

The influence of platinum (II) on TiO₂ photocatalyzed dye decolourization by rutile, P25 and PC500

Terry A. Egerton*, Herry Purnama¹, John A. Mattinson

School of Chemical Engineering & Advanced Materials, Newcastle University, NE1 7RU, UK

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ABSTRACT

The effect of deposition of 0.38% Pt(II) on the UV photocatalyzed decolouration of Reactive Orange 16 (RO16) and Malachite Green (MG) is reported for rutile TiO₂, for anatase PC500, and for the mainly anatase P25. The metal loading and oxidation state were those that previously [17], gave the largest enhancement ($\times 37$) of the UV photocatalyzed degradation of DCA, when Pt was deposited on rutile. For rutile, Pt(II) deposition enhanced the rate of UV decolouration ($\times 20$, for RO16, or $\times 8$, for MG). For PC500, Pt(II) deposition on PC500 reduced the decolouration of RO16 and increased the UV photocatalyzed decolouration of MG by only $\times 1.2$. On P25, Pt(II) significantly reduced the UV photocatalyzed decolouration of both dyes. Previously, [17], Pt(II) deposition on P25 enhanced DCA degradation by a factor of only 1.5. Complementary measurements showed that visible-light photocatalytic decolouration rates were small on all the catalysts. It was inferred that platinum influences the UV photocatalysis by facilitating the electron transfer to adsorbed oxygen, and that this facilitation is much more important for rutile than for anatase because formation of O₂⁻ is more difficult on Pt-free anatase than on Pt-free rutile.

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1. Introduction

Photocatalytic oxidation of organic molecules by TiO₂ has been extensively studied [1–4]. Particular attention has been given to the decolouration of dye solutions [5–16], either as a convenient test of photocatalytic activity [9–11], or, as with azo-dyes [12–15], with the ultimate aim of environmental remediation. In practice, anatase is generally found to be more effective catalyst than rutile [1,2] and the most widely studied TiO₂ photocatalyst is Evonik (formerly Degussa) P25, which is $\sim 80\%$ anatase.

Platinum deposition is well known to affect the photocatalytic activity of TiO₂ [8–12,14,15,17–26] and in most cases it probably modifies UV photocatalysis by providing an electron sink, which reduces charge carrier recombination [19]. Increases (typically $\times \sim 2.5$) of photocatalytic activity are often observed at low loadings but decreases have also been reported especially at high platinum loadings; usually the optimum loading is between, 0.25% and 1% [22–24]. Emilio et al. [25] reported that addition of 0.5% Pt on Evonik P25, Sachtleben Hombikat UV100 and Millennium Tiona PC50 increased catalytic activity for NTA degradation, although both 0.5% and 1% platinum decreased the degradation of 5 mM EDTA solutions. They concluded that the effect of Pt depends more

on the nature of the compound to be degraded than on the properties of the TiO₂. By contrast, the importance of the TiO₂ is evident in the results of Sclafani and Herrmann [22] who reported that for oxidation of 0.5 M aqueous propan-2-ol to acetone, 0.5% Pt on a 20 m² g⁻¹ rutile increased the rate $\times 3.5$ but decreased the rate on 14 m² g⁻¹ anatase by 10% and on 50 m² g⁻¹ P25 by 25%.

Egerton and Mattinson [17] summarized earlier studies on the effect of platinum on degradation of chloro-compounds and reported that platinum deposition reversed the relative activities of P25 and rutile for the decomposition of dichloroacetic acid (DCA). This was because Pt deposition on P25 increased the rates of DCA photodegradation by factors of less than 2, whereas deposition on a high area rutile enhanced activity by factors of up to 37. This increase is so large as to merit an examination of the generality of the effect, especially in view of the suggestion [25] that the effect of Pt depends more on the nature of the compound to be degraded than on the properties of the TiO₂.

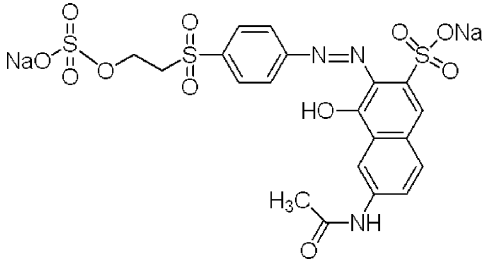
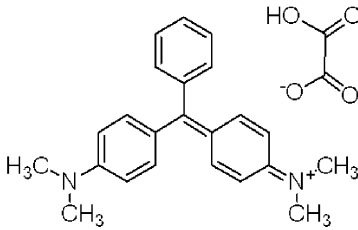
Decolouration of two different dyes, Reactive Orange (RO16) and Malachite Green (MG) was chosen to test the generality of the earlier observations because of the wide interest [5–16,26–36] in dye decolouration, because the molecules are more complex than the previously studied CHCl₂COO⁻ [17], and because their degradation involves attack on moieties which differ significantly from those in chloroacetic acids. The UV-photocatalyzed decolouration of the anionic azo dye Reactive Orange has been studied by Chen [27] Mahvi et al. [28] and Tizaoui et al. [29] and visible-light decolouration has been reported by Chatterjee et al. [30]. These studies have

* Corresponding author. Tel.: +44 0 191 222 5618.

E-mail address: T.A.Egerton@ncl.ac.uk (T.A. Egerton).

¹ Present address: Muhammadiyah University of Surakarta, Indonesia.

Table 1
Characteristics of the Reactive Orange (RO16) and Malachite Green (MG) dyes and the wavelengths of the visible absorption.

Name	Structure/molecular formula	Type	MW	λ_{\max}
Reactive orange 16 Remazol Brilliant Orange 3R	 $C_{23}H_{25}N_2 \cdot C_2HO_4 \cdot 0.5C_2H_2O_4$	Azo dye; anionic	617.54	493
Malachite green <i>N,N,N',N'</i> -tetramethyl-4,4'-diaminotriphenyl-carbenium oxalate Basic Green 4	 $C_{25}H_{28}N_4^+ \cdot C_2O_4^{2-}$	Triphenyl methane dye; cationic	463.50	617420

shown that the decolouration follows pseudo first-order kinetics and Chen's GC-MS results [27] demonstrate that cleavage of the N=N bond is an important step in the degradation. By contrast malachite green is a cationic triphenyl methane dye; it has been suggested previously [31] that its difficult and complicated UV-photocatalyzed decolouration may require catalyst properties that differ from those required for effective degradation of an acetic acid. Similar considerations prompted our choice of this dye. The reaction has been studied by Chen et al. [32], by Bojinova et al. [33], by Sayilkan [34], and by Asilturk et al. [35] and dye sensitized decolouration has also been reported [34–36]. At alkaline pH *N*-de-methylation takes place in a stepwise manner, but at low pH adsorption of the cationic dye on the positively charged TiO₂ surface is small, and cleavage of the whole conjugated chromophore system is believed to dominate [32]. Therefore a pH of ~4 was selected for the MG decolouration studies reported below.

The background to this study of dye decolouration by Pt deposited on anatase (PC500), on a mixed anatase/rutile (P25) and on a high area rutile is that Pt deposition on TiO₂ is generally considered to cause only modest improvements in decolouration rates. Thus, 0.8% Pt enhanced the activity of P25 for Acid Green 16 decolouration by 2.5 [26]. 1% Pt on an isopropoxide derived TiO₂ increased its activity for Acridine Orange decolouration by 2.5 [8]. Enhancements from 2.0 to 2.5 were reported for the effect of 1% Pt on methyl orange decolouration, [10–12]. 1% of adsorbed Pt ions increased decolouration rates of the azo-dye, ethyl orange by a factor of 3.2 [15] and of Rhodamine B by 2.5 [9].

2. Experimental

2.1. Materials

Reactive Orange 16 (RO16 or Remazol Brilliant Orange 3R) and Malachite Green (Basic Green 4) were both supplied by Sigma Aldrich, and were used as received; their characteristics are shown in Table 1. The high area rutile (120 m² g⁻¹; Croda Chemicals formerly Uniqema) was prepared by hydrolysis of titanium tetrachloride; its characterization has been reported previously [17,38]

and its morphology is compared with that of P25 in Fig. 1. Previous studies suggested that the long axes of the acicular rutile crystals are in the *c* direction. P25 (rutile:anatase = 20:80, ~50 m² g⁻¹; Evonik formerly Degussa) and PC500 (anatase, 325 m² g⁻¹; Millennium) were used as received.

2.2. Preparation of Pt(II)-TiO₂

The catalyst was prepared by photochemical deposition of 0.38% platinum from K₂PtCl₆ (Fluka, 40 wt% Pt). At pH ~3, with methanol present as an electron donor the Pt would be deposited as Pt(0) but (without methanol) at pH 10 it is deposited as Pt(II) [37]. The earlier work, on enhancement of DCA degradation [17], had shown that enhancement by Pt(II) was marginally greater than on Pt(0), and therefore deposition at pH 10 was selected. Transmission electron micrographs confirmed the presence of platinum on high area rutile [17]. XPS measurements [17] of peaks with binding energies of 72.85 and 76.13 eV confirmed the presence of Pt(II) on the high area rutile. Zhang et al. [37] demonstrated that this deposition method also gave Pt(II) on P25. In contrast to samples prepared at pH 3, all of these samples were light green in colour. Pt(0) samples were much darker consistent with the much stronger visible absorption seen in the reflectance spectra (Fig. 2). Although the deposition of both Pt(0) and Pt(II) changed the visible reflectance as shown in Fig. 2, there was no sign of a shift in the TiO₂ absorption edge. Nor was any shift in the absorption edge apparent in a Kubelka–Munk transformation of the reflectance data. A fuller description of the synthesis method and of the sample characterization has been given elsewhere [17].

2.3. Photoactivity measurement

The photoreactor was a cylindrical concentric system with the lamp in the axial well (Fig. 3). In preliminary measurements, with Millennium PC500, the highest rates of reaction were obtained at TiO₂ loadings of 1.0 and 2.0 g dm⁻³ and therefore all comparisons were carried out with 2 g dm⁻³ TiO₂ catalyst. The TiO₂ was pre-dispersed by 30 min milling, as described elsewhere [38]. The stirred

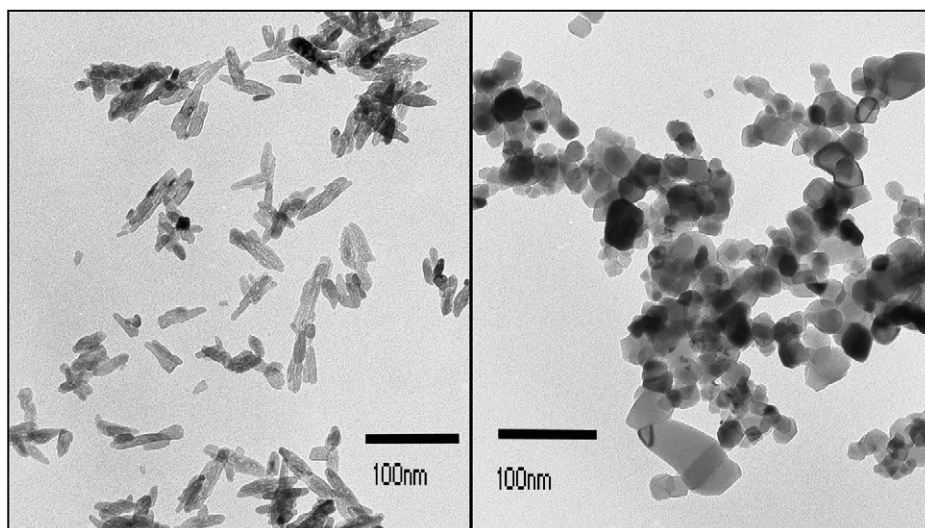


Fig. 1. A comparison of TEM images of rutile (left) and Degussa P25 (right) showing the acicularity of the high area rutile.

suspension in 0.05 mM dye solution was equilibrated in the dark at the natural pH of the suspension (~ 6.5 for RO16, ~ 4 for MG) for 30 min to allow adsorption equilibrium to be achieved. During this time the solution concentration of dye fell, by $\sim 10\%$, and the absorbance A_0 , corresponding to the lower concentration, C_0 , was taken as the initial absorbance in rate constant determinations. The suspension was then irradiated by UV (Philips PL-L 36 W).

Samples of the coloured suspension were taken every 30 min and centrifuged to remove TiO_2 prior to measuring their absorbance spectrophotometrically (Shimadzu UV mini 1240).

This paper is concerned with UV photocatalysis but dye decolouration can also be by additional mechanisms. The first, dye sensitization, allows visible-light excitation of dye molecules followed by transfer of an electron from the excited dye to the TiO_2 and has been demonstrated for both azo dyes [39–41] and malachite green [28,35,36]. TiO_2 may also sustain photocatalytic activity as a result of absorption of visible-light by platinum clusters and salts. [9,42] Therefore, visible-light experiments were conducted using a visible-light lamp (Osram Dulux L 36W/835). The outputs of the UV and visible lamps are compared in Fig. 4, which shows that at 405 nm the two lamps had a similar output. The UV lamp has a maximum output near 365 nm and transmission measurements at this wavelength show that the TiO_2 absorbance is ca. 2 orders of magnitude stronger than that of the 0.05 mM dye solutions.

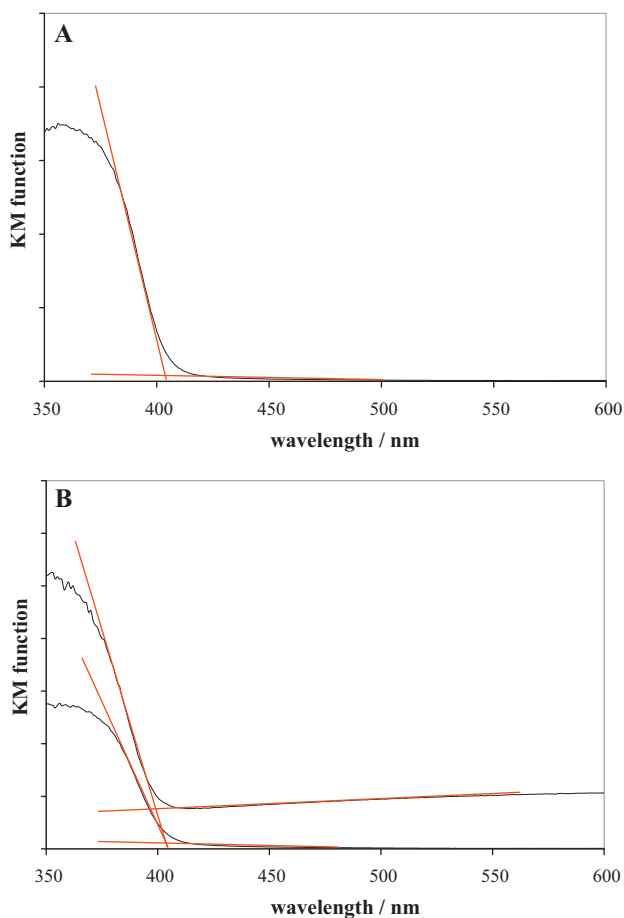


Fig. 2. Kubelka–Munk transformations of the reflectance profiles of. (A) The high area rutile and (B) Pt(0)/rutile (top line) and Pt(II)/rutile (bottom line).

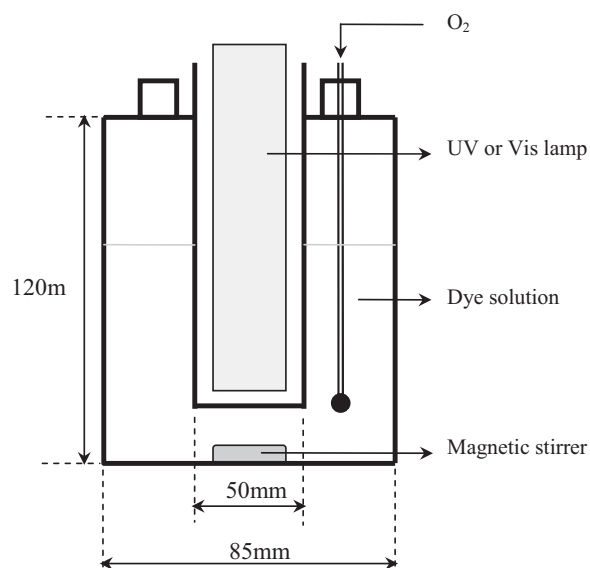


Fig. 3. Side view of cylindrical pyrex-glass photoreactor.

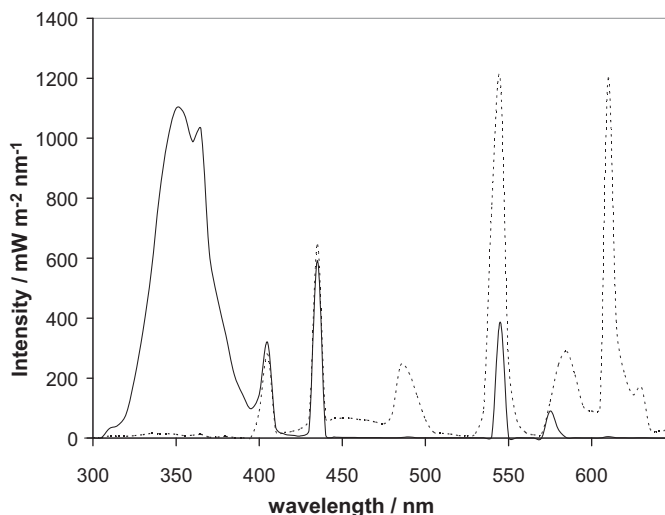


Fig. 4. The intensity of radiation from the UV lamp (—) or the visible lamp (---) placed inside the well of the reactor (see Fig. 3). The radiometer detector was positioned against the outer wall of the empty reactor. Taken from Ref. [17].

3. Results

3.1. UV photocatalysed dye decolouration

Reactive Orange 0.05 mM solutions had absorption maxima at 493, 385, 293 and 254 nm, with absorbances of ca. 1.2, 0.75, 1.2 and 1.4 respectively, consistent with previously published [43] spectra. The adsorption of RO16 on TiO₂ was briefly investigated using PC500, selected because its high area ($\sim 325 \text{ m}^2 \text{ g}^{-1}$) facilitated the measurements. (It is assumed that the behaviour of the other two catalysts would be broadly similar.) Absorbance measurements made on 0.05 mM RO16 solutions in the presence of 2 g dm^{-3} PC 500 TiO₂ varied little between pH 10 and 6 but decreased from pH 6 to pH 2. This implies that between pH 10 and 6 the adsorption changes little, although at low pH there is significant adsorption of the anionic dye onto the TiO₂, because below its pH of zero charge (p.z.c.) the TiO₂ surface is positively charged. A Langmuir analysis of the adsorption isotherm at pH 6 suggested that the adsorption was small with a surface footprint of $2900 \text{ nm}^2 \text{ molecule}^{-1}$.

Direct UV photochemical decolouration of RO16 was 2–3 orders of magnitude slower than photocatalytic decolouration, and was ignored. Preliminary photocatalytic measurements showed that the 385, 293 and 254 nm peaks all decreased at the same rate. The 493 nm absorption, mainly due to the N=N bond, decreased at a similar but $\sim 10\%$ larger rate. Since the 493 nm absorption dominates the visual colour of the solutions the results below are based on the decrease in this absorbance. Decolouration was quantified as A_t/A_0 where A_t was the absorbance after irradiation for time t , and plots of $\ln(A_t/A_0)$ vs. t for photocatalytic decolouration (Fig. 5a) were approximately linear – consistent with pseudo first-order kinetics – and were conveniently represented by the gradient of a best-fit straight line, as collated in Table 2. Although there is some scatter in the points the differences between individual rates are clear.

The decolouration rate of RO16 by rutile, $\sim 0.8 \times 10^{-2} \text{ min}^{-1}$, was much lower than by PC500, 10×10^{-2} , or by P25, 13.3×10^{-2} . On predominantly anatase samples, the decolouration rates were lower on Pt(II) samples; by a factor of 0.62 for PC500, by a factor of 0.32 for P25. However, on rutile, platinum increased the decolouration rate by a factor of ~ 20 to $15.7 \times 10^{-2} \text{ min}^{-1}$. Consequently decolouration on Pt/rutile was faster than on any of the other catalysts studied.

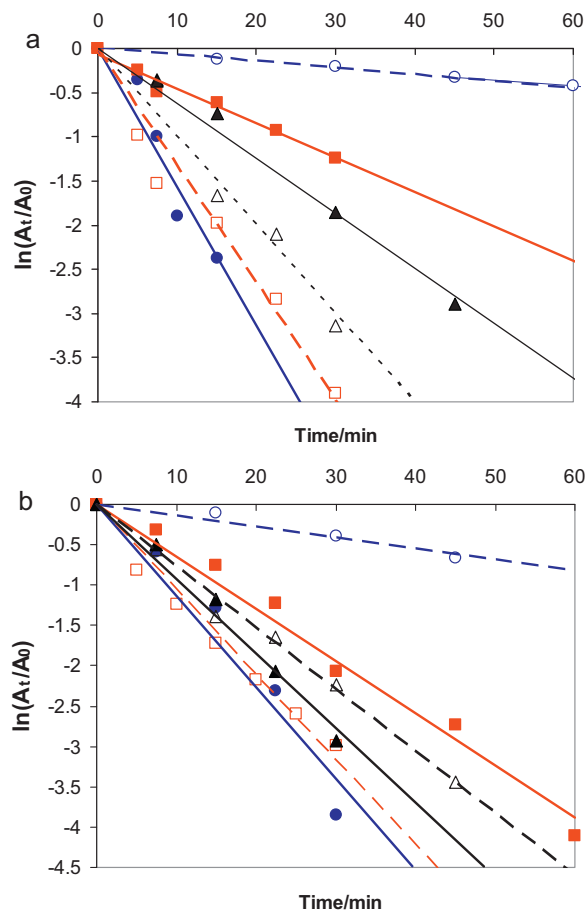


Fig. 5. (a) Photocatalytic decolouration of 0.05 mM Reactive Orange dye under UV irradiation by 2 g dm^{-3} TiO₂ [Rutile (○) P25 (□), PC500 (Δ)] and Pt/TiO₂ [Pt/Rutile (●) Pt/P25 (■), Pt/PC500 (▲)]. (b) Photocatalytic decolouration of 0.05 mM Malachite Green dye under UV irradiation by 2 g dm^{-3} TiO₂ [Rutile (○) P25 (□), PC500 (Δ)] and Pt/TiO₂ [Pt/Rutile (●) Pt/P25 (■), Pt/PC500 (▲)].

Malachite Green 0.05 mM solutions absorbed near 617, 420 and 310 nm, with absorbances of ca. 3.6, 0.8 and 0.8 respectively, consistent with published spectra [33,44,45]. Because Malachite Green is an amphoteric dye, its extinction coefficient changes with pH and therefore changes in absorbance as a function of pH are less easily interpreted in terms of its adsorption behaviour. However the results of others [44] indicate that at low pH the cationic malachite green adsorption does not adsorb extensively on the positively charged TiO₂ surface. The extinction coefficient of the strongest absorption, near 617 nm, which changes only slightly between pH 4 and pH 9, was used to follow the decolouration. Results for MG decolouration are shown in Fig. 5b. On PC500, platinum increased the decolouration rate by a modest amount ($\times 1.2$); although modest, the effect is opposite to that for Reactive Orange. On P25, Pt (II) decreases the MG decolouration rate to 6.5×10^{-2} , 61% of the rate without platinum, but for RO16 the Pt(II)/P25 rate was only 4.2×10^{-2} , 32% of the rate without platinum. On high area rutile Pt(II) increases the MG decolouration rate from 1.4×10^{-2} to $11.3 \times 10^{-2} \text{ min}^{-1}$, although this increase by a factor of ~ 8 , is less than the factor of 20 for RO16, Pt(II)/rutile is the most active catalyst for MG decolouration, as well as for RO16.

3.2. Dye decolouration photocatalysed by visible radiation

To assess the extent to which processes such as dye sensitization might contribute to decolouration, and hence perturb the photocatalytic results, the decolouration of RO16 and MG by the

Table 2

The rates of decolouration of reactive orange and malachite green solutions by TiO₂ and Pt/TiO₂ under UV and visible radiation. The figures in square brackets, [], are derived by dividing the rate for the Pt(II) catalyst by that for the Pt-free catalysts.

Catalyst	Dye	UV light Rate k_{UV}/min^{-1}	Visible-light Rate k_{vis}/min^{-1}	k_{vis}/k_{UV} (rounded ratio)
PC500	Reactive orange	10.0×10^{-2}	$0.8(5) \times 10^{-2}$	0.09
Pt(II)/PC500		6.2×10^{-2} [0.62]	0.1×10^{-2} [0.1]	0.02
P25	Reactive orange	13.3×10^{-2}	0.9×10^{-2}	0.07
Pt(II)/P25		4.2×10^{-2} [0.32]	0.2×10^{-2} [0.2]	0.05
Rutile	Reactive orange	0.8×10^{-2}	$0.1(5) \times 10^{-2}$	0.2
Pt(II)/Rutile		15.7×10^{-2} [20]	0.5×10^{-2} [3.3]	0.03
PC500	Malachite green	7.7×10^{-2}	1.1×10^{-2}	0.15
Pt(II)/PC500		9.2×10^{-2} [1.2]	1.2×10^{-2} [1.1]	0.15
P25	Malachite green	10.6×10^{-2}	1.0×10^{-2}	0.09
Pt(II)/P25		6.5×10^{-2} [0.61]	0.3×10^{-2} [0.3]	0.05
Rutile	Malachite green	1.4×10^{-2}	0.5×10^{-2}	0.35
Pt(II)/rutile		11.3×10^{-2} [8.1]	0.4×10^{-2} [0.8]	0.04

same catalysts was then measured under visible radiation (Osram Dulux L 36W/835). The results, shown in Table 2, demonstrate that for all catalysts the decolouration induced by visible radiation was a small fraction of the UV-photocatalyzed rate. Except for platinum free rutile, RO16 decolouration by visible-light was <0.1 of the UV rate. The higher relative rate of 0.2 on rutile only occurs because the UV rate on rutile is small, 0.8×10^{-2} , and the absolute rate of visible-decolouration on rutile is amongst the smallest of those measured. For MG the highest relative rate, $\times 0.35$, of visible-decolouration again occurred on rutile but, again, this is because the UV rate on rutile is small, 1.4×10^{-2} . Pt(II) had little effect on the visible-decolouration rate. The relative (to UV) rate of visible-decolouration was generally higher for MG than RO16 but in no case was it increased as a result of platinum deposition. Pt(II) made little difference to the visible-light decolouration of MG on PC500 but significantly decreased MG decolouration on P25, and of RO16 on both PC500 and P25.

4. Discussion

4.1. The implications of the results of visible-radiation decolouration for mechanism

As indicated above, azo dyes and malachite green can decolour by dye sensitization [28,30,35,36,40,41] or by absorption of visible-light by platinum clusters [9,42] and the visible-light experiments were conducted to determine whether the 1st or 2nd of these mechanisms contributed significantly to the measured decolouration.

For RO16 decolouration by visible radiation, the decolouration by as-received rutile was only 20% of the UV rate. Pt(II) increased the measured activity from 0.15×10^{-2} to $0.5 \times 10^{-2} \text{ min}^{-1}$ to a level $\sim 60\%$ that of the rate of UV activated decolouration unadorned rutile. Even so, the enhancement was much less than the increase from 0.8×10^{-2} to $15.7 \times 10^{-2} \text{ min}^{-1}$ in the UV decolouration rate. It is tentatively, because the rates are low, suggested that the 405 nm photons in the visible radiation (Fig. 2) are harvested and then used more effectively by the Pt(II) rutile. (The action spectrum for rutile extends to 405 nm [4]). For MG the decolouration rate ($0.5 \times 10^{-2} \text{ min}^{-1}$) induced by visible radiation on as received rutile was 35% of the UV rate, which may indicate that dye sensitization makes a larger contribution for MG than for RO16; the rate on Pt(II)/rutile was similar ($0.4 \times 10^{-2} \text{ min}^{-1}$). For both the anatase catalysts the rate constants for visible radiation, k_{vis} were much

smaller than those for UV, k_{UV} . For RO16 decolouration the values of k_{vis} (PC500, $0.85 \times 10^{-2} \text{ min}^{-1}$; P25, $0.9 \times 10^{-2} \text{ min}^{-1}$) were less than 10% of the corresponding rates for UV radiation and were further reduced by Pt(II) deposition. For MG decolouration by PC500, k_{vis}/k_{UV} was 15% and was unaffected by deposition of Pt(II). For MG decolouration by P25, k_{vis}/k_{UV} was 9%, but fell to 5% after deposition of Pt(II).

As the dye-sensitized reaction contributes little to the measured UV decolouration rate, and any changes associated with Pt(II) are either small or negative it is concluded that the large increases in UV decolouration rate caused by platinization of rutile are unlikely to be due to dye-sensitization or absorption of visible-light by platinum clusters.

4.2. Dye decolouration photocatalyzed by UV radiation

UV photocatalyzed decolouration of RO16 [27–29] and MG [31–35] has been widely reported and it has also been demonstrated that when doping extends the TiO₂ absorption into the visible region [34,35] photocatalysis may be initiated by visible wavelengths. Holes in the valence band are generated when electrons are photo-excited and may react either directly, by electron capture from the dye, or indirectly, by the formation of hydroxyl radicals. The involvement of hydroxyl radicals in MG decolouration has been demonstrated [44]. The excited electrons are captured by oxygen to form O₂⁻ and this reaction is often considered to be rate-limiting [45].

The UV photocatalyzed decolouration rates of both RO16 and MG on Pt-free anatase were much higher than on Pt-free rutile. P25 was $\times 17$ more active than rutile for RO16, and $\times 8$ times more active for MG, and these figures compare with the $\times 16$ greater activity for DCA degradation. The superior activity of the anatase is consistent with previous reports. Tayade et al. [46] reported rutile to be ~ 3 more active than anatase for MG decolouration, whilst Bojinova et al. [33] have reported that in mixed anatase/rutile catalysts increased anatase content always leads to higher activity. Kominami et al. [31] also reported a higher activity in their anatase HyCOM(823) than in the rutile-containing HyCOM(1023), though factors such as crystallinity were also considered to influence the activity.

The effect of platinum on the anatase catalysts was negative or small (for MG on PC500), as has been found in many other studies of UV catalysed dye decolouration by Pt/anatase

[8–12,17,18,22,25,26]. The reasons for the decreased decolouration rate of MG on Pt(II)/P25 and of RO16 on both Pt(II)/PC500 and Pt(II)/P25 are unclear. As stated in the introduction, the optimum level of platinum deposition is usually between 0.5% and 1%. Possible reasons for the decrease in activity above this optimum include reduced access of UV to the TiO₂ surface, blockage of active sites by metal, and increased charge recombination, as with silver, reducing desorption of intermediates which promote charge recombination [47]. Since the areas of the three TiO₂s vary from 50 to 325 m² g⁻¹ it is possible that the optimum loading also varies. If Pt(II) concentrations were to be adjusted (on a surface area basis) to be equivalent to the 0.38% on 120 m² g⁻¹ rutile, the 325 m² g⁻¹ PC500 would require 1% Pt(II) and the actual level of 0.38% could be significantly sub-optimum. On the 50 m² g⁻¹ P25, the same surface concentration would correspond to 0.16% Pt(II). However, for DCA degradation [17] 0.15% Pt(II)/P25 was only slightly more active (5.3×10^{-3}) than 0.38%Pt(II)/P25 (4.7×10^{-3}) and both were more active than P25 (3.2×10^{-3}). Also, though 0.38%Pt(II) gave the highest activity on rutile, the fall in the activities from 3.1×10^{-3} to 3.0×10^{-3} and then 2.4×10^{-3} min⁻¹, as the Pt(II) loading increased from 0.38% to 0.7% and then 1%, is small and all these catalysts were more active than rutile (8.4×10^{-5}). It would appear that if 'overloading' is responsible for the observed decreases, it must have a much greater effect on dye decolouration than on DCA degradation. A fuller analysis would require measurements on a series of catalysts with different amounts of platinum.

In marked contrast to the results for anatase, dye decolouration on rutile showed significantly higher rates, ($\times 20$ for RO16, $\times 8.1$ for MG) in the presence of Pt(II). These may be compared with increased rates of dichloroacetate degradation by rutile of $\times 37$ for 0.38% Pt(II), and $\times 33$ for 0.38%Pt(O) [17]. However, the decolouration rates of the Pt(II)/rutile samples were only slightly higher than those for the as-received P25. The increased rate could not be attributed to a shift of the absorption edge to longer wavelengths, because Fig. 2 shows that unlike the results of, e.g., Sayilkan [34] or Asilturk et al. [35] the absorption edge was unchanged. Following others [2,48], it is suggested, that one important reason why the photocatalytic activity of anatase is larger than that of rutile is that the rate-determining transfer of electrons to O₂ is faster on anatase than on rutile. (The higher energy (by ~ 0.2 eV) of the anatase conduction band may facilitate more rapid transfer of electrons to O₂, reduce surface electron-hole recombination and consequently increase the photocatalytic activity.) Because the transfer of excited electrons to oxygen is more facile on anatase (and leads to its higher photocatalytic activity), any benefits associated with deposition of platinum on the anatase surface are small and may be offset by the other effects of platinum. By contrast, because transfer of electrons to oxygen on rutile is less easy the benefits of transfer to platinum are more apparent. This implies that the decolouration rates on platinised rutile should be comparable with those on platinum-free anatase and the measured rates are in fact close. For RO16 they are 15.7×10^{-2} min⁻¹ for Pt/rutile, 13.3×10^{-2} min⁻¹ for P25 and 10×10^{-2} min⁻¹ for PC500. For MG they are 11.3×10^{-2} min⁻¹ for Pt/rutile, 10.6×10^{-2} min⁻¹ for P25 and 7.7×10^{-2} min⁻¹ for PC500. The differences can be partially attributed to the additional photons, between 385 and 405 nm that are absorbed by rutile but not by anatase. Different extents of dye adsorption may influence activity [7,49] but it is unlikely that the changes in surface area control the activity pattern because the surface area of the rutile is intermediate between the two anatase samples.

5. Conclusion

The main conclusion of this work is that the deposition of Pt(II) on rutile greatly increases the UV photocatalyzed decolouration of

both reactive orange and malachite green. Although the deposition of 0.38% Pt(II) had only a small effect on the decolouration rates on both P25 and PC500, the decolouration rates on rutile increased by factors of 8 for MG green and 20 RO16. As a result the decolouration rates on Pt-rutile catalysts were comparable with (though slightly larger than) the rates on the predominantly anatase samples. These large increases for 0.38% Pt(II) on rutile are analogous to the previously observed [17] large increase, $\times 37$, of the rate of DCA photocatalytic degradation and broaden the evidence that the rate enhancement observed may be a general effect. It is suggested that, in both DCA and dye decolouration studies, the photoactivity of rutile increased because the Pt reduced electron-hole recombination by acting as an electron sink. On anatase Pt deposition has less effect, or a negative effect, in both studies, probably because there is more facile transfer of electrons to adsorbed oxygen.

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