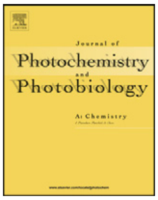
Journal of Photochemistry and Photobiology A: Chemistry 216 (2010) 268–274

Contents lists available at ScienceDirect

Journal of Photochemistry and Photobiology A: Chemistry

journal homepage: www.elsevier.com/locate/jphotochem



Effects of particle dispersion on the measurement of semi-conductor photocatalytic activity

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ARTICLE INFO

Article history:
Available online 23 June 2010

Keywords:
Titanium dioxide
Photocatalysis
Dispersion

ABSTRACT

Milling changes the particle size distribution of TiO_2 suspensions and this is reflected in the changed optical characteristics. Typically, the visible transmission is increased, as large TiO_2 agglomerates are broken down, and the UV absorption is increased. It has been shown that the rates of dye decolouration, alcohol oxidation, and carboxylic acid degradation are all changed by milling. For all the TiO_2's tested (anatase and rutile, surface areas from ~8 to 140 $m^2 g^{-1}$) photocatalytic oxidation of propan-2-ol is reduced by milling. It is suggested that this is a consequence of the $I^{0.5}$ dependence of reaction rate on UV intensity. This argument was supported by demonstrating that the rate of salicylic acid degradation (which also exhibits $I^{0.5}$ dependence), is reduced by milling. By contrast there was no significant decrease in the rate of degradation of dichloroacetate (which exhibits I^1 dependence).

Fourfold changes in the rate of salicylic acid degradation were induced when the same catalyst was milled for increasing times. This implies that two catalysts which differ in activity by a factor of four may do so because of differences in their dispersion rather than because they have different intrinsic activities. It is also shown the relative performance of two catalysts which differ in their surface properties changes when they are milled. However, the relative activities of a series of iron doped catalysts with no deliberate differences in surface properties were not changed by milling.

1. Introduction

Many research programmes seek to rank the activity of TiO_2 photocatalysts. In a study of 8 commercial TiO_2 catalysts using 19 test reactions (phenols, acids, amines, chlorohydrocarbons, dyes, inorganic ions), Ryu and Choi found that the catalyst ranking depended on the test reaction and that each TiO_2 could be ranked as best in at least one reaction [1]. Pichat and Agrios proposed that the order of activity depends on whether the chosen test reaction proceeds by direct transfer of the UV generated holes or *via* hydroxyl radical intermediates [2]. Recent comparisons of the relative activities of P25 and PC500 and other TiO_2's have included investigations of the liquid phase photocatalytic degradation of aromatic sulphonic acids [3,4], the pesticide diuron [5], uracil and 5-bromouracil [6] and herbicides [7,8] the decomposition of microcystin-LR [9] and the photocatalytic reduction of selenium ions [10]. These careful studies, and others, addressed the effects of catalyst loading, surface area, and medium pH. This emphasis reflects the prime importance of reactant adsorption, which in conventional/dark heterogeneous catalysis, depends on both the amount of available surface and the surface charge. By contrast the initial step in photochemical reactions is photon absorption. This is controlled by the optical properties of the TiO_2 suspensions and these depend on the particle dispersion. Therefore, this paper focuses on the effects of changes in catalyst dispersion.

The scattering and absorption of radiation by dispersed semi-conductor particles depend on the refractive index of the medium and on the intrinsic properties of the particle (the real and imaginary parts of the refractive index of the semi-conductor at the wavelength of interest) and on the size of the particles *in suspension* [11]. 10 nm particles are too small to significantly scatter visible light but, in practice, suspensions of such nanoparticles usually appear white. For example, although both BET and XRD (Debye Scherrer) measurements imply that the primary particle size of PC500 is ~5 nm [4–10], unmilled suspensions are white and, as shown below, their transmission spectra show a maximum at about 750 nm [12] which is consistent with a particle size of ~400 nm. This estimate is of the same order as the 'dispersive particle size' of 600–700 nm based on the ZetaPALS (Brookhaven instrument) measurements reported by Amal and co-workers [10]. The difference between the primary particle size of 5 nm and a dispersed particle size of 400–700 nm implies that the 5 nm primary particles of PC500 are extensively aggregated or agglomerated in suspension. This agglomeration is also present in suspensions of many other

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doi:10.1016/j.jphotochem.2010.06.023

Table 1
A summary of the TiO_2's considered in this study.

Identification code	Surface area ($m^2 g^{-1}$)	Crystalline form	Origin (formerly known as)
PC500	~320	Anatase	Cristal Global (Millenium) [3–10,12]
P25	50	Mainly (~70%) Anatase	Evonik Degussa (Degussa) Ref. [12]
LAR	~8	Rutile	Huntsman (Tioxide)
LAA	~10	Anatase	Huntsman (Tioxide)
LAR/1-AL	1% Alumina coated LAR	Rutile	Huntsman (Tioxide)
HAR	120–140	Rutile	Uniqema (Croda) Ref. [13]
MAR/ASt	76, Aluminium stearate treated	Rutile	Tayca–MT100T Ref. [13]
HAR/Fe	120–140	Fe doped rutile	Newcastle University [16]

TiO_2 photocatalysts. (The words 'aggregate' and 'agglomerate' are often used interchangeably. However, in this paper 'agglomerate' is used to designate a secondary particle which is relatively loosely bound and can be broken down to its component primary particles whilst maintaining the integrity of the primary particles.)

The widespread occurrence of agglomeration can be inferred from the use of stirrers to prevent catalyst sedimentation in photocatalytic reactors [3–9]. The steady state sedimentation rate, U, of particles of radius r and density ρ in a fluid of density ρ_f is described by Stokes Law:

$$U = \frac{2r^2(\rho - \rho_f)g}{9\eta} \quad (1)$$

where g is the acceleration due to gravity and η the viscosity of the fluid (for water η = 1 mPa s). For 100 and 10 nm particles Eq. (1) gives sedimentation rates of 0.70 and 0.7 nm s^{-1} respectively, and in both cases the figures would be greatly reduced by Brownian motion. If a photocatalytic experiment lasts 30 min, the maximum sedimentation distance would be ~0.1 mm which is too small to account for significant catalyst deposition. However, particle flocculation and agglomeration lead to much higher sedimentation rates and the consequent general use of stirrers in even small-scale catalytic reactors [3–9]. The actual size of the dispersed particles varies widely; it depends on the solids content, the dispersion conditions, and on the colloidal stability of the particles.

The measurements reported in this paper used a simple mill, described earlier [13], to change the size of the particles in suspension. Mild milling reduces the size of the catalyst agglomerates and alters the optical properties of the suspension. If milling acts mainly to breakdown extensive agglomerates and thus make more surface accessible to reactant molecules, an increase in the rate of photocatalysis would be expected. However, if the main effect of milling is to change the optical properties of the particle suspensions the changes in activity are less predictable. Therefore, this paper uses a range of reactions to explore the effect of milling TiO_2.

2. Experimental

2.1. TiO_2 samples

The different TiO_2 types used in this study are summarized in Table 1. A series of HAR/Fe samples, similar to the HAR high area rutile but with iron levels from 0.001 to 5 at.% was prepared by coprecipitation of iron acetate and titanium tetrachloride [16]. X-ray diffraction showed that all of these doped samples were rutile. X-ray line broadening showed that the iron-free sample had a crystal size of 9.5 nm; all the crystal sizes of the iron doped samples fell in the range 8.8 ± 1.3 nm.

2.2. Milling procedure

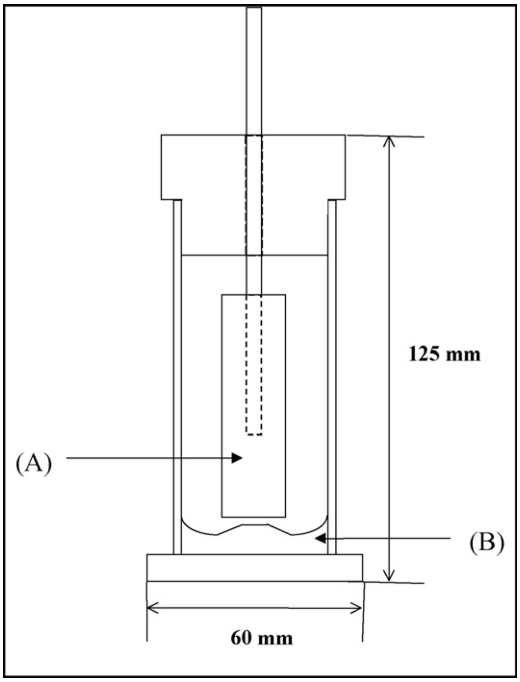

Fig. 1. The mill used for treatment of TiO_2 suspensions prior to catalytic measurements. 'A' is a polyurethane rubber impeller. 'B' is a silicone inset.

The milling procedure employed a simple attritor mill (sand-mill) shown in Fig. 1 and described earlier [13]. The mill was charged with an appropriate amount of TiO_2 (e.g. 0.4 g for propan-2-ol oxidation, 1 g for DCA oxidation) in 40 cm^3 of liquid and 50 g of ~200 μm glass balls (ballotini). An impeller rotating at 900 rpm imparted kinetic energy to the ballotini which then collided with, and broke down, agglomerated particles in suspension. The ballotini are sufficiently small (200 μm) to avoid the damage to TiO_2 primary particles because prolonged milling with 6 mm alumina cylinders [14] has been shown to fracture pigmentary TiO_2 of 200 nm primary size. After a fixed time, the milled suspension was decanted from the milling media which were washed to remove residual TiO_2. The washings were combined with the decanted liquid and the combined liquid was then diluted to 50 cm^3. In this way the samples of TiO_2 were not dried, and were therefore not reaggregated after milling. Changes in the optical properties were monitored by measuring the transmission of quantitatively diluted suspensions, using 1 mm path length cells.

2.3. Particle size measurements

The size distribution of selected dispersions was measured using an X-ray disc centrifuge (Brookhaven Instruments, B1-XDC) in which a centrifugal force induced by spinning the disk was used to sediment the particles. The sedimentation was then monitored by measuring the attenuation of a collimated X-ray beam and the particle size distribution calculated by the application of Eq. (1). Measurements were made on aqueous dispersions milled with a silicate dispersant. For agglomerates, the density of the water/TiO_2

composite is less than that of its constituent primary particles. Because the calculation uses the density of the primary particles (4.26 g cm^{-3} for rutile) the calculated radius underestimates the agglomerate size. For an agglomerate in which only 50% of the volume is TiO_2 the true particle size may be 40% larger than the instrument output. (Estimates derived from dynamic light scattering methods would be similarly in error because the refractive index of the agglomerate would be less than that of the primary particle.) Despite these caveats it is clear that milling decreased particle size, as detailed previously [13]. In a typical experiment the mean size of a sample of HAR milled for 30 min in the laboratory attritor mill had a nominal mean size of 29 nm compared with ~10 nm estimated from the surface area, or 7 nm from X-ray line broadening. An MAR/ASt sample decreased from a nominal 55 to 28 nm (compared with a BET derived size of 19 nm) after milling in a manner similar to, but not identical, with that described above.

2.4. Measurements of photocatalysis

2.4.1. Decolouration of Reactive Orange

Photocatalytic decolouration of 0.05 mM Reactive Orange (Aldrich: Remazol Reactive Orange RO16 $C_{20}H_{17}N_3Na_2O_{11}S_3$) was carried out in a 0.6 dm^3 cylindrical reactor with two 8 W lamps (Sylvannia BL-350) placed in annular lamp well, described previously [15]. The TiO_2 loading was 2 g dm^{-3} and the reaction suspension was sparged with oxygen (0.5 dm^3 min^{-1}). The extent of decolouration was monitored by measuring the absorbance at 493 nm.

2.4.2. Propan-2-ol oxidation

Measurements of the photocatalytic oxidation of propan-2-ol (isopropanol) to propanone (acetone) have been described previously [13]. 50 cm^3 of a milled suspension of TiO_2/isopropanol were placed in a 45 mm diameter cylindrical pyrex reactor, stirred from above. Prior to reaction, oxygen was bubbled through the suspension and during the reaction a flow of oxygen was slowly bled across the dead volume. (Air, not oxygen, was used in the work carried out by Harrison [16].) During the reaction the suspension was irradiated from below by two Philips 36 W actinic lamps (PL-L 09). Samples of the reaction mixture were withdrawn at appropriate intervals, and after removal of the TiO_2, analysed for propanone by gas chromatography, using a diethyl ether internal standard. Rate constants measured in replicate experiments agreed to within ±3%.

2.4.3. Salicylic acid degradation

Measurement of the photocatalytic degradation of salicylic acid solutions (0.36 mM) by TiO_2 (2 g dm^{-3}) were made [16] using the same reactor and lamp as used for the propan-2-ol oxidation experiments. The reaction mixtures were prepared by adding 5 cm^3 of 3.6 mM salicylic acid solution to 45 cm^3 of the milled TiO_2 suspension. The pH was adjusted to 4 with HCl. The degradation of the salicylic acid was followed using HPLC (Dionex UVD 170S). Elution from the C_{18} reverse phase column was monitored spectrometrically at 201 nm.

2.4.4. Degradation of dichoracetate anion at pH 3

Full details of the degradation of dichloracetate anion at pH 3 have been described previously [17]. The oxidation of 36 mM dichloracetate (DCA) was carried out using a TiO_2 loading of 4 g dm^{-3} in a 250 cm^3 annular reactor with 36 W lamp (Philips PL-L-09) with a broad output between 320 and 400 nm and a peak near 360 nm. The degradation was followed electrochemically using an ion selective electrode (Orion 96-17) to monitor the Cl$^-$ product released from the DCA during the experiment. Rate constants measured in replicate experiments agreed to within ±5%.

The UV intensity incident on the reaction mixture was varied by interposing solutions of UV-absorbing nitrophenol between the lamp and the reactant solution.

3. Results and discussion

3.1. Decolouration of Reactive Orange by PC500

The photocatalytic decolouration of 0.05 mM solutions of the azo dye, Reactive Orange RO16, by unmilled and milled suspensions of the high area anatase catalysts PC500 was compared. Even though the primary particle size (the crystal size) of PC500 is ~5 nm [10] the unmilled suspension was white and the transmission spectra, which is shown in Fig. 2a, had a maximum at about 750 nm. Using the approximate estimate that TiO_2 particles of diameter d give maximum scattering at wavelengths λ_{max} for which $\lambda_{max} = 2d$ [18,19] the TiO_2 particles in suspension are estimated to be ~400 nm. A single laser diffraction measurement (Beckman Coulter LS 13-320) gave a size of ~1300 nm, of the same order of magnitude as 600–700 nm reported by Amal and co-workers [10] on the basis of ZetaPALS (Brookhaven instrument) measurements. All these estimates suggest that unmilled dispersions of PC500 are extensively agglomerated. As shown in Fig. 1, the optical properties were significantly changed by milling. The transmission at 350–750 nm increases and the transmission at $\lambda < 350$ nm decreased. These changes are fully consistent with the large agglomerates present in the original, unmilled suspension being broken down by milling.

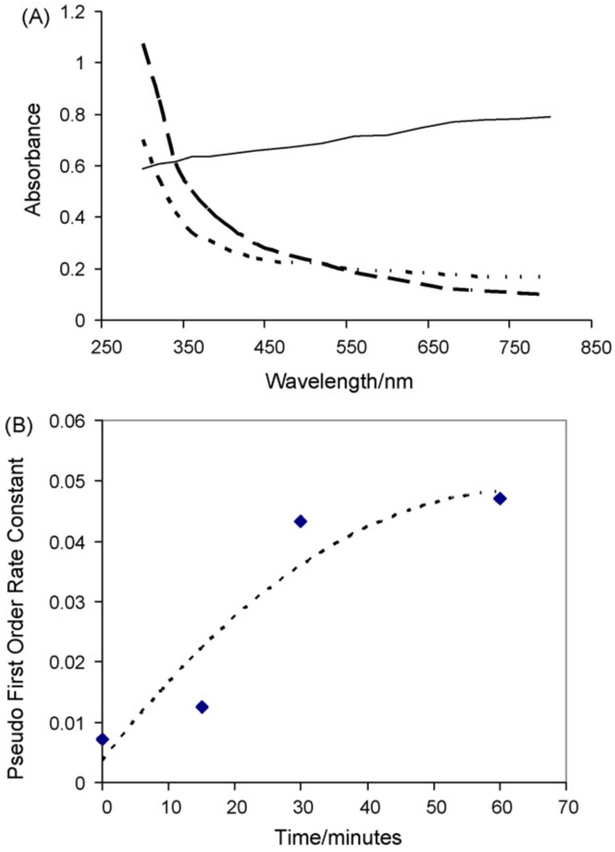

Fig. 2. (a) The effect of milling on the transmission of suspensions of PC500. Spectra after 15 min (broken line) and 30 min (dotted line) milling are compared with the spectrum of the unmilled sample (full line). (b) The increase with milling time of the pseudo first order rate constant for decolouration of a 0.05 mM Reactive Orange solution.

Table 2
The effect of 30 min milling on the photocatalytic oxidation of propan-2-ol by different TiO_2's.(P25 180 min milling). Measurements on different samples were made at different times and are not be strictly comparable because of small differences in experimental conditions.

Identification code and reference	Type and preparation route	Unmilled TiO_2 rate $10^5 \times$ rate mol dm^{-3} min^{-1}	Activity after 30 min milling, relative to activity of unmilled TiO_2
MAR/ASt [13]	Stearate coated	3.5	0.64
Different HAR preps. [13,16,21]	High area rutile Liquid phase hydrolysis (For Ref. [16] oxidation by air.)	15.4 (Ref. [13]) 4.1 (Ref. [16]) 4.8 (Ref. [21])	0.24 (Ref. [13]) 0.62 (Ref. [16]) 0.50 (Ref. [21])
P25 [13]	$TiCl_4$ flame hydrolysis	9.0	0.68
LAA (This study)	Precipitation/calcination	3.3	0.49
LAR (This study)	Precipitation/calcination	4.2	0.42
LAR/1-AL (This study)	Precipitation/calcination + 1% alumina coating	1.9	0.24

Measurements were then made of the photocatalytic decolouration of an sulphonated azo dye, Reactive Orange RO16, by milled and unmilled suspension of the PC500. The decolouration was followed by comparing the 493 nm absorption, A, after a time t, with A_0, the absorbance measured before irradiation but after allowing 30 min contact between the TiO_2 and the dye solution to permit any adsorption to reach equilibrium. Plots of $\ln(A/A_0)$ against t were good straight lines from which pseudo first order rate constants could be derived. Fig. 2b shows that the derived rate constants increased with milling time, which suggests that the breakdown of agglomerates has significantly increased the measured activity. Since adsorption is considered to be a necessary step in the degradation of related dyes such as reactive red and other sulphonated dyes [20], this could suggest that milling has increased the accessible surface area and has allowed the photocatalytic decolouration rate to increase. Comparisons of dye-adsorption kinetics and adsorption-equilibria on unmilled and milled dispersions under UV irradiation would allow this hypothesis to be tested.

3.2. *Isopropanol oxidation*

The photocatalytic oxidation of isopropanol to acetone was measured on a low area rutile (LAR) before and after milling for 30 min. No acetone was produced in the absence of TiO_2 nor was acetone produced in the absence of UV radiation. During irradiation, the concentration of acetone increased linearly with time. As shown in Fig. 3, which compares acetone production of unmilled and milled TiO_2, the rate of acetone formation was significantly lower for the milled TiO_2.

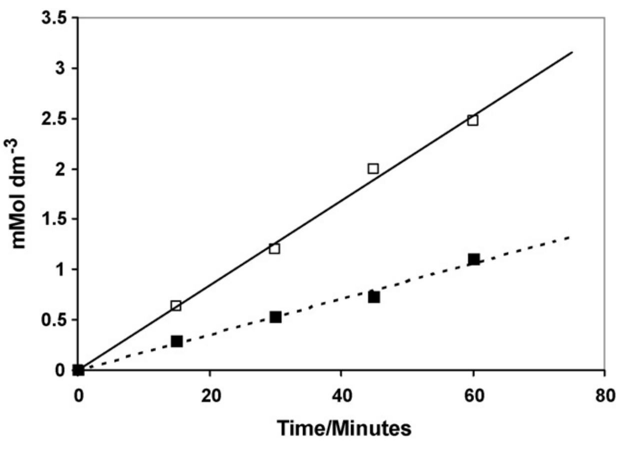

Fig. 3. Oxidation of isopropanol to acetone by a rutile of ~8 m^2 g^{-1} measured before, □, and after, ■, 30 min milling in the mill shown in Fig. 1.

For the unmilled TiO_2 the propanone formation rate was $4.2_1 \pm 0.1 \times 10^{-5}$ mol dm^{-3} min^{-1}; for the milled material it was $1.7_6 \pm 0.1 \times 10^{-5}$ mol dm^{-3} min^{-1}. A decrease in the measured rate of propanone formation when TiO_2 is milled has been demonstrated previously for a series of high area TiO_2's including P25 (~50 m^2 g^{-1}), a high area rutile (HAR: 140 m^2 g^{-1}) and a medium area rutile coated with aluminium stearate (MAR/ASt: 76 m^2 g^{-1}) [13] but no measurements on low area rutiles have previously been reported. To further explore the generality of the observed decrease of measured oxidation activity associated with milling, the experiments were repeated using the same low area rutile after surface treatment with alumina (LAR/1-AL) and also on a anatase of similar low area (LAA: 10 m^2 g^{-1}). These, and previous, results are summarized in Table 2. They confirm that the reduction in propan-2-ol oxidation rate occurs with a wide range of TiO_2's and that the reduction is always greater than 35% and typically about 50%. Since this trend is opposite to that observed in the dye decolouration study, it is useful to summarize the reason why increased milling decreased the photocatalytic oxidation of propan-2-ol.

It has been reported earlier [13] that milling increased UV absorption and that for a sample of HAR milled for increasing times the distance corresponding to 90% absorption of 350 nm radiation decreased from 2.2 mm (0 min) to 0.48 mm (7.5 min) to 0.24 mm (30 min). Since milling breaks down agglomerates but does not change either the mass of TiO_2 or the number of primary particles per unit volume the incident photons must be absorbed by the smaller number of crystals, say $1/F$ of the original number, within the reduced attenuation length. Correspondingly, each crystal must absorb F times as much UV. The photocatalytic oxidation of propan-2-ol is known to depend on the square root of the UV intensity, I [22,23], and it has been demonstrated previously [13] that this I^{05} is the cause of the decreased activity for propanol oxidation when the dispersion is improved. Because activity depends on $I^{0.5}$, the extra activity of each crystal increases by $F^{0.5}$. Now,

$$\begin{aligned}\text{The measured activity} &= \text{Number of crystals}\\ &\quad\times \text{Activity of each crystal}\\ &= \left\{\frac{1}{F}\right\} \times F^{0.5} = F^{-0.5}\end{aligned}$$

Consequently there is a reduction in oxidation rate when milling increases the UV absorption.

The above argument depends on the $I^{0.5}$ dependence of reaction rate. Therefore, it has been further tested by measurements on

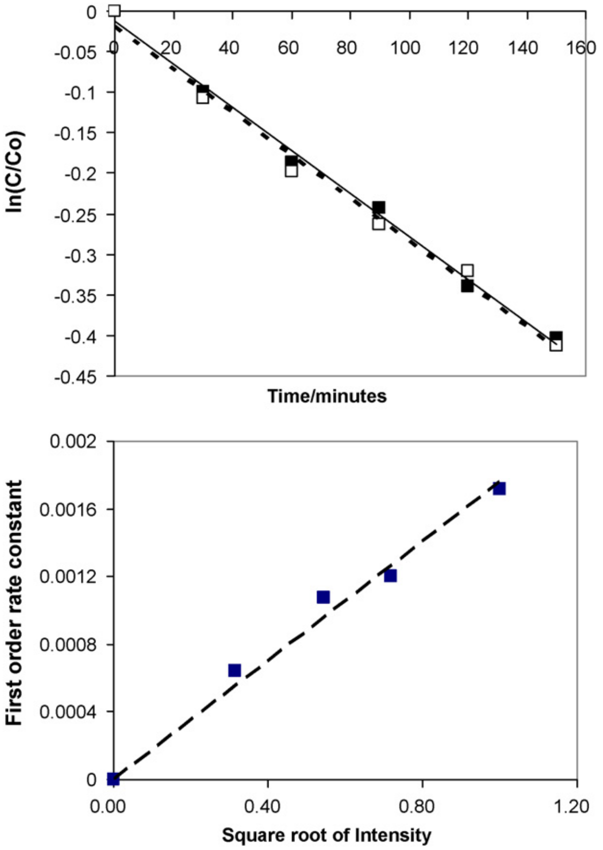

Fig. 4. (a) Degradation of 0.036 mM salicylic acid by an unmilled suspension of high area rutile (HAR) in water ■ ––, and water/propan-2-ol □- - - -. (b) Reduction of the rate of photocatalytic degradation of unmilled 0.036 mM salicylic acid solution as the UV intensity is progressively reduced by interposing neutral density filters between the lamp and the reactor.

the degradation of salicylic acid, since the rate of this reaction also depends on $I^{0.5}$, and on the degradation of dichloroacetic acid, the rate of which depends on I^1.

3.3. Photocatalytic degradation of salicylic acid

These experiments were carried out using the high area rutile, HAR. The disappearance of salicylic acid was well represented by a plot of $\ln(C/C_o)$ vs. time (Fig. 4a) and the pseudo first order rate constant was used as a measure of reaction rate. As shown in Fig. 4b the rate constant varied as $I^{0.5}$. The results in Fig. 5 show that milling the TiO_2 decreases the measured rate constant by approximately 80%.

The TiO_2 became yellow after contact with the salicylic acid solution, as has previously been reported [24,25], and, as shown in Fig. 4a, the rate of degradation of salicylic acid was unaffected by the addition of propan-2-ol. Both observations support the suggestion of Tunesi and Anderson [24] that photocatalytic degradation of salicylic acid is by direct hole transfer, unlike propan-2-ol oxidation, which proceeds by a hydroxyl radical mechanism [26]. Thus these results show that milling decreases reaction rate not only for the hydroxyl mediated propanol oxidation but also for a direct hole transfer reaction.

3.4. Degradation of dichloracetate anion

The photocatalytic degradation of dichloracetic acid and of the dichloroacetate anion (the major species in solution at pH 3) has been studied by a number of groups [27,28]. In general agreement with these previous workers, our results showed a linear increase of the chloride ion concentration with time and a rate of DCA degradation that was sensitive to pH. Bahnemann had also demonstrated [28] that at pH 3 the dichloracetate degradation increases *linearly* with increasing UV intensity and our own results (Fig. 6) confirmed this.

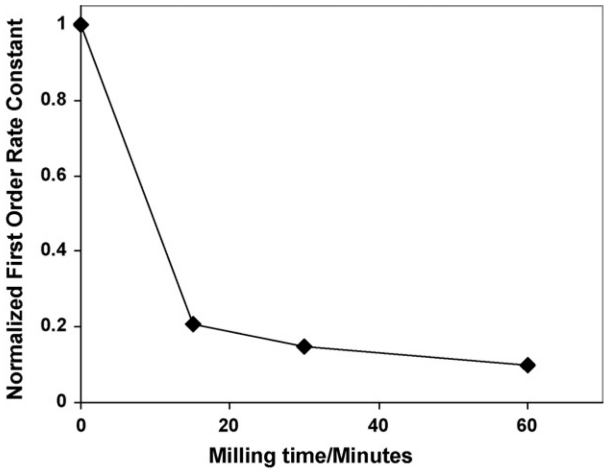

Fig. 5. Relative first order rate constants for the photocatalytic degradation at pH 4 of 0.36 mM salicylic acid by a high area rutile, HAR.

The transmission spectra of the 4 g dm^{-3} suspensions of HAR in 36 mM DCA were measured in a 1 mm path length cell after 15-fold dilution and without pH adjustment.

The results shown in Fig. 7 demonstrate that as with previous measurements the UV attenuation increased as the sample was milled.

The results for degradation of DCA at pH 3 on HAR rutile are shown in Fig. 8a and those for HAR and P25 are summarized in Fig. 8b. They demonstrate that in neither case does activity decrease significantly.

The results in Fig. 7 confirm that increased milling leads to increased UV attenuation of for HAR TiO_2/DCA suspensions. DCA degradation was selected for inclusion in this study because of the I^1 dependence of degradation rate on UV absorption. Consequently, if the decrease in measured photoactivity of propan-2-ol oxidation and salicylic acid degradation results from the $I^{0.5}$ relationship, milling would *not* be expected to decrease the DCA degradation rate. The results in Fig. 8a and b show that for P25 there was negligible change in degradation—increased UV absorption by individual crystals compensates for the reduced number of nanoreactors. For

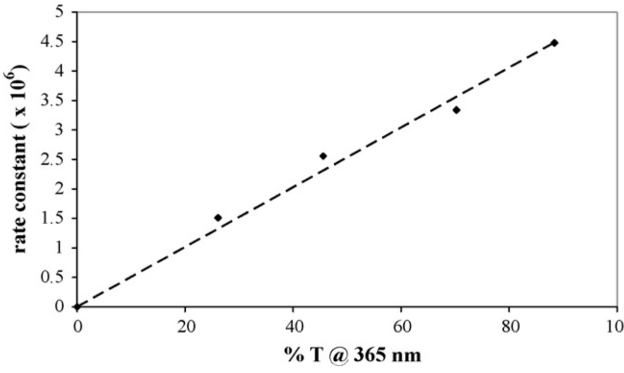

Fig. 6. The decrease in the rate of dichloracetate degradation at pH 3 by unmilled high area rutile (HAR) as the percentage transmission of the UV filter is gradually reduced.

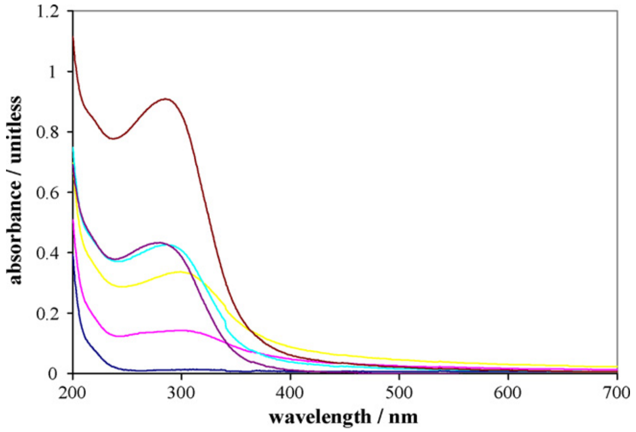

Fig. 7. Optical transmission of suspensions of HAR in DCA after milling for increasing times.

HAR the activity increased significantly (even though the adsorption of DCA did not increase significantly when the TiO_2 was milled for 1 h). As a consequence of these different responses to milling, P25 is only ∼3 times as active as HAR if both are milled for 30 min even though the unmilled P25 is ∼15 times more active than unmilled HAR.

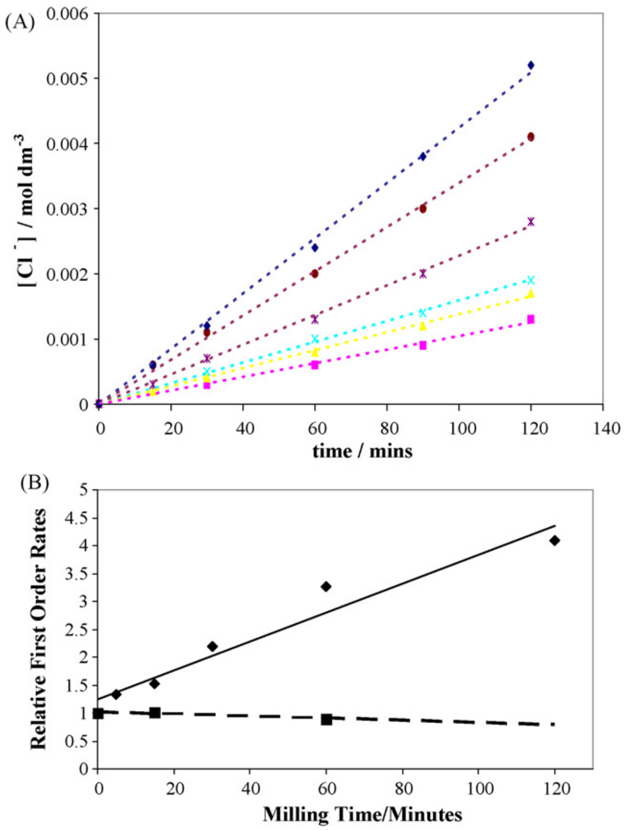

Fig. 8. (a) Effect of milling on DCA oxidation rate by HAR rutile: 0 min (- - - ■); 5 min (- - - ▲); 15 min (- - - ×); 30 min (_ _ _ *); 60 min (- - - ●); 120 min (- - - ♦). (b) Rates of photocatalytic degradation of dichloroacetate ion at pH 3. For both P25 ($k = 0.159$ mmol dm^{-3} min^{-1}, ■ . . . . . .) and HAR ($k = 0.0104$, mmol dm^{-3} min^{-1} ♦ ––) the rates have been normalized to the degradation rate of the unmilled suspension for which the rate constants are given in brackets. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of the article.)

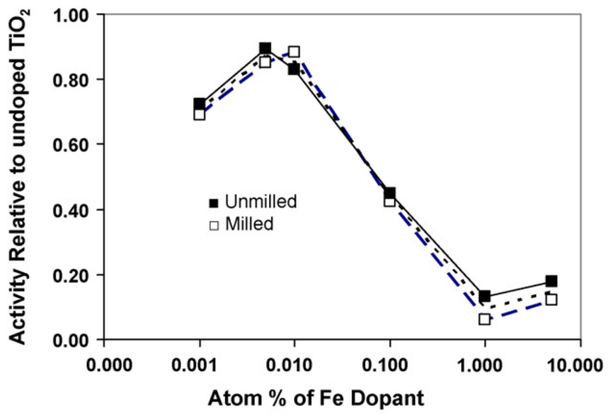

Fig. 9. The effect of 30 min milling on the photocatalytic activity for propan-2-ol oxidation of iron doped high area rutiles. For both unmilled and milled catalysts the activity of the undoped material is taken to be 1. {unmilled ■ ––; milled □– – – –; averaged. . . . .}.

3.5. *The influence of milling on the relative photocatalytic activity of different TiO_2's*

Since the previous sections have established that milling affects the measured photocatalytic activity of a wide range of TiO_2's, the effect of changes in the state of dispersion (the main consequence of milling) on the measured ranking of different photocatalysts is now addressed. The activities of a range of TiO_2's of similar size and surface characteristics are considered first and then the effect of milling on TiO_2's of different types and surface properties is reported.

The activities of a range of iron doped TiO_2's have been measured before and after milling. Each TiO_2 was laboratory-prepared and the only deliberate change was the amount of iron dopant introduced during the preparation. For each sample the photocatalytic activity for propan-2-ol oxidation was measured before and after 30 min milling. Milling reduced the activity by about 40% but for each series of measurements (one on unmilled and one on milled catalysts) the activities, which are shown in Fig. 9, were normalized to the activity of the undoped material. It is clear that the milling these catalysts has not significantly altered the measure of the efficacy of iron.

In Table 3 results of propan-2-ol oxidation are presented for TiO_2 of a similar crystal size but with either different structures (LAR cf LAA) or different surfaces (LAR cf LAR/1-AL). Milling did not change the ranking of these samples, but it did give a particularly large reduction in the activity of the alumina coated LAR/1-AL. Since LAR and LAR/1-AL differ only in the surface alumina on the LAR/1-AL, the result supports the argument that particle dispersion, which is known to be influenced by surface treatment, causes

Table 3
The effect of milling on the propan-2-ol photocatalytic oxidation rates on three catalysts. The figures in brackets have been normalized to the corresponding results for LAR rutile.

TiO_2 type	UnmilledTiO_2 rate $10^5 \times$ rate mol dm^{-3} min^{-1} Figures in brackets are normalized to the LAR result	Milled TiO_2 rate $10^5 \times$ rate mol dm^{-3} min^{-1} Figures in brackets are normalized to the LAR result	Relative rates unmilled/milled
LAR untreated rutile ∼8 m^{2}g^{-1}	4.2_0 (1)	1.7_8 (1)	2.4
LAA untreated anatase∼10 m^{2}g^{-1}	3.3_0 (0.79)	1.6_2 (091)	2.0
LAR/1-AL: 1% alumina coating on LAR	1.9_0 (0.45)	0.4_6 (0.26)	4.1

the difference. Although both milled and unmilled measurements show that the alumina surface treatment has significantly reduced the activity of the low area rutile, consistent with earlier studies of higher area material [29] the unmilled LAR/1-AL is *more* active than the milled LAR parent material which has not been surface treated. The relative activity of the alumina coated sample is much higher for the unmilled than for the milled sample. In this case, changes in agglomeration cause larger changes in the measured activity than does the surface treatment with alumina.

4. Conclusions

The results have demonstrated that the rates of four different photocatalytic reactions, decolouration of Reactive Orange dye, propanol oxidation, salicylic acid degradation and dichloroacetate degradations are affected by milling. Two other reactions (methyl viologen reduction [13] and nitrophenol oxidation [16] not been reported here) show the same effects. For photocatalysed propan-2-ol oxidation, the effect of milling has been demonstrated for the six different TiO_2 types shown in Table 2, and also for iron doped variants of HAR. The possibility that even the mild milling used in this study affects photocatalytic activity by inducing defect states, as has been proposed by Heller et al. [14] seems unlikely. First the milling media used in this study are much less massive than the 6 mm alumina cylinders used by Heller. Second, Heller found that many days milling was necessary (No photoactivity change was reported for samples taken after 1 day milling—presumably the change was insignificant.) and changes continued to be observed when the milling time was increased from 12 to 21 days. By contrast, we observed differences after only a few minutes and beyond 60 min further changes were minimal. Thirdly, in our experiments the effect of milling has been to sometimes increase and sometimes decrease oxidation rates.

The decrease in oxidation rate occurs for reactions whose reaction rate has been shown to vary as $I^{0.5}$ and can be explained by a mechanism that has been proposed previously for propan-2-ol oxidation [13]. It is significant that for DCA oxidation whose rate does not vary as $I^{0.5}$, milling does not decrease the rate. For DCA oxidation by high area rutile and Reactive Orange decolouration by PC500 milling increases the reaction rate. The reasons for these changes merit further investigation. Both reactions probably involve adsorption of the reactant [30,31] but preliminary measurements suggest that milling did not affect the equilibrium adsorption of DCA by the high area rutile. However, the possibility that milling alters the adsorption kinetics, by increasing the accessibility of the adsorption sites, cannot be excluded.

The finding that milling a photocatalyst may make a fourfold differences to the rate of a photocatalytic reaction implies that such a difference in the measured activity of two different catalysts may be a consequence of dispersion differences, not of intrinsic photoactivity change. Differences in dispersion are particularly likely if the catalysts have been made in different ways—for example, a TiO_2 made by a gas phase route may be less agglomerated and more easily dispersed than one made by calcination. The degree of catalyst agglomeration or flocculation may also be influenced by suspension pH, since flocculation will occur more readily at the isoelectric point. Changes in surface charge are known to affect reactant adsorption [4,6,20] but little attention has been given to how changes of UV absorption/scattering caused by changed colloidal stability influence photocatalytic reaction rates. Similarly, comparisons of the relative activity of the same catalyst when used as a suspended powder or on fibre [8] diatomite [20] or paper supports [5], may be affected by the different degrees of dispersion in the two conditions.

Acknowledgements

It is a pleasure to acknowledge financial support through the Muhammadiyah University, Surakarta, Indonesia (HP) and the UK EPSRC CASE award schemes with Huntsman (SEH) and Uniqema (RWH, JAM).

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