ELSEVIER

Catalysis Today 39 (1997) 219–231

CATALYSIS TODAY

Supported titanium oxide as photocatalyst in water decontamination: State of the art

Roberto L. Pozzo, Miguel A. Baltanás, Alberto E. Cassano*

INTEC (Instituto de Desarrollo Tecnológico para la Industria Química), UNL and CONICET (Universidad Nacional del Litoral and Consejo Nacional de Investigaciones Científicas y Técnicas), Güemes 3450, 3000 Santa Fe, Argentina

Abstract

Over the last two decades the interest on systems based on supported titanium oxide as a photocatalyst for water decontamination has grown significantly. A variety of supporting materials, coating methods, and reactor arrangements have been investigated from engineering as well as from more fundamental points of view. A thorough search of the published reports of these investigations was carried out and they are analyzed in this paper. An overview of the state of the art in the subject is given. © 1997 Elsevier Science B.V.

Keywords: Water decontamination; Supported photocatalyst; Titanium dioxide

1. Introduction

The photocatalytic degradation of different toxic organic compounds – particularly chlorinated ones – has been proposed as viable alternative in the decontamination process of either waste water or drinking water for human use (see for example [1–4]). Indiscriminate use of agrochemicals, inadequate industrial waste disposal and even the worldwide employed method of potabilization by using chlorine are the main causes for the pollution of water sources.

The UV activation of a finely divided semiconductor, usually titanium dioxide, in intimate contact with an aqueous solution of the pollutants, develops a redox environment capable of oxidizing them into nontoxic substances such as carbon dioxide, hydrogen chloride and water.

Basically, the process is initiated by the photogeneration of hole/electron pairs in the semiconductor valence and conduction bands, respectively, upon absorption of UV light with energy equal to or higher than the corresponding band gap (>3.2 eV). Energized electrons and holes may either recombine, dissipating energy, or be available for redox reactions with electron donor or acceptor species adsorbed on the semiconductor surface or being nearby in the electrical double layer surrounding the particle [5,6].

Charge carrier pairs that avoid recombination are separated by the electric field created in the solid side at the semiconductor/liquid junction [7] which favors migration of holes to the illuminated zones and of electrons to the unlit zones of the semiconductor particle surface. It is generally accepted that the primary steps initiating the subsequent degradation processes are the formation, by hole trapping, of extremely reactive radicals (such as $^{\cdot}OH$) [8], in the highly hydroxylated semiconductor surface, and/or the

---

*Corresponding author. Tel.: (042) 559174/75/76/77; fax: +54 42 550944; e-mail: acassano@arcride.edu.ar

0920-5861/97/$32.00 © 1997 Elsevier Science B.V. All rights reserved.
PII S0920-5861(97)00103-X

direct oxidation of the pollutant species. Charge balance would be sustained by electron consumption via reduction of adsorbed oxygen species derived from dissolved molecular oxygen, or other electron acceptors.

Even though a rigorous understanding of all the complex mechanisms involved in this heterogeneous, photochemical system is not yet established, some technological applications have been developed which have demonstrated its feasibility.

The finely divided catalyst can be either dispersed in the irradiated aqueous solution as a slurry, or anchored on a suitable support as a fixed or fluidized bed. According to various reports [9–13], mainly from laboratory scale investigations, slurry type reactors seem to be more efficient than those based on immobilized catalyst. However, for engineering applications, there is an intrinsic drawback to the first option: the need of a post-radiation treatment of particle-fluid separation, for catalyst recycling and for the ultimate goal of obtaining a clean, powder-free water. Because of the small particle size of the catalyst usually synthesized by the industry (somewhere between 30 and 300 nm of particle size) the cost requirements for this downstream operation may even invalidate altogether the claimed energy saving for a solar induced decontaminating process.

Albeit phase-separation energy-costly processing can be avoided by using fixed or fluidized bed reactors with a supported catalyst, it is not less true that mass transfer limitations might outweigh this intrinsic advantage. Also, the catalyst surface availability for reactants and photons could be significantly better in a well mixed, pseudo-homogeneous small particle slurry than in any supported catalyst arrangement.

The penetration length of light in the solid–liquid medium is another important parameter, which is a function of particle size, catalyst charge (slurry concentration in one case, support surface coverage in the other) and support transparency to radiation, among other variables. Actually, given the complexity of the photocatalytic process, and the multiplicity of variables involved it is not an easy task to carry out an effective variable control and to find a common ground for comparison of supported vs. unsupported catalyst performances.

Many alternatives have been proposed in the last few years which have tried a variety of supporting materials and coating methods in different arrangements for the degradation of several organic compounds. A first valuable effort to systematize this field was recently presented by Bideau et al. [9].

It is the purpose of the present paper to give an actualized overview of the state of the art in this specific photocatalytic type of reactors in terms of its potential capability as a water pollution control technology.

2. General background

In general, it is assumed that a good supporting material for titania as a photocatalyst should have the following attributes: (a) to be transparent to UV radiation; (b) to favor strong surface chemical–physical bonding with the TiO_2 particles without negatively affecting their reactivity; (c) to offer a high specific surface area; (d) to have good adsorption capability for the organic compounds to be degraded; (e) to be in a physical configuration which favors the ultimate liquid–solid phase separation; (f) to allow reactor designs that facilitate the mass transfer processes; and (g) to be chemically inert.

Several substrates have already been proposed as catalyst supports for the photodegradation of water pollutants. Most of them are based on SiO_2 as raw material, either as a simple glass reactor wall [13–25] or in the form of sand [11,26,27] and silica gel [28–31]. Quartz optical fibers [32,33], glass fiber (in the form of mesh [34], fabric [35–38] or wool [39]), glass beads [9,40] and microporous cellulose membranes [41] were other experimented options. Some alumina clays [42], ceramics in the form of membranes [43–45] and monoliths [46,47], zeolites [48,49], and even stainless steel [50,51], anodized iron [52] and polythene films [53] have also been tried as bearing composites.

From the coating point of view, the ideal situation is given by two basic conditions: (1) a good adherence catalyst/support, and (2) no degradation of the catalyst activity by the attachment process.

The first quality is essential, since the support-catalyst junction should resist strain derived from particle to particle and particle-fluid mechanical interactions in the reactor environment, in order to avoid comminution and/or detachment of catalyst particles from the support.

Catalyst activity, of obvious and paramount importance, can be affected by several factors, for example:

- changes in the TiO_2 energy band structure because of chemical bonds with the support and/or the small particle size of the film;
- alteration of catalyst crystal structure (originated on temperature treatments for fixing);
- decreasing of catalyst active surface area due to catalyst particle agglomeration, and catalyst support binding; and
- catalyst particle trapping inside support micropores, where the radiation cannot penetrate.

Two main routes have been explored to fix the titania on any suitable support. In one of them, the fixing is intended by manipulation of previously made titania powder (PMTP). The other way is based on different alternatives of "in situ" catalyst generation such as the so-called "sol-gel process" (SGP), chemical vapor deposition (CVD) and grafting.

As the reactor system is a concern, a variety of configurations have also been investigated. Arrangements of the catalyst as fixed [6,26,29,34,37,39, 40,46,52], fluidized [27] and floating beds [54] were tested. In many cases, the fixed bed was on the same reactor wall [14–16,19–21,52,53], on the surface of fiber-optics cables [32,33,55] or covering a glass plate immersed in the reactor chamber [56] or an electrode plate in an electrochemically assisted photocatalysis [57,58]. A kind of membrane "sandwich" between "pyrex" plates [41] was also tried. The reactors were operated either in a batch mode (in some cases with recirculation) or in a continuous flow fashion.

3. Catalyst fixation by PMTP methods

The use of a previously made catalyst (PMTP) seems to be the simplest starting point to procure a support coating. The basic scheme for this alternative can be described as follows [9]: (1) an intimate mixing or contacting of aqueous TiO_2 suspensions with the support, usually in a microsized powder form; (2) filtering, evaporation or other solid–fluid separating operation; (3) drying of the adhered catalyst by heating; (4) flushing with the suspension liquid support; (5) drying once again; and (6) calcining at an appropriate temperature.

There is no clear understanding of the bonding forces acting at the catalyst/support interface when a PMTP is used. Electrostatic interactions between charged particles are probably involved [27] but it is possible that some kind of chemical bonding might also occur. In an investigation carried out by Siffert and Metzger [59] on the coating of fiber cotton liners with rutile (related with paper making), they found that van der Walls attractive forces were involved with fibers and that mainly rutile aggregates are retained. On the contrary, with tiny fibrils, electrostatic forces were predominant and individual particles were attached.

Some modifications to the above described approaches have been investigated, as for instance, the use of 2-isopropanol instead of water as suspension matrix in the coating of quartz sand [27]. An explicit reason was not given for this selection, but it is likely to be based on the higher volatility of this alcohol compared with that of water, facilitating the evaporation and drying operations. The authors reported good mechanical stability and an acceptable photoactivity for the coating they obtained.

Another interesting novelty – which will be referred from now on as the silane coupling (SC) method – was introduced by Jackson et al. [54]. Aiming at sea water cleaning from oil spills, they tried triethoxysilane (TES) as a binder between the previously made catalyst (powdery titania) and borosilicate or aluminosilicate glass hollow beads. The silane would develop bonding bridges upon reacting with hydroxide groups on both the catalyst and support surfaces. According to their procedure the glass beads are refluxed with TES and with TiO_2 powder in glacial acetic acid.

In a different approach Brezová et al. [20] immobilized a thin film, composed by Degussa P25 TiO_2 and polyvinyl acetate. In this approach the layer is formed by coating a photochemical reactor wall with a previous mix of titania powder and a commercial dispersion of the polymer, followed by drying and calcining. Initial decomposition rates of *p*-toluenesulfonic acid, used as a testing photoreaction, were reported as being independent of the initial concentration. This outcome was attributed by the authors to a lowering of the amount of the catalyst active surface sites because of fixation. It might be also due to mass transfer limitations, although this possibility was not analyzed in their work.

A porous thin film of nano-colloidal titania was developed by Matthews et al. [60] on conducting glass, by electrophoretic deposition from a Degussa P25 dispersion. In this approach a colloid is obtained by grinding a thick paste made of titania and 2-methoxyethanol in a ceramic mortar, and by subsequent dilution with the same solvent. After deposition, the film is aerated and annealed at 500°C.

Vinodgopal and Kamat [57], succeeded in building an optically transparent electrode, coated with a semiconductor thin film, by partially "painting" a plate of a conducting glass with a sonicated suspension of titania (Degussa P25), and by further drying in oven at 400°C. The said electrode was successfully employed by these authors in the photodegradation of acid orange 7,4-chlorophenol, and textile dyes [61] in a UV illuminated electrochemical cell, in which a biasing potential was applied.

An atypical and apparently simple technique for catalyst fixation on polymer membranes was proposed by Tennakone et al. [53]. In their work they coated a polythene film, functioning as the catalyst support, by a dry process. The method involves an even spreading of the powdery catalyst all over the support film by rubbing with a cotton wool, a subsequent ironing (with an iron plate at 74°C), followed by rinsing with sodium hydroxide, and washing out loosely bonded particles. The resulting coated film was tested after drying, in the degradation of phenol with promising results, according to the authors' reports.

4. Coating by in situ catalyst generation

The "in situ" formation of a TiO_2 deposit on the surface of any appropriate support, by the SGP, can be the result of a combined series of physical and chemical transformations of a precursor such as a titanium salt (usually an alcoxide) in adequate solvent and/or acid–base conditions. Major efforts on the development of this technique appeared many decades ago as a method to synthesize ceramics and glasses of several metal oxides (such as: Al_2O_3, SiO_2, and TiO_2) with high purity and great homogeneity [62].

These ceramics are the result of the combined process of simultaneous hydrolysis, polycondensation and drying of a colloidal suspension. By hydrolyzing the metal salt alcoxide a hydroxide sol is obtained, which can be gelated, dried and calcined. By an adequate handling of the sol-suspension it is possible to obtain a monolith type of structure. This technique is also employed in the development of film coatings such as indium tin oxide (ITO) on glass to improve insulation properties.

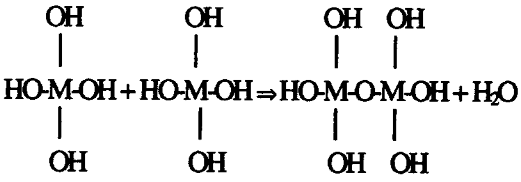
The general process for these metal oxide formations, either as self-supported structures or as a support coating, can be summarized as follows [63]:

1. Controlled hydrolysis of an alcoxide precursor.

   $$M(OR)_4 + 4H_2O \Rightarrow M(OH)_4 + 4R(OH)$$

2. Condensation by forming

   $\equiv M{-}O{-}M \equiv$ bonds :

   $$\mathrm{HO{-}\underset{OH}{\overset{OH}{M}}{-}OH + HO{-}\underset{OH}{\overset{OH}{M}}{-}OH \Rightarrow HO{-}\underset{OH}{\overset{OH}{M}}{-}O{-}\underset{OH}{\overset{OH}{M}}{-}OH + H_2O}$$

   (where M is the central metal and R is the hydrocarbon fraction)

3. Polycondensation with formation of colloidal (submicrometer) particles, by formation of a network of multiple M–O–M bonds. The particles size is mainly a function of pH and the [water]/[alcoxide] ratio.
4. Gelation, by formation of a three-dimensional structure, with linkage and properties determined by particle size and extent of gel cross linking.
5. Molding or coating of a suitable support.
6. Dehydration and densification by heating to temperatures as high as 1700°C with some ceramics.

Two different alternatives have been proposed for the first step (hydrolysis). In one of them the hydrolysis is brought about by adding alcohol with a small amount of water to the alcoxide solution, forming inorganic polymers. With the other option, the hydrolysis is made just in water, generating a particulate sol and a subsequent gelation.

In this last method, peptization of precipitates by acidification becomes necessary to obtain a stable colloidal solution. This effect is a consequence of the electrical charging of the hydroxide particles by proton adsorption, hence avoiding agglomeration and preserving small size particles. This method facilitates a highly uniform gelation process and a more coherent deposit or membrane structure.

With regards to the specific titania coatings, a sol-gel process has been adopted, based on the typical basic scheme described below. With some minor variants from one reference to another [9,23,56, 64,65]: an alcoholic colloidal suspension of an alcoxide is hydrolyzed to Ti(OH) by adding an acidic water/alcohol solution. The support is coated by the resulting sol directly onto the supporting surface. The titania deposit is then fixed by gelling through evaporation, drying and calcining.

Anderson and co-workers [12,22,23,43–45] carried out a research program aimed at developing supported and unsupported ceramic type membranes of TiO_2 by using an SGP. (A typical procedure is described in [21].) These ceramics were photochemically tested as thin films on the inner wall of an annular reactor [21], as a "screening" photoreactor (a glass plate covered with a TiO_2 ceramic film immersed in the reaction chamber) [66], as a coating on an optical fiber type of reactor [55] and as membrane functioning as a potential biased photoelectrode suspended on a Tin(IV) oxide-covered glass [58].

As a part of their program, this research group carried out systematic studies to elucidate the correlations between controlling variables of the sol-gel formation chemistry and sintering processes with the physicochemical properties of the resulting membranes [43,63,67,68].

The crystalline forms of the resultant TiO_2 depend on calcining temperature and atmosphere [69]. Heating in air atmosphere at temperatures in between 400°C and 600°C will preferentially produce anatase, while at more than 700°C, rutile will be predominant. However, by heating in a hydrogen environment, the crystal type dividing temperature range is confined between 525°C and 550°C.

Titanium chlorides ($TiCl_3$ and $TiCl_4$) were also tested as precursors, trying out two different routes: by hydrolyzing the chloride (in a sol-gel process type) and by CVD. As illustrative examples for the first alternative Sobzynski et al. [70] precipitated $Ti(OH)_3$ from $TiCl_3$ on SiO_2 and then oxidized to $Ti(OH)_4$ by oxygen bubbling; Munoz-Paez and Malet [71] precipitated a monolayer of TiO_2 on silica (Degussa Aerosil 200) from an acidified water solution of $TiCl_3$ by a controlled neutralization with a dilute solution of Na(OH). Castillo et al. [72] deposited titania on silica support by neutralizing with ammonium hydroxide an acidic $TiCl_4$ suspension and, alternatively, by evaporating a dispersion of $TiCl_4$ in *n*-hexane (grafting).

Quite representative of the CVD alternative is the investigation made by Anpo et al. [73] in the coating of porous Vycor glass by reacting $TiCl_4$ with superficial OH groups at the glass/gas interface at 453–473 K and further processing with water vapor to substitute the chlorides, and the work published by Jackson et al. [54] where borosilicate glass beads were exposed alternatively to $TiCl_4$ and water vapors in a fluidized bed arrangement at 300–500°C. Sato et al. [74] deposited titania in the form of ultrathin anatase films by CVD on fused silica and studied their photochemical properties. Photodeposition of silver from silver nitrate solution was used as the testing reaction by these investigators.

Thin films of ultrafine titania have been obtained on quartz and silicon substrates, by hydrolyzing and condensing titanium tetraethoxide, dispersed in a hydroxypropylcellulose polymer, in a mixture of alcohol and water [75]. Also, ultrasonic nebulization (USN), followed by pyrolysis of an alcohol solution of dipropoxy-titanium-*bis* (acetylacetonate) was the method chosen by Gao et al. [50] to deposit titanium oxide thin films on various plate substrates.

5. Supporting materials and performance of the titania coatings

5.1. *Different types of glass supports*

One of the first candidates that emerged as a supporting material was simply the glass reactor wall, probably due to the tenacious sticking capability between titania powder and the lab glassware, observed by numerous researchers in many laboratories around the world. According to Zeltner et al. [22] the strong adhesion between titania and Pyrex glass could be attributed to some kind of sintering occurring between the catalyst particles and the glass during the calcining process of these devices.

Glass coiled tubes, internally coated with catalyst [14–16,19] or annular cylindrical reactors, with coating in the inner tube [12,13,21,25] acted as continuous flow reactors in these arrangements, with the irradiation source localized either internally, coincident with the system axis, or outside [24] the reactor. An internally coated photochemical immersion well was also tried [20].

Using these type of reactors, initial rates and reaction mechanisms (Langmuir–Hinshelwood kinetics) were investigated for 22 common organic water contaminants [14,15], and for chlorinated phenols [16], dichlorvos [19] (organic insecticides), 3-chlorosalycilic acid [21], formic acid and anthracene [13], methyl vinyl ketone [25], TCE [24], and *p*-toluenesulfonic acid [20]. Boundary layer mass transfer limitations, inherent to this type of reactor system, were overlooked, in general, in these investigations (with some exceptions [15,16,19,21]). No reports are given about the performance regarding mechanical stability of the catalyst coating.

Massive glass beads (3 mm diameter) were also investigated as catalyst bearing material. They were tested either as a filling of the annular space (0.6 cm) between the irradiation source and the external cylindrical glass tube [16] (in a continuous flow fixed bed type of reactor) or as a layer at the bottom of the reactor illuminated from top to bottom [9].

In this last quote, the authors reported detachment of catalyst from the support during the reaction process, and a partial loss of photoactivity suffered by the titania in aqueous suspension after attachment and detachment treatments. They also found, in a vis-à-vis comparison of the two previously mentioned forms of coatings, PMTP (with TiO_2 Degussa P25) and SGP (from titanium tetra-isobutoxide), that the titania coating originated from PMTP was more stable mechanically but catalytically less active than that produced by the SGP. This last finding is in apparent contradiction with results reported by Dorion et al. [56], showing exactly the opposite trend in a similar testing, for titania deposited on a glass plate.

However, the apparently polemical results between these two papers should be taken with care, since the photocatalytic reaction rates with fixed catalyst were determined under conditions where both anchored and detached titania were present in the reaction vessel, in one case [9], and mass transport limitation effects were likely to be involved in both of them [9,56].

The increasingly serious ecological disasters generated by the spilling of oil on sea water from damaged freight vessels and/or by industrial accidents lead to the consideration of a solar assisted catalyzed clean up procedure as an alternative. Aiming at the development of an in situ photodegrading method, and since crude oil strongly absorbs in the UV [76], it came out as a requirement to keep floating the dense photocatalyst at the air/oil interface. Low density floating glass spherules emerged as a good alternative for making up a photocatalyst support. Jackson et al. [54] and Schwitzgebel et al. [77] investigated the performance of hollow glass microbeads for this purpose. The photooxidation of ethanol, and of several olefines were their testing reactions. Nair et al. [78] tested alumino silicate microspheres in the photooxidation of crude oils.

They studied different methods for coating: deposition from $TiCl_4$ by a CVD technique; the SC method and their own version of a PMCP deposition, identified by them as the "thermal attachment" (TA) method. According to their reports only the last two techniques yielded photocatalytically stable deposit for as long as two days of irradiation. Beads coated by the TA method performed the best.

Pretreatment temperatures and surface water content on glasses were variables considered relevant by these investigators. They concluded that the presence of superficial water favors the catalyst attachment to glass when CVD is used. Pretreatment temperatures higher than 400°C were necessary to produce an active catalyst. They also found that hydrogen chloride etching improved the performance of beads coated by the SC method but had no effect on those treated with the TA technique.

Based on SEM micrographs, Jackson and co-workers could show significant differences in the patterns of the coatings they obtained by different processing and supporting glasses. For instance, while the TA method yielded a quasihomogeneous film, covering the entire microbeads surface, deposits obtained by both the CVD and the SC techniques looked as an irregular and randomly distributed coating constituted by small isolated catalyst particles (0.5–1 μm), in the first case, and by titania aggregates in the second one.

5.2. *Fiber optics and quartz light guides*

An interesting concept for a catalytic reactor system was developed by Hofstadler and Bauer [79] and

Bauer [80] and by Peill and Hoffmann [32,33], based on quartz fiber optics coated with titania. In the arrangement of Hofstadler and Bauer, light is conducted by fused silica fibers coated with a sol-gel processed titania film, all of them placed inside a glass tube. Successive reflection/refraction phenomena at the fiber/titania interface would generate both catalyst excitation and light transport.

Peill and Hoffman conceived driving the light with a bundle of fibers through a reaction vessel via radial refraction while activating the catalyst particles on the fibers. Attachment of TiO_2 onto the previously exposed fiber cores was carried out by dipping them into an aqueous concentrated slurry of TiO_2 (Degussa P25), followed by drying and heating at temperatures ranging from 200°C to 500°C.

Both systems were photochemically tested in the degradation of 4-chlorophenol. The investigation of Hofstadler and Bauer focused on the influence on quantum yield of intensity and wavelength of light; temperature, addition of hydrogen peroxide and flow rate. Shorter wavelength (ranging from 280 to 320 nm), higher temperatures (ranging from 10°C to 60°C) and hydrogen peroxide addition favored higher reaction rates, whereas changes in the flow rate did not appreciably affect the quantum yield. In a comparison with a slurry of free catalyst the authors reported an apparently better performance for the fixed titania. However, this conclusions must be taken cautiously since comparable conditions were not guaranteed by the authors. The coating was reported as very stable without any appreciable loss of photochemical activity.

On the other hand, the thickness of the coating film, the extension of interfacial coverage, the angle of irradiation incidence on the tip of fibers [32], and the distribution of light as a function of fiber diameter were the parameters [33] found relevant by Peill and Hoffman in order to calculate quantum efficiency (which was claimed to be of the same order as that of a slurry reactor under declared comparable conditions). Quantum efficiency was defined by the authors as the ratio between the initial rate of reaction and the radiation absorbed by the catalyst.

From their conclusions, it follows that a compromise between a minimum coated area and the existence of a film thickness capable of absorbing most of the incident refracted photons should be achieved, together with an angle of irradiation close to 90°, in order to optimize the axial propagation of light, the catalyst surface activation and consequently, the quantum efficiency.

In a different approach to a quite similar concept, Tada and Honda [81] investigated the performance of a titania film coated on a 10 mm diameter quartz rod, which functioned as an internal light guide. By using SGP, they obtained a catalyst thin film of approximately 100 nm, and assessed its photocatalytic activity by monitoring the photodeposition of Pt (on the same catalyst surface) and the rate of decarboxylation of acetic acid. Its efficiency, defined here as the ratio of the rate of reaction to mass of catalyst, is reported to be up to 50 times higher (in the photodeposition of Pt) than that yielded by a P25 TiO_2 slurry reactor.

By SEM, TEM micrograph and electron diffraction pattern analyses carried out in the same work, the coating film was identified as anatase in a well-defined polycrystalline structure constituted by 50 nm particles involving smaller ones of less than 5 nm. The measured specific surface area was about three times larger than that of a P25 titania. The platinum deposited on the titania film was also characterized – via XPS analysis and by SEM micrographs – as a highly dispersed coating of particles of less than 2 nm size.

Tada and Honda also reported in their work, a significant efficiency enhancement in the decarboxylation of acetic acid by the catalyst photodoping with platinum. A similar behavior was reported by Aguado and Anderson [66], in the degradation of formic acid. The enhancement effect was attributed by the former authors to the inhibition of the charge carrier recombination by electron trapping on the metal surface [81]. However, the enhancement appeared to be more accentuated for the supported catalyst than for the free catalyst system. In addition, in the quartz rod supported titania, the efficiency increased with increasing amount of Pt and reached a plateau at about 16% by weight of metal deposition. In the slurry system, on the other hand, the same trend was observed, but a maximum in the reaction rate occurred at about 2% Pt w/w and then an abrupt efficiency decay was apparent when the Pt loading was increased further.

According to the authors, this behavior was quite expectable, since in the first arrangement the catalyst particles are illuminated from inside the quartz rod, and the Pt coverage would not interfere with light activation. On the contrary, in the slurry system the Pt free area available for light activation on each particle would compete with the opaque platinized area.

5.3. *Sands and silica gel*

Studies with titania immobilized on common beach sand were carried out by Matthews and McEvoy, under near UV [26] and sun illumination [31] by using an open dish illumination arrangement, and a PMTP coating method. Phenol [31] and "colored organic" degradation [26] were the testing reactions. No detachment of catalyst was reported after several days of reaction. However, this is not surprising since the fixed bed type of reactor used in these investigations does not severely strain the composite. Also, the degradation rate efficiency, almost three times lower with the immobilized catalyst than upon using a free suspension was reported. Mass transfer limitations in the first case were given as the main reason for this behavior.

Haarstrich et al. [27] investigated the behavior of commercial quartz sand, in a fluidized bed arrangement, in the photodegradation of 4-chlorophenol and *p*-toluenesulfonic acid. They also used a PMTP coating method. Good stability of the TiO_2 coating was reported for a reaction time as long as 2 h. No comparison of efficiency with other arrangements was given.

Silica gel was investigated as catalyst support by Matthews [30] in an annular tubular photoreactor for the destruction of several organic compounds, such as: fluorescein, salycilic acid, phenol, 4- and 2-chlorophenol, 2-naphthol and catechol. A method of PMTP deposition type was chosen for catalyst coating, with a final drying under vacuum at 368 K, without further calcining. The process in fact combines an adsorption chromatographic column with in situ photodegradation.

Crittenden et al. [28,29] tried also silica gel coated with platinized TiO_2 in a fixed bed type of arrangement in the photodegradation of several fuel contaminants of groundwater. A pretreatment of water with a filter and an ion-exchange resin to remove suspended particles and dissolved ionic species to prevent catalyst fouling and severe destruction inhibition was reported as necessary for the viability of the system. It is worth noticing that they also reported that catalyst fouling is partially photoinduced.

5.4. *Glass fibers*

Glass fiber cloth coated with titania was another catalyst support investigated in different arrangements. Murabayashi et al. [37] coated this type of material with titania by thermal decomposition of Ti-tetraisopropoxide. The test reaction systems were the degradation of chloroform dissolved in water. Some chemical bond between TiO_2 and SiO_2 was postulated from SEM and EPMA observations. Commercial fiberglass fabric covered with TiO_2 either by sol-gel technique or by PMTP processing was reported as mechanically stable materials by Brezová et al. [35,36], even under common ultrasonic treatment. They were tested in the photodegradation of phenol with a declared efficiency comparable to that of P25 slurry suspensions. However, a decrease of photoactivity was reported during repeated degradation experiments. This decrease, which was quite significant after 20 h of irradiation, was attributed by the authors to TiO_2 surface saturation with intermediate reaction products. It could be partially reversed, though, by further regeneration.

In a work carried out by Matthews [39] titania covered glass mesh was used to fill a cylindrical annular type of reactor to induce photodegradation of salicylic acid, phenol and chlorophenols by UV irradiation. The TiO_2 was attached by immersion of the mesh in a P25 suspension with further air drying. In a comparison between this arrangement and a coiled reactor internally coated by immersion with titania, the second one apparently performed better. Good performance was reported by Pugh et al. [34], who also tried fiberglass mesh as supporting material in the photodegradation of atrazine, in indoor and outdoor tests. Wyness et al. [82], on the other hand, have conceived a pond configuration for solar decomposition of 4-chlorophenol. In this case the TiO_2 loaded mesh is fixed close to the pond surface.

A summary of the referenced works classified by supports and deposition methods is given in Table 1.

Table 1
Catalyst supports and deposition methods

Supports			Deposition methods								
			PMTP					In situ generation			
								SGP		CVD	USN
Raw material	Physical form	Specific charact.	Water or alcohol immers.	SC by reflux.	Electro-foresis	Electro-deposit.	Dry coating	From alcoxide	From Ti(Cl)$_n$		
Glass	Reactor wall	Coiled tube	[14–17,19,39,76][a]								
		Annul. reactor						[12,13,21,23–25]			
		Immers. well	[20][a]								
	Beads	Massive	[9,17,85][a]					[9,40]			
		Hollow	[54,77][a]	[54]						[54]	
	Plate		[56,57][a]		[60]	[97]		[56,58,86]	[73]		[50]
Quartz	Fiber optics		[32,33][a]					[79,80,83]			
	Light guide rod							[81]			
	Plates							[86]			
Silica	Sand		[11,26,27,31,85][a]					[48,72]	[72]		
	Silica gel		[28,29][b][30,31,85][a]					[84]			
	Monolith							[47]			
Glass fibers	Cloth/Fabric		[36,37][a]					[36,38]			
	Mesh		[35,39,84][a]								
Cellulose	Membrane		[41]								
Zeolites	Grains			[48]				[48,49]			
Alumina	Ceramic composite	Annul. Cylind.						[42,48]			
Alumino silicates	Microspheres		[78]								
S. Steel	Plate							[51,86]			
Iron	Plate		[52][a]								
Polythene	Film						[53]				

PMTP: previously made titania process, SGP: sol-gel process, CVD: chemical vapor deposition, USN: ultra sonic nebulization.

[a] Degussa P25.

[b] Aldrich.

6. Fundamental studies on structure, morphology and preparation techniques of titania coatings as related to their photocatalytic properties

Many studies have been carried out aiming at elucidating the correlation among titania coating structure and morphology with preparation methods and resulting catalyst system performance. All kinds of spectroscopic studies (XPS, UV–vis, NZR, diffuse reflectance spectra, X-ray diffraction), electron microscopy, Z potential measurements and BET analysis, and many other analytical techniques have been used to help in understanding the relevant mechanisms and physicochemical variables which may control and ultimately lead to the development of stable coatings, with good catalyst efficiency and practical feasibility. In spite of that, there is not yet a clear understanding on how the structure and texture of supported titania affects its photoactivity.

Nevertheless, there is general agreement about the convenience of synthesizing homogeneous coatings with high specific surface area. As for the crystal structure, the anatase form of TiO_2 appears to be most efficient from the catalytic point of view. According to this, calcining temperatures not higher than 400°C would favor anatase crystal formation in unsupported films originated by SGP, and not higher than 600°C in glass supported films. However, there are still contradictory reports on how the particle size affects the catalyst photoactivity: Kim et al. [83] looked for larger crystal sizes which would favor charge transport. On the other hand, Anpo et al. [73] and Yasumori et al. [84] have argued in favor of small particles (of about single digit nanometer size) and consequently have privileged highly dispersed coating films.

There are also some studies on different supporting materials and their influence on the catalyst behavior. For instance, from the point of view of the supported catalyst performance a systematic investigation was carried out by Zhang et al. [85] considering five different silica based materials and various parameters such as particle size, catalyst dosage, support bonding and calcination temperature. Also, Xu and Langford [48] correlated the larger adsorptivity capacity of zeolites compared with alumina and silica gel to a better catalytic performance, whereas Fernandez et al. [86] carried out a comparative study of photoactivity and characterization of rigid supports made of glass, quartz and stainless steel.

Some basic investigations can be accounted as related to precursor/support chemical interactions in the sol-gel deposition, which supposedly affect the catalyst performance. Along this research line there are several recent papers published by Srinivasan et al. [87,88], Lassaletta et al. [89], Castillo et al. [72,90,91], Zaharescu et al. [92] and by Matsuo and Nakano [93] are typical representatives. Most of these investigations correlate these type of substrate/photocatalyst interactions with energy band gap alterations of the fixed TiO_2. The report by Zaharescu et al. focused on the influence of the sol-gel chemistry with different alcoxides and support materials on the optical properties of thin film titania coatings.

Munoz-Paez and Malet [71] have employed X-ray absorption spectroscopy to investigate the feasibility of a titania monolayer formation on silica, by using either impregnation of an alcoxide or precipitation from an aqueous solution of $TiCl_3$. From the point of view of mechanical stability of the coating, Mills et al. [94] studied the effect of pH on titania/glass bonding strength. No detachment of TiO_2 was detected by these investigators in the pH range from 2 to 9. Easy stripping of the coating was observed at pH higher than 12.

In other aspects of the problem, studies on specific surface area of the titania on TiO_2 coated silica were reported by Hanprasopwattana et al. [95]; and on aggregation/disaggregation kinetic of TiO_2 particles on glass beads under shear conditions by Newman et al. [96]. Fox et al. [49] focused their attention on the influence of the pore size on the photocatalytic behavior of different type of zeolites, working as support for titania composites in the oxidative decomposition of alcohols. Ohkuba et al. [69] investigated the electrophotochemical properties of rutile and anatase thin films on a titanium plate prepared by sol-gel methods and Vinodgopal and Kamat [97] analyzed the feasibility of the oxidation of textile dyes in a photoelectrochemical cell with a biased and illuminated anode made of an optically transparent electrode (OTE) coated with TiO_2.

Takahashi et al. [98] studied thin films of Pt–TiO_2 deposited on a Vycor glass plate by spray-coating a titanil acetyl acetonate solution, and by using the coating thickness as a parameter, they found that amorphous TiO_2 occurs at a thickness of less than 50 nm. Anatase crystallites started to form at a higher thickness, with a paralleled increment of reactivity.

Relevant to this survey are the studies made by Montoya et al. [99] on the effects of several variables on the properties of titania made by the sol-gel process. These authors investigated parameters such as the alcohol/alcoxide ratio, the pH, type of solvent and calcination temperature in relation with textural, structural and morphological characteristics on the obtained product.

7. Conclusions and prospectives

It can be concluded from this overview that titania supported catalyst appears to be a promising alternative for water pollution remediation. However, in spite of significant advances in the understanding of the subject, numerous aspects still remain that should be clarified before this approach becomes a technological reality from an engineering point of view. Among these unresolved problems we can mention:

- It is still unclear which are the most convenient method and support in terms of mechanical stability and photocatalytic activity of the resulting product.
- Up to now no method seems to guarantee both the mechanical and/or the photocatalytical stability of a TiO_2 coating on any support. This is particularly valid under conditions of prolonged use of the catalyst in a reaction system with an acceptable quantum efficiency.
- In general, good adherence catalyst/support and photoactivity of the resulting catalyst appear to be in an inverse relation.
- Mass transport limitations and radiation field distribution should be given more attention in future work.

Acknowledgements

The authors are grateful to Consejo Nacional de Investigaciones Científicas y Técnicas (CONICET) and to Universidad Nacional del Litoral (UNL) for their support to produce this work.

References

[1] D. Ollis, H. Al-Elkabi, Photocatalytic Purification and Treatment of Water and Air, Elsevier, Amsterdam, 1993.
[2] N. Serpone, E. Pellizzetti, Photocatalysis: Fundamentals and Applications, Wiley, New York, 1989.
[3] D. Ollis, E. Pellizzetti, N. Serpone, Environ. Sci. Technol. 25 (1991) 1523.
[4] K.J. Green, R.J. Rudham, J. Chem. Soc., Faraday Trans. 89 (1993) 186.
[5] A.J. Bard, J. Photochem. 10 (1979) 59.
[6] M.A. Fox, CHEMTECH 22 (1992) 680.
[7] A. Heller, Acc. Chem. Res. 14 (1981) 154.
[8] C.S. Turchi, D.F. Ollis, J. Catal. 122 (1990) 178.
[9] M. Bideau, B. Claudel, C. Dubien, L. Faure, H. Kazouan, J. Photochem. Photobiol. A 91 (1995) 137.
[10] M. Murabayashi, K. Itoh, S. Suzuki, K. Kawashima, R. Masuda, Proc.-Electrochem. Soc. 93(18) (1993) 131.
[11] R. Matthews, S.Mc. Evoy, J. Photochem. Photobiol. A 64 (1992) 231.
[12] J. Sabate, M. Anderson, M. Aguado, J. Gimenez, S. Cervera-March, J. Mol. Catal. 71 (1992) 57.
[13] G. Chester, M. Anderson, H. Read, J. Photchem. Photobiol. A 71 (1993) 291.
[14] R. Matthews, J. Catal. 111 (1988) 264.
[15] R. Matthews, J. Phys. Chem. 91 (1987) 3328.
[16] M. Abdullah, G.K.C. Low, R. Matthews, J. Phys. Chem. 94 (1990) 6820.
[17] H. Al-Elkabi, W. Serpone, J. Phys. Chem. 92 (1988) 5726.
[18] C. Turchi, D. Ollis, J. Phys. Chem. 92 (1988) 6852.
[19] M.C. Lu, G.D. Roam, J.N. Chen, C.P. Huang, J. Photochem. Photobiol. A 76 (1993) 103.
[20] V. Brezová, M. Jankoviæová, M. Soldan, A. Blazcová, M. Rehákova, M. Surina, M. Ceppan, B. Havlinová, J. Photochem. Photobiol. A 83 (1994) 69.
[21] J. Sabate, M.A. Anderson, H. Kikkawa, M. Edwards, C.G. Hill Jr., J. Catal. 127 (1991) 167.
[22] W.A. Zeltner, C.G. Hill, M. Anderson, CHEMTECH (1993) 21.
[23] J. Sabate, M.A. Anderson, H. Kikkawa, Q. Xu, S. Cervera-March, C.G. Hill Jr., J. Catal. 134 (1992) 36.
[24] H.D. Chun, J.K. Park, Hazard Waste Hazard Mat. 11(4) (1994) 501.
[25] M. Muneer, S.J. Das, V.B. Manilal, A. Haridas, J. Photochem. Photobiol. A 63 (1992) 107.
[26] R. Mattews, Water Res. 25 (1991) 1169.
[27] A. Haarstrick, O.M. Kut, E. Heinzle, Environ. Sci. Technol. 30 (1996) 817.
[28] J.C. Crittenden, Y. Zhang, D.W. Hand, D.L. Perram, E.G. Marchand, Water Environ. Res. 68 (1996) 270.
[29] Y. Zhang, J.C. Crittenden, D.W. Hand, D.L. Perram, J. Sol. Energy Eng. 188 (1996) 123.
[30] R.W. Matthews, Chem. Ind. 1 (1988) 28.
[31] R.W. Matthews, S.R. McEvoy, Solar Energy 49 (1992) 507.
[32] N.J. Peill, M.R. Hoffmann, Environ. Sci. Technol. 29(12) (1995) 2974.

[33] N. Peill, M.R. Hoffman, Environ. Sci. Technol. 30(9) (1995) 2806.
[34] K. Pugh, D. Kiserov, J. Sullivan, J.H. Grinstead Jr., ACS Symp. Ser. 607 (1995) 174.
[35] V. Brezová, A. Blazová, M. Breznan, P. Kottas, M. Ceppan, Collect. Czech. Chem. Commun. 60 (1995) 788.
[36] M. Mikula, V. Brezová, L. Ceppan, L. Pach, L. Karpinsky, J. Mater. Sci. Lett. 14 (1995) 615.
[37] M. Murabayashi, K. Itoh, S. Kuroda, R. Huda, R. Masuda, W. Takahashi, K. Kawashima, Denki Kagaku 8 (1992) 741.
[38] M. Murabayashi, K. Itoh, K. Kawashima, R. Masuda, S. Susuki, Trace Met. Environ. 3 (1993) 783.
[39] R. Matthews, Solar Energy 38(6) (1987) 405.
[40] N. Serpone, E. Borgarello, R. Harris, P. Cahill, M. Borgarello, Sol. Energy Mater. 14 (1986) 121.
[41] J.R. Bellobono, M. Bonardi, L. Castellano, E. Selli, L. Righetto, J. Photochem. Photobiol. A 67 (1992) 74.
[42] K. Kato, J. Ceramic Soc. Japan, Int. Ed. 101 (1993) 240.
[43] M. Anderson, M.J. Gieselmann, Q. Xu, J. Membrane Sci. 39 (1988) 243.
[44] S. Tunesi, M. Anderson, J. Phys. Chem. 95 (1991) 3399.
[45] M. Anderson, S. Tunesi, Q. Xu, US Patent No. 5 035 784 (1991).
[46] M. Sauer, D. Ollis, J. Catal. 149 (1994) 81.
[47] R. Mariscal, J.M. Palacios, M. Galan-Ferreres, J.L.G. Fierro, Appl. Catal. A 116 (1994) 205.
[48] Y. Xu, H. Langford, J. Phys. Chem. 99 (1995) 11501.
[49] M.A. Fox, K.E. Doan, M.T. Dulay, Res. Chem. 20(7) (1994) 711.
[50] Y.M. Gao, H.S. Shen, K. Dwight, A. Wold, Mater. Res. Bull. 27 (1992) 1023.
[51] Y.H. Ha, M. Anderson, J. Environ. Eng. (1996) 217.
[52] N. Muradov, Solar Energy 52 (1994) 283.
[53] K. Tenakone, C.T.K. Tilakaratne, I.R.M. Kottegoda, J. Photochem. Photobiol. A 87 (1995) 177.
[54] N.B. Jackson, C.M. Wang, Z. Luo, J. Schwitzgebel, J.G. Ekerdt, J.R. Brock, A. Heller, J. Electrochem. Soc. 138(12) (1991) 3660.
[55] D.C. Gapen, Jr., MS Thesis, University of Wisconsin – Madison.
[56] C. Dorion, O. Zahraa, M. Bouchy, Proceedings of the V Congres du Groupe Francais du Giníc des Procedés, Lyon, Set (1995).
[57] K. Vinodgopal, P.V. Kamat, Sol. Energy Mater. Sol. Cells 38 (1995) 401.
[58] D.H. Kim, M.A. Anderson, Environ. Sci. Technol. 28 (1994) 479.
[59] B. Siffert, M. Metzger, Colloids and Surfaces 53 (1991) 79.
[60] D. Matthews, A. Kay, M. Grätzel, Aust. J. Chem. 47 (1994) 1869.
[61] K. Vinodgopal, P.V. Kamat, CHEMTECH (1996) 18.
[62] L. Hench, J. West, Chem. Rev. 90 (1990) 33.
[63] M.A. Anderson, F. Tiscareno-Lechuga, Q. Xu, C.G. Hill Jr., Novel Mater. in Heterogeneous Catal., ACS Symp. Ser. 437 (1990) 198.
[64] O. Rodriguez, F. Gonzalez, P. Bosh, M. Portilla, T. Viveros, Catal. Today 14 (1992) 243.
[65] M. Toba, F. Mizukami, S.I. Niwa, T. Sano, K. Maeda, A. Annila, V. Komppa, J. Mol. Catal. 91 (1996) 277.
[66] M.A. Aguado, M.A. Anderson, Sol. Energy Mater. Sol. Cells 28 (1993) 345.
[67] M.J. Gieselmann, M. Anderson, M. Moosemiller, C.G. Hill, Separation Sci. Technol. 23(12,13) (1988) 1695.
[68] Q. Xu, M. Anderson, Mater. Res. Soc. Proc. 132 (1989) 41.
[69] Y. Hamasaki, S. Ohkubo, K. Murakami, H. Sei, G. Nogami, J. Electrochem. Soc. 141 (1994) 660.
[70] A. Sobzynsky, A.J. Bard, A. Campion, M.A. Fox, S.E. Malloux, S.E. Webber, J.M. White, J. Phys. Chem. 91 (1987) 3316.
[71] A. Munoz-Paez, P. Malet, Appl. Surf. Sci. 56–58 (1992) 873.
[72] R. Castillo, B. Koch, P. Ruiz, B. Delmon, in: G. Poncelet et al. (Eds.), Preparation of Catalysis VI, Scientific Bases for the Preparation of Heterogeneous Catalysis, Elsevier, Amsterdam, 1995, p. 291.
[73] M. Anpo, N. Aikawa, Y. Kubokawa, M. Che, C. Louis, E. Giamelllo, J. Phys. Chem. 89 (1985) 5689.
[74] S. Sato, A. Sobczynski, J.M. White, A.J. Bard, M.A. Campion, T.E. Malloue, S.E. Webber, J. Photochem. Photobiol. A 50 (1989) 283.
[75] V.J. Nagpal, R.M. Davis, J. Mater. Res. 10(12) (1995) 3068.
[76] I. Rosemberg, J.R. Brock, A. Heller, J. Phys. Chem. 96 (1992) 3423.
[77] J. Schwitzgebel, J.C. Ekerdt, H. Gerischer, A. Heller, J. Phys. Chem. 99 (1995) 5633.
[78] M. Nair, Z. Luo, A. Heller, Ind. Eng. Chem. Res. 32 (1993) 2318.
[79] K. Hofstadler, R. Bauer, Environ. Sci. Technol. 28 (1994) 670.
[80] R. Bauer, Chemosphere 29(6) (1994) 1225.
[81] H. Tada, H. Honda, J. Electrochem. Soc. 142(10) (1995) 3438.
[82] P. Wyness, J.F. Klausner, D.Y. Goswami, K.S. Schance, Trans. ASME 116 (1994) 8.
[83] D.H. Kim, M.A. Anderson, W.A. Zeltner, J. Environ. Eng. (1995) 599.
[84] A. Yasumori, K. Yamasaki, S. Shibata, M. Yamane, J. Ceramic Soc. Japan 102(8) (1994) 702.
[85] Y. Zhang, D. Crittenden, D.W. Hand, D. Perram, Environ. Sci. Technol. 28 (1994) 435.
[86] A. Fernandez, G. Lassaletta, V.M. Jimenez, A. Justo, A.R. Gonzalez-Elipe, J.M. Herrman, H. Tahiri, Y. Ait-Ichou, Appl. Catal. B 7 (1995) 49.
[87] S. Srinivasan, K. Datye, M. Hampden-Smith, E. Wachs, G. Deo, J.M. Jehno, M. Turek, C.H.F. Peden, J. Catal. 131 (1991) 260.
[88] S. Srinivasan, A.K. Datye, M.H. Smith, C.H.F. Peden, J. Catal. 145 (1994) 565.
[89] G. Lassaletta, A. Fernandez, J.P. Espinos, A.R. Gonzalez-Elipe, J. Phys. Chem. 99 (1995) 1484.
[90] R. Castillo, B. Koch, P. Ruiz, B. Delmon, J. Mater. Chem. 4(6) (1994) 903.
[91] R. Castillo, B. Koch, P. Ruiz, B. Delmon, J. Catal. 161 (1994) 524.

[92] M. Zaharescu, M. Crisan, D. Crisan, M. Gartner, F. Moise, Revue Roumaine 40(10) (1995) 993.
[93] K. Matsuo, K. Nakano, Appl. Surf. Sci. 34 (1988) 269.
[94] A. Mills, D. Worseley, R.H. Davies, J. Chem. Soc., Chem. Commun. (1994) 2677.
[95] A. Hanprasopwattana, S. Srinivasan, A.G. Sault, A.K. Datye, Langmuir 12 (1996) 3173.
[96] K. Newman, D. Stozenbach, Colloids and Surf. A 107 (1996) 189.
[97] K. Vinodgopal, P.V. Kamat, CHEMTECH (1996) 18.
[98] M. Takahashi, K. Mita, H. Toyuki, M. Kume, J. Mater. Sci. 24 (1989) 243.
[99] J.A. Montoya, T. Viveros, J.M. Dominguez, L.A. Canales, I. Schifter, Catal. Lett. 15 (1992) 207.