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Silver metallisation of titania particles: effects on photoactivity for the oxidation of organics

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Abstract

The effects of silver metallisation of titania on the photoactivity were investigated for the oxidations of sucrose, salicylic acid and phenol. The activity of silver/titania particles was dependent on the nature of the organic photooxidised. This dependence was linked to the influence of the parent organic and the intermediate organics on the overall rate of reaction.

Silver/titania enhanced the rates of sucrose oxidation by four times but possessed similar activities to bare titania for salicylic acid and phenol oxidation. The enhanced activity of silver/titania for sucrose oxidation was postulated to be due to improved charge separation and to the operation of an alternative reaction mechanism involving both oxidative and reductive pathways.

The lack of enhancement in salicylic acid oxidation was postulated to be due to the ability of salicylic acid and the intermediates to function as deep hole traps and mediate efficient charge separation on both bare and modified titania surfaces. Thus, surface metallisation was not required to further enhance charge separation.

The absence of rate enhancement in phenol oxidation was explained by a reported oxidation–reduction recombination cycle between the intermediates, hydroquinone and benzoquinone. The recombination of holes and electrons in the cycle was promoted with silver/titania particles. It is postulated that this nullified the beneficial effects of enhanced charge separation.

Keywords: Photocatalysis; Silver; Sucrose; Salicylic acid; Phenol; Surface metallisation

1. Introduction

Over the last 30 years, one particular water purification technique that has received much attention is heterogeneous photocatalysis. In this process, light-induced redox reactions take place on the surface of a catalyst [1]. Photocatalysis can be used for the treatment of waters polluted with toxic organic compounds and metal ions [2,3]. An excellent feature of this technique is that organic compounds may be completely mineralised to carbon dioxide, water and simple mineral acids in the presence of oxygen [4]. In addition, sunlight may be used as an attractive and possible source of photons to initiate photocatalytic reactions [5]. The fact that the end products of photocatalytic oxidation reactions are harmless and the added advantage of utilising a solar component has seen photocatalysis described as “green” technology [5,6].

Photocatalysis has been successfully used to degrade organics such as phenols, ketones, alcohols, alkanes, chlorinated alkenes and nitrogen-containing aromatics [3,4]. Precious metals such as Ag^+, Au^{3+} and Pt^{4+} can also be recovered from contaminated waters by their photocatalytic reduction to the metallic state [7–9]. The metal ions are reduced to the metal and deposited on the surface of the photocatalyst. The metal can be separated from the photocatalyst particles by centrifuging [10] or by digestion of the particles in aqua regia [9]. In aqueous systems containing both organic compounds and metal ions, the oxidation and reduction reactions can occur simultaneously [11,12].

Titanium dioxide (TiO_2) is widely used as a photocatalyst as it is inexpensive and non-toxic. The particles are stable in aqueous media and display high activity [6,13]. When titania particles are illuminated with near-ultraviolet light of energy equal to or greater than the bandgap energy ($\lambda < 380$ nm), electrons residing in the valence band are excited into the conduction band creating positively charged

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holes in the valence band (Eq. (1)). Holes and electrons migrate to the surface of the photocatalyst where they initiate oxidation and reduction reactions with adsorbed species. In aqueous titania suspensions, organic molecules, hydroxyl ions and water molecules are oxidisable species. Hydroxyl ions and water molecules are oxidised to hydroxyl radicals (Eqs. (2)–(4)). Electrons can reduce dissolved oxygen molecules to superoxide radicals and metal ions (Eqs. (5) and (6)). It is also possible that electrons reduce organic species as the potential of the conduction band electron is sufficient to reduce many organic molecules [14]. Holes and electrons can also recombine, leaving them unavailable for participation in useful redox reactions (Eq. (7)):

$$\mathrm{TiO_2} \xrightarrow{h\nu \geq E_g} \mathrm{e^-_{cb}} + \mathrm{h^+_{vb}} \tag{1}$$

$$\mathrm{h^+_{vb}} + \mathrm{OH^-_{ads}} \rightarrow \mathrm{OH^{\bullet}{}_{ads}} \tag{2}$$

$$\mathrm{h^+_{vb}} + \mathrm{H_2O_{ads}} \rightarrow \mathrm{OH^{\bullet}{}_{ads}} + \mathrm{H^+} \tag{3}$$

$$\mathrm{h^+_{vb}} + \mathrm{D_{ads}} \rightarrow \mathrm{D^+_{ads}} \tag{4}$$

$$\mathrm{e^-_{cb}} + \mathrm{O_2} \rightarrow \mathrm{O_2}^{\bullet -} \tag{5}$$

$$\mathrm{e^-_{cb}} + \mathrm{M}^{n+} \rightarrow \mathrm{M}^{(n-1)+} \tag{6}$$

$$\mathrm{e^-_{cb}} + \mathrm{h^+_{vb}} \rightarrow \mathrm{TiO_2} + \text{energy} \tag{7}$$

One drawback of photocatalytic reactions is the low efficiency or quantum yields usually achieved. The efficiency of photocatalytic reactions is governed by how effectively electrons and holes are channelled into oxidation and reduction reactions before recombination takes place [15]. Typically, the quantum yields of photocatalytic reactions achieved with commercial titania samples are quite low (of the order of 1% or less) [16]. Therefore, increasing the efficiency of photocatalytic processes is important for applications of this technique in the future [5]. To improve the efficiency of photocatalytic reactions, the lifetimes of electrons and holes in TiO_2 particles must be increased before recombination takes place [17].

One approach that has been applied to improve the photoactivity of titania particles in organic oxidation reactions is by the deposition of metals such as silver, gold, platinum and palladium on the photocatalyst surface [18,19]. The deposition of noble metal crystallites on the titania surface is said to accelerate both the removal of electrons from the particles and their transfer to molecular oxygen [20]. According to Gerischer and Heller [21], the reduction of oxygen to superoxide radicals is proposed to be the rate-limiting step in the photocatalytic oxidation of organics. When oxygen reduction is rate-limiting, electrons accumulate on the photocatalyst surface and increase the rate of electron–hole recombination [22]. Thus, in the presence of metal deposits, the quantum yield of the reaction may be increased by improving the separation of charge carriers and the rate of oxygen reduction.

The findings of various studies on the effects of surface metallisation on titania activity are contradictory. While some reported that surface modification of TiO_2 particles improved the photoactivity considerably [4,19], others reported that the effect was detrimental [23,24]. For example, platinised titanium dioxide particles (Pt/TiO_2) enhanced the mineralisation of dichloroacetic acid by 160% and the mineralisation of 4-chlorophenol by 39% compared to bare titania particles [19]. In contrast, the activity of Pt/TiO_2 particles was lower than bare TiO_2 particles for the photooxidation of cyclohexane to cyclohexanone [23].

Thus, further work is required in order to clarify the effects of surface metallisation on titania photoactivity in organic oxidation reactions. In this work, the activities of bare titania and silver metal surface-modified titania particles were compared for the photooxidations of sucrose, salicylic acid and phenol to carbon dioxide and water under ambient and oxygen-enriched conditions. Some explanations have been proposed to understand the differences and the similarities in the activities of bare and surface metallised titania particles in these oxidation reactions.

2. Experimental

2.1. Chemicals

Milli-Q water (Millipore, Milli-Q PLUS) was used in the preparation of all solutions. Stock solutions of sucrose (>99% pure, Fisons Scientific Equipment), salicylic acid (>99% pure, Aldrich) and phenol (>99% pure, Aldrich) of various concentrations (1–20 g carbon (C)/l) were prepared. A stock solution of silver(I) nitrate (99.9999 wt.%, Aldrich) was also prepared at a concentration of 10 g/l. Degussa P25 was used as the titanium dioxide photocatalyst (primary particle size −30 nm, surface area −50 m^2/g). Titanium dioxide suspensions were prepared at a loading of 2.0 g/l and mixed well by ultrasonic agitation. The suspension pH was adjusted to 3.0–3.5 with perchloric acid (Aldrich). Modified TiO_2 suspensions were prepared by adding the required quantities of silver nitrate to the suspension such that the desired Ag^+/Ti atom:atom ratio was obtained. Silver ion loadings of 2.0 and 20.0 at.% were used in study. The various silver/titania (Ag/TiO_2) samples prepared in this work were identified by the silver ion loading added to the suspension prior to illumination.

2.2. Dark adsorption experiments

Suspensions of bare titania and silver/titania particles (prepared at a silver ion loading of 2.0 at.%) were prepared (0.2 wt.%, pH 3.5). Sucrose, salicylic acid and phenol loadings of 2000 μg C were added to 20 ml aliquots of the photocatalyst suspension and mixed well by magnetic stirring for 0.5, 1 and 24 h to promote adsorption/desorption equilibrium. At a carbon loading of 2000 μg (μg C), the concentrations of sucrose, salicylic acid and phenol present in the suspension initially were equivalent to 238, 164 and 131 ppm, respectively. After mixing, the suspension was filtered (0.22 μm filter, Millipore) and the clear filtrate was analysed for the concentration of sucrose, salicylic acid or phenol. The amount of organic adsorbed was determined by difference between the amount of organic present in the suspension initially and the amount of organic remaining in the suspension after mixing.

The concentration of sucrose was measured by total organic carbon (TOC) analysis (ANATOC Series II analyser). The concentration of salicylic acid was measured by UV-Vis absorbance spectroscopy (Varian CARY 1E) at 294 nm. The concentration of phenol was measured by gas chromatography–mass spectrometry (GC–MS) on a Varian GC/MS/MS Saturn 2000 instrument. The stationary phase was a SGE DB5 column. The filtered samples were acidified with concentrated sulphuric acid (H_2SO_4) and extracted with dichloromethane prior to analysis.

2.3. *Photoactivity tests*

The photocatalytic oxidation reactions of sucrose, salicylic acid and phenol were conducted using a spiral, slurry-type photoreactor. The apparatus and the procedure used in this work are similar to that previously described by Matthews [25] and Abdullah et al. [26]. A brief description of the experimental procedure is given here. A detailed description can be found in a previous publication [27].

The reactor consisted of two glass coils (with 45 turns each) of similar height. A blacklight lamp (NEC, 15 W, maximum emission at −350 nm, emission range 300–400 nm) was fitted through each coil. The combined light intensity of the lamps was 1.554×10^{20} photons/min (4.30 μE/s or 0.258 mmol photons/min) at 350 nm as measured by potassium ferrioxalate actinometry [28]. The glass coils were connected to a peristaltic pump (Masterflex® Quick Load, Cole Parmer Instrument Co., Extech Equipment Pty Ltd.), a gas–liquid separator and a conductivity cell ($K = 0.1\,\mathrm{cm}^{-1}$) by Viton tubing. The conductivity cell consisted of a probe dipped in 10 ml of Milli-Q water with a gas inlet at the bottom and an air outlet at the top of the cell.

The photocatalyst slurry (20 ml) was introduced into the reactor and circulated at a flow rate of 72 ml/min. The suspension was air-equilibrated. The desired amount of organic solution equivalent to 2000 μg C was injected into the suspension and mixed for 30 min to allow dark adsorption of organic molecules on the photocatalyst surface. When illumination was initiated, carbon dioxide was generated during the reaction. Carbon dioxide in the liquid phase was separated into the gas phase in the gas–liquid separator and pumped through to the conductivity cell. As the generated carbon dioxide dissolved in the conductivity cell water, the conductivity readings increased. The conductivity readings were displayed on an Alpha 800 conductivity meter and recorded every 10 s until no further change in the conductivity values was detected.

A calibration curve was used to convert the conductivity readings to the mass of carbon generated as carbon dioxide. For each experimental run, the values obtained for the mass of carbon generated as CO_2 were normalised to account for the differences in the amount of ambient carbon dioxide dissolved in water prior to the reaction from day to day. The reactions were conducted at ambient temperature and pressure.

For mineralisation experiments using oxygen-enriched suspensions, oxygen gas was purged into the reactor for 90 min prior to starting the reaction. As the suspension was purged with oxygen for 90 min, the new dissolved oxygen concentration is expected to be significantly higher than ambient dissolved oxygen levels or close to saturation levels.

3. Results and discussions

3.1. *Control experiments*

In the absence of illumination, the mineralisation of sucrose, salicylic acid and phenol did not proceed in both bare titania and silver ion-modified titania suspensions. In the presence of illumination (30 min illumination) and in the absence of titania particles, the mineralisation of the organics did not occur. Similar observations were made in the absence of both illumination and titania particles. These findings showed that both illumination and titania particles were required for the photocatalytic oxidation reactions to proceed.

3.2. *Dark adsorption studies*

The adsorption of 2000 μg C sucrose on both bare titania and silver metal-modified titania particles was negligible. The adsorption studies on salicylic acid showed that approximately 198 μg C (9.9%) and 352 μg C (17.6%) were adsorbed on bare titania and silver/titania particles, respectively, at a salicylic acid loading of 2000 μg C. The adsorption of salicylic acid on bare titania resulted in a colour change of the particles from white to yellow. This was due to the formation of charge transfer complexes between salicylate ions and titanium atoms on the titania surface [29,30]. A colour change was not observed with silver/titania particles as these particles were light brown in colour. However, salicylic acid can also adsorb on silver metal surfaces by the formation of silver–salicylate complexes [31,32]. At pH 3.5, salicylic acid (pK_a 2.97) dissociates to form negatively charged salicylate ions. At pH 3.5, titania and silver/titania particles are positively charged (Degussa P25 TiO_2 point of zero charge 6.8) [33]. Thus, the adsorption of salicylate ions on the photocatalyst particles is favoured.

The adsorption studies of phenol showed that at the 2000 μg C phenol loading, 73 and 31% of the initial phenol loading was adsorbed onto bare titania and silver/titania surfaces, respectively. The different amounts of salicylic acid and phenol adsorbed on bare titania and silver/titania surfaces indicated that the presence of silver deposits on the titania surface affected the adsorption properties of the organics on titania particles before and after surface modification.

3.3. Photocatalytic mineralisation of sucrose, salicylic acid and phenol under ambient and oxygen-enriched conditions

The photocatalytic oxidations of sucrose, salicylic acid and phenol to carbon dioxide and water were performed using titanium dioxide and silver ion-modified titanium dioxide suspensions. In silver ion-modified titania suspensions, silver ions were reduced to silver metal and deposited on the titania surface during the simultaneous oxidation of the organics. The presence of metallic silver on the titania surface was confirmed by X-ray diffraction analysis of the modified particles [34]. The deposition of metallic silver on the TiO_2 surface during the reaction was indicated by a colour change of the particles. At the 2.0 at.% Ag^+ loading, the colour of the slurry changed from white to light brown. At the 20.0 at.% Ag^+ loading, the colour of the suspension changed to dark brown initially and then to yellow as the reaction progressed. Similar colour changes were observed by Herrmann et al. [7]. At the 2.0 at.% silver ion loading, the mass of silver deposited on the TiO_2 surface as a percentage of the initial mass of silver ions added to the suspension during the simultaneous oxidation of sucrose, salicylic acid and phenol was 46.1, 48.8 and 38.0%, respectively [27,35]. Thus, the compositions of these particles were equivalent to 1.3, 1.3 and 1.0 wt.% Ag^0, respectively. Transmission electron microscopy analysis of silver/titania particles prepared at nominal silver ion loadings of 2.0 and 20.0 at.% showed that nanosized (5 nm or less) silver particles were present on the titania surface. Agglomerates of silver metal up to 125 nm were also observed on silver/titania particles prepared at the 20.0 at.% silver ion loading [27,35].

In the first part of the study, bare titania and silver ion-modified titania suspensions were used for the oxidation of sucrose. In Fig. 1 the activities of TiO_2 and Ag^+-modified TiO_2 suspensions for the mineralisation of sucrose are compared in terms of the 90% overall oxidation rates achieved by the photocatalysts under ambient conditions. The 90% overall oxidation rate is the oxidation rate achieved by the photocatalyst after 90% of the initial carbon mass had been mineralised to carbon dioxide.

Fig. 1 shows that silver ion-modified titania suspensions were more active than bare titania suspensions for the photooxidation of sucrose. In separate experiments it was verified that the enhanced activity of silver ion-modified titania suspensions was predominantly due to the metal deposited on the surface rather than the metal ions present in the suspension initially [27,34]. Therefore, silver/titania particles prepared at the 2.0 at.% silver ion loading showed the highest photoactivity. Silver/titania particles prepared at the 2.0 and 20.0 at.% silver ion loadings enhanced the rates of sucrose oxidation by approximately 400 and 260%, respectively, compared to bare titania particles (based on the 90% overall oxidation rates). The illumination times required for the complete mineralisation of sucrose with bare titania and silver/titania particles prepared at the 2.0 at.% silver ion loading were 29 and 10 min, respectively.

The illumination times given above for the reaction were used to determine the apparent quantum yields for the mineralisation of sucrose. The quantum yield is the ratio of the moles of organic mineralised to the moles of photons striking the suspension during the reaction. The moles of photons striking the suspension during the reaction were calculated from the combined light intensity of the lamps. The quantum yields were calculated as 0.18 and 0.53% with bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading, respectively. The quantum yields calculated are apparent

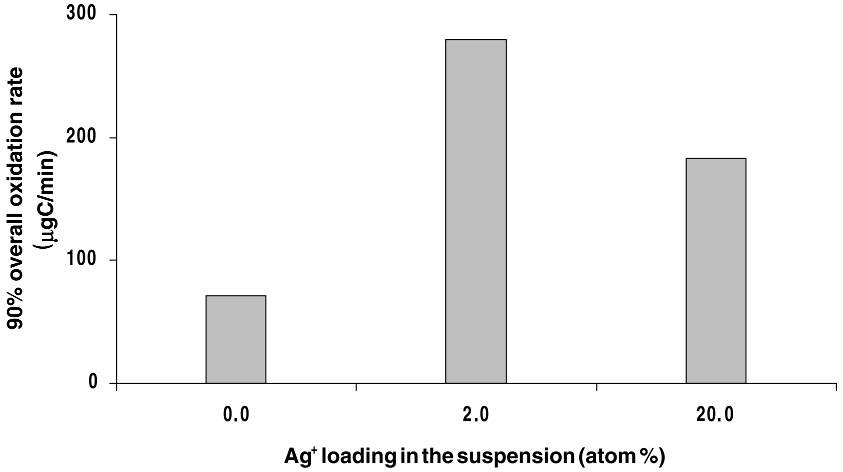

Fig. 1. Mineralisation of 2000 μg C sucrose using bare titania and silver ion-modified titania suspensions.

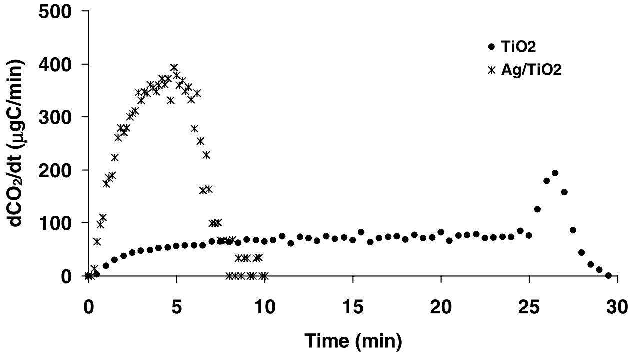

Fig. 2. Plots of the instantaneous rates of carbon dioxide generation as a function of the illumination time for the oxidation of 2000 µg C sucrose with bare titania and silver/titania particles.

quantum yields rather than true quantum yields as the moles of photons absorbed do not account for the moles of incident light scattered by the photocatalyst particles.

The enhanced photoactivity of silver/titania particles for the oxidation of sucrose is further illustrated in plots of the instantaneous rates of carbon dioxide generation (dCO_2/dt) as a function of the illumination time. The instantaneous rate of carbon dioxide generation reflects the rate at which sucrose and the intermediate organic products generated during the reaction are mineralised to carbon dioxide and water. The plots obtained with bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading are shown in Fig. 2.

As shown in Fig. 2, the profiles obtained with bare titania and silver/titania particles are significantly different in shape. The enhanced activity of silver/titania particles for sucrose mineralisation was reflected in the higher instantaneous rates of carbon dioxide generation achieved compared to bare titania particles.

In further experiments to compare the photoactivities of bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading, the mineralisation of sucrose was conducted under oxygen-enriched conditions. The photoactivities of bare titania and silver/titania particles under ambient and oxygen-enriched conditions are compared in Fig. 3. The chart shows the mass of carbon oxidised to carbon dioxide as a function of the illumination time.

With bare titania particles, the presence of additional oxygen improved the rates of sucrose mineralisation by 59%. In contrast, with silver/titania particles, the photoactivity decreased by 25% under oxygenated conditions. However, silver/titania particles still outperformed bare titania particles under oxygenated conditions.

The enhanced photoactivity of silver/titania particles compared to bare titania particles under ambient and oxygen-enriched conditions could not be attributed to differences in the surface areas of bare titania and silver/titania particles. It has been shown previously that the external surface area of titania particles was unchanged regardless of the metal loading present on the surface based on Brunauer–Emmett–Teller surface area measurements [27]. The difference in the photoactivities could not relate to the extent of sucrose adsorbed on bare and modified surfaces either as negligible amounts of sucrose were adsorbed at the 2000 µg C sucrose loading, as stated in Section 3.2.

The enhanced photoactivity of silver/titania particles compared to bare titania particles for the photooxidation of sucrose is firstly explained by a favourable change in the surface properties of the photocatalyst [36]. Metal particles on the TiO_2 surface behave as sites on which electrons accumulate. Under illumination, electrons are spontaneously transferred from the titania support to the silver metal particles [2,37,38]. The spontaneous transfer of electrons from the titanium dioxide conduction band to the metallic silver particles is possible due to the fact that the work function of titania particles (4.6 eV) is less positive than that of silver metal (4.7 eV) [37]. Therefore, electrons are removed from the TiO_2 surface near the vicinity of each silver particle [2]. The accumulation of electrons on silver particles results in the negative charge enrichment of the metal deposits. This

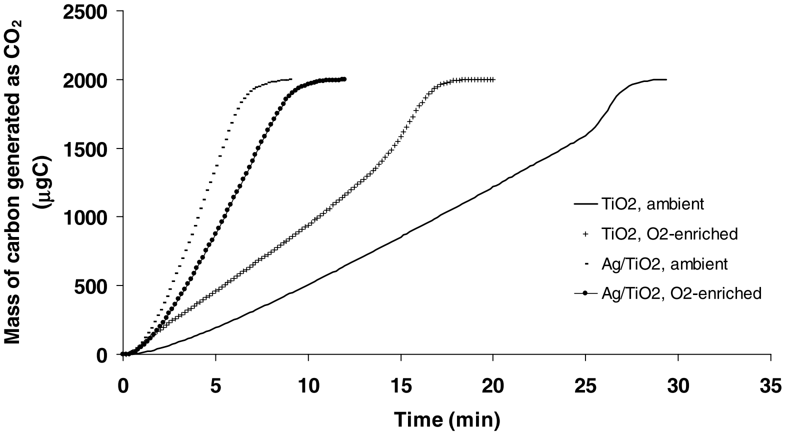

Fig. 3. Comparing the photoactivities of bare titania and silver/titania particles for the mineralisation of 2000 µg C sucrose under ambient and oxygen-enriched conditions.

enhances the separation of reduction and oxidation surface sites [39]. Hence, the extent of surface recombination is lowered and the availability of holes and electrons for redox reactions is improved [40].

The observations made from the results obtained for the oxygen-enriched conditions shed a new light on the photomineralisation mechanism of sucrose. In bare titania suspensions, the higher mineralisation rates of sucrose under oxygen-enriched conditions is explained by firstly, the improved separation of electrons and holes when more oxygen molecules are present in the system [41]. Oxygen molecules scavenge photogenerated electrons and improve charge separation. Secondly, the higher mineralisation rates are attributed to the increased rates of reaction between organic radicals ($R^\bullet$) and oxygen. Organic radicals produced by hole or hydroxyl radical attack of organic species (R) react with oxygen molecules and superoxide radicals to generate organoperoxy radicals ($ROO^\bullet$) and unstable tetraoxides ($ROOOO^-$) which rapidly decompose to carbon dioxide and water [42,43].

In silver/titania suspensions, the fact that the rates of sucrose mineralisation decreased with silver/titania particles under oxygen-enriched conditions suggests that at a sufficiently high dissolved oxygen concentration, oxygen molecules begin to compete effectively for electrons on the silver sites which may be required for a possible reduction reaction involving organic intermediate species generated during the reaction [14,44,45]. Thus, in the presence of silver deposits on titania particles, it is postulated that the reduction of oxygen molecules as well as organic species can occur on silver deposits [45,46]. The detrimental effect of increasing the dissolved oxygen concentration on the rates of organic degradation has been observed previously [14,44,46–48]. Such studies explained that the negative effect was due to the competition for electrons between organic species and oxygen molecules.

The reduced sucrose mineralisation rate under oxygen-enriched conditions was observed in silver/titania suspensions only. This suggests that the reduction of organic species is favoured in silver/titania suspensions but not in bare titania suspensions [45]. It is also suggested that while certain organic specie(s) are reduced in silver/titania suspensions, these organic specie(s) may also undergo oxidation to other by-products in parallel pathways [14,44]. The postulation that oxidative and reductive pathways simultaneously operate in the photocatalytic oxidation of sucrose in silver/titania suspensions implies that differences exist in the reaction mechanisms using bare and silver/titania suspensions in the photooxidation of sucrose. The operation of different reaction mechanisms may explain the significantly different shapes of the dCO_2/dt versus illumination time profiles for sucrose obtained with bare titania and silver/titania particles as shown in Fig. 2. With a different reaction mechanism operating, different intermediate products are generated during the sucrose photooxidation reaction in bare titania and silver/titania suspensions. Thus, the rates at which these intermediates are converted to carbon dioxide and water differ. This is reflected in the different magnitudes of the instantaneous rates of carbon dioxide generation and in the different shapes of the oxidation profiles obtained in bare titania and silver/titania systems. The occurrence of reductive pathways in the photocatalytic oxidation of sucrose with silver/titania particles was supported by further experiments in our laboratories involving the analysis of the intermediate products of the reaction. These results will be discussed in detail in a future publication.

Thus, it is proposed that the enhanced photoactivity of silver/titania particles for the photocatalytic oxidation of sucrose is due to the enhanced separation of charge carriers as well as the operation of a different reaction mechanism compared to the bare titania system. The reaction mechanism followed in silver/titania suspensions is believed to provide a more efficient route for the complete mineralisation of sucrose compared to the reaction mechanism followed in bare titania suspensions.

In the second part of this study, bare titania and silver/titania particles were used for the photooxidation of salicylic acid. The results of the photoactivity studies of bare titania and silver/titania particles on the oxidation of salicylic acid under ambient conditions are presented in Fig. 4.

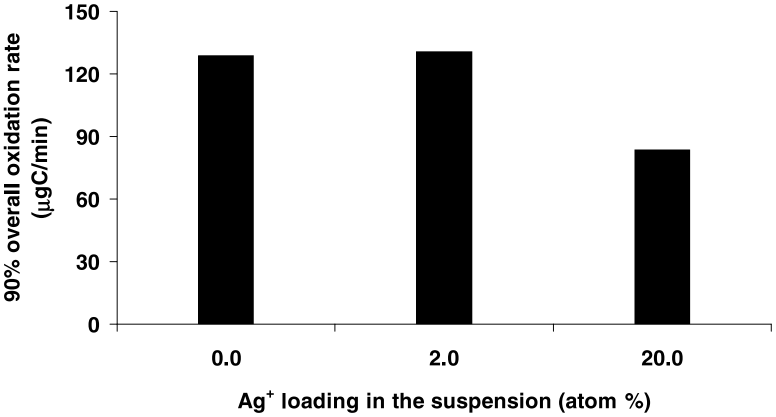

Fig. 4. Mineralisation of 2000 µg C salicylic acid using bare and silver ion-modified titania suspensions.

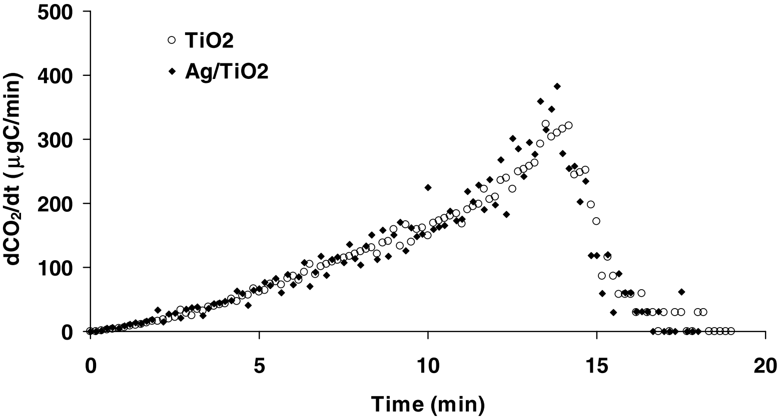

Fig. 5. Plots of the instantaneous rates of carbon dioxide generation as a function of the illumination time for the oxidation of 2000 μg C salicylic acid with bare titania and silver/titania particles.

The results obtained in Fig. 4 illustrate that the photoactivities of bare titania and silver/titania particles prepared at the 2.0 at.% silver ion loading were identical for the mineralisation of salicylic acid. With silver/titania particles prepared at the 20.0 at.% Ag^+ loading, the presence of silver metal on the TiO_2 surface had a detrimental effect on catalyst activity, such that the activity of the modified particles was 30% lower than that of bare titania particles. An illumination time of 19 min was required for the complete mineralisation of salicylic acid with bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading. The quantum yields of the reaction were determined to be 0.49% for both bare titania and silver/titania particles.

The similar photoactivities of bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading for salicylic acid photooxidation are also illustrated in plots of dCO_2/dt versus the illumination time. These plots are shown in Fig. 5.

Fig. 5 shows that the oxidation profiles obtained with both bare titania and silver/titania photocatalysts are identical in shape. This suggests that salicylic acid and the intermediate products of the reaction are mineralised to carbon dioxide at similar rates in both photocatalyst systems. In further experiments, the photoactivities of bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading were compared in oxygen-enriched photocatalyst suspensions. The photoactivities of bare titania and silver/titania particles under ambient and oxygen-enriched conditions are compared in Fig. 6.

Fig. 6 showed that in the presence of a higher dissolved oxygen concentration in the system the rates of salicylic acid mineralisation were improved with both bare titania and silver/titania photocatalysts. The rates of salicylic acid mineralisation improved by 36 and 24% in bare titania and silver/titania suspensions, respectively.

The lack of enhancement in the photoactivity of silver/titania particles for salicylic acid oxidation is in contrast to the findings of other researchers. For example, Suri et al. [49] reported that the mineralisation of salicylic acid was enhanced by 2.3 times with platinised titanium dioxide particles (1.0 wt.% Pt). Silver/titania and palladium/titania

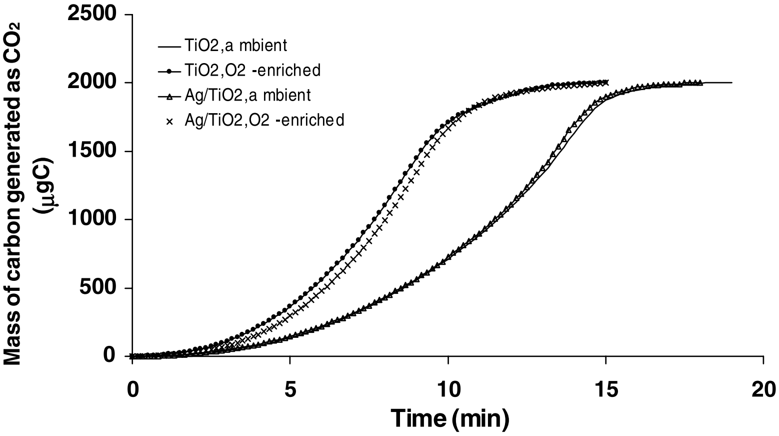

Fig. 6. Comparing the photoactivities of bare titania and silver/titania particles for the mineralisation of 2000 μg C salicylic acid under ambient and oxygen-enriched conditions.

thin films also enhanced the rates of salicylic acid degradation by 30% [17,50,51]. However, in another study it was reported that the mineralisation rates of salicylic acid were lower using titania particles modified with crystallites of gold (0.5 wt.% Au) and platinum (0.5 wt.% Pt) [5].

The different observations reported in this study and in those mentioned above on the effects of surface modification on salicylic acid photooxidation are attributed to the different experimental procedures followed in the various studies. For example, different titania samples were used in the preparation of the modified photocatalysts. The sol–gel process was used to prepare the titania samples in the studies of Suri et al. [49], Lee et al. [50], Papp et al. [51] and Wold [17], while commercial grade Degussa P25 particles prepared by flame synthesis were used by Parent et al. [5], and in this work. The use of different titania samples has been reported to affect the activity of the metallised photocatalyst [18,19,52]. Next, different methods of metal deposition were employed. Papp et al. [51], prepared palladium/TiO_2 films by thermal reduction while Suri et al. [49] and Lee et al. [50] prepared platinised/TiO_2 and silver/TiO_2 photocatalysts by photodeposition. The silver/titania particles used in this work were also prepared by photodeposition. The use of different methods of metal deposition can influence the size and the dispersion of the metal deposits which in turn affect the photoactivity [53]. In addition, different experimental conditions were used in the various studies, such as the pH, different initial concentrations of salicylic acid and light intensity. Parent et al. [5] conducted their reactions at pH 1, while a pH of 4 was used by Suri et al. [49] and pH 3.5 was used in this work. These parameters can affect the adsorption properties of salicylic acid on the bare and metallised photocatalysts, for example. Thus, these differences influence the activity of titania particles before and after surface modification.

The similar photoactivities of bare titania particles and silver/titania particles could not be related to the amounts of salicylic acid adsorbed on the photocatalyst surface in the dark. Although, approximately 198 and 352 μg C salicylic acid were adsorbed on bare titania and silver/titania surfaces, respectively, the extent of adsorption clearly did not affect the rates of salicylic acid mineralisation achieved by bare titania and silver/titania particles.

The similar photoactivities of bare titania particles and silver/titania particles for the oxidation of salicylic acid may be explained by considering the effects of the intermediate products of salicylic acid oxidation on the overall rate of oxidation. An explanation is proposed in terms of the strong affinity of salicylic acid and its intermediate oxidation products for both bare titania and silver/titania surfaces. The intermediate products of salicylic acid oxidation have been identified as catechol and a mixture of dihydroxybenzoic acids in previous studies [54,55]. The adsorption of salicylic acid on bare titania and silver/titania surfaces was described by the formation of Ti^{IV}–salicylate surface complexes and silver–salicylate complexes, as mentioned previously in Section 3.2. Similarly, catechol is known to adsorb strongly to titania through charge-transfer Ti^{IV}–catecholate surface complexes [56,57]. The chemisorption of dihydroxybenzoic acids on titania also results in the formation of surface complexes via the carboxylate group [24,29,58].

In bare titania suspensions, it is proposed that the strongly adsorbed organic species such as salicylic acid, catechol and dihydroxybenzoic acids behave as deep hole traps on the photocatalyst surface and improve the separation of charge carriers during the oxidation reaction [29,30,59,60]. Hence, salicylic acid and its intermediate oxidation products mediate the efficient separation of holes and electrons for redox reactions during the reaction. The ability of chelating organics to improve charge separation and the rates of electron transfer to electron acceptors such as metal ions in titania suspensions has been demonstrated in several studies [30,59–61]. Under these conditions, holes are efficiently trapped by organic species and other oxidisable species such as adsorbed hydroxyl groups and water molecules while electrons are efficiently trapped by oxygen molecules.

In silver/titania suspensions, the accumulation of electrons on silver deposits enhances the separation of holes and electrons on the photocatalyst surface compared to the bare titania system. However, in the presence of chelating species such as salicylic acid and its intermediate products on the photocatalyst surface which mediate efficient charge separation, it is proposed that the rate of hole transfer to organic species, hydroxyl ions and water molecules is not rate-determining. Similarly, the efficient rates of electron transfer to oxygen in the presence of chelating organics suggest that the reduction of oxygen molecules is not rate-limiting in the photooxidation reaction either. Thus, any further improvement in the separation of charge carriers by silver metal surface modification does not significantly affect the rates of oxidation. Hence, similar rates of oxidation are achieved in both bare titania and silver/titania systems.

The similar behaviour of bare titania and silver/titania particles under oxygen-enriched conditions further supports the postulation that the reduction of oxygen is not the rate-limiting step in the photooxidation of salicylic acid. However, this finding is in disagreement with those reported in the literature [17,50,51]. In addition, the findings of this work do not support the argument of Gerischer and Heller [21] who determined that the rate-controlling step of photooxidation reactions was associated with the reduction of oxygen.

In both bare titania and silver/titania systems, it is proposed that the enhanced rates of salicylic acid mineralisation under oxygen-enriched conditions is due to the higher rates of reaction between oxygen, superoxide radicals and organic species [42,43]. This facilitates the faster degradation and mineralisation of salicylic acid and the intermediate products of the reaction to carbon dioxide and water.

In the third part of this work, the photoactivities of bare titania and silver/titania particles were compared for the mineralisation of phenol under ambient conditions. The results obtained are presented in Fig. 7.

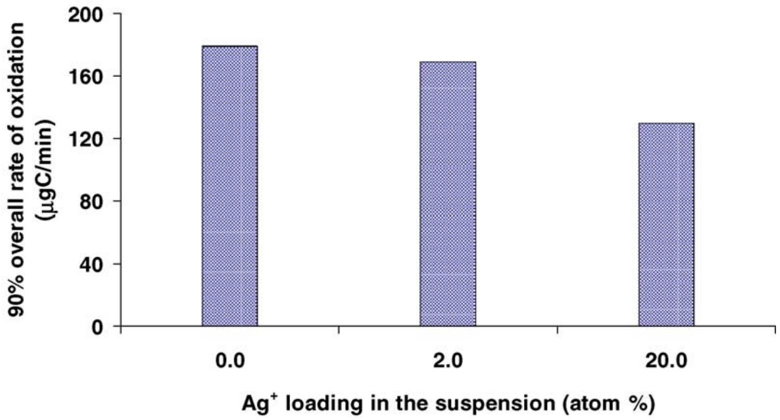

Fig. 7. Mineralisation of 2000 μg C phenol using bare and silver ion-modified titania suspensions.

Fig. 7 shows that the activities of bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading were similar for the mineralisation of phenol. However, the deposition of silver metal on the titania surface at the 20.0 at.% Ag^+ loading inhibited the photoactivity. The photoactivity of these silver/titania particles was 28% lower than that of bare titania particles. The illumination times required for the photooxidation reaction of phenol with bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading were 13 and 14 min, respectively. The quantum yields of the reaction were 0.83 and 0.77%, for bare titania and silver/titania particles, respectively. The similar behaviour of bare titania and silver/titania particles for the mineralisation of phenol is illustrated further in plots of dCO_2/dt versus the illumination time. These plots are presented in Fig. 8.

As shown in Fig. 8, the shapes of the curves obtained with bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading are similar. This indicated that the rates at which phenol and its intermediate oxidation products were mineralised to carbon dioxide were similar in both bare titania and silver/titania systems.

In a further series of experiments, the photocatalytic mineralisation of phenol was conducted under oxygen-enriched conditions using bare titania and silver/titania particles prepared at the 2.0 at.% Ag^+ loading. The activities of the two photocatalysts are compared under ambient and oxygen-enriched conditions in Fig. 9.

Fig. 9 shows that the rates of phenol mineralisation were increased with both bare titania and silver/titania photocatalysts under oxygen-enriched conditions. The rates of phenol mineralisation increased by 22 and 11% with bare titania and silver/titania particles, respectively. Similar results were observed by Almquist and Biswas [41].

The similar photoactivities of bare titania and silver/titania photocatalysts for the oxidation of phenol under both ambient and oxygen-enriched conditions are in contrast to the findings of others who have reported an enhancement in the rates of phenol oxidation with silver/titania photocatalysts [62,63]. Sclafani et al. [63] reported that the rates of phenol oxidation were enhanced by approximately two times. Alberici and Jardim [64] reported that the rates of degradation and mineralisation of phenol were enhanced by 24 and 46%, respectively.

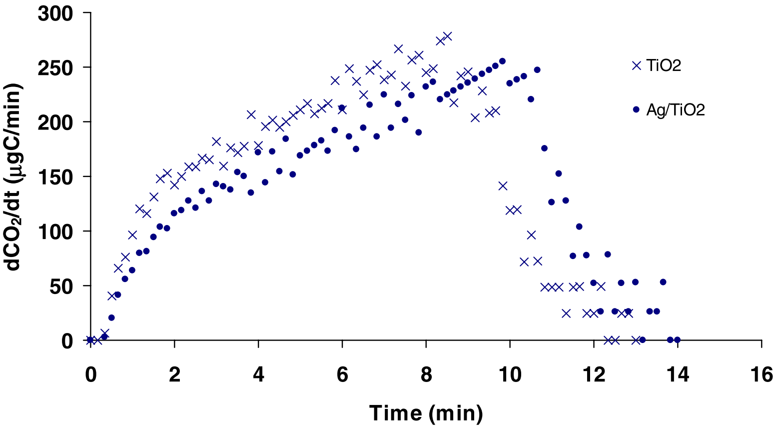

Fig. 8. Plots of the instantaneous rates of carbon dioxide generation as a function of the illumination time for the oxidation of 2000 μg C phenol with bare titania and silver/titania particles.

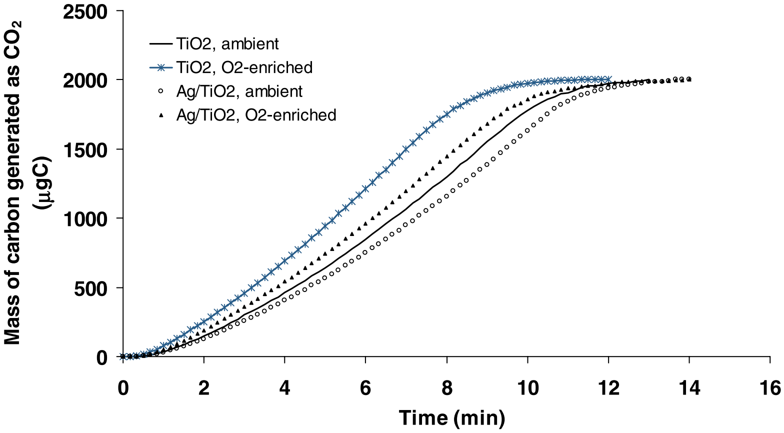

Fig. 9. Comparing the photoactivities of bare titania and silver/titania particles for the mineralisation of 2000 µg C phenol under ambient and oxygen-enriched conditions.

The different effects of surface modification on the photoactivity of titania particles observed in this work and in others are attributed to the different experimental procedures used in the various studies. Alberici and Jardim [64] used commercial grade Aldrich TiO_2 while Sclafani et al. [63] used Tioxide TiO_2. Degussa P25 TiO_2 was used in this work. In addition, the modified photocatalysts were prepared by thermal impregnation in the study by Alberici and Jardim [64] while the photodeposition method was used by Sclafani et al. [63] and in this work. Finally, different experimental conditions were employed in the various studies. For example, a pH of 6.5 was used in the study by Alberici and Jardim [64] compared to pH 3.0 and 3.5 used by Sclafani et al. [63] and in this work, respectively. These differences in the preparation of the modified photocatalysts and the reaction conditions are known to affect the activity of titania particles before and after surface metallisation. This was previously discussed in the photooxidation of salicylic acid.

The similar photoactivities of bare titania and silver/titania particles could not be explained in terms of the extent of phenol adsorption on the photocatalysts. The adsorption studies of phenol showed that at the 2000 µg C phenol loading, 73 and 31% of the initial phenol loading was adsorbed onto bare titania and silver/titania surfaces, respectively. Thus, although large differences in the amounts of phenol adsorbed on bare titania and silver/titania particles were measured, this was not reflected in the corresponding photoactivities of the two photocatalysts. Thirdly, the similar activities of bare and modified titania particles could not be explained by the affinity of phenol molecules for titania and silver/titania surfaces, as was proposed to explain the similar activities of the two photocatalysts in salicylic acid photooxidation. At pH 3.5, the adsorption of phenol on titania and silver/titania surfaces occurs by physical adsorption rather than by the formation of surface complexes as the pK_a of phenol is 9.1 [65]. Thus, other factors are considered to explain the results.

The similar photoactivities of bare titania and silver/titania particles are explained in terms of a rate-limiting "short-circuiting" cycle involving the intermediate products of the phenol oxidation reaction. A wide array of intermediate products has been identified in the photooxidation of phenol. Some of the major intermediate products formed include hydroquinone and benzoquinone. Other intermediate products include hydroxyhydroquinone and hydroxybenzoquinone [66–68]. The intermediate products formed during the oxidation reaction undergo further hole and hydroxyl radical oxidation to form other by-products en route to carbon dioxide formation. For example, hydroquinone is oxidised by holes to benzoquinone or to hydroxyhydroquinone by hydroxyl radical attack [69]. Benzoquinone can be oxidised by hydroxyl radicals to form hydroxybenzoquinone [69]. However, it is also possible that benzoquinone is reduced by electrons back to hydroquinone in a parallel reaction [44,68–70].

In bare titania suspensions, it is proposed that a "short-circuiting" oxidation–reduction cycle operates involving the intermediate organics, hydroquinone and benzoquinone, which limits the rate of phenol mineralisation. The transfer of holes and electrons between hydroquinone and benzoquinone inhibits the rates of degradation of hydroquinone and benzoquinone. Furthermore, if it is assumed that ring cleavage occurs following the degradation of hydroquinone and benzoquinone (or their oxidised derivatives), then the operation of the oxidation–reduction cycle between these intermediates limits the rates of formation of ring-opening by-products and ultimately the rate of carbon dioxide generation [69].

In silver/titania suspensions, the accumulation of electrons on silver deposits improves the availability of charge carriers for redox reactions. It is proposed that the improved availability of holes and electrons encourages the occurrence of the "short-circuiting" cycle to a greater extent than in bare titania suspensions. While the oxidation of hydroquinone is promoted by the increased availability of holes, the reduction of benzoquinone to hydroquinone via a back-reaction is similarly promoted by the increased availability of electrons in silver/titania systems. The consumption of the additional holes and electrons in this cycle effectively nullifies the beneficial effects of improved charge separation. Thus, bare titania and silver/titania particles perform similarly in the oxidation of phenol.

The transfer of photogenerated electrons to benzoquinone in both bare titania and silver/titania suspensions occurs in competition with the reduction of oxygen. In fact, benzoquinone has been shown to behave as an efficient electron scavenger in competition with oxygen in both air-saturated and oxygen-saturated photocatalyst suspensions [44,68,70]. Ilisz and Dombi [68] also showed that the reduction of benzoquinone to hydroquinone occurred in silver/titania suspensions in the presence of oxygen.

The similar activities of bare titania and silver/titania particles in air-saturated and oxygen-saturated conditions suggest that the rate-limiting step in the oxidation of phenol is not the reduction of oxygen. These findings again do not support Gerischer and Heller's [21] argument that the rate-controlling step of photooxidation reactions is oxygen reduction. Rather, it is proposed that the rate-limiting step may be associated with the rate of oxidation of the intermediate organic benzoquinone. In fact, in a previous study, it has been reported that the oxidation of benzoquinone was the rate-limiting step in the oxidation of phenol [71]. In addition, the rate of benzoquinone degradation was found to be slower than the rate of phenol degradation [71].

Therefore, the improvement in the rates of phenol mineralisation under oxygen-enriched conditions in both bare titania and silver/titania suspensions is attributed to firstly, the higher rates of reaction between organic radicals and oxygen and superoxide radicals. This increases the rate of conversion of organic species to carbon dioxide and water [42,43]. Secondly, at higher oxygen concentrations, it is also possible that oxygen molecules are able to compete more effectively against benzoquinone for photogenerated electrons [70]. This results in the improved rates of oxidation of the intermediate organics which increases the rate of carbon dioxide generation.

Finally, in the photooxidations of sucrose, salicylic acid and phenol, it was observed that the photoactivities of silver/titania particles prepared at the 20.0 at.% silver ion loading were lower than that of silver/titania particles prepared at the 2.0 at.% silver ion loading. This was shown in Figs. 1, 4 and 7. The decrease in activity is attributed to several factors. Firstly, at excessively high metal loadings, the probability of hole capture by the numerous, negatively charged silver deposits on the titania surface is increased. This is due to the inefficient distribution and lower dispersion of the deposits at the higher metal loadings [37,72]. As a consequence, the probability of hole trapping by organic species is reduced which detrimentally affects the rate of reaction. Hence, the metal deposits behave as recombination centres [24,37,53]. It is also possible that at high metal loadings, the metal deposits provide excessive coverage of the photosensitive surface [4,53]. Thus, metal deposits block the illuminating light from reaching the titania surface. This decreases the concentration of electrons and holes generated and the overall rate of reaction [4].

Further experiments are required to verify the postulations made in this study for a complete understanding of the effects of surface metallisation on titania activity in the photocatalytic oxidations of sucrose, salicylic acid and phenol. The identification of the intermediate products of the reaction as well as their adsorption characteristics and the photoactivities of bare titania and silver/titania photocatalysts for the oxidation of these intermediates organics are areas of investigation. These results will be presented in a future publication.

4. Conclusions

The results of this study showed that the photocatalytic activity of silver metallised titania particles was a function of the nature of the organic compound oxidised in photocatalytic reactions. While silver/titania particles enhanced the rates of sucrose photooxidation by approximately four times compared to bare titania particles, both bare titania and silver/titania photocatalysts possessed similar activities for the photooxidation of salicylic acid and phenol. The similarities and differences in the photoactivities of bare titania and silver/titania particles were not related to the different extents of organic adsorption on bare and modified surfaces in the absence of illumination. The substrate dependence of the photoactivity of silver/titania particles could be explained by the influence of the both the parent organic and the intermediate organic products on the overall rates of reaction.

The enhanced activity of silver/titania particles for sucrose oxidation was attributed to the improved separation of charge carriers and to the operation of a different reaction mechanism compared to the bare titania system. The new reaction mechanism followed in the silver/titania system is believed to involve both oxidative and reductive pathways by which sucrose and the intermediate oxidation products were rapidly degraded. In bare titania systems, the photooxidation of sucrose was proposed to proceed solely via oxidative pathways.

A possible explanation for the similar activities of bare and modified titania particles for the oxidation of salicylic acid was given as being due to the strong affinity of salicylic acid and the intermediate oxidation products for the photocatalyst surface. The chemisorbed organics mediated the efficient separation of charge carriers. Hence, the rates of hole transfer to electron donor species and electron transfer to oxygen were not rate-limiting. Thus, further improvements in charge separation by the surface metallisation of titania were not of significant benefit for the rates of salicylic acid oxidation.

A possible explanation for the similar activities of bare titania and silver/titania particles for phenol oxidation was given as being due to the occurrence of a "short-circuiting" oxidation–reduction cycle between the intermediate organics, hydroquinone and benzoquinone in both bare titania and silver/titania systems. Silver/titania particles promoted the operation of the recombination cycle. This nullified the beneficial effects of enhanced charge separation. The rate of benzoquinone oxidation was proposed to be the rate-limiting step in the photooxidation of phenol.

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