Irradiation with AM1 simulated sunlight ($\lambda > 340$ nm) precludes reaction (10) as a major source of hydroxyl radicals since the concentration of H_2O_2 formed is small.[17]

Several years ago, we pointed out that both O_2 and H_2O are essential species in the photomineralizaiton of 4-chlorophenol in the presence of irradiated TiO_2 [18]; no photodegradation occurs in the absence of either O_2 or H_2O, or both. Adsorbed oxygen traps e^- (Eq. (8)) thereby delaying electron/hole recombination (k_{rec}). It should be emphasized that even trapped electrons and holes rapidly recombine on the particle surface. To prevent recombination of holes and electrons, the latter carrier is scavenged by pre-adsorbed (and photoadsorbed) molecular oxygen to give the superoxide radical anion, $O^{-\bullet}_{2(ads)}$, (Eq. (8)), which can be reduced further to the peroxide dianion, $O^{2}_{2(ads)}$ (Eq. (11)). Alternatively, surface peroxo-species can be formed[19] either by hydroxyl radical (hole) pairing (Eq. (12)) or by sequential two-hole capture by the same OH group (Eqs. (7) and (14)) or by dismutation of $O_2^{-\bullet}$ (Eq.

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(15)). Careful identification of surface peroxo-species has been performed electrochemically by cyclic voltammetry.[20]

$$O_{2(ads)}^{-\cdot} + e^- \rightarrow (O_2^{2-})_{surface}, \qquad (11)$$

$$2\ ({}^\cdot OH)_{surface} \rightarrow (H_2O_2)_{surface}, \qquad (12)$$

$$(H_2O_2)_{surface} \rightleftarrows (O_2^{2-}) + 2\ H^+, \qquad (13)$$

$$(Ti^{IV}\text{–}O^{2-}\text{–}Ti^{IV})\text{–}OH^\cdot + h_{VB}^+ \rightarrow (O)_{surface} \rightarrow \tfrac{1}{2}\ O_{2(ads)}, \qquad (14)$$

$$2\ O_{2(ads)}^{-\cdot} \rightarrow O_{2(ads)} + O_{2(ads)}^{2-}. \qquad (15)$$

In acidic media (pH < 3), the superoxide radical anion protonates to give the hydroperoxide radical, $HO_2^\cdot$ (pK_a 4.88[21]). Other reactions that no doubt occur on the TiO_2 particle surface and that are solvent (water) related are summarized in Eqs. (16) to (20).

$$O_{2(ads)}^{-\cdot} + H^+ \rightarrow HO_{2(ads)}^\cdot, \qquad (16)$$

$$2\ HO_2^\cdot \rightarrow H_2O_2 + O_2 \qquad (17)$$

$$O_2^{-\cdot} + HO_2^\cdot \rightarrow O_2 + HO_2^- \xrightarrow{+H^+} H_2O_2, \qquad (18)$$

$$H_2O_2 + e^- \rightarrow OH^\cdot + OH^-, \qquad (19)$$

$$H_2O_2 + {}^\cdot OH \rightarrow H_2O + HO_2^\cdot. \qquad (20)$$

As far as the nature of the oxidizing species is concerned (that is, hole vs. radical species), chemical evidence of hydroxylated species originating during degradation of phenol[22] and halophenols[23] supports other studies, like kinetic deuterium isotope experiments[24] and ESR studies,[15d,25] claiming that the hydroxyl radical is the reactive species. It should be remarked that product identification may not lead, if at all, to a delineation of ${}^\cdot OH$ versus hole oxidation, since the product may be identical in both cases. For example, the products identified in the photo-oxidation of phenol may originate either by ${}^\cdot OH$ radical attack of the phenol ring or by direct hole

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oxidation to give the cation radical that subsequently undergoes hydration in solvent water. Thus product analysis alone will in most cases be insufficient to establish unambiguously the process(es) in the primary photochemical event.

Holes, as primary oxidizing species, have been described in nonaqueous photo-assisted oxidations.[26] In aqueous solution, besides an early study carried out on a TiO_2 modified surface,[27] recent strong evidence in favor of direct hole oxidation comes from a study that failed to detect any of the expected hydroxylated intermediate ˙OH-adducts following diffuse reflectance flash photolysis of several TiO_2/substrate combinations.[28] Experimental difficulties together with the fact that an ˙OH-adduct often possess absorption bands in the UV region where TiO_2 absorption interferes, thereby obstructing observation of such expected hydroxylated species, do not obviate the intermediary of ˙OH radicals (possibly by an electron transfer process) in photo-oxidations.

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B. Physico-chemical Properties of TiO_2 Particles

Photoreactions occurring at TiO_2 are markedly affected by the surface properties of this material.[29,30] There is abundant evidence that the TiO_2 surface exposed to an aqueous solution undergoes hydroxylation. Temperature programmed desorption experiments have placed the number of surface $-OH$ groups at ca. 5 per nm^2, representing less than 50% of surface coverage. A theoretical report[31] puts the number of $-OH$ groups at 5–10 per nm^2, with the exact number dependent on the type of crystal plane examined. The consensus seems to be $7 \simeq 10$ $-OH$ nm^{-2} for TiO_2 at ambient temperature.[32] Chemisorbed water (H_2O bound directly to surface Ti^{IV} ions) amounts to about 2–3 molecules nm^{-2} for rutile TiO_2.[33] Thus, most if not all the Ti^{IV} sites are occupied. The surface density of $-OH$ has an important role in the efficiency of the photocatalytic process and strongly affects the rate of oxygen evolution and of photodegradation of organic molecules.[33-35]

Due to the Lewis base character of the surface oxide ions, that act as donor surface states, the chemisorption of water at the Ti^{IV} site is likely to be followed by the proton transfer to the $-O-$ site. Two kinds of surface $-OH$ groups are then formed. The acidic one has a pK value of ca. 2.9, while the remainder behaves as weak acid with a pK 12.7.[36]

The amphoteric ionization reaction[37] of the surface –OH groups (Eqs. (21) and (22)) determines the surface charge of the oxide-solution interface.

$$\text{Ti–OH} \rightleftarrows \text{Ti–O}^- + \text{H}^+_{\text{aq}}, \tag{21}$$

$$\text{Ti–OH} + \text{H}^+_{\text{aq}} \rightleftarrows \text{Ti–OH}_2^+. \tag{22}$$

The surface charge density, σ_s, is usually calculated from the uptake of the potential-determining ions, H^+ and OH^-, measured as a function of the pH of the oxide suspension:

$$\sigma_S = F(\Gamma_{H^+}) - \Gamma_{OH^-}) \tag{23}$$

where Γ_{H^+} and Γ_{OH^-} are the surface excesses (the adsorption densities) of the corresponding ions, expressed in mol cm^{-2}, and F is the Faraday constant. The pH value at which the oxide surface carries no fixed charge, i.e., $\sigma_S = 0$, is defined as the point of zero charge (PZC)[38] (see Table I for PZC of metal oxides of interest). A closely related parameter, the isoelectric point (IEP), obtained from electrophoretic mobility and streaming potential data, refers to the pH value at which the electrokinetic potential equals zero. The PZC and IEP should coincide when there is no specific adsorption in the inner region of the electric double layer at the oxide-solution interface. In the presence of the specific adsorption, the PZC and IEP values move in opposite directions as the concentration of supporting electrolyte is increased.

The observation of the low adsorption processes involving the potential-determining ions, which are expected to reflect low changes in the PZC,[39] may be of interest in relation to long-term photochemical or photoelectrochemical experiments with TiO_2 dispersions or TiO_2 electrodes.

Recent careful measurements of the surface charge density of a titanium dioxide (rutile) suspension as a function of pH,[39] employing aqueous KNO_3 solutions of various concentrations, place the PZC at pH = 5.8 ± 0.1. The sample used in this study was a thoroughly purified synthetic rutile prepared by hydrolysis of

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titanium tetrachloride. For a similar rutile sample in a KNO_3 solution, an IEP value of 5.8 (i.e., equal to the PZC) was determined.[40] This would suggest that potassium nitrate behaves as a classical "indifferent electrolyte" and that the above PZC and IEP of TiO_2 may be considered as intrinsic values.

The available data regarding the point of zero charge of anatase are not markedly different from those for rutile and range from pH = 6 to pH = 6.4.[41] There is abundant evidence, especially in earlier literature, that the values of the PZC and IEP are strongly affected by a high-temperature pre-treatment of the oxide. In fact, calcining of the TiO_2 sample above 1100 K (in general, at 1273 K) results in a drop of the PZC and IEP to pH 4.7–4.8. Such a decrease of the PZC and IEP values, exceeding one unit of pH, reflects apparently irreversible changes in the surface chemistry of titanium dioxide. It is significant, in this connection, that the TiO_2 samples, after being calcined above 1100 K, undergo only partial rehydroxylation when exposed to water, and, as previously observed, relevant changes in photocatalytic activity result.

The variation of the point of zero charge of TiO_2, PZC_T, with the temperature of the impregnating solution has been observed. An increase in the impregnation temperature from 10 to 45°C brings about an increase in the PZC_T from 3.84 to 7.06. Therefore, an extension of the pH range in which negative species can be adsorbed on titania should be expected by increasing the impregnation temperature.[42] As electrophoretic mobility measurements show, under illumination of TiO_2 particles in the absence of an easily reducible species in solution, there is a build-up of negative charge on the particle surface.[43]

C. Adsorption of Ions on the Surface of TiO_2

Surface charge density (σ_S) versus pH isotherms, derived from the results of potentiometric titrations, are also an important source of information about the adsorption of ions on the oxide surfaces. Comparison of the σ_S against pH curves obtained in solutions of different electrolytes allowed the establishment sequences of preferential adsorption of cations and anions on titanium dioxide. This phenomenon can affect photodegradation process in two ways: (a) if the organic compound to be degraded has an acid or basic char-

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acter; (b) if inorganic ions are initially present or formed during the degradation and can compete for adsorption sites.

Whereas the degradation rate of a non-ionizable substrate, such as chloroform, is only slightly affected by pH variations, a dramatic effect is shown by trichloroacetate ($pK_a = 0.7$) and chloroethylammonium ($pK_a = 8$).[44] A further complicating factor is, however, the changes induced by pH variations on the redox potential of semiconductor bands,[45] as well as redox potentials of dissociable compounds.[46]

Inorganic ions present in the medium or originated during the degradation (case b) can chemisorb and change the surface properties. Whereas perchlorate and nitrate show very little effect, sulphate, phosphate and chloride are rapidly adsorbed by the catalyst and cause relevant reduction of the reaction rate.[44,47]

D. Degradation Process Location

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Another issue, often raised in the discussion of the photocatalyzed mineralization of organic substrates, is whether the initial oxidation of the organic substrate occurs on the photocatalyst's surface or in solution. In analyzing the kinetic data of photocatalyzed oxidations (and reductions), mediated by photo-activated semiconductor particles, several studies in the 1980s literature have fitted the results to the simple rate expression of Langmuir type.[2,48]

A rigorous treatment[49] of the kinetic of the photocatalyzed oxidations of organic substrates on an irradiated semiconductor under a variety of conditions has recently examined whether it was possible to delineate surface vs. solution bulk reactions. The derived kinetic model considered four cases implicating $^{\bullet}OH$ radical attack of the organic substrate: (i) reaction occurs while both species are adsorbed; (ii) reaction occurs between the adsorbed substrate and the free radical; (iii) reaction occurs between a surface bound $^{\bullet}OH$ radical and the substrate in solution; and (iv) reaction occurs while both species are in solution. In all cases, the analytical form of the derived complex rate expression was identical and was similar to that from the Langmuir model. Clearly, kinetic studies alone are silent on whether photo-oxidations are surface processes or solution processes.[50]

The overall reaction mechanism leading to the final decomposition is in fact rather complex. Once the active oxidizing species are generated at the catalyst surface, the subsequent reaction sequence, which leads to the final degradation of the pollutant, can be envisaged to occur through several steps. If the reaction site is at the surface of the photocatalyst, the following processes can occur: (i) diffusion of the reactant from the bulk solution (i,a) or from an "inert" surface (i,b) to the photocatalyst surface; (ii) diffusion of the reactant from surface (ii,a) or pore (ii,b) sites to the active centers at the surface of the photocatalyst; (iii) reaction at the catalytic centers; (iv) diffusion of the reaction products from the surface to the bulk solution. If reaction occurs exclusively (or also) in the bulk solution, the steps are: (v) diffusion of photogenerated reactive species from the surface to the bulk solution; (vi) reaction in solution; or, if the compound to be degraded is adsorbed on an "inert" surface, (vii) reaction of the photogenerated reactive species at the surface of the "inert" support.

An interesting aspect shown by the accumulation of kinetic data on related compounds is that their rates of disappearance are quite similar. This is the case for p-alkylphenol that, on going from the parent phenol (<2% adsorption on TiO_2) to p-nonylphenol (>99% adsorbed on TiO_2), shows only a 3-fold increase in the degradation rate.[51] For a highly adsorbing species, paths (i,b)–(iii) or (v),(vii) are the two expected routes, whereas for a weakly (or non) adsorbed species paths (i)–(vi) could be contributing.

Some studies have sought chemical evidence and inferences to ascertain whether or not the oxidation is a surface process. The selective inhibiting influence of iso-propanol, which modifies only two terms in the kinetic expression that are independent of the furfuryl alcohol (FA) concentration, was taken by Lemaire *et al.*[52] to mean that oxidation of FA by a $^{\bullet}OH$ radical over ZnO dispersion occurs in the homogeneous phase. The relative importance of the formation of glycolate and glyoxylate via $^{\bullet}OH$ oxidation of acetate increases with increasing pH.[53] It was inferred that, since in alkaline media little adsorption of acetate takes place on the negatively charged TiO_2 surface, the hydroxyl radical must diffuse away from the surface of the photocatalyst to oxidize acetate in solution. By contrast, suppression of the degradation rate of trichloroacetate when TiO_2 bears a negative charge seems to support the surface location of the process.[44] Similarly, degradation of pentachloro-

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phenol occurs at a sustained rate also in an alkaline medium.[54] It was inferred that the photo-oxidative process does not need to occur at the catalyst's surface, as the reactive $^{\bullet}OH$ species can diffuse several hundred angstroms in the solution. Other workers have suggested that the diffusion length of an $^{\bullet}OH$ radical in the presence of TiO_2 may only be a few atomic units in distance or less.

A recent photoelectrochemical study[55] is supportive of solution $^{\bullet}OH$ reactive species in photocatalyzed oxidations. The two important anodic and cathodic reactions on the working metal electrode are embodied in Eq. (24).

$$TiO_2^- \rightarrow TiO_2 + e^- \text{ (anodic)}, \tag{24a}$$

$$^{\bullet}OH \rightarrow OH^- + h^+ \text{ (cathodic)}. \tag{24b}$$

In a slurry photochemical reactor containing an organic substrate, the initial photocurrent was cathodic that rapidly became anodic under steady state conditions. Immobilization of the TiO_2 onto a conducting carbon paste in a nonuniform manner, in which presumably no TiO_2 come in contact with the electrode, gave similar results as the slurry cell reactor. The results suggested[55] that a photo-generated surface-originating $^{\bullet}OH$ radical must diffuse into solution to generate the observed cathodic photocurrent.

Recent studies seem, however, to give privilege to the surface location of the photo-oxidative process. Time-resolved microwave conductivity studies[56] on TiO_2 Degussa P25 showed a definite increase in the lifetime of the mobile charge carrier (electron) in the presence of isopropanol, resulting either from (i) scavenging of surface $^{\bullet}OH$ radicals by isopropanol or (ii) to displacement of a deep surface trap by the alcohol. Observation of a small signal growth in the last pulse of a 100-pulse train (5 Hz) in the TiO_2/isopropanol sample was inferred to arise from electron ejection from the $CH_3C\cdot(OH)CH_3$ radicals, formed in an irradiated (with 3 MeV from a Van de Graaff accelerator) isopropanol solution of TiO_2, via Eq. (25). A similar process explained the observed photocurrent doubling effect by alcohols or other oxidizable organics,[57] a process that could only take place at the TiO_2 surface.

$$CH_3C\cdot(OH)CH_3 + TiO_2(h^+) \rightarrow CH_3COCH_3 + TiO_2 + H^+. \tag{25}$$

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In a study by means of the pulse radiolysis method,[58] the reaction of TiO_2 colloids with $^{\bullet}OH$ radical produced by irradiation of N_2O-saturated aqueous solutions with high energy electrons has been investigated. The observed growth rate of the product, which we presently define simply as (TiO_2 + $^{\bullet}OH$), varies linearly with [TiO_2] giving $k = 6.0 \times 10^{11}\ M^{-1}s^{-1}$ (concentration in terms of particles). Since the $^{\bullet}OH$ radical reacts with TiO_2 at a diffusion controlled rate, the reverse reaction, that is desorption of $^{\bullet}OH$ to the solution, seems highly unlikely.

The absence of inhibition of hydrogen carbonate may be considered other evidence of surface reaction. Hydrogen carbonate effectively scavenges $^{\bullet}OH$ radicals in the homogeneous phase, generated by O_3-UV and H_2O_2-UV systems.[59]

A further indication that the $^{\bullet}OH$ radical is surface bound, and is unlikely to desorb into the solution, emanates from a study[60] which notes that decafluorobiphenyl (DFBP) is tenaciously adsorbed ($\geq 99\%$) on metal oxide particle surfaces (Al_2O_3 and TiO_2) and does not undergo facile exchange between the two oxide materials ($\leq 5\%$). When adsorbed on the alumina surface in dispersions into which H_2O_2 or a TiO_2 colloidal solution (particle size ca. 0.05 μm) is added, followed by UV irradiation, the DFBP is photodegraded. This indicates that the $^{\bullet}OH$ radical from H_2O_2 and TiO_2 sol (particle adsorbed on alumina) migrates to the reaction site on the DFBP/Al_2O_3 system to initiate the photo-oxidative events. By contrast, if TiO_2 beads (size ca. 1000 μm) or even TiO_2 P25 are used instead of H_2O_2 or the TiO_2 sol to generate the oxidizing species, the photodegradation is nearly suppressed and is identical to the behavior of the DFBP/Al_2O_3 system alone, irradiated with UV light under otherwise identical conditions. Pentafluorophenol, which readily exchanges between the two metal oxide surfaces, undergoes fast photodegradation under the same conditions. We concluded that the photogenerated oxidizing species ($^{\bullet}OH$ radical, if any) does not migrate far from the photogenerated active site on TiO_2 (i.e., step vii is unlikely), and that the degradation process must occur at the photocatalyst surface or within a few atoms of distance from the surface.

With regard to the location at the surface of the photocatalyst,

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the reaction of active oxidizing species with the substrate can be described by the expression:

$$\text{rate} = k_{\text{app}}\,[\text{organic}]. \tag{26}$$

Here, k_{app} is a complex function of several parameters:

$$k_{\text{app}} = \frac{\Phi I_a^n \beta A_p \dfrac{k_{\text{trap}}}{k_{\text{rec}}} \tau_{\text{OH}}\, k K_{\text{ORG}}\, [\text{site}]_o}{1 + \sum_i K_i\,[\text{S}_i]} \; \frac{K_{\text{O}_2}[\text{O}_2]}{1 + K_{\text{O}_2}[\text{O}_2]} \tag{27}$$

where Φ is the fraction of photons generating e^-/h^+ pairs; I_a^n is the illumination intensity, where $n = 1$ for low light fluxes; βA_p is the fraction of the catalyst particle surface (A_p) irradiated; τ_{OH} is the lifetime of $^\bullet$OH radicals; K_{ORG} and K_{O_2} are the respective adsorption coefficients for the organic molecule and molecular oxygen; the species S comprises the initial organic substrate, the intermediates formed, the final product(s), the solvent and any ions present in the suspension; K_i are the appropriate adsorption coefficients for the different species.[61]

As mentioned above, although Eq. (27) is reminiscent of the Langmuir–Hinshelwood relationship, this is not conclusive for the operational mechanism in heterogeneous photocatalysis.

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IV. PHOTOCATALYTIC TRANSFORMATION OF INORGANIC SUBSTANCES

Photocatalytic processes may transform/recover inorganic substances from the environment. Specifically, H_2S and CN^- can be converted in less toxic materials and various strategic and/or toxic metals can be recovered from waste effluents.

A. Photocatalyzed Transformation of Hydrogen Sulfide

Hydrogen sulfide is a group VI hydride and like water is a potential source of hydrogen, an excellent energy vector. It is a major un-

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wanted constituent of natural gas and is the principal product in the hydrodesulfuration of petroleum and coal. Its toxicity is comparable to that of HCN and its impact on the environment must also be assessed for its role in equilibria involving SO_2 and thus on acid rain.

Unlike water, oxidation of H_2S is thermodynamically facile. In the presence of light and a semiconductor catalyst, the oxidation products are molecular hydrogen and sulphur.

The reaction has been examined in some detail using CdS as the photocatalyst.[62] Although CdS is not a particularly good electrode for water reduction, photo-evolution of H_2 does proceed at reasonable rates without the intervention of a redox catalyst (Pt or RuO_2). The complete cleavage of H_2S at pH 14 in the presence of SO_2 yields dihydrogen and thiosulfate, $S_2O_3^{2-}$, in a 1:1 stoichiometric ratio (reaction (28)).

$$S^{2-} + SO_3^{2-} + 2\,H_2O \xrightarrow{2\,h\nu} S_2O_3^{2-} + 2\,OH^- + H_2 \qquad (28)$$

Coupling the process in reaction (28) with one capable of recycling the $S_2O_3^{2-}$ back to S^{2-} and SO_3^{2-} can sustain dihydrogen evolution in a cyclic system (reaction (29)).

$$3\,H_2O + S^{2-} \xrightarrow{h\nu} SO_3^{2-} + 3\,H_2 \qquad (29)$$

No accumulation of S and $S_2O_3^{2-}$ would take place in such a photosystem. By operating with two semiconductors to accomplish vectorial displacement of charges, the visible light-induced process leads to a more efficient conversion of H_2S.[64] This strategy, called Interparticle Electron Transfer (IPET), is depicted in Fig. 3 and is summarized by reactions (30)–(34) for H_2S.

$$CdS \xrightarrow{h\nu} e^-_{(CdS)} + h^+_{(CdS)}, \qquad (30)$$

$$2\,h^+_{(CdS)} + S^{2-} \rightarrow S, \qquad (31)$$

$$2\,e^-_{(CdS)} + 2\,H_2O \rightarrow H_2 + 2\,OH^-, \qquad (32)$$

$$e^-_{(CdS)} + TiO_2 \rightarrow e^-_{(TiO_2)} + CdS, \qquad (33)$$

$$2\,e^-_{(TiO_2)} + 2\,H_2O \rightarrow H_2 + 2\,OH^-. \qquad (34)$$

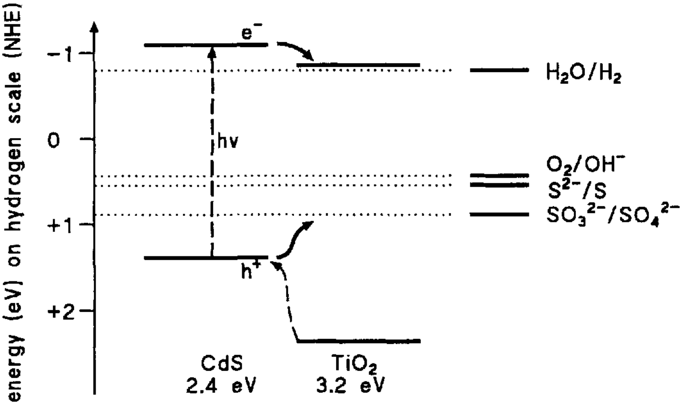

FIGURE 3 Flatband potentials of CdS and TiO_2 at pH 14 and 0.1 M Na_2S in aqueous media. Positions of other redox couples are also indicated.

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An energy conversion efficiency of 1% is attained; in the presence of SO_3^{2-} ions the efficiency is about 2%. Through the combination of the two semiconductors, the extent of e^-/h^+ recombination is diminished. Charge separation is achieved through the selective transfer of e^- from CdS to TiO_2; the transfer of h^+ is thermodynamically inhibited.[64a] An analogous process was noted in the photo-oxidation of alcohols[64a]; the coupled semiconductor materials are CdS and platinized TiO_2. The IPET strategy in photocatalysis has since been confirmed photoelectrochemically[65] by photoconductance[66] and by spectrofluorimetric techniques.[67]

Evolution of H_2 occurs with a quantum efficiency of ≈23% and an energy conversion efficiency close to 3% for a Rh-loaded CdS catalyst in alkaline media of H_2S and SO_2 has been achieved.[64d] The high quantum yield and the facile preparation of the CdS/Rh catalyst make it practical in photogenerating H_2 and disposing of two hazardous pollutants like H_2S and SO_2.

B. Photocatalyzed Conversion of Cyanide

As is well known, cyanide is extensively used in mining, electroplating and other industries, and its safe destruction often poses significant problems. Photocatalytic oxidation can be a potentially promising option and this procedure is receiving renewed attention.

In the early studies on CN^- photocatalytic oxidation on TiO_2,[68] quantitative formation of cyanate was established, according to

$$CN^- + 2\,OH^- + 2\,h^+ \rightarrow OCN^- + H_2O. \tag{35}$$

Although cyanate is expected to further oxidate, more investigations confirmed or assumed this finding.[69] More recent work has shown that cyanate is quantitatively photo-oxidized to carbonate. Since nearly all the organic materials in aqueous aerated suspensions of irradiated TiO_2 are oxidized to carbon dioxide, this result is not surprising. However, a different fate has been suggested for the nitrogen. Whereas oxidation to molecular nitrogen has been proposed in two works,[70] formation of nitrate via nitrite has been shown[71] according to

$$OCN^- + 3\,H_2O + 6\,h^+ \rightarrow NO_2^- + CO_2 + 6\,H^+, \tag{36}$$

$$NO_2^- + H_2O + 2\,h^+ \rightarrow NO_3^- + 2\,H^+. \tag{37}$$

Since reaction (36) necessitates six holes, more steps are to be considered and several (labile) intermediates are possibly formed.

When cyanide is complexed by metal ions, as in jewellery wastes, photocatalytic disposal requires previous treatment with peroxides and/or addition of a hole scavenger, like methanol, in order to accomplish total reduction of the complexes.[72]

An alternative photocatalytic route uses another waste (H_2S) as the oxidizing agent. The catalyst is CdS/Rh, which can be irradiated with visible light. The efficiency of the system is quite high.[73] The stoichiometry of the transformation reaction is

$$CN^- + S^{2-} + 2\,H_2O \xrightarrow[\lambda > 405\ \text{nm}]{\text{CdS/0.2 wt\% Rh}} SCN^- + H_2 + 2\,OH^-. \tag{38}$$

The photogenerated holes oxidize sulfide and mediate the CN^-

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to SCN^- conversion. Conduction band electrons reduce water to H_2 and are involved in e^-/h^+ recombination.

C. Photocatalytic Reductions and Selective Recovery of Metals

Near UV-irradiation of semiconductor suspensions containing soluble metal complexes represents a viable route for the deposition of noble metals on the catalyst[74] and for investigation of the electron scavenging process. In particular, kinetic and mechanistic studies have been done for the deposition of Pt on UV-irradiated TiO_2 suspended in aqueous $PtCl_6^{2-}$ solutions[75] under different conditions of light intensities, salt concentrations, and pH, among others. Deposition occurs in two stages: a rapid initial process followed by a second slower process in which the rate is less sensitive to process parameters. The main conclusions are (a) the initial rate of Pt deposition varies as the square root of the light intensity, (b) the quantum yield of the process varies only slightly with initial $[PtCl_6^{2-}]$ (for a 10-fold increase) and decreases with increasing pH, (c) the ionic strength affects only the slower second stage with greater efficiencies at the higher ionic strengths, (d) both stages of the deposition process are temperature dependent, (e) the presence of O_2 decreases the rate of the initial deposition but has no effect on the slower process, and (f) increasing photocatalyst (TiO_2) loading increases the quantium yield of the process. From a practical standpoint, the optimal conditions for the photoreduction and deposition of Pt on irradiated TiO_2 are low pH, low light fluxes, high ionic strength, low oxygen content and higher than ambient temperatures.

The photocatalyzed reduction and deposition of Pt on TiO_2 using different Pt(IV) complexes (H_2PtCl_6, Na_2PtCl_6, $H_2Pt(OH)_6$, and $Pt(NH_3)_2$–$(NO_2)_2$) have also been examined; for the latter Pt(II) complex the rate of deposition is smaller than for the Pt(IV) species.[76]

A potential and attractive practical application of the light-driven reduction process is in the recovery of metals of strategic and economic importance (Pt, Pd, Cr, Au, Rh, Ag, and others) from industrial waste effluents. The method affords selective recovery of one specific metal over others in solution by appropriately chosen experimental conditions: pH, O_2 presence, electron donors

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(e.g., methanol) and TiO_2 amount. The metal is reduced on the particle surface and is subsequently extracted from the slurry by mechanical and/or chemical means (aqua regia).[77]

For their environmental concern, Pb(II) and Hg(II) will be described in more detail.

C.1. Lead(II)

Lead(II) in aqueous suspension of platinized TiO_2 is both reduced to Pb(0) on the platinum islands, in the absence of which no removal occurs, and is oxidized to PbO_2 by valence band holes as well as by $O_2^{\cdot -}$ radical species (see Fig. 4). An optimal pH = 3.7 has been found.[78] The concentration of Pb^{2+} remaining in solution after irradiation of a platinized TiO_2 suspension at various initial pH's is depicted in Fig. 5.

C.2. Mercury(II) and Methylmercury(II)

Mercury and its salts have attracted much attention as environmental contaminants. Their removal from aqueous media is efficient in air-equilibrated suspensions of TiO_2 on irradiation by AM1

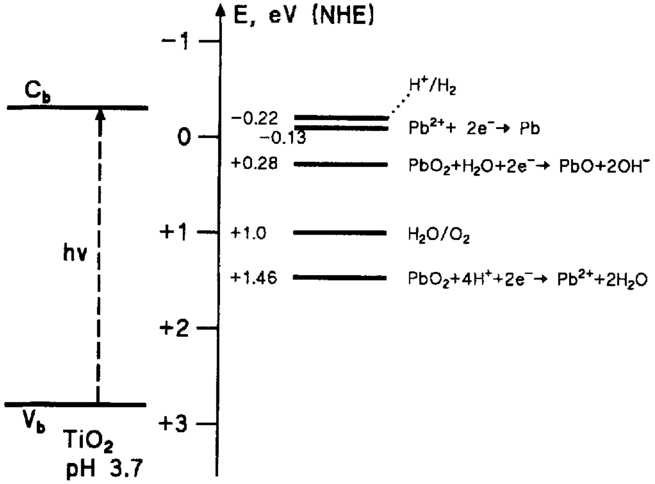

FIGURE 4 Flatband potentials of TiO_2 anatase at pH = 3.7 and some relevant redox couples of water and lead species.

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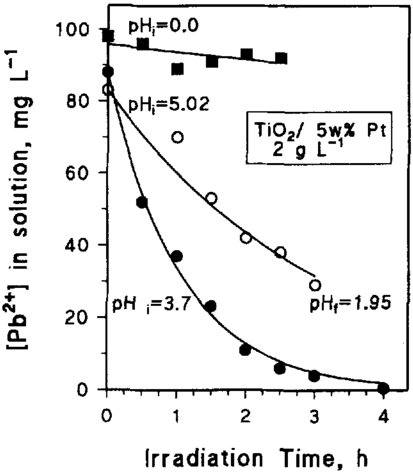

FIGURE 5 Plots of Pb^{2+} concentration remaining in solution against irradiation time for aqueous TiO_2/5 wt.% Pt dispersions. Concentration of photocatalyst, 2 g/L. From Ref. 78.

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simulated sunlight, on alteration of the pH and on addition of methanol to the slurry.

The chemistry of Hg(II) is complex and is very sensitive to the nature of the medium. In aqueous media and at natural pH, $HgCl_2$ is 99% undissociated. Only 1% of $HgCl_2$ exists as Hg^{2+} (K_{diss} = 6.0×10^{-14}). In 1 M Cl^- media, $HgCl_4^{2-}$ predominates. However, in 0.1 M Cl^-, the species present are $HgCl_2$, $HgCl_3^-$, and $HgCl_4^{2-}$. Some of these species hydrolyze in water (reaction (39)); $[Hg^{2+}] = [Hg(OH)_2]$ at pH 3.0.

The photoreduction of $HgCl_2$ in air-equilibrated TiO_2 aqueous suspensions (initial pH 4.65) occurs efficiently in <20 min of irradiation. Photoreduction of 0.5 mM of Hg(II) yields 1 mM H^+ as per the stoichiometry of reaction (39); the final pH after total disposal of Hg was 3.0.

$$\mathrm{Hg(II)} + \mathrm{H_2O} \xrightarrow[\mathrm{TiO2}]{h\nu} 2\,\mathrm{H^+} + \tfrac{1}{2}\,\mathrm{O_2} + \mathrm{Hg(0)} \qquad (39)$$

At pH 0, no photoreduction in aqueous media and no adsorption of $HgCl_4^{2-}$ takes place. Addition of 20 vol.% methanol leads to total reduction in ca. 3 hrs. At more alkaline pH's, photoreduction occurs but in a very complex way, the result of complex and varied nature of the chemistry of the mercury species present.

The elimination of Hg(II) from aqueous solutions by photocatalytic action of UV-irradiated WO_3,[80] ZnO[81] and TiO_2[77f,80] has been reported under various conditions.

The aqueous chemistry of $CH_3Hg(II)$ chloride is mostly dominated by pH-dependent reactions yielding the species CH_3HgOH, $(CH_3Hg)_2OH^+$, CH_3Hg^+ and CH_3HgCl (pH 5.7). Methylmercury(II) is not photoreduced at pH 5.7 in a TiO_2 aqueous suspension. In methanolic aqueous media, photoreduction occurs readily and complete elimination of the $CH_3Hg(II)Cl$ occurs after 30 min of AM1 solar illumination. The stoichiometry of the reduction is indicated in reaction (40):

$$CH_3HgCl + H_2O \xrightarrow[TiO_2]{h\nu} \tfrac{1}{2}O_2 + H^+ + Cl^- + Hg + CH_4. \qquad (40)$$

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V. PHOTOCATALYTIC DEGRADATION OF ORGANIC COMPOUNDS

The extraordinary oxidizing properties of holes in semiconductors like TiO_2 can promote easy oxidation and degradation of organic materials. Complete mineralization, that is stoichiometric formation of carbon dioxide and eventually of inorganic anions, has been observed in aqueous aerated dispersions of TiO_2 under band gap illumination. Water and O_2 are crucial for complete mineralization.

The stoichiometric equation (41) generally holds for an organic compound of general formula $C_nH_mO_p$:

$$C_nH_mO_p + \left(\frac{(m-2p)}{4} + n\right)O_2 \rightarrow n\,CO_2 + \frac{m}{2}H_2O. \qquad (41)$$

In the case of organic compounds containing halogens, the corresponding halide is formed according to

$$C_nH_mO_pX_q + \left(\frac{(m - 2p)}{4} + n\right) O_2 \rightarrow n\,CO_2 + \frac{(m - q)}{2} H_2O + q\,HX. \quad (42)$$

Whereas sulfur and phosphorous are recovered as sulfate and phosphate irrespective of their initial oxidation state, nitrogen has a more intriguing fate, as will be mentioned below.

Many classes of compounds of low to medium molecular weight, both aliphatic and aromatic, have been so far investigated. An exhaustive list of investigated compounds has been reported in recent reviews.[11d,48,82]

The intermediates identified by HPLC methods, together with the present status of knowledge of events on semiconductor particle surfaces, at least for TiO_2, permit the inference of mechanistic pathways. There are two adsorption sites on the surface of the TiO_2 photocatalyst particles. Organics adsorb on surface hydroxyls,[83] while molecular O_2 (and other electron acceptors) adsorbs on the Ti(III) sites[84] giving $O_2^{\cdot -}$. Taking phenol as a model substrate, our views on the most plausible events in a typical photocatalyzed oxidation process are illustrated in Scheme I.[85]

Phenol is dissociatively chemisorbed on a surface Ti^{IV} displacing an OH^- surface group. Following irradiation, the photogenerated e^- and h^+ are subsequently trapped: the electron as surface Ti^{III} (e_{tr}^-) and the hole as a sub-surface lattice $Ti^{VI}\text{–}O^{\cdot -}\text{–}Ti^{IV}$ entity (h_{tr}^+), and this in competition with e^-/h^+ recombination. Adsorbed molecular O_2 scavenges the surface trapped electron to give $O_2^{\cdot -}$ which yields the $HO_2^{\cdot}$ radical in acid media. The h_{tr}^+ species may now oxidize directly either the chemisorbed phenoxide to give the phenoxyl radical[28] (step a) or the surface $Ti\text{–}OH^-$ groups to give a chemisorbed $^{\cdot}OH$ radical (step b) which in turn may produce the phenoxyl, the dihydroxycyclohexadienyl, and the semiquinone radicals, all of which have been observed for pentachloro- and

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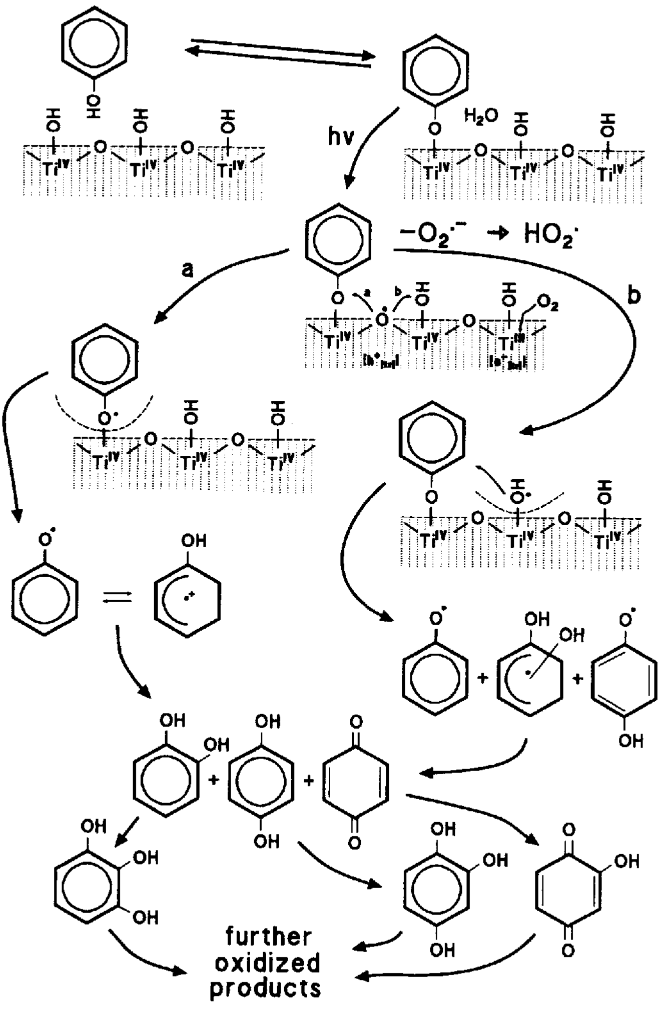

SCHEME I

pentabromophenols.[86] The available data suggest this primary oxidation event occurs at the particle surface; unfortunately nothing is known about whether the subsequent steps are surface related or take place in solution.

Scheme I also notes that hydration of the phenoxyl radical to the same intermediate products (catechol, hydroquinone and benzoquinone, and others[22]) as those from $^{\bullet}OH$ radical oxidation of the $Ti^{IV}-O-Ph$ moiety, establishes that product analysis is indeed silent as to the course of events in photo-oxidation. Continued oxidation of these intermediate products ultimately yields carbon dioxide. At some point along the photo-oxidation path, the phenyl ring cleaves to form various aliphatic aldehydes and carboxylate species.[87]

The greater number of intermediate products identified for the fluorinated phenols permits a description of plausible pathways for their ultimate photo-oxidation to carbon dioxide and fluoride.[23] Scheme II summarizes the events that lead to the formation of the aromatic intermediates, by analogy with a pulse radiolytic study on pentahalophenols.[86]

The first step (a) in Scheme II yields a fluorodihydroxycyclo-

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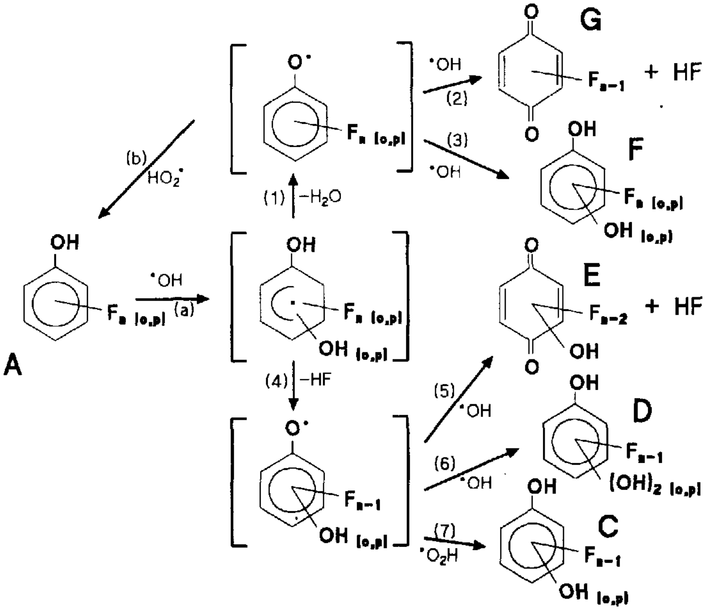

SCHEME II

hexadienyl radical which through loss of H_2O (step 1) forms a phenoxyl radical intermediate; this can interact with the $HO_2^{\cdot}$ radical (see Scheme I) to give back the original substrate. Further attack of the $^{\cdot}OH$ radical on the phenoxyl radical species products G and/or F. Loss of fluoride occurs in the formation of G to give benzoquinone for the monofluorinated phenols (observed for 4-fluorophenol). The expected products from intermediate F are fluorocatechol and fluorohydroquinone as seen for the monofluorophenols but not for the difluorinated analogs. Loss of fluoride by the cyclohexadienyl radical (step 4) yields a fluorohydroxyphenoxyl radical which interacts further with $^{\cdot}OH$ radicals to give E (step 5) and D (step 6), while reaction with $HO_2^{\cdot}$ gives C (step 7). Species E is not a possible intermediate for the monofluorophenols, but difluorophenols would produce hydroxybenzoquinone (not observed). For the monofluoro analogs, D gives trihydroxybenzene, observed for both 2-FPh and 4-FPh. No fluorinated trihydroxybenzenes were identified[23]; these species must

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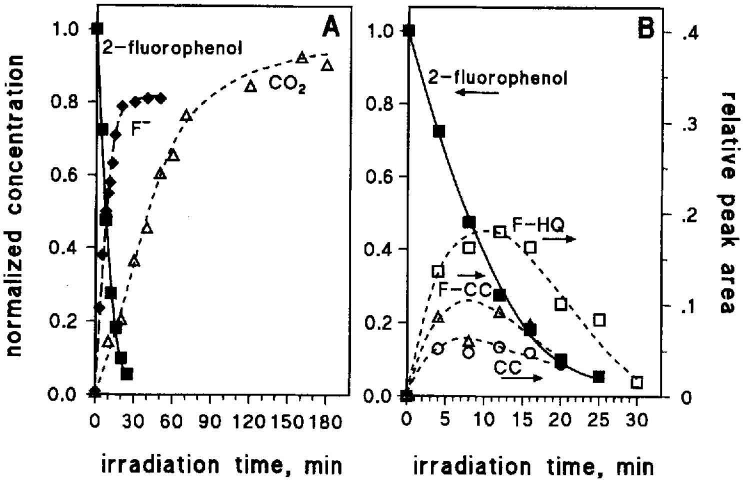

FIGURE 6 (a) Degradation of 2-fluorophenol, formation of fluoride and carbon dioxide in the presence of 100 mg L^{-1} of illuminated TiO_2 at initial pH 3. (b) Degradation of 2-fluorophenol and time evolution of some selected intermediates (F-HQ = 2-fluoro-1,4-benzenediol, F-CC = 4-fluoro-1,2-benzenediol, CC = 1,2-benzenediol) in the presence of 50 mg L^{-1} of illuminated TiO_2. Adapted from Ref. 23.

be thermally unstable as are the trihydroxybenzenes which rapidly oxidize and fragment to aliphatic species. In the case where C forms, the intermediate products are hydroquinone for 4-FPh and cathecol for 2-FPh. For the difluorinated phenols, both fluorohydroquinone and fluorocatechol were identified.[23] Figure 6 shows the disappearance of the initial compound (2-fluorophenol), the time evolution of some intermediates and the formation of final products.

A. Nitrogen Containing Compounds

Titanium dioxide mediated illumination of organic compounds containing nitrogen heteroatoms yields both ammonia and nitrate ions. The relative concentration of these species depends largely on the nature of the nitrogen atom in the compound, illumination time and initial solute concentration. Aliphatic amines produce a higher ammonium to nitrate concentration ratio than compounds containing ring nitrogen. This showed that reactions involving ring nitrogen compounds are more complex and that there are significant reaction paths leading to nitrate ions in addition to ammonium ions. The nitrate ion formed at significant rates in the photocatalytic oxidation of ammonia and at much lower rates than from ammonium ions. Nontrivial quantities of ammonium ions were found with the photocatalytic oxidation of compounds containing nitro and nitrate groups. Although the conversion of ammonia to nitrate was facile, the reverse process was not. The conversion of nitrate to ammonium ion was enhanced when the reacting solution contained a hole scavenger.[88]

A particular case in which complete transformation into inorganic ions is not realized is represented by the class belonging to s-triazine derivatives.[89] Under oxidative photocatalytic conditions the trihydroxyderivative, i.e., cyanuric acid, is formed. This product is remarkably stable to further degradation at wavelengths of irradiation above 300 nm.[90]

In conclusion, with the exception of these triazines, all the elements present in low to medium molecular weight organics are converted to their inorganic forms under TiO_2 mediated photocatalytic oxidative conditions, e.g., carbon is converted to carbon dioxide, sulfur to sulfate, phosphorous to phosphate, halogens (F,

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Cl, Br) to halides and nitrogen to both ammonium and nitrate ions.

VI. MATERIALS FOR PHOTOCATALYSIS

A. Different Preparations of the Photocatalysts

Expression (27) implies that the properties of the catalyst surface will have a strong influence on the overall efficiency of a material destined to perform a photocatalytic degradation. Specifically, these properties can be summarized into four categories.

(1) Electronic properties: Quantum yield of light absorption by the photocatalyst (Φ).

(2) Textural properties: Surface area of the catalyst (A_p) and the fraction of the irradiated surface (β).

(3) Active species generation: Lifetimes of active species (e^-/h^+ pairs, radicals),[1,56] rate of generation of electrons and holes at the surface (k_{trap}); rate of e^-/h^+ recombination (k_{rec})[91]; the presence of recombination centers, or dopants, or retardants; the presence of surface states and surface species formed in the process.[6,20] The effect of mechanical and chemical etching on the photonic efficiency and on the recombination rates has been described.[92]

(4) Surface chemistry: A molecular architecture during the interfacial catalysis as favorable as possible (k)[93]; adsorption of the organic molecule,[94] and adsorption of anions and solvent which are poised at the surface ready to compete for the available catalytic sites where the degradation process originates (K_i). In addition and not least, there is also the adsorption of molecular O_2 (K_{O_2})[95] and/or other electron scavengers; the surface density of hydroxyl groups[96] which reflects (but is not necessarily equal to) the concentration of catalytic sites which will influence k_{trap}.

Wherever different semiconductor materials have been tested under comparable conditions for the degradation of the same compound, TiO_2 has generally exhibited the highest activity.[97] Only ZnO possesses an activity similar to that of TiO_2 which has also been observed for chlorofluoromethanes and chloroaromatic derivatives.[98] However, zinc oxide dissolves in acidic and alkaline solutions[99] and therefore cannot be used for most technical appli-

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cations. The anatase modification of titanium dioxide shows much higher photocatalytic activity than the rutile form,[100] which has been explained by a faster recombination of charge carriers in rutile and also by a considerably lower amount of reactants adsorbed on the surface of the semiconductor particle. The latter effect can be rationalized by a lower number of surface hydroxyl groups present on rutile. Different anatase samples show different photocatalytic activity and properties.[95b,100,101] It should be pointed out at this point that only relative values for the efficiency of a particular photocatalytic system are given in the majority of the literature cited above. Absolute determinations of quantum yields are usually not presented, and the available experimental details are normally not sufficient to estimate yields. Therefore it is almost impossible to compare data from different laboratories. However, a detailed discussion of this argument is available.[61]

Titanium dioxide, the material with the highest photocatalytic detoxification efficiency, is a wide band gap semiconductor ($E \cong 3.2$ eV). Thus, only light below 400 nm is absorbed and capable of forming e^-/h^+ pairs.[102] Therefore only less than 5% of the solar energy reaching the surface of the earth could, in principle, be utilized when TiO_2 is used as a photocatalyst. Hence it is evident that, especially for solar applications, other materials have to be found or developed which exhibit similar efficiencies as anatase but possess spectral properties more closely adapted to the terrestrial solar spectrum. Moreover, reactors using artificial light sources will be much cheaper in their setup and running costs when lamps with a radiant flux in the visible can be employed.

Unfortunately, the choice of convenient alternatives to substitute for titanium dioxide in photocatalytic detoxification systems is limited. The appropriate semiconducting material should

—not contain any toxic constituents,
—be stable in aqueous solutions containing highly reactive and/or toxic chemicals, and
—not be subject to photocorrosion under band gap illumination.

Generally, metal oxides fulfill these requirements rather well and have been shown to be extremely stable in an aqueous environment even under continuous illumination.[12] Unfortunately, most metal oxides are large band gap semiconductors or insulators.[103]

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Iron (III) oxide is one of the few exceptions, with a band gap energy of ca. 2.2 eV (for hematite, α-Fe_2O_3). Hence, α-Fe_2O_3 absorbs already in the visible below 560 nm. However, hematite particles exhibit satisfactory photocatalytic activity in a limited number of cases, e.g., for the oxidation of sulfite.[103] For most other reactions which have been studied, α-Fe_2O_3, which exhibits by far the highest photolytic activity of all iron (III) oxide modifications, shows very little if any photocatalytic action as compared with TiO_2 or ZnO.[103] Often, photochemical transformations in the presence of iron (III) oxides are well explained by the formation of light-absorbing surface complexes capable of LMCT or MLCT transitions rather than by their solid state properties.[104]

Following the early observations on the phototropy of titanates in the presence of transition metal impurities,[105] various attempts have been made to extend the action spectrum of the otherwise "ideal" photocatalyst, TiO_2, into the visible part of the absorption spectrum.[106] In particular, the incorporation of transition metal dopants at relatively high concentrations of ($0.1 \approx 10\%$) results in the anticipated visible light response of the material.[106a–i] Goodenough has presented a model using localized, metastable occupied states to explain these observations.[106e] Transition metal doping did not only result in a change of the material's absorption spectrum but also in its photochemical activity upon excitation in the visible. Several authors observed the generation of hydrogen and oxygen, detected the reduction of carbon dioxide and of molecular nitrogen (to ammonia).[106j–l] While most of the authors agreed that Cr-doped TiO_2 was the most active material for the above transformations, it was recently shown that the addition of Cr ions is detrimental to the photodegradation of phenol.[106l] Following an earlier observation that doping with 0.5% Fe(III) augments the charge-carrier lifetime in titanium dioxide from 30 ns to minutes or even hours,[106m] it has been assessed that, whereas the presence of less than 0.5% iron ions is beneficial to the photoreduction of methylviologen (MV^{2+}), an increased amount of iron sharply reduces the MV^+ yield.[106n] Various iron/titanium photocatalysts have been prepared and their structural and morphological properties were extensively investigated.[106o–q]

Investigations of the effect of transition metal doping on the material's activity as a potential photocatalyst for the detoxification

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of polluted water have only been started recently. Using Nb-doped membranes, a drop in the rate of degradation of 3-chlorosalicylic acid compared with an undoped membrane was observed.[106s] On the other hand, a considerable increase in the rate of degradation of dichloroacetate was observed when Ti(IV)–Fe(III) mixed oxide colloids have been employed instead of pure TiO_2 colloids as photocatalysts.[107] However, photodissolution of these mixed oxide colloids is still a serious drawback of these novel catalysts.

Several other attempts reporting on the photocatalytic activity of mixed oxides based on TiO_2 are present in the literature.[108] Incorporation of microcrystalline TiO_2 into sheet silicates of clay exhibited higher photocatalytic activity toward isopropanol dehydrogenation and decarboxylation of carboxylic acids.[109] Another approach to improve the photocatalytic activity of titanium dioxide involves the deposition of minute amounts of noble metal on its surface, like silver[110] and gold.[111] This treatment does not extend the spectral response above the limit determined by the band gap energy, but efficient visible light sensitization of TiO_2 can be achieved by surface complexation with, e.g., transition metal cyanides.[112]

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B. Supported Catalysts

The vast majority of the studies reported so far have been carried out in aqueous suspensions of small semiconductor particles. From a practical viewpoint, however, an immobilized catalyst would be preferred (if it exhibits similar photocatalytic activity) since its separation from treated water would be simplified. Several different methods for the immobilization of the photocatalyst have been described in the literature.[106o,113–116] Most of the authors coated the surfaces of plates, coils, tubes, or glass beads with TiO_2 particles. TiO_2 membranes were also prepared. Recently, millimeter-sized TiO_2 beads have been prepared showing satisfactory photocatalytic activity.[101] Generally, the efficiency of the overall process decreases as the catalyst is immobilized, e.g., suspended particles exhibit a fourfold higher rate for the reduction of chromium(VI) than the respective membrane system. It is not clear whether mass-transfer limitations can account for all these differences.

VII. SOLAR DRIVEN PILOT PLANTS

Various reactor designs have been tested, initially by Matthews, for their applicability in solar driven pilot plants.[117] He compared the efficiency of titanium dioxide attached to glass mesh with that of a thin film coated on the inside of a glass coil using a parabolic trough solar concentrator. In his study with the model compound salicylic acid, the maximum destruction rate was achieved with the glass coil set up. The latter reactor type has in fact been chosen for the first solar detoxification loops constructed in the US at Sandia National Laboratories in Albuquerque[118] and in Europe at the Plataforma Solar de Almeria/Spain.[119] While the glass-tube trough system indeed exhibits considerable activity for the destruction of the model compounds salicylic acid,[118a] trichloroethylene[118b] and pentachlorophenol,[119] an alternative falling film/heliostat system tested under comparable conditions permitted even higher degradation rates.[118] A similar falling film reactor has recently been constructed at the University of Campinas, Brazil and showed very high activity for the degradation of dichloroacetate.[107] However, much remains to be done to understand the events during degradation processes that employ concentrated sunlight.[120] Very little is known about high temperature and/or high light intensity photochemistry.

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VIII. CONCLUDING REMARKS

Heterogeneous photocatalysis represents a promising route for the conversion of organic and metalloorganic contaminants to harmless mineral products and to retrieve precious and strategic metals from dilute solutions and/or industrial effluents.

This comment has attempted to give some information on the complexity of the photochemical and photophysical events that occur when an aqueous semiconductor dispersion is irradiated with light of proper wavelengths in the presence of various solutes. Although many questions concerning the primary events and the degradation mechanism remain to be definitely answered, research on photocatalytic materials (new photocatalysts, different preparations and treatments, doping, sensitization, supported catalysts) coupled with reactor design should contribute to demonstrate the feasibility of this decontamination process.

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