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Enhancing the catalytic oxidation capacity of Pt/TiO₂ using a light pre-treatment approach



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ABSTRACT

The role of UV light pre-treatment in enhancing Pt/TiO₂ activity for the catalytic oxidation of formic acid in an aqueous environment and under ambient conditions has been examined. The impact of light pre-treatment, relaxation time (the period between light pre-treatment and formic acid addition) and re-illumination on the oxidation rate were considered. Pre-illuminating Pt/TiO₂ provided an almost seven-fold increase in the formic acid oxidation rate compared with the untreated case. The oxidation rate decreased with increasing relaxation time, whereby after 16 h of relaxation it had stabilised at a value still around three times greater than the untreated sample. Re-illuminating the Pt/TiO₂ led to a complete recovery of the transient element of the activity. The Pt deposits were observed to undergo partial oxidation over the course of the reaction and, when coupled with a lower activity being observed upon purging the system with N₂, imply the participation of dissolved oxygen in the overall oxidation mechanism. The findings suggest the platinum deposits can inject electrons into adsorbed molecular oxygen where the oxygen remains in an active state ready for oxidising the formic acid. Pre-treating the catalyst with light accentuates this effect as additional photogenerated electrons are drawn into the Pt deposits from the TiO₂ and transferred to and held by the adsorbed oxygen. Striking features of this particular system is the light pre-treatment effect prevails for an unexpectedly long period (in the order of hours) and is completely recoverable with re-illumination.

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1. Introduction

Platinum is a versatile and widely used catalyst, capable of imparting high activities for a range of reaction types including hydrogenation [1], dehydrogenation [2], isomerisation [3] and oxidation reactions [4]. Often the support has a marked influence on the suitability of the Pt catalyst for a specific reaction as well as its catalytic activity, selectivity and lifetime. Metal oxides are regularly employed as supports for Pt catalysis and can introduce characteristics such as acidity/basicity, enhanced oxygen mobility or strong metal support interaction (SMSI) which may be beneficial for the particular reaction. Common metal oxide supports such as TiO₂, ZnO, and WO₃ also exhibit semiconducting properties – a trait of utmost importance for photocatalysis but seldom associated with thermal catalysis.

From a photocatalysis perspective, electron and hole separation within the metal oxide can be improved by the presence of a metal,

such as Pt in the form of small deposits, on the semiconductor surface. Photogenerated electrons accumulate in the Pt deposit which mediates molecular oxygen reduction through both O₂ adsorption on the Pt surface and an increased opportunity for electron transfer to the adsorbed O₂. Interestingly, Pt has been reported to be an effective catalyst for thermal-catalytic reactions involving oxygen activation such as catalytic wet air oxidation (CWAO) [5] as well as the oxygen reduction reaction (ORR) at the Pt cathode in fuel cells [6]. This implies some overlap exists regarding the action of Pt during photocatalytic and catalytic oxidation reactions and is a commonality which has rarely been exploited.

During selected photocatalytic studies, Pt/TiO₂ has been observed to oxidise formic acid without illumination and under ambient conditions, suggesting catalytic action by Pt may be contributing to its photocatalytic performance. He et al. [7] reported formic acid oxidation without any illumination by a Pt/TiO₂ film supported on indium-tin-oxide glass, achieving up to 30% Chemical Oxygen Demand (COD) removal in a solution initially containing 6300 µg carbon. Under illumination COD removal was approximately 60% indicating catalysis by Pt could be contributing to the overall photocatalytic effect. Denny et al. [8] observed complete formic acid oxidation within 4 min for a pre-illuminated Pt/TiO₂

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suspension initially containing 2000 μg carbon. Pre-illumination, which is in essence a light pre-treatment step, refers to the Pt/TiO₂ suspension initially being illuminated, with the light then turned off and formic acid added with no further illumination provided. They observed formic acid oxidation in the pre-illuminated Pt/TiO₂ case occurred at a rate similar to formic acid oxidation by Pt/TiO₂ under illuminated conditions, again suggesting catalytic action by the Pt deposits could be a contributing factor. However neither study explicitly appraised the extent by which Pt catalysis contributed to photocatalytic performance nor the effect of light on Pt thermal-catalytic activity.

The work presented here explores the use of light pre-treatment to augment the catalytic performance of Pt/TiO₂ during oxidation, using formic acid as the probe reactant. Aspects including the light pre-treatment duration, the relaxation period (i.e. time between ceasing illumination and adding formic acid) and re-illumination and their impact on catalyst activity are investigated. In addition, the impact of light pre-treatment and the abovementioned variants on Pt deposit oxidation state were studied.

2. Experimental

2.1. Materials

Aeroxide® TiO₂ P25 (primary particle size ~25 to 30 nm, surface area ~50 m² g⁻¹, anatase to rutile ratio of 4:1) was used as the catalyst support in all experiments. Chemicals were analytical grade and used as supplied: formic acid (>98%, Riedel-Haën), methanol (>99.9%, Ajax Finechem), hexachloroplatinic acid (99%, Sigma-Aldrich®), potassium permanganate (99%, Ajax Finechem), and perchloric acid (70%, Frederick Chemical).

2.2. Pt/TiO₂ synthesis

Pt/TiO₂ particles were prepared by photodepositing Pt on Aeroxide P25 using an annular reactor as described in Lee et al. [9]. The annular reactor was purged with 700 mL of a 1 g/L TiO₂ suspension and illuminated with UV light (Sylvania, 18 W black light blue, maximum emission = 365 nm) for 30 min to remove organic impurities. The light was switched off and a pre-determined amount of Pt precursor (to give 1 at.% Pt with respect to Ti) was added along with 24.7 mL of methanol as a sacrificial hole scavenger. The suspension pH was adjusted to 3 ± 0.05 using 1 M perchloric acid. The mixture was circulated for 20 min to allow precursor adsorption on the TiO₂ surface. During the final 10 min of adsorption the suspension was purged with 50 mL min⁻¹ N₂ gas to decrease the dissolved oxygen concentration. Illumination was provided for 1 h to photodeposit Pt on the TiO₂ surface. N₂ purging was maintained during the photoreduction period to minimise the dissolved oxygen level. The Pt/TiO₂ particles were recovered and washed five times with water to remove residual precursor and chloride ions, after which they were dried in an oven for 24 h at 343 K.

2.3. Pt/TiO₂ characterisation

Platinum deposit size and distribution were determined by HR-TEM. The images were obtained on a Phillips CM200 at an electron accelerating voltage of 200 kV. Platinum oxidation state and the presence of surface carbon before and after reaction were assessed by XPS. Particle recovery following reaction involved centrifuging particle suspension and air drying in an oven at 343 K for 48 h. XPS data were collected using a monochromatic X-ray source (Al-K α , 6.68 eV) operating at 164 W. All spectra were referenced to the Ti 2p (TiO₂) peak at 458.7 eV and checked against the C 1s peak at 285 eV from surface carbon [10].

2.4. Light pre-treatment and reaction

Formic acid oxidation was undertaken in a 70 mL spiral-type reactor as detailed elsewhere [11] with the catalyst activity evaluated with and without pre-irradiation. In a typical pre-irradiation experiment, the reactor was charged with a 1 g/L Pt/TiO₂ suspension adjusted to pH 3 ± 0.05 with perchloric acid. In the case of pre-irradiated Pt/TiO₂, the suspension was initially illuminated (Sylvania, 18 W black light blue, maximum emission = 365 nm) for 30 min. Following pre-irradiation the system was opened to the atmosphere for 10 min to allow for air equilibration. The system was then resealed and an ensuing relaxation period (10–60 min) allowed before 100 μmol of formic acid was added. The catalytic performance of Pt/TiO₂ was assessed by monitoring CO₂ generation during the dark (i.e. no UV irradiation) mineralisation of formic acid. Reactions involving no light pre-treatment followed the same procedure but without the illumination step. Experiments were also performed at a reduced O₂ concentration whereby following pre-irradiation, the system was purged with N₂ for 10 min prior to the 10 min relaxation period. Total organic carbon (TOC) analysis was undertaken at the end of each reaction to ensure complete formic acid mineralisation was achieved. TOC analysis was performed on a Shimadzu TOC-V_{CSH} analyser equipped with a non-dispersive infrared detector.

2.5. Formic acid adsorption

Formic acid adsorption experiments were performed using a 100 glass bottle at room temperature. One hundred μmol of formic acid was added to 50 mL of a 1 g/L TiO₂ suspension and the pH adjusted to 3 ± 0.05 using perchloric acid. The mixture was magnetically stirred for 20 min to promote adsorption/desorption equilibrium at which time samples were collected for analysis using a Waters 2695 High Performance Liquid Chromatograph with a Waters 2996 photodiode array detector. Formic acid identification was achieved using a T3 Atlantis column with a 20 mM NH₄H₂PO₄ mobile phase (pH 2.5) flowing at 0.5 mL min⁻¹ at 30 °C.

2.6. Reactive oxygen species evaluation

The presence of reactive oxygen species (H₂O₂, O₂⁻) in the solution following light pre-treatment was assessed. H₂O₂ generated during the light pre-treatment stage was measured by the permanganate method [12]. Following illumination, samples (6 mL) were taken from the reactor and immediately mixed with a 2 mL 10⁻³ M KMnO₄ solution. The solution volume was adjusted to 10 mL by adding water and allowed to sit for 30 min while reaction between the permanganate and the peroxide occurred. The mixture was then filtered through a 0.20 μm PTFE-membrane filter prior to analysis. KMnO₄ remaining in solution was evaluated by a Cary 300 UV/Vis spectrometer at λ = 525 nm. To identify whether superoxide radicals were present following light pre-treatment 2.5 mL of the pre-irradiated sample was added to 2 mL of nitro blue tetrazolium solution (Sigma 74032, 0.6 mg/L) and 0.5 mL of H₂O. The solution was allowed to mix for 30 min at ambient conditions and then filtered and the light intensity at λ = 260 nm measured using a Cary 300 UV/Vis spectrometer.

3. Results

3.1. Pt/TiO₂ characteristics

The TEM image in Fig. 1(a) depicts the platinum photodeposit dispersion on Aeroxide P25. The deposits appear to be arbitrarily located on the TiO₂ surface. The average Pt deposit size was estimated as 2.0 ± 0.3 nm for a 60 deposit count.

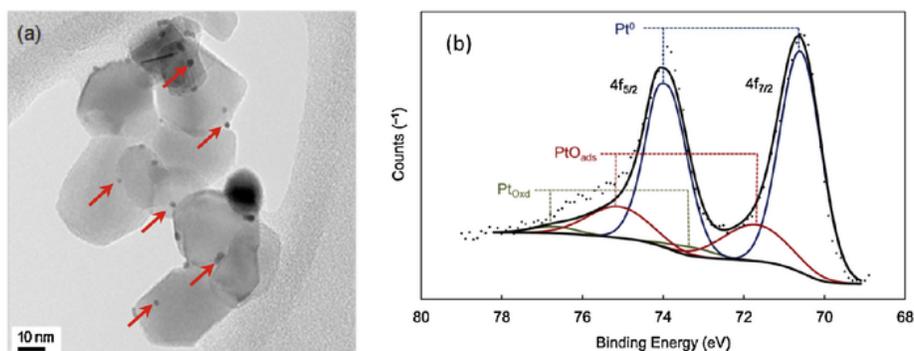


Fig. 1. (a) TEM micrograph of Pt photodeposits on Aerioxide P25. Examples of Pt deposits indicated by red arrows; (b) XPS profile of Pt species for Pt photodeposits on Aerioxide P25. Pt^0 represents metallic Pt, PtO_{ads} represents Pt with surface-adsorbed oxygen and PtO_{oxd} represents oxidised Pt (PtO and PtO_2). The dotted profile represents the original XPS spectra while the solid black profile represents the sum of the deconvoluted Pt spectra.

The XPS profile for the Pt deposits is provided in Fig. 1(b). Two strong peaks with binding energies centred at 70.6 eV and 74.0 eV, representative of the $4f_{7/2}$ and $4f_{5/2}$ electrons in Pt metal (Pt^0) [13], can be seen. Also apparent are shoulders on the upper binding energy sides of the XPS profile, suggesting the existence of positively charged Pt species. Assuming the ratio of the $4f_{7/2}$ and $4f_{5/2}$ peak areas is constant (1.33) for each Pt species [13], the spectrum can be deconvoluted into several sets of peaks. The corresponding peak parameters are listed in Table S1 with peaks assigned as representing either Pt^0 , Pt with surface-adsorbed oxygen (PtO_{ads}) and oxidised Pt (PtO_{oxd} , i.e. PtO and PtO_2).

On the basis of the peak positions defined in Table S1, the Pt deposits are predominantly Pt^0 (~77%), with the remainder existing as oxidised Pt (PtO_x – comprising PtO_{ads} and PtO_{oxd}). Pt photodeposition is routinely expected to provide metallic deposits however the ratio of Pt metal to Pt oxides in the photodeposits can be influenced by a number of factors including the ratio of hole scavenger to metal precursor, solution acidity, illumination period, dissolved oxygen content and TiO_2 support characteristics. For instance, Lee and Choi [10] found at acidic pH and under electron donor (ED)-rich conditions (i.e. methanol to chloroplatinic acid molar ratio = 10,000) Pt metal dominated the Pt photodeposits while under ED-deficient conditions (i.e. methanol to chloroplatinic acid molar ratio = 100) the deposits were mainly comprised of PtO . Additionally, they reported under the ED-rich environment the Pt deposits initially formed as PtO and then were reduced to Pt metal as illumination continued. In this study the Pt was photodeposited under conditions favouring an ED-deficiency (methanol to chloroplatinic acid molar ratio ≈ 285) however an oxygen lean environment was used, compared with the air-equilibrated circumstance employed by Lee and Choi. That is, an oxygen lean environment should aid in providing reduced metal deposits. Murcia et al. [14] found the maximum attainable Pt metal to Pt oxide ratio they were able to achieve for their Pt photodeposits was ~60%. In their case they performed the photodeposition at pH 3 and under an N_2 environment but used isopropanol as the hole scavenger and pretreated their TiO_2 with sulphuric acid beforehand.

3.2. Catalytic results

The impact of light pre-treatment on formic acid oxidation by Pt/TiO_2 is displayed in Fig. 2 (Run number 1). Catalyst performance is compared on the basis of the R_{50} value which describes the rate for mineralising 50% of the carbon. Also included in the figure is the effect of repeated formic acid additions (without light pre-treatment between additions) on the R_{50} value.

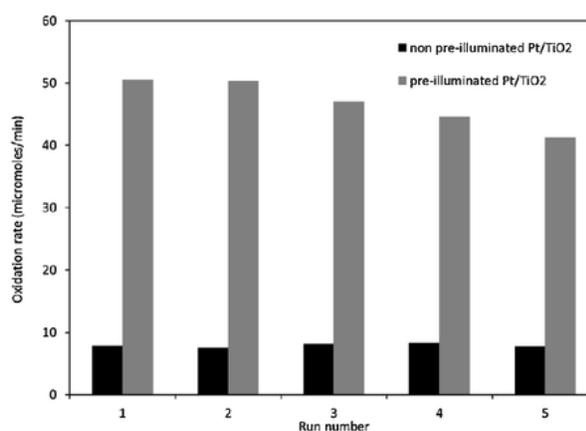


Fig. 2. The change in formic acid oxidation rate (R_{50}) upon repeated formic acid additions for Pt/TiO_2 with and without light pre-treatment. Catalyst loading = 1 g/L. Formic acid loading = $100 \mu\text{mol}/\text{addition}$. Initial pH = 3 ± 0.05 . Pre-illumination period = 30 min with 10 min relaxation time. No re-illumination was performed between formic acid additions.

Results for the initial run in Fig. 2 show light pre-treatment produces an approximately seven times greater formic acid oxidation rate for the Pt/TiO_2 , clearly illustrating the substantial boost this approach can give to catalytic performance. Moreover, the ability of Pt/TiO_2 to retain the benefits imparted by light pre-treatment is also demonstrated. The findings indicate without light pre-treatment the Pt/TiO_2 maintains an approximately constant R_{50} value of around 7.5–8.5 $\mu\text{mol}/\text{min}$ over the five additions. In contrast, while the R_{50} value for light treated Pt/TiO_2 is consistently higher over the five additions it is also apparent there is a decrease in the oxidation rate, particularly from the third addition onwards. Compared to the rate for the first run (50.5 $\mu\text{mol}/\text{min}$), the formic acid oxidation rate decreased by ~18% to 41.2 $\mu\text{mol}/\text{min}$ for the fifth addition.

Control experiments were performed (see Figure S1) to confirm whether the Pt deposits were responsible for the observed phenomenon. Pre-treating neat TiO_2 with light provoked a small but constant conductivity increase in the conductivity cell. A second control experiment where no photocatalyst was present and no light pre-treatment was employed exhibited a similar conductivity profile to the neat TiO_2 . The conductivity increase in both instances may be due to minor base-line drift within the system. In any case, the maximum rate for the control experiments was a factor of

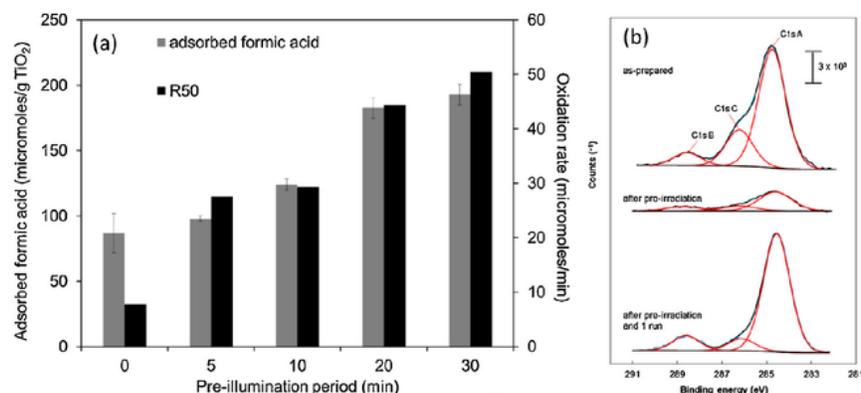


Fig. 3. (a) The change in formic acid oxidation rate (R_{50}) with light pre-treatment period for Pt/TiO₂. Catalyst loading = 1 g/L. Formic acid loading = 100 μ mol/addition. Initial pH = 3 \pm 0.05. Relaxation time = 10 min. Also included is the influence light pre-treatment time has on the extent of formic acid adsorption on neat TiO₂; (b) XPS spectra of C 1s core levels for Pt/TiO₂ without light pre-treatment (top), following 30 min light pre-treatment (centre) and following 30 min light pre-treatment and formic acid oxidation (bottom).

70 times less than for the light pre-treated Pt/TiO₂ system, indicating the enhanced activity derived from the Pt deposits.

The findings indicate that while the higher activity invoked by light pre-treatment is retained for repeated formic acid additions, there is a mild decay in the oxidation rate for each ensuing reaction. The effect could originate from phenomena such as: (1) fouling due to the accumulation of carbon-based compounds on the surface during the reaction; and/or (2) the gradual consumption of active species (formed during light pre-treatment) by the formic acid. The question then arises as to what extent each of these phenomena contribute to the activity improvement with the ensuing study further probing this aspect.

To explore the impact of light pre-treatment on the formic acid oxidation rate, the illumination and relaxation times were systematically varied. Fig. 3(a) illustrates the effect of varying the illumination period on the formic acid oxidation rate (R_{50}). It is apparent from the figure that as illumination time is increased (up to 30 min) there is a corresponding increase in formic acid oxidation rate from 7.8 μ mol/min to 50.5 μ mol/min.

Pre-illumination is regularly used to prime the surface of TiO₂ and other semiconductors prior to assessing photocatalytic performance. That is, pre-illumination is often used to oxidise adsorbed carbon species originally present on the semiconductor surface which may interfere with its photocatalytic activity during assessment [15]. To evaluate the impact of light pre-treatment on surface carbon on Pt/TiO₂, XPS spectra depicting the C 1s core levels before and after illumination are compared in Fig. 3(b). The spectra indicate light treatment lowers the incidence of carbon species on the Pt/TiO₂ surface (from 19.7 atom% to 4.6 atom%) which may contribute to the improved catalytic performance. A hint as to the reason for improved activity upon removing carbon-containing species from the Pt/TiO₂ surface is provided in Fig. 3(a). The figure shows an increase in the light pre-treatment time promoted formic acid adsorption on neat TiO₂, with the adsorption increase roughly correlating with the increase in formic acid oxidation rate. The increased formic acid adsorption may derive from the removal of carbon species facilitating its access to the active sites on the catalyst, akin to increasing the accessible surface area, in turn increasing catalytic activity. The importance of surface area in relation to organic adsorption for improving photocatalyst performance has been reported by others. Li et al. [16] observed a link between photocatalyst surface area, reactive brilliant red X3B (an organic dye) and its rate of photodecolourisation for both ZnO and TiO₂ particles. Xu and Langford [17] also found a relationship between surface area, organic adsorption and photoactivity for reactive brilliant red

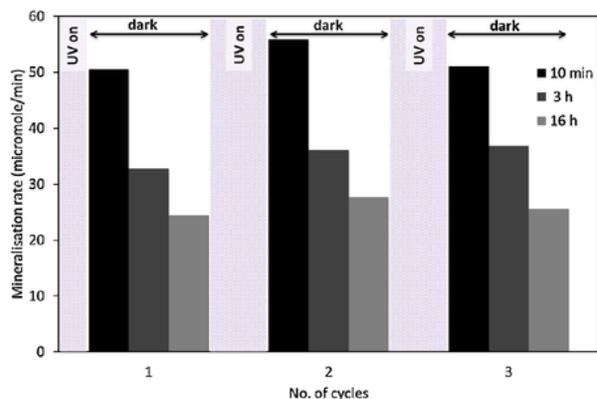


Fig. 4. The influence of relaxation period and re-irradiation on the formic acid oxidation rate (R_{50}) by light treated Pt/TiO₂. Catalyst loading = 1 g/L. Formic acid loading = 100 μ mol/addition. Initial pH = 3 \pm 0.05. Light pre-treatment and re-illumination periods = 30 min.

X3B but only after accounting for the contribution of adsorption to the 'apparent' photodecolourisation rate during the reaction.

To assess the impact relaxation time had on formic acid oxidation rate by Pt/TiO₂, formic acid was sequentially added at different times following the light pre-treatment step. Additionally, the system was pre-treated with light for 30 min and the formic acid addition sequence repeated twice following the 16 h relaxation time condition. The formic acid R_{50} values for the experimental sequence are provided in Fig. 4.

Fig. 4 indicates increasing the relaxation time from 10 min to 16 h decreased the mineralisation rate from 50.5 μ mol/min to 24.4 μ mol/min, illustrating that while light pre-treatment activates the catalyst for a surprisingly long time the active species gradually decay with time. Although not to the same degree, as the total relaxation time was shorter, a similar effect was evident in Fig. 2. Fig. 4 also demonstrates that re-illuminating the catalyst restores the activity to its original value, signifying the active species can be readily regenerated. The active species again then undergo a repeated decay process with increasing relaxation time. The third re-illumination/relaxation cycle mirrored the first two cycles. An analogous effect was observed by Einaga et al. [18] during the oxidation of CO in the presence of Pt/TiO₂. They found the Pt/TiO₂ was only able to oxidise CO at room temperature when

pre-illuminated. The activity decayed with time (over approximately 1 h) and was able to be recovered upon re-illumination. The observed capacity of the Pt/TiO₂ to completely recover activity upon illumination indicates catalyst activity could be maintained by periodic illumination and has positive implications for reactions such as CWAO where processing times can be lengthy.

Pt oxidation state, R_{50} values and surface carbon loading on the Pt/TiO₂ prior to light pre-treatment as well as at various points during the light treatment process are provided in Table 1. Note the carbon content values reported in Table 1 are derived from XPS data and can be used only as a guide for determining surface carbon content. They may not reflect the true carbon content as the particle recovery and analytical process could result in deterioration/evaporation of some of the surface carbon species. From Table 1, Pt deposits prior to light treatment are dominated by Pt metal with a considerable presence of surface carbon. Light pre-treatment (without any formic acid addition) invokes a small (~5%) degree of Pt deposit oxidation while substantially (~75%) reducing the surface carbon level (as was depicted earlier in Fig. 3(b)).

The addition of formic acid and its reaction in the system without light pre-treatment leads to a mild (~15%) increase in oxidised Pt content. Conversely, formic acid addition and reaction after pre-treating the Pt/TiO₂ with light leads to considerable Pt oxidation (~40%) whereby the deposits are subsequently dominated by oxidised Pt species. During reaction the surface carbon content also increased to a level comparable to the as-prepared Pt/TiO₂. The C 1s profile (from XPS) for the light pre-treated Pt/TiO₂ after one reaction cycle is provided in Fig. 3(b) and illustrates the carbon accumulates to an amount similar to what was present on the surface prior to illumination. It is apparent that while light pre-treatment and formic acid oxidation on their own invoke some oxidation of the Pt deposits, when combined the effect is markedly larger. Table 1 also indicates variations to the Pt deposits (and surface carbon content) imparted after the first formic acid oxidation run are retained during at least a further four formic acid additions for both the light pre-treated and untreated systems. The only noticeable difference is a ~18% loss in activity (R_{50}) by the light treated Pt/TiO₂ over the five cycles, as was previously illustrated in Fig. 2. Following the five formic acid additions, re-illumination of the light treated sample leads to considerable reduction of the oxidised Pt species and no lowering of the carbon content on the sample surface.

The relaxation time is also shown to influence the extent of Pt oxidation as demonstrated in Table 1. After a 60 min relaxation time, formic acid addition promotes oxidation of the Pt deposits but not to the same degree as for the shorter (10 min) relaxation time. The R_{50} value for the longer reaction time is also lower, supporting the result observed in Fig. 4.

Oxidation of the light treated Pt deposits during formic acid oxidation suggests the presence and role of oxygen in the reaction could be important and may interact with the Pt deposits as part of the reaction mechanism. Table 1 indicates upon formic acid addition, and even with light pre-treatment, decreasing the oxygen content within the system (via N₂ purging) leads to minimal Pt deposit oxidation and an R_{50} value only mildly (~55%) greater than the untreated case. This finding suggests oxygen is important to the reaction but more interestingly may also be responsible for partially oxidising the Pt deposits with this phenomenon potentially comprising part of the reaction process.

To determine whether other reactive oxygen species (i.e. H₂O₂, O₂⁻) were generated as a result of light pre-treatment and then played a significant role in the formic acid oxidation mechanism their potential presence was investigated. H₂O₂ was the only compound observed (see Figure S2) and it was detected in the pre-irradiated Pt/TiO₂ system alone. The lack of O₂⁻ does not mean these species were not present following light pre-treatment as

the employed analysis technique may not have been suitable for this system or alternately they may have contributed to H₂O₂ generation (i.e. Eqs. (1) and (2)). A maximum H₂O₂ concentration of ~80 μM was observed for the 30 min light treatment and given this equates to 4 μmole its contribution to the formic acid oxidation process was considered to be minor.



4. Discussion

The study has demonstrated that a 30 min light pre-treatment step markedly increases the catalytic activity of Pt/TiO₂ for oxidising formic acid under ambient conditions. Others have described the ability of Pt/TiO₂ to oxidise formic acid under ambient conditions but have not explicitly considered light pre-treatment effects [7,8]. Here we found pre-illuminating the Pt/TiO₂ provided an approximately 6.5-fold increase in catalytic activity with the activity retained for repeated formic acid additions. The activity was observed to decay with time but could be recovered by re-illumination. The effect of light pre-treatment/re-illumination can be two-fold: (1) it removes carbon-containing species from the Pt/TiO₂ surface allowing for greater formic acid adsorption and accessibility to reaction sites; and/or (2) it increases electron transfer from the TiO₂ to the Pt deposits where the additional electrons reduce (and are stored in) adsorbed oxygen which then participates in the oxidation reaction. Evidence implying both these phenomena are occurring has been found with the respective contributions of each considered in the ensuing discussion.

4.1. Surface cleanliness

Light pre-treatment (and potentially the accompanying removal of carbon-based species from the surface) enhances formic acid adsorption which appears to play a role in improving catalytic performance. The XPS results (Fig. 3(b)) indicated light treatment removes carbon-based surface species with the amount removed presumably a function of the illumination time. Removing these carbon species from the surface could promote greater formic acid adsorption which in turn impacts on catalytic activity (Fig. 3(a)). Fig. 3(b) and Table 1 suggests carbon-based species accumulate on the catalyst surface during formic acid oxidation, with this occurring during the first reaction cycle. It also appears the amount of carbon-based species on the surface remains at an elevated level irrespective of further illumination as upon re-illumination (after five reaction cycles) the carbon content does not decrease to the values seen following the original light treatment step. These reaction-derived carbon-based species also appear to not hamper subsequent formic acid oxidation reactions. That is, the amount of surface carbon present after the first formic acid oxidation cycle (16.1 atom%) is comparable to the carbon level on the as prepared (no pre-illumination) Pt/TiO₂ (19.7 atom%) however the R_{50} value of the sample following the first reaction cycle (41.2 μmol/min) remains considerably higher than the as prepared sample (7.8 μmol/min). Moreover, the carbon-based species formed on the Pt/TiO₂ during the reaction appears to be photostable as illustrated by its persistence even following re-illumination. Gong et al. [19] used in situ ATR-FTIR to probe ethanol photooxidation by Pt/TiO₂ in the aqueous phase. As their system was unable to detect gas-phase products (i.e. CO₂) they used an indirect means to observe CO₂ formation by looking for carbonate signals within the spectra. To confirm whether this approach could be used they bubbled CO₂ through water above the Pt/TiO₂ film and observed carbonate species formation on the Pt/TiO₂ surface. A similar effect could be occurring here whereby generated CO₂ potentially

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Table 1

Percentage of Pt oxidation states (from XPS) for Pt/TiO₂ following various light pre-treatment and relaxation conditions before and after formic acid addition. Also provided are corresponding R₅₀ values and the amount of carbon present on the surface. FA = formic acid.

Pt/TiO ₂ treatment	Pt ⁰ (%)	PtO _x ^a (%)	R ₅₀ (μmol/min)	C (atom%) ^b
As prepared (no pre-treatment)	76.7	23.3	n.a.	19.7
10 min relaxation, FA reaction	60.1	39.9	7.8	8.4
After 5 reaction cycles	59.5	40.5	7.8	12.6
30 min light treatment	71.9	28.1	n.a.	4.6
10 min relaxation, FA reaction	33.9	66.1	50.5	16.1
After 5 reaction cycles	34.2	65.8	41.2	12.1
After 5 reaction cycles and re-irradiated	64.2	35.8	n.a.	17.2
30 min light treatment	71.9	28.1	n.a.	4.6
60 min relaxation, FA reaction	50.1	49.9	40.7	9.7
30 min light treatment,	69.1	30.9	n.a.	6.8
10 min N ₂ bubbling, FA reaction	69.4	30.6	13.1	13.7

n.a.: not available.

^a PtO_x encompasses PtO_{ads} and PtO_{oxd} species.

^b C (atom%) represents the sum of the C 1s A, C 1s B and C 1s C XPS spectra peaks.

forms carbonate species on the Pt/TiO₂ surface. Tanaka and White [20] also used FTIR to probe gas-phase CO₂ adsorption and surface interaction with a commercial (Matheson Coleman and Bell (MCB) Chemicals) anatase sample under different scenarios (oxidised, oxygen pre-adsorbed and water pre-adsorbed). In the water pre-adsorbed case the CO₂ rapidly interacted with the adsorbed water to form surface bicarbonate and bidentate carbonate species. Likewise, on the oxidised anatase surface bicarbonate/bidentate carbonate was observed to form but at a much slower rate. However, Tanaka and White found these carbonate-based species were removed upon evacuation. This suggests carbonate species may not be responsible for the C 1s peaks seen in the XPS profiles in our work as the XPS analysis was performed under a vacuum.

Interestingly though, the study by Gong et al. [19] reported a persistent Pt-CO_{ad} species was formed during aqueous ethanol photooxidation (its formation was also observed during acetaldehyde and acetic acid photooxidation), which was suggested to derive from decarbonylation of adsorbed ethoxy, acetaldehyde and/or acetate species. While unable to confirm at this time whether Pt-CO_{ad} is forming during formic acid degradation in our study (or whether the Pt-CO_{ad} species are sufficiently stable to survive the rigours of particle recovery (i.e. drying) and XPS analysis (i.e. evacuation)) the findings by Gong et al. indicate carbon-based species can accumulate on Pt/TiO₂ and remain on the surface even in the presence of UV light.

4.2. Oxygen activation and stabilisation

The findings in Fig. 4 indicated relaxation time governed the extent to which light pre-treatment influenced activity and activity was recoverable by re-illuminating the catalyst. Closer inspection of this data (see Figure S3, Supplementary Information) indicates there is a decrease in the deactivation rate with increasing relaxation time. At the 16 h relaxation time, the formic acid oxidation rate appears to have essentially stabilised at ~25 μmole/min with this effect being consistent for each of the re-illumination cycles. This value is considerably higher than the formic acid oxidation rate for the non-pre-illuminated system (~8 μmole/min) with the difference between these values suspected as due to the impact of surface cleaning during the initial 30 min light treatment period as discussed above.

More significantly though, Figure S3 indicates light pre-treatment invokes a phenomenon which coincides with the surface cleaning, further promoting formic acid oxidation. This striking effect is impermanent in nature, gradually deteriorates with time (over 16 h) and is recoverable by re-illumination. The origin of

this transient activity component is thought to relate to the ability of Pt deposits to accumulate photogenerated electrons from the TiO₂ when illuminated [21] and readily transfer them to adsorbed oxygen species where they effectively remain 'trapped' in a quasi-stable state. In relation to the experimental findings and in conjunction with supporting literature a tentative mechanism detailing the impact of light pre-treatment on oxygen activation and stabilisation by the Pt deposits is proposed below.

The initial step in the process would require the adsorption of molecular O₂ on the Pt deposits. As part of a theoretical study by Muhich et al. [22] on the effect of Pt deposits (Pt₃₇) on TiO₂ photocatalytic activity they probed molecular oxygen adsorption on neat and Pt/TiO₂. Their findings indicated that in aqueous solutions O₂ rarely interacts with the TiO₂ surface due to preferential adsorption of water. In contrast, when Pt deposits are present on the surface O₂ adsorption is significantly enhanced as the Pt preferentially adsorbs O₂ over H₂O. They proposed that the beneficial role of Pt deposits during photocatalysis stemmed from the Pt offering a greater number of O₂ adsorption sites which may also be the case in our system.

Following molecular O₂ adsorption on the Pt deposits the oxygen may: (1) undergo electron injection to give a superoxide radical, O₂⁻ (Eq. (3)); (2) undergo electron injection to give O₂⁻ followed by dissociation into atomic oxygen species, O and O⁻ (Eq. (4)); (3) dissociate to give atomic oxygen, O (Eq. (5)), which then undergoes electron injection to give O⁻ (Eq. (6)). While it is not clear which mechanism dominates, partial oxidation of the Pt deposits to give PtO_x (including PtO_{ads} – Table 1) in this study provides some evidence of oxygen dissociation (i.e. O₂ dissociates when oxidising Pt⁰ to form PtO (or PtO_{ads})). The capacity for molecular oxygen to adsorb and dissociate on Pt has been investigated by others. For instance, Lim and Wilcox [6] used Density Functional Theory (DFT) to predict the outcomes of molecular oxygen interaction with Pt₁₃ nanoparticles loaded on a defective graphene support. They found the preferred initial reaction to be the dissociation of molecular oxygen, bridged across adjacent Pt atoms, into two adsorbed atomic O species (i.e. O₂^{*} → O* + O* where the asterisk represents adsorbed species on the Pt). Bray and Schneider [23] also used DFT to probe molecular O₂ dissociation on a Pt(3 2 1) surface, indicating the barrier to dissociation on this surface structure was low. The ease of O₂ dissociation on the Pt(3 2 1) surface was suggested to be a function of the type of Pt atoms across which the oxygen was bridged (i.e. kink-kink or kink-step) with the kink-kink arrangement providing the lowest energy dissociation pathway. The findings also indicated the barrier for O₂ dissociation on the Pt(3 2 1) surface was lower than on a clean Pt(1 1 1) surface arising from a greater

energetic mismatch between O₂ adsorption and dissociation processes for the Pt(321) surface. Additionally, the degree to which molecular oxygen dissociates on a Pt surface is a function of both temperature and oxygen coverage. For instance, Gland [24] demonstrated that below ~150 K oxygen remains in a molecular state on the Pt(111) surface while above this temperature it undergoes dissociation with the extent of dissociation governed by the oxygen surface coverage.



Experimentally, electron spin resonance (ESR) studies on neat and Pt/TiO₂ have also (indirectly) indicated the generation of active oxygen species, O₂⁻ and O₃⁻, during illumination. An ESR study by Sano et al. [25] probing the oxygen species formed on neat TiO₂ (Aeroxide P25) and Pt/TiO₂ under UV illumination provided an increased O₂⁻ signal intensity for the Pt/TiO₂ compared with the neat TiO₂. The difference in the O₂⁻ signals was suggested to derive from the Pt deposits enhancing O₂⁻ formation or stabilising the species. Einaga et al. [18] also employed ESR to survey the oxygen species formed on Pt/TiO₂, in their case probing the surface following 10 min pre-illumination at room temperature and in the presence of water vapour. Their ESR spectra demonstrated O₂⁻ and O₃⁻ species were present and that implied the Pt enhanced O₃⁻ stability in the dark. Einaga et al. went further to suggest O₃⁻ formation derived from interaction between O₂ and an O⁻ although they inferred the O⁻ originated from a lattice oxygen hole centre generated upon illumination (Eq. (7)):



The suppositions by Sano et al. and Einaga et al. advocate the idea that Pt facilitates the 'trapping' of photogenerated electrons within the form of activated oxygen species.

The transient relationship between photoactivity and relaxation time exhibited in Fig. 4 suggests that while the Pt facilitates charge trapping the resulting active oxygen species are not incessantly stable. A somewhat similar phenomenon was observed by Hwang et al. [26] during gas-phase CO oxidation by Pt/TiO₂. They found that if they decreased the 'dark time' between successive photocatalytic cycles the CO photo-oxidation rate increased although they did not comment on reasons for the differences in oxidation rate with changing dark time. The gradual deterioration of the pre-illumination effect is thought to derive from relaxation of the system possibly via recombination of atomic oxygen accompanied by return of the electron(s) to the Pt deposit and/or the TiO₂ (via the Pt). Supporting this notion, the DFT study by Bray and Schneider [23] also considered the diffusion of atomic oxygen on a Pt(321) surface, reporting the barrier to oxygen leaving the most stable adsorption site on the Pt(321) was relatively low and that the atomic oxygen can diffuse across the surface. While the Pt(321) surface differs from the arrangement of Pt atoms in the 2 nm deposits here, their work indicates the potential for atomic oxygen mobility and opens the way for eventual collision and recombination between the atomic species.

Overall, the benefit invoked by light treatment can potentially be used for improving catalytic activity for chemical processes using Pt-loaded semiconductors including CWAO processes at elevated temperature and pressure. Much like the reactions during photocatalysis, the oxygen activation step in CWAO is considered as the rate limiting step during processing [27]. If the presence of electrons in the Pt deposits can be harnessed and subsequently transferred to adsorbed oxygen during CWAO, then the potential exists for

enhancing the oxygen reduction reaction (ORR) and improving catalyst performance by simple light pre-treatment.

5. Conclusions

This work has demonstrated that treating Pt/TiO₂ with light can promote its catalytic activity, in this instance for the oxidation of formic acid. Pre-treating the Pt/TiO₂ with UV light for 30 min provided an almost seven-fold increase in the formic acid oxidation rate which is attributed to a combination of: (1) cleaning the surface which allows for increased formic acid adsorption and; (2) the injection of photo excited electrons from the TiO₂ into the Pt deposits and their subsequent trapping, possibly as activated oxygen species. The captured, photo excited electrons possess strikingly long lifetimes which are in the order of hours. However, the activity enhancement gradually decayed with time whereby re-illuminating the Pt/TiO₂ with UV light completely recovered the transient component of the improved activity. Partial oxidation of the Pt deposits during reaction and a decrease in activity under oxygen-lean conditions indicates oxygen plays an important part in the overall reaction mechanism. It is thought adsorbed molecular oxygen is the species primarily responsible for trapping and stabilising electrons from the Pt, an action which is enhanced by increased electron injection during light pre-treatment. While work is underway to confirm whether this is the case, pre-treatment with light could be a simple means by which oxygen reduction/activation by Pt catalysts could be further enhanced. Beyond formic acid oxidation, the improved catalytic oxidation activities arising from light pre-treatment have potentially positive implications for more significant applications based on the ORR such as CWAO or fuel cell systems.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatt.2014.08.042>.

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