

# Platinum and Palladium in Semiconductor Photocatalytic Systems

## FACTORS AFFECTING THE PURIFICATION OF WATER AND AIR

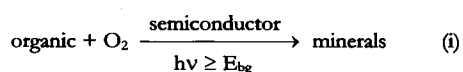
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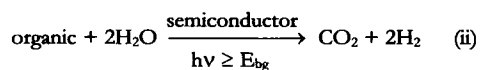
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*A wide range of organic pollutants can be destroyed by semiconductor photocatalysis using titania. The purification of water and air contaminated with organic pollutants has been investigated by semiconductor photocatalysis for many years and in attempts to improve the purification rate platinum and palladium have been deposited, usually as fine particles, on the titania surface. Such deposits are expected to improve the rate of reduction of oxygen and so reduce the probability of electron-hole recombination and increase the overall rate of the reaction. The effectiveness of the deposits is reviewed here and appears very variable with reported rate enhancement factors ranging from 8 to 0.1. Semiconductor photocatalysis can be used to purify air (at temperatures > 100°C) and Pt deposits can markedly improve the overall rate of mineralisation. However, volatile organic compounds containing an heteroatom can deactivate the photocatalyst completely and irreversibly. Factors contributing to the success of the processes are considered. The use of chloro-Pt(IV)-titania and other chloro-platinum group metals-titania complexes as possible visible light sensitisers for water and air purification is briefly reviewed.*

The overall (photomineralisation) process of semiconductor photocatalysis for water and air purification can be summarised by the equation:



The other thermodynamically favoured photomineralisation reaction:



which can take place in theory does not do so in practice under the usual conditions employed in the photomineralisation of organic pollutants, namely, under aerobic conditions and in the absence of a platinum group metal (pgm). This is because the overpotential for the photoreduction of water to hydrogen is large on most non-platinised semiconductors, making the generation of hydrogen impossible. Indeed, for this reason, no significant degree of photomineralisation of the organic upon ultra-bandgap irradiation of a suitable

semiconductor usually occurs unless something more easily reducible than protons is available on the surface of the semiconductor. Oxygen fulfils this role. If the semiconductor has a pgm on its surface, then water reduction can take place (and mineralisation occurs via Equation (ii)) but only if oxygen is excluded. Interestingly, this was an early

Table I  
Classes of Organics Able to be Photomineralised

|                            |                           |
|----------------------------|---------------------------|
| Alkanes                    | Phenols                   |
| Haloalkanes                | Halophenols               |
| Aliphatic alcohols         | Aromatic carboxylic acids |
| Aliphatic carboxylic acids | Polymers                  |
| Alkenes                    | Surfactants               |
| Haloalkenes                | Herbicides                |
| Aromatics                  | Pesticides                |
| Haloaromatics              | Dyes                      |
| Nitrohaloaromatics         | Hormones                  |

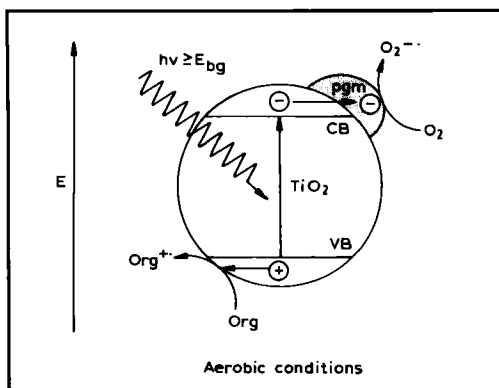


Fig. 1 Schematic illustration of the electron energetics and basic electron-transfer processes associated with the mineralisation of an organic by oxygen, photocatalysed by a particle of semiconductor with a pgm deposited on its surface

suggested approach to the treatment of biomass. However, if, as is usually the case, oxygen is present in the photocatalytic system then oxygen rather than water will be reduced.

In Equation (i) the semiconductor photocatalyst, invariably titania, mediates the cold combustion of the organic pollutant dissolved in water or airborne. Carbon dioxide ( $\text{CO}_2$ ),  $\text{H}_2\text{O}$  and any mineral acids (if the original organic contained heteroatoms, such as S or N) and/or salts (if the original organic contained metals, such as Na or K) are generated (1–3). The range of organics that can be destroyed via this route is extensive and is summarised in Table I (1).

Given the large number of classes of organics listed in Table I, especially aromatics, pesticides, dyes, hormones and surfactants, it is not surprising that semiconductor photocatalysis has been promoted as a new and promising method of water purification, and commercial enterprises have been established (4). Attempts to improve the performance of such systems have often focused on the efficacy of pgm deposits, usually Pt, on titania (5). The basic principles of operation of platinised titania particles as mediators in the photomineralisation of organic pollutants are illustrated in Figure 1 (1–3).

As Figure 1 shows, upon absorption of a photon of ultra-bandgap energy, an electron-hole pair is generated. These pairs can recombine in the

bulk or at the surface, but at the surface they can also react with adsorbed species. Thus, the photo-generated hole can react with an adsorbed hydroxyl group to produce an adsorbed hydroxyl radical which can then oxidise the organic substrate. Alternatively, it can react directly with the adsorbed organic substrate. For some organics there is evidence that both oxidation mechanisms can occur on titania (1–3). However, for the overall process in Equation (i) to work effectively, the photogenerated electrons must not be allowed to accumulate on the titania particles as this would lead to an increase in the rate of electron-hole recombination.

Oxygen is frequently used as a scavenger of photogenerated electrons. It is often suggested that Pt (or Pd) deposits on titania act as trap sites (electron wells) for the photogenerated electrons and mediate the reduction of oxygen to superoxide much more effectively than a plain titania surface (6). Any superoxide generated by this initial reduction process will be further reduced to hydrogen peroxide which itself can act as a secondary supply of hydroxyl radicals. The basic overall process illustrated in Figure 1 must usually be repeated many times over to bring about the eventual mineralisation of the organic (Equation (i)). Consideration of the relevant redox potentials:

$$\begin{aligned} E^{\circ}_{\text{CB}}(\text{anatase}) &= -0.32 \text{ V} \\ E^{\circ}_{\text{CB}}(\text{rutile}) &= -0.11 \text{ V} \\ E^{\circ}(\text{O}_2/\text{HO}_2^{\bullet}) &= +0.12 \text{ V and} \\ E^{\circ}(\text{HO}_2^{\bullet}/\text{H}_2\text{O}_2) &= +1.44 \text{ V} \end{aligned}$$

where all redox potentials are for pH 0 and versus the standard hydrogen electrode, shows that the reduction of  $\text{O}_2$  to  $\text{HO}_2^{\bullet}$  (or  $\text{O}_2^{\bullet-}$ ) and its subsequent further reduction to  $\text{H}_2\text{O}_2$  by titania conduction band electrons are thermodynamically feasible processes.

In this area of research the semiconductor is invariably titania; however, titania photocatalysts can be prepared by many methods and consequently may exhibit very different characteristics, such as specific surface area, pzc, i.e. point of zero charge (in the case of titania this is the pH at which the overall charge on the semiconductor particles is zero), porosity, dispersibility, etc. In order to

| Table II<br>Characteristics of Common Commercial Forms of Titania |                   |                      |                      |            |  |
|---|-------------------|----------------------|----------------------|------------|--|
| Product name  | Company           | Crystallite size, nm | Phase                | Porosity   | Surface area, m <sup>2</sup> g <sup>-1</sup> |
| P25   | Degussa-Hüels     | 21–30                | 70:30 anatase:rutile | non-porous | 55   |
| Hombikat UV 100   | Sachtleben Chemie | 6                    | 100% anatase         | mesoporous | 250  |
| Anatase   | Aldrich           | 47                   | 100% anatase         | –          | 10   |

focus on the effects of Pt and Pd deposits in semiconductor photocatalytic systems for water and air purification, the literature in this review has been restricted to systems where the titania used is one of the three most common commercial forms: P25 (Degussa-Hüels), Hombikat UV 100 (Sachtleben Chemie) and Anatase (Aldrich Chemicals). Some key characteristics of these sources are summarised in Table II (7). Aldrich anatase titania has a low surface area and is 100% anatase, Degussa P25 is typically a 70:30 mixture of anatase titania to rutile titania and is non-porous, with a moderately high surface area and Hombikat UV 100 is a mesoporous, high surface area form of anatase TiO<sub>2</sub>. The most popular form of titania for semiconductor photocatalysis is Degussa P25, often taken as the optimum quality reference titania photocatalyst. Its popularity is due to its high photocatalytic activity, ready availability and well-defined physical characteristics.

### Photocatalytic Purification of Water

The 'enhancement factor', E-factor, for a photo-process is defined as:

$$\text{E-factor} = \frac{\text{rate of process with pgm}}{\text{rate of process without pgm}} \quad (\text{iii})$$

There are many reports of enhanced rates for the photocatalytic purification of water (E-factors  $\geq 1$ ) for Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> semiconductors compared to their non-metallised counterparts. Table III contains details from a selection of these reports in terms of the titania source, method and amount of pgm deposited, organic pollutant under test and reported E-factor (9–15).

In most of the systems listed in Table III the amount of Pt (or Pd) deposited on the titania particles is invariably ca. 1% w/w. This amount is a consequence of the vast majority of previous work on hydrogen evolving photocatalytic systems: too much pgm will result in a greatly reduced photocatalytic efficiency due to enhanced electron-hole combination and UV-shielding of the TiO<sub>2</sub> particles by the pgm deposits, whereas too little pgm will result in low photocatalytic activity due to the paucity of low-overpotential water reduction sites. The optimum pgm value is usually ca. 1 wt.%.

From Table III (and later Tables) the most popular method of depositing Pt/Pd onto titania is by photodeposition (16, 17). The E-factors in Table III are generally low, typically from 2 to 4. By contrast, for the reduction of water to H<sub>2</sub> by sacrificial electron donors, such as methanol, photocatalysed by a Pt/TiO<sub>2</sub> or Pd/TiO<sub>2</sub> dispersion, the E-factor is  $> 1000$  if not infinitely large. But, as noted earlier, if pgm is not present little or no hydrogen is usually evolved (16, 17). In many cases, the major difference between these two types of photocatalytic systems: i.e. those focused on organic mineralisation (Equation (i)) and those centred on water reduction (Equation (ii)) is the presence or absence of oxygen. Thus, one type of photosystem can be converted to function as the other simply by purging the system with nitrogen or air.

Finally, it is clear from Table III that for apparently identical photocatalytic systems, that is the same pgm, semiconductor and organic pollutant, there are significant variations in the E-factors (for instance, for methanol or trichloroethylene (TCE)) reported by different research groups (8, 10–12).

| TiO <sub>2</sub> type | Deposition method                      | Metal, wt. % | Pollutants                             | E-factor | References |
|-----------------------|--|--------------|--|----------|------------|
| P25                   | photocatalytic                         | Pt, 1        | methanol (pH 5.1)                      | 7.8      | 8          |
| UV 100                | photocatalytic                         | Pd, 0.01–2   | DCP                                    | 3–7      | 9          |
| Aldrich (anatase)     | photocatalytic                         | Pt, 1        | TCE                                    | 6        | 10         |
| Aldrich (anatase)     | photocatalytic                         | Pt, 1        | TCE                                    | 5        | 11         |
| P25                   | photocatalytic                         | Pt, 0.5      | TCE, BTEX                              | 4.8      | 12         |
| P25                   | photocatalytic                         | Pt, 1        | ethanol (pH 5.1)                       | 4.2      | 8          |
| P25                   | photocatalytic                         | Pt, 1        | DCA                                    | 3        | 13         |
| Aldrich (anatase)     | chemical reduction (Zn)                | Pt, 1        | TCE                                    | 3        | 11         |
| P25                   | thermal reduction under H <sub>2</sub> | Pt, 1        | ethanol (pH 10.9)                      | 2.4      | 8          |
| P25                   | photocatalytic                         | Pt, 1        | methanol (pH 10.9)                     | 2.4      | 8          |
| Aldrich (anatase)     | photocatalytic                         | Pt, 0.5      | TCE                                    | 2.4      | 12         |
| UV 100                | photocatalytic                         | Pt, 0.1–1    | DCA                                    | 2–3      | 13, 14     |
| Aldrich (anatase)     | photocatalytic                         | Pt, 1        | toluene                                | 1.5      | 10         |
| P25                   | photocatalytic                         | Pd, 1        | methanol (pH 5.6)                      | 1.4      | 8          |
| P25                   | thermal and photocatalytic             | Pd, 0.15     | 1,4-dichlorobenzene and salicylic acid | 1.3–1.4  | 15         |
| Aldrich (anatase)     | photocatalytic                         | Pt, 1        | toluene                                | 1.2      | 10         |
| P25                   | photocatalytic                         | Pd, 1        | ethanol (pH 5.5)                       | 1.2      | 8          |
| P25                   | physical mixing                        | Pd, 1        | TCE (pH 5.4)                           | 1.1      | 8          |

P25 is from Degussa; UV 100 Hombikat is from Sachtleben Chemie.

DCP = sodium 2,2-dichloropropionate; TCE = trichloroethylene; BTEX = benzene, toluene, ethylbenzene and xylene; DCA = dichloroacetic acid

Table IV contains details of photocatalytic systems for water purification where E-factors  $\leq 1$  have been reported (8, 11, 14, 18–20). It is clear that Pt/TiO<sub>2</sub> and Pd/TiO<sub>2</sub> photocatalysts are not necessarily always more effective photocatalysts for water purification compared to the original unmetallised titania forms.

Initially the variation in the E-factor appears to be due to the variation in the nature of the pollutant rather than a variation in the photocatalyst. For example, from Table III the photodestruction of dichloroacetic acid (DCA) always appears to be more active (E-factor  $\geq 1$ ) for a Pt/TiO<sub>2</sub> or Pd/TiO<sub>2</sub> photocatalyst than for the original TiO<sub>2</sub> (E-factor = 1) (13, 14) whereas, from Table (IV), the photodestruction of 4-chlorophenol (4-CP) sensitised by the same UV 100 titania photocatalyst is often found to be unaffected or inhibited (E-factor  $\leq 1$ ) by deposits of Pt or Pd (13, 14). These results and others indicate that the E-factor varies from pollutant to pollutant. This variation

could be attributed to the effect of the pgm on one or more of the key reaction parameters which include: the adsorption isotherms of the reactants, the kinetics of the electron-transfer processes and the desorption isotherms of the products. However, Tables III and IV also show examples where, for apparently the same or very similar photosystems, E-factors > 1 and < 1 have both been reported for the same pollutant, for example TCE, (8, 10–12).

Significant differences in the E-factor for apparently identical photocatalytic systems may occur because the systems are not as alike as they first appear. In fact, one problem in semiconductor photocatalysis is that the systems have many critical variables. These variables include: source and history of the semiconductor, method of depositing the pgm, method of agitation, method of aeration, photoreactor design and construction (material of which it is made), illumination source (the wavelength(s) and intensity of excitation),

| TiO <sub>2</sub> type | Deposition method                          | Metal, wt. % | Pollutants                      | E-factor | References |
|-----------------------|--|--------------|---------------------------------|----------|------------|
| UV 100                | photocatalytic                             | Pt, 1        | 4-CP                            | 1        | 13, 14     |
| P25                   | photocatalytic                             | Pt, 0.1      | nitroglycerine and rhodamine 6G | 1        | 18         |
| P25                   | photocatalytic                             | Pt, 1        | 2,4-dichlorophenoxy acetic acid | 1        | 19         |
| P25                   | photocatalytic and chemical reduction (Zn) | Pt, 1        | TCE                             | < 1      | 11         |
| P25                   | photocatalytic                             | Pt, 1        | chloroform (pH 5.4)             | 0.6      | 8          |
| P25                   | photocatalytic                             | Pd, 1        | DCP                             | 0.5      | 8          |
| P25                   | thermal reduction under H <sub>2</sub>     | Pt, 1        | chlorobenzoic acid              | 0.4      | 20         |
| P25                   | photocatalytic                             | Pt, 1        | chloroform (pH 5.6)             | 0.3      | 8          |
| P25                   | physical mixing                            | Pd, 1        | ethanol (pH 5.1)                | 0.3      | 8          |
| P25                   | photocatalytic                             | Pt, 1        | TCE (pH 5.2)                    | 0.1      | 8          |

4-CP = 4-chlorophenol

pollutant concentration, pH, ionic strength, and temperature. Various combination of these factors could easily lead to an overall E-factor > 1 or < 1.

In the case of the photomineralisation of TCE (11), using Pt deposited by a chemical reduction method using zinc, it appears that the variation in E-factors in Tables III and IV is due to the source of titania, with Aldrich anatase (E-factor = 3) appearing more active than Degussa P25 (E-factor < 1). The reason for this is presently unclear.

In other cases, the cause for the E-factor variation may be hidden in the experimental detail. Thus, the work of Chen *et al.* gives the E-factor for the photomineralisation of methanol by Pt/TiO<sub>2</sub> as 7.8 at pH 5.1, but as 2.4 at pH 10.9 (8). Thus, it is even possible for different groups studying the same photocatalytic system to report different E-factors and the difference is due simply to a difference(s) in one or more of the key experimental parameters (pH or ionic strength, for instance).

In fact, the rate of photomineralisation of methanol sensitised by unplatinated titania is ten times faster at pH 10.9 than at pH 5.1, so in this system, increasing the pH improves the overall rate of photocatalysis much more for TiO<sub>2</sub> than for Pt/TiO<sub>2</sub> (8). The reasons for the apparent variation in E-factor and rates with pH remain as yet unclear.

One of the classic works in semiconductor photocatalysis, by Wang *et al.*, concerns the efficiency of Pd as an oxygen reduction catalyst in the photocatalytic destruction of sodium 2,2-dichloropropionate (DCP) by titania (9). This work is often cited by researchers as an example of a pgm (Pd) that significantly enhances the overall rate of photomineralisation by catalysing the, presumed slow, oxygen reduction step by photogenerated electrons on TiO<sub>2</sub>. In the destruction of DCP, dissolved HCl is produced, along with CO<sub>2</sub>. Wang used the HCl production, via the associated change in pH of the reaction solution, to monitor the progress of the reaction (9). [H<sup>+</sup>] versus irradiation time profiles for this system, using titania impregnated with 0, 0.01 or 2 wt.% Pd as the photocatalyst, are illustrated in Figure 2(a) and show that the overall rate of the photocatalytic oxidation of DCP is increased 3-fold with 0.01 wt.% Pd, but 7-fold for 2 wt.% Pd (9).

Recent work has shown that the presence of a pgm does not always enhance a photocatalytic system even when the organic pollutant, pgm and semiconductor are the same. For instance, in a study of the role of Pt and Pd in semiconductor photocatalysis, Chen and coworkers (8) investigated the same DCP/(Pd/TiO<sub>2</sub>) system as used by

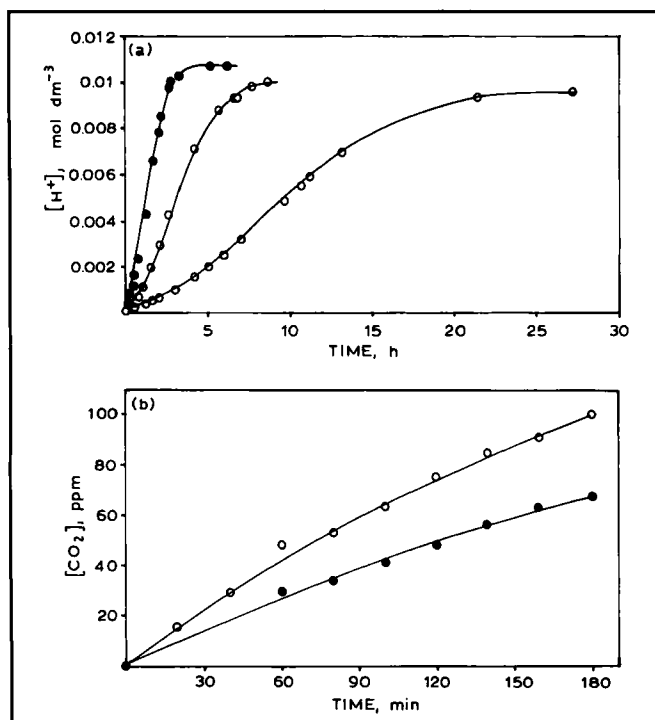


Fig. 2 (a)  $[H^+]$  versus irradiation time profiles from data by Wang et al. (9) for the photomineralisation of DCP by Pd/TiO<sub>2</sub>. The titania photocatalyst was impregnated with:  
 right: no Pd  
 middle: 0.01 wt.% Pd  
 left: 2 wt.% Pd

(b)  $[CO_2]$  versus irradiation time evolution curves by Chen et al. (8) for the photomineralisation of DCP by:  
 ○ TiO<sub>2</sub>  
 ● 1 wt.% Pd/TiO<sub>2</sub>

Wang (9). Figure 2(b) illustrates some results of this work which show that 1 wt.% Pd significantly depresses ( $E$ -factor = 0.5), rather than enhances, the overall kinetics of photomineralisation (8)! The only obvious difference between the two studies is the source of the titania: Hombikat UV 100 (Wang (9)) and Degussa P25 (Chen (8)). The type of the titania used thus appears to be a critical factor in determining whether a ppm will have a positive or negative effect on the overall kinetics of photomineralisation. In fact, despite more than two decades of research, it is still not clear why some forms of titania are better than others at destroying particular organic pollutants. For instance, why is unplatnised Hombikat UV 100 usually found to be excellent at destroying DCA but less effective for 4-CP? Why is this situation reversed when unplatnised Degussa P25 is used as a photocatalyst? Only more detailed work will reveal the elusive answers to these apparently simple questions.

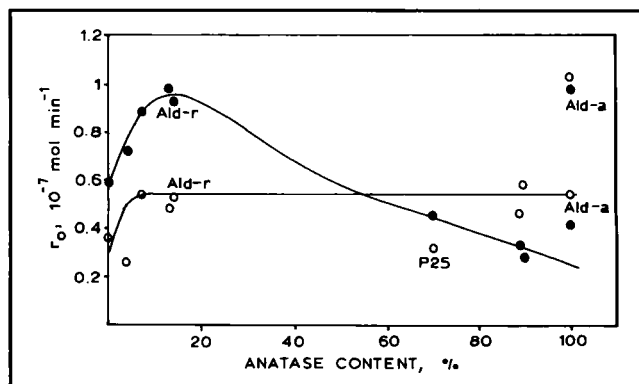
Another example of the unpredictable and contradictory nature of semiconductor photocatalysis has been provided by Tanaka and coworkers in a

study of the effect of the crystallinity of titania on its photocatalytic activity (21). Twelve different commercial samples of titania, with and without Pt deposits, were tested as photocatalysts for the destruction of phenol. The results, in the form of plots of initial rate as a function of the % anatase content of the photocatalyst, are illustrated in Figure 3 (21). They indicate that whereas platinisation of rutile TiO<sub>2</sub> generally enhances the rate of destruction of phenol, it depresses it for anatase TiO<sub>2</sub>. Just as progress seems to be made towards a general rule, a glance at the data in Figure 3 reveals that Aldrich anatase is an exception, that is, platinisation of a 100% sample of anatase titania significantly enhances its rate of destruction of phenol! It was also noted that platinisation has only a small effect if the organic pollutant is TCE or chloroacetic acid (21)! There appears to be no obvious explanation for this exceptional behaviour by Aldrich anatase, or why the 'rule' that: platinised rutile is better than anatase (if it exists) is pollutant specific.

The most likely explanation for the results in Tables III and IV and the examples discussed is

Fig. 3 Plots of the observed variation of the rates of photomineralisation of phenol by:

○  $\text{TiO}_2$   
 ● 1 wt.% Pt/ $\text{TiO}_2$   
 as a function of % anatase content for 12 commercial samples of titania; reported by Tanaka et al. (20)



that Pt and Pd may enhance or depress the kinetics of the semiconductor photocatalytic destruction of organic pollutants in aqueous solution, depending upon a combination of negative or positive effects arising from the selected reaction conditions. The variation in E-factor is due to the complicated nature of the overall process, the rate of which depends upon factors such as: adsorption of pollutant, oxidation of pollutant and the concomitant reduction of oxygen and desorption of products. All these processes may be positively, negatively or unaffected by the presence of a pgm, and are likely to depend upon:

- the nature of the pollutant
- the source and history of the semiconductor
- the method of pgm deposition employed (and amount deposited), and
- the reaction solution pH, ionic strength and temperature.

From Tables III and IV it can be seen that if the E-factor is positive it is never very large, typically 2–4, and may often be negligible or  $< 1$ . This seems to cast doubt on the future role of pgms in semiconductor photocatalysis for purifying water.

It is worth commenting on recent work by Kamat and colleagues on Au/ $\text{TiO}_2$  photocatalysts, from which it appears that nanoparticle deposits of Au are photooxidised to  $\text{Au}^+$  ions by photogenerated holes and/or hydroxyl radicals on the surface of the titania particles (22). The authors suggest that adsorbed or intercalated  $\text{Au}^+$  ions may then act as electron-hole recombination centres and so cause a reduction in the efficiency of such photocatalytic systems during long-term irradiation. It is

not clear how much of a problem this oxidative dissolution mechanism represents in the photocatalytic destruction of organic pollutants in water or air. Certainly the photooxidative dissolution of Pt or Pd deposits on titania has not been recognised as a major complicating process despite the many photocatalytic studies carried out using Pt/ $\text{TiO}_2$  and Pd/ $\text{TiO}_2$  photocatalysis. However, pgm oxidative dissolution is worth bearing in mind, especially as it may be partly or fully responsible for any observed slow loss of photocatalytic activity in such systems on prolonged irradiation.

### Photocatalytic Purification of Air

More recently the photocatalytic purification of air has become a focus of attention and air conditioning devices and air purifying tiles and paving stones are now available, based on the process summarised by Equation (i) and Figure 1. The organic to be treated in this case is a volatile organic carbon (VOC), usually at a low level (typically  $< 100$  ppm). While not obvious from Equation (i) or Figure 1, water vapour plays an essential role in the overall process even in the gas phase. The nature of the role is uncertain but it is generally agreed that if water vapour were not present the overall photomineralisation process would rapidly grind to a halt. This is because in most photocatalytic systems for air purification, water vapour is the major source of adsorbed hydroxyl groups. However, it is often also a major product, thus, in most instances Equation (i) can proceed quite efficiently under very dry conditions. In some examples of Equation (i) for air purification, a high

| TiO <sub>2</sub> type | Pt deposition method                    | Pt, wt. % | Pollutant(s) | E-factor | References |
|-----------------------|---|-----------|--------------|----------|------------|
| P25                   | photocatalytic                          | 0.4       | toluene      | 3        | 25         |
| P25                   | photocatalytic                          | 0.2       | ethanol      | 2.2      | 26         |
| P25                   | photocatalytic                          | 0.2       | benzaldehyde | 1.5      | 27         |
| P25                   | photocatalytic                          | 0.2       | toluene      | 1.3      | 27         |
| Sol-gel               | chemical reduction (NaBH <sub>4</sub> ) | 0.1       | benzene      | 1.25     | 28         |
| Sol-gel               | chemical reduction (NaBH <sub>4</sub> ) | 0.3       | ethylene     | 0.8      | 29         |
| UV 100                | photocatalytic                          | 0.4       | acetone      | 0.6      | 25         |
| P25                   | photocatalytic                          | 0.5       | acetaldehyde | 0.5      | 30         |
| P25                   | thermal reduction under H <sub>2</sub>  | 0.1–2     | TCE          | 0.1      | 31         |

partial pressure for water vapour appears partly to inhibit the photomineralisation process, possibly due to competitive adsorption between the water and VOC molecules on the semiconductor surface (23). In other examples, increasing the partial pressure of the water vapour appears to have either little effect or to promote the overall photocatalytic process (23).

A possible concern about the real usefulness of Equation (i) as a method of air purification, comes from Peral and Ollis in their study of the deactivation of titania photocatalysts by heteroatom-containing VOCs, such as decamethyl tetrasiloxane (DMTS), indole and pyrrole (24). These workers found that VOCs containing Si or N heteroatoms appear to generate products that cause the irreversible and complete deactivation of titania photocatalysts. The nature of the poisons is unknown. These findings and the concerns they raise about the usefulness of Equation (i) for air purification appear to have been largely ignored by other researchers in the field. Obviously, more work on heteroatom VOCs and their possible poisoning effects needs to be conducted.

There have been many attempts to improve the performance of photocatalytic air purification systems by incorporating a pgm, such as Pt or Pd, on the semiconductor surface. But, as with the water purification work, there has been mixed success. Table V contains data from reports on the enhancement, or otherwise, by Pt and Pd in Equation (i) for air purification (25–31). The E-

factors are not large and may be  $\leq 1$ . Again they appear to vary considerably, depending on the source and nature of the titania, method of pgm deposition and nature of the pollutant (amongst other things).

One major difference between the photocatalytic systems for air and water purification is the relative ease of carrying out the process at elevated temperatures ( $T > 100^\circ\text{C}$ ). This ease has been exploited recently by Kennedy and Datye in a study of the photomineralisation of ethanol by platinumised and unplatinsed titania (26). The study shows that while the rate of photocatalytic mineralisation of ethanol by TiO<sub>2</sub> is largely unaffected when the reaction temperature is increased from 50 to 170°C, with Pt/TiO<sub>2</sub> the rate is markedly increased at temperatures  $> 140^\circ\text{C}$ . This is illustrated in Figure 4(a) using plots of the rates of CO<sub>2</sub> generation as a function of reaction temperature for UV-illuminated TiO<sub>2</sub>, Pt/TiO<sub>2</sub> and non-illuminated Pt/TiO<sub>2</sub> photocatalysts (26). The results show that the enhanced rates of ethanol destruction recorded for Pt/TiO<sub>2</sub> at  $T > 140^\circ\text{C}$  are not due simply to the catalysed thermal oxidation of ethanol by the Pt deposits, a measure of which is given by the plot of the dark rate of CO<sub>2</sub> generation as a function of temperature in Figure 4(a). Instead, there seems to be a synergistic effect between the semiconductor photocatalytic and the Pt-catalysed thermal oxidation modes of ethanol mineralisation at temperatures over 140°C, that is, region B in Figure 4(a). It is suggested that this



Fig. 4 (a) Plots of the observed % conversion of ethanol to  $\text{CO}_2$  by oxygen as a function of reaction temperature for:

- $\text{TiO}_2 + \text{UV light}$
- 1 wt.%  $\text{Pt/TiO}_2 + \text{UV light}$ , and
- 1 wt.%  $\text{Pt/TiO}_2 - \text{UV light}$  (25).

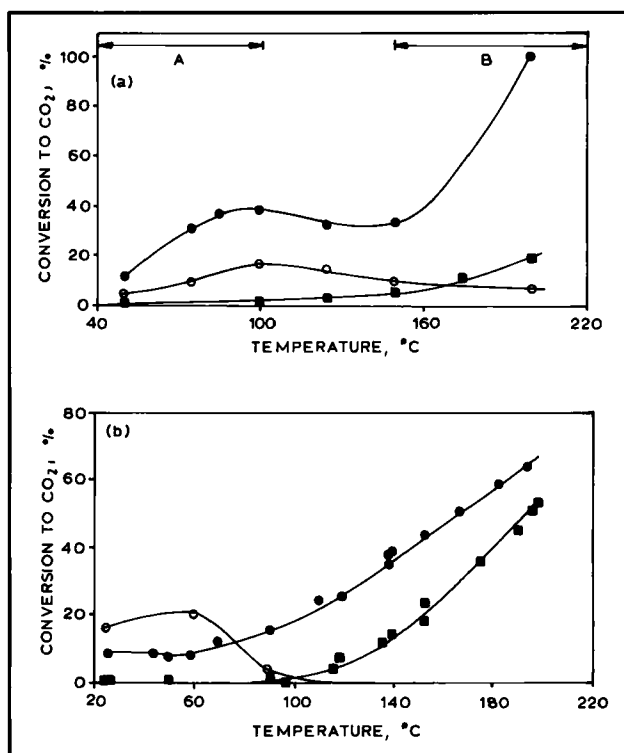
In region A no catalysis of the thermal oxidation of ethanol by the Pt deposits takes place and the overall mineralisation process proceeds on  $\text{Pt/TiO}_2$  under UV light via semiconductor photocatalysis alone.

In region B there appears to be a synergistic effect between the action of the semiconductor photocatalyst and the Pt thermal oxidation catalyst

(b) Plots of the observed % conversion of acetaldehyde to  $\text{CO}_2$  by oxygen as a function of reaction temperature for:

- $\text{TiO}_2 + \text{UV light}$
- 1 wt.%  $\text{Pt/TiO}_2 + \text{UV light}$ , and
- 1 wt.%  $\text{Pt/TiO}_2 - \text{UV light}$  (30).

In this system there appears to be no synergy between the semiconductor photocatalyst and the Pt thermal oxidation catalyst, but rather an additive effect



synergistic effect arises because the  $\text{TiO}_2$  photocatalyst generates acetaldehyde as an intermediate and this species is then rapidly oxidised on the Pt islands via a thermal process at the elevated temperatures associated with region B (26).

The findings of Kennedy and Datye (26) are very encouraging with regard to Pt and Pd usage in Equation (i): they indicate that air purification by semiconductor photocatalysis may be achieved more efficiently if the process is carried out at elevated temperatures and in the presence of a pgm, such as Pt or Pd.

However, generalising from one result is not possible. This is shown in recent work by Falconer *et al.* (30) on the photomineralisation of gaseous acetaldehyde by  $\text{Pt/TiO}_2$  at elevated temperatures. The titania they used was the same as used by Kennedy and Datye, Degussa P25 (26). Some of Falconer's results (30) are illustrated in Figure 4(b) as plots of (aldehyde) % conversion to  $\text{CO}_2$  versus reaction temperature for their UV-irradiated  $\text{TiO}_2$  and  $\text{Pt/TiO}_2$  and non-irradiated  $\text{Pt/TiO}_2$  photocatalysts. The titania photocatalyst becomes

poisoned at  $T > 100^\circ\text{C}$  and while platinisation depresses the rate of mineralisation of acetaldehyde at ambient temperatures, the observed enhanced rates at elevated temperatures appear to be associated with additional thermal oxidation of acetaldehyde on the Pt islands, rather than a synergistic effect. As a consequence, the variation in % conversion of acetaldehyde versus reaction temperature profile for  $\text{Pt/TiO}_2$  in Figure 4(b) appears to be the sum of the average % conversion of acetaldehyde due to photomineralisation at ambient temperature on  $\text{TiO}_2$  plus the variation with temperature in the % conversion due to thermal oxidation of acetaldehyde by oxygen, catalysed by Pt. The presence of Pt on the titania prevents, or slows down, the formation of poisoning agents associated with this system, especially at elevated temperatures (30).

These two studies show that pgms may have an important role to play in the semiconductor photocatalytic purification of air at elevated temperatures (26, 30). This role may be as a synergistic catalyst that enhances the rate of photomineralisation

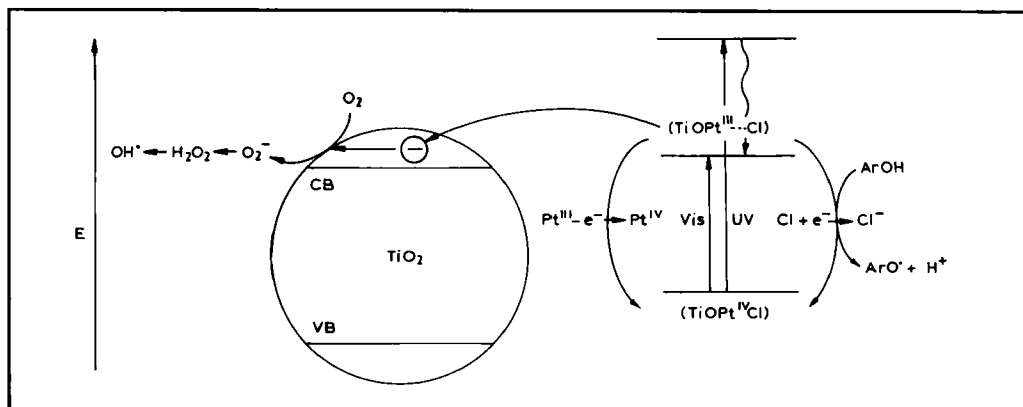


Fig. 5 Schematic illustration of the electron energetics and basic electron-transfer processes associated with the mineralisation of an organic by oxygen, photocatalysed by a particle of semiconductor with a Pt(IV) chlorocomplex chemisorbed on its surface

of the VOC (as with the Pt/TiO<sub>2</sub>-ethanol system of Kennedy and Datye (26)), or as a simple catalyst to thermally oxidise the VOC under test and/or any poisoning intermediates that may be generated (as in the Pt/TiO<sub>2</sub>-acetaldehyde systems of Falconer (30)). Thus, the exact nature of the role played by a pgm deposit in semiconductor photocatalysis for air purification appears to depend, amongst other things, on the pollutant.

Looking to the near future, it is probable that, tempted by the promise of synergy and greatly enhanced purification rates, many more studies of air (and possibly water) purification by semiconductor photocatalysis will be conducted at elevated temperatures,  $T > 100^{\circ}\text{C}$ , and this work will be dominated by semiconductor photocatalysts with pgm deposits.

### Visible Light Studies

The review so far has focused on the role of Pt and Pd as catalytic materials to purify water and air by semiconductor photocatalysis, dominated by the semiconductor titania. However, titania as a photocatalyst has one major drawback: it absorbs only UV light and so can only utilise 2–3% of the solar spectrum. One major objective of semiconductor photocatalysis research is therefore to develop a stable, active photocatalyst that utilises a wider part of the solar spectrum.

Despite much effort little progress had been made until recently, when Kisch and coworkers

looked at the visible light sensitisation of the photodegradation of 4-CP by TiO<sub>2</sub> (amorphous or crystalline) impregnated with pgm chlorides, such as chlorides of Pt(IV), Pd(II) and Rh(III) (32). Their most active sample appeared to be a TiO<sub>2</sub>-chloroplatinate(IV) photocatalytic material, prepared by stirring the TiO<sub>2</sub> powder into a H<sub>2</sub>PtCl<sub>6</sub> solution and calcining the yellow-brown filtered product at 200°C for 2 hours. Rutile TiO<sub>2</sub> (from Aldrich) did not appear to chemisorb the H<sub>2</sub>PtCl<sub>6</sub> and so did not work as a photocatalyst using visible light. The activity of the P25 TiO<sub>2</sub>-chloroplatinate(IV) product appeared low due to presence of Pt in both the (II) or (0) oxidation state, as well as in the desired (IV) oxidation state.

Their most active and effective TiO<sub>2</sub>-Pt(IV) chloride samples generated to date for visible light photocatalysis use 100% anatase TiO<sub>2</sub> (from Kerr-McGee) and amorphous TiO<sub>2</sub> (prepared by a sol-gel process) (32). The suggested role of the Pt(IV) chloride in such TiO<sub>2</sub>-Pt(IV) chloride photocatalytic systems for water purification is illustrated in Figure 5 (32) for the destruction of the test pollutant, 4-CP.

In this scheme the electronically-excited Pt complex, created by the absorption of UV or visible light, undergoes homolytic cleavage of a Pt–Cl bond to generate intermediates of Pt(III) and an adsorbed chlorine atom. The former species injects an electron into the conduction band of the semiconductor which subsequently reduces oxygen

to superoxide and, eventually, leads to the generation of a hydroxyl radical. Hydroxyl radicals and the adsorbed chlorine atoms are assumed to oxidise the 4-CP, eventually converting it to CO<sub>2</sub> and HCl. The yellow-brown TiO<sub>2</sub>-Pt(IV) powders appear quite stable under visible light irradiation and can be used for several days as photosensitisers for water purification (32).

However, this system inevitably degrades, especially under UV light illumination, as the Pt(IV) chloride is slowly photoreduced by the organic pollutant, in this case 4-CP. Other, less effective TiO<sub>2</sub>-noble metal chloride, visible light photosensitisers for water purification have been prepared by Kisch and coworkers, using gold and rhodium chlorides (33). It appears likely that these other sensitizers operate via a mechanism similar to that indicated in Figure 5, and thus also suffer from the same problem of a slow but, ultimately limiting, photoinstability. Therefore, although such systems have attracted a great deal of attention, their future as a route to sensitising Equation (1) with visible light, appears to be very limited.

## Conclusions

Semiconductor photocatalysis can effect the complete mineralisation of a wide range of organic pollutants, invariably using a UV-absorbing titania semiconductor, generally either Aldrich anatase, Hombikat UV 100 or Degussa P25. The efficacy of Pt and Pd deposits on titania as oxygen reduction catalysts has been extensively studied, aimed at improving the overall purification rate. Enhanced and depressed rates of photomineralisation with platinisation (or palladisation) have been reported for both water and air purification systems. Any positive E-factor is not usually large, typically 2–4, and can vary considerably. The large variation in the E-factor is attributed to the complicated nature of the overall process and depends on many factors including: adsorption of pollutant, oxidation of pollutant and concomitant reduction of oxygen and desorption of products, all of which may be positively or negatively affected by the presence of a pgm. Important rate-determining reaction conditions include: (a) the nature of the pollutant, (b) the source and history of the semi-

conductor, (c) the method (and amount) of pgm deposited, and (d) the reaction solution pH and temperature.

Although semiconductor photocatalysis can be used to purify air, VOCs containing a heteroatom, such as N and Si, appear able to deactivate the photocatalyst. Air purification can be conducted easily at temperatures > 100°C and the presence of Pt deposits markedly improves the overall rate of VOC photomineralisation. For some VOCs, such as ethanol, the effect is a synergistic combination of semiconductor photocatalysis and thermal oxidation of the pollutant, catalysed by Pt. With other VOCs, such as acetaldehyde, this effect appears to be the sum of the two processes, although the Pt deposits may protect the semiconductor from poisoning at very elevated temperatures. Chloro-Pt(IV)-titania and other chloro-pgm-titania complexes have recently attracted attention as possible visible light sensitizers for water or air purification. However, at present they lack long term photostability.

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## References

- 1 A. Mills and S. Le Hunte, *J. Photochem. Photobiol. A: Chem.*, 1997, 108, 1 and references therein
- 2 M. R. Hoffmann, S. T. Martin, W. Choi and D. W. Bahnemann, *Chem. Rev.*, 1995, 95, 69 and references therein
- 3 A. L. Linsebigler, G. Lu and J. T. Yates, *Chem. Rev.*, 1995, 95, 735 and references therein
- 4 A. Mills and S.-K. Lee, *J. Photochem. Photobiol. A: Chem.*, 2002, 152, 233
- 5 M. I. Litter, *Appl. Catal. B: Environ.*, 1999, 23, 89 and references therein
- 6 J. W. M. Jacobs, *J. Phys. Chem.*, 1986, 90, 6507
- 7 U. Sieman, D. Bahnemann, J. J. Testa, D. Rodriguez, M. I. Litter and N. Bruno, *J. Photochem. Photobiol. A: Chem.*, 2002, 148, 247
- 8 J. Chen, D. F. Ollis, W. H. Rulkens and H. Bruning, *Water Res.*, 1999, 33, 661
- 9 C. Wang, A. Heller and H. Gerischer, *J. Am. Chem. Soc.*, 1992, 114, 5230
- 10 K. A. Magrini, A. Watt and B. Rinehart, *Solar Eng.*, 1995, 415
- 11 J. C. Crittenden, J. Lui, D. W. Hand and D. L. Perram, *Water Res.*, 1997, 31, 429

- 12 K. A. Magrini, R. M. Goggin, A. S. Watt, A. M. Taylor and A. L. Baker, *Solar Eng.*, 1994, 163
- 13 M. Lindner, J. Theurich and D. W. Bahnemann, *Water Sci. Technol.*, 1997, 35, 79
- 14 D. Bockelmann, M. Lindner and D. W. Bahnemann in "Fine Particles Science and Technology", ed. E. Pelizzetti, NATO ASI Ser., Ser. 3, Kluwer, Amsterdam, 1996, Vol. 12, pp. 675–689
- 15 J. Papp, H.-S. Shen, R. Kershaw, K. Dwight and A. Wold, *Chem. Mater.*, 1993, 5, 284
- 16 T. Sakata, T. Kawai and K. Hashimoto, *Chem. Phys. Lett.*, 1982, 88, 50
- 17 A. Mills and S.-K. Lee, *Platinum Metals Rev.*, 2003, 47, (1), 2
- 18 N. Z. Muradov, *Sol. Energy*, 1994, 52, 283
- 19 M. Trillas, J. Peral and X. Domenech, *Appl. Catal. B: Environ.*, 1995, 5, 377
- 20 H. Tahiri, Y. A. Ichou and J. M. Herrmann, *J. Photochem. Photobiol. A: Chem.*, 1998, 114, 219
- 21 K. Tanaka, V. Capule and T. Hisanaga, *Chem. Phys. Lett.*, 1991, 187, 73
- 22 V. Subramanian, E. Wolf and P. V. Kamat, *J. Chem. Phys. B*, 2001, 105, 11439
- 23 J. Peral and D. F. Ollis, *J. Chem. Technol. Biotechnol.*, 1997, 70, 117 and references therein
- 24 J. Peral and D. F. Ollis, *J. Mol. Catal. A: Chem.*, 1997, 115, 347
- 25 A. V. Vorontsov, E. N. Savinov, G. B. Barannik, V. N. Troitsky and V. N. Parmon, *Catal. Today*, 1997, 39, 207
- 26 J. C. Kennedy and A. K. Datye, *J. Catal.*, 1998, 179, 375
- 27 M. C. Blount and J. L. Falconer, *J. Catal.*, 2001, 200, 21
- 28 X. Fu, W. A. Zeltner and M. A. Anderson, *Appl. Catal. B: Environ.*, 1995, 6, 209
- 29 X. Fu, L. A. Clark, W. A. Zeltner and M. A. Anderson, *J. Photochem. Photobiol. A: Chem.*, 1996, 97, 181
- 30 J. L. Falconer and K. A. Magrini-Bair, *J. Catal.*, 1998, 179, 171
- 31 M. D. Driessen and V. H. Grassian, *J. Phys. Chem. B*, 1998, 102, 1418
- 32 G. Burgeth and H. Kisch, *Coord. Chem. Rev.*, 2002, 230, 41 and references therein
- 33 L. Zang, W. Macyk, C. Lange, W. F. Maier, C. Antonius, D. Meissner and H. Kisch, *Chem. Eur. J.*, 2000, 6, 379

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## Nanostructured Palladium in Methane Detection

In potentially hazardous atmospheres, the speedy detection of combustible gases is a priority, and for the natural gas industry early detection of methane is essential. One common method of detecting combustible gases is with pellistor sensor technology. Pellistors detect a rise of temperature in a gas on combustion. Typical pellistor construction has a coil of fine platinum (Pt) wire embedded in a refractory bead that is loaded with a catalyst, usually palladium (Pd). The Pt wire heats the catalyst to its operating temperature. The Pt wire also detects any extra heat produced if gas burns on the catalyst, by a change in its resistance as the catalyst temperature increases. However, as the Pt wire is very fine (10–50  $\mu\text{m}$  in diameter) pellistors are fragile. The power consumption of the device is high (120–500 mW) and they also have to be individually produced.

Recently micromachined 'hotplate' planar sensor structures, where a supported thin etched  $\text{SiO}_2$  or  $\text{SiN}$  membrane carries a Pt track on one side and a catalyst layer on the other, have been fabricated. The technology has resulted in smaller structures, less power use and should allow parallel production on the wafer level. However, due to the poor performance of the catalyst

layer, reliable devices have not been achieved.

Now, scientists at the University of Southampton have produced a micromachined pellistor structure that has low power consumption and a controllable catalyst structure (P. N. Bartlett and S. Guerin, *Anal. Chem.*, 2003, 75, (1), 126–132). Nanostructured Pd films were electrochemically deposited (e) from the hexagonal ( $\text{H}_1$ ) lyotropic liquid crystalline phase of a nonionic surfactant, octaethyleneglycol mono-hexadecyl ether, onto micromachined Si hotplate structures.  $(\text{NH}_4)_2\text{PdCl}_4$  served as the source of Pd. The electrodeposited nanostructured Pd catalyst layer can be formed into metal or alloy powders and films with regular nanoarchitecture. The  $\text{H}_1$ -e Pd films have high surface areas ( $\sim 28 \text{ m}^2 \text{ g}^{-1}$ ) and are effective and stable catalysts for the detection of methane in air on heating to 500°C. The response of the  $\text{H}_1$ -e Pd-coated planar pellistors was linearly proportional to a concentration of 0 to 2.5% methane in air with sensitivity of  $\sim 35 \text{ mV}/\%$  methane and good stability. Pd adhesion to the structure is excellent. The detection limit for devices is  $< 0.125\%$  methane in air.

There is optimism that practical commercial devices can be achieved from this technology.