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Modelled kinetics of the rate of hydrogen evolution as a function of metal catalyst loading in the photocatalysed reforming of methanol by Pt (or Pd)/TiO₂

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Abstract

The rate of hydrogen evolution, $r(\text{H}_2)$, due to the photocatalysed reforming of methanol, MeOH, is studied as a function of Pt loading on P25 TiO₂ both in the aqueous (at room temperature) and gas phase (at 100 °C). A similar study, using Pd on P25, has been reported earlier [M. Bowker et al. J. Catalysis, 2003, 217, 427-433] and a perimeter-based Metal-Support Interface (MSI) kinetic model used to interpret the results. Here a new kinetic model is introduced which appears to provide a better fit to all the $r(\text{H}_2)$ vs wt% metal data sets, in which the rate of reaction is proportional to an extended *area* around each metal island, rather than its *perimeter*. A simple theoretical rationale is provided for this expanding photocatalytic *area* and overlap (EPAO) kinetic model in which each metal island forms an electric field with the surrounding TiO₂ so as to act as a sink for electrons photogenerated in the surrounding TiO₂ film, thereby allowing it to effect the reduction of water, leaving the remaining photogenerated holes to oxidise the methanol adsorbed on the TiO₂. Some support for this very simple kinetic and theoretical model is provided by the results of a brief study of the oxidation of soot deposited on and around a Pt 'dot' on a sol-gel TiO₂ film, in that, upon irradiation of this system a zone of activity is visibly revealed by the gradual disappearance of the soot around the Pt 'dot', the radius of which appears to be proportional to the radius of the metal 'dot'.

Key words: methanol; reforming; hydrogen; platinum, loading

1. Introduction

As the concern with global warming increases, there is renewed interest in a hydrogen economy in which hydrogen, rather than hydrocarbons, is the fuel for transport and homes [1]. In addition, unlike hydrocarbons, hydrogen works very well as a fuel in polymer electrolyte fuel cells to provide electricity efficiently and largely free of pollutants [2]. An indication of the increasing interest in hydrogen as a fuel for the future is the fact that in 2017 a number of renowned international companies associated with energy, transport and industry, formed the Hydrogen Council to promote the use of hydrogen [3]. However, although a versatile fuel, the economic storage of hydrogen on a large scale continues to pose a major challenge and, as a result, there is a considerable effort to explore other, easier to store, fuels, like methanol, MeOH, which can act as an indirect source of hydrogen, e.g. in the case of MeOH, *via* the reforming reaction:

Unfortunately, most catalysts for reaction (1) are only effective above 200 °C [4, 5] and so there is a need for a process that can effect reaction (1) at much lower temperatures. One such method is semiconductor photocatalysis and, as a result, numerous studies of its application to reaction (1) have been conducted in recent years, mainly in *aqueous* solution using TiO₂ particles as the photocatalyst, decorated with a fine (usually < 5 nm diameter) distribution of islands of a platinum group metal, such as Pt or Pd [6-14]. In this process, it is usually suggested that the metal acts as a sink for the photogenerated electrons, as it has a lower fermi level than the conductance band of the TiO₂, and has a low overpotential for the reduction of water [15, 16].

Interestingly, despite the growing research efforts in the photocatalysed reforming of methanol *via* reaction (1) [6-14], the effect of %wt metal loading on the rate has not been well studied or modelled, with the notable exception of the work of the Bowker and his group [9-12, 17], who proposed a Metal-Support Interface (MSI) kinetic model to explain the striking rate of hydrogen evolution, $r(\text{H}_2)$, vs wt% Pd profile they observed for reaction (1) photocatalysed by Pd/TiO₂ and which is illustrated in figure 1 [11, 17]. In this work, 0.2 g of a Pd/TiO₂ photocatalyst, with various metal loadings (0.001 – 5 wt%) prepared by the incipient wetness method, were dispersed in a 27 mM aqueous methanol solution, which were then exposed to UV irradiation using a 400 W Xe arc lamp. Only H₂ and CO₂ generation were observed in the headspace [11, 17], suggesting that reaction (1) provides an adequate description of the overall photocatalytic process.

The MSI kinetic model [11, 17] is based on a number of assumptions including:

- a) the metal is uniformly distributed as hemispherical islands of radius, r , across the surface of the semiconductor photocatalyst particles, each spaced a distance, R , apart, where the distance depends upon their packing (hexagonal or square packed);
- b) the rate of hydrogen generation due to the photocatalysed reforming of MeOH, $r(\text{H}_2)$, is proportional to the total perimeter length, P_T' , per m^2 associated with the metal particles;
- c) the perimeter around each metal island is described by a circle of radius, r ;
- d) the increase in $r(\text{H}_2)$ with wt% metal (the increasing rate stage) is due to an increase in r and so in P_T' ;
- e) when $r(\text{H}_2)$ is at a maximum the metal islands touch so that $r = r_{\text{touch}}$;
- f) the sudden and striking loss in rate above a maximum wt% metal is due the metal islands gradually merging into each other, thereby causing P_T' to decrease (the decreasing rate stage)

This model continues to be cited in recent reviews on the sacrificial production of hydrogen over TiO_2 -based photocatalysts [18-21]. The variation in rate with Pd (or Pt) metal loading does not appear to be related to plasmonic effects [21], given that the surface plasmon resonances of these metals are below 300 nm [22] and no visible light photocatalysis has been reported for this system [21].

However, Bowker *et al.* [11, 17] subsequently revised this model because they correctly noted that for most studies, including the ones reported by Bowker *et al.* [11, 17] and here, it is simply not possible for metal particle overlap to occur even at the maximum %wt metal levels usually employed in such studies (typically 1-10 wt% maximum). Indeed, even if Pd atoms, say, (radius = 163 pm) were employed as a hexagonal-packed monolayer on the P25 (specific surface area (SA) = $50 \text{ m}^2 \text{ g}^{-1}$), rather than the usual 1-2 nm diameter particles that decorate the TiO_2 powder particles, a loading of ca. 11.8 % would be required to achieve complete coverage. This figure rises to a heady 72 wt% of Pd, if hexagonal-packed, 1 nm radius hemispherical particles of Pd square were used to cover the same surface. As we shall see, electron microscopy of the Pd and Pt decorated TiO_2 particles discussed in this work confirms that even at a loading 10 wt% of Pt or Pd, where the photocatalyst appears very dark grey, much of the surface of the TiO_2 remains metal deposit free.

The above observations suggest that the reason for the often observed sudden decrease in photocatalytic activity at high metal wt% loadings is not due to blocking of the incident UV light by the metal islands as often suggested [23-25] nor overlap of the metal islands [11, 17], and that there must be another cause. In order to address the latter concern, Bowker *et al.* [11] subsequently made an additional assumption to their initial model, namely:

- g) that in both (d) and (f), i.e. during the increasing and decreasing rate stages, the radius of the activity perimeter extends beyond that of the metal islands themselves, so that the effective radius is r_z , where $r_z \gg r$, and $r_z = r + d$, where d is the width of the extended zone.

This simple revised model was then used by Bowker *et al.* [11] to fit their observed variation of $r(\text{H}_2)$ vs. wt% Pd data derived from a study of reaction (1) photocatalysed by Pd/TiO₂, as illustrated by the solid line plot in figure 1. As illustrated in figure 1, Bowker *et al.* [11] reports the average rates after 2 and 5 h, presumably to identify any marked difference in values and profile shape, due to catalyst conditioning say. A brief inspection of the results suggest that while there is some non-systematic variation in values there is little in profile shape.

Figure 1: Plot of rate of hydrogen evolution due to the photocatalysed reforming of MeOH by Pd/TiO₂ with different metal loadings (open and closed circles refer to measured rates at 2 and 5 h respectively). The solid line has been generated using the revised metal-support interface kinetic model proposed by Bowker *et al.* [11, 17].

A brief inspection of figure 1, suggests that the fit of this simple model to the data is encouraging but not great and Bowker *et al.* [11] suggest two model assumptions that may be behind this lack of good fit, namely that the metal particles are: (i) all of the same shape and number and invariant with wt% metal loading and (ii) distributed in an ordered (square planar or hexagonal) arrangement on the surface, whereas electron microscopy suggests that not all the metal particles are the same shape and that the particles are randomly distributed. However, given the obvious simplifications made in the model, the fit of the MSI kinetic model appears promising although, in order to get the fit illustrated in figure 1, Bowker *et al.* [11, 17] had also to assume that, at the maximum rate of H₂

evolution, the extended zone exists ca. 15 nm from the edge of the 2 nm diameter Pd particles, for a 0.5 wt% Pd/TiO₂ photocatalyst, i.e. very far away (7.5x's the Pd particle diameter) from the actual metal-support interface. The latter assumption is difficult to rationalise in theory and has prompted us to explore an alternative model described below.

Despite the concerns noted above, the MSI kinetic is not without merit, since there is evidence of spill-over and extended reaction zones from other photocatalytic studies of metal-deposited photocatalytic films [11, 26, 27]. In particular, in a recent paper from this group on the photocatalysed oxidation of soot by a TiO₂ film with a photodeposited line, or 'wire', (ca. 1 mm) of Pt on its surface [27] clear evidence of an extended zone of photocatalytic activity around the Pt 'wire' was presented. More importantly, as we shall see, this extended zone appeared to develop gradually *as a whole*, rather than as a *perimeter* of activity growing out from the edge of the Pt 'wire'. These findings suggest that it is the *area*, rather than the *perimeter*, of the extended zone that is the photocatalytically active zone that surrounds a deposited metal, such as Pt, and that a modified version of the initial Bowker kinetic model [11, 17], based on *area*, rather than *perimeter*, growth and overlap, may be more appropriate to interpret the kinetic data illustrated in figure 1, for the photocatalysed reforming of MeOH in aqueous solution, using a Pd/TiO₂ photocatalyst. In order to test this hypothesis, in this paper an *area* model of the kinetics of photocatalysis of reaction (1) is developed, along the same lines used by Bowker *et al.* [11, 17] in the MSI *perimeter* kinetic model, and used to fit not only the results illustrated in figure 1, for the photocatalysed reforming of MeOH in aqueous solution using a Pd/TiO₂ photocatalyst, but also those arising from a study of the same reaction, with the MeOH and water in the *liquid* and *gas* phase and Pt/TiO₂ as the photocatalyst.

2. Experimental

2.1 Materials

Unless stated otherwise, all chemicals were purchased from Sigma Aldrich and used as received. The Aeroxide® P25 TiO₂ powder was a gift from Evonik (formerly Degussa). All gases were purchased from BOC and certified to be of 99.999% purity.

2.2 Photocatalyst preparation

All Pt/TiO₂ photocatalysts were prepared using the incipient wetness method [11, 28]. Thus, for the typical photocatalyst Pt/TiO₂ (0.2 wt% Pt), 58 mg of the metal salt (H₂PtCl₆·6H₂O) were dissolved in 80 cm³ of water and the solution then added dropwise to 10 g of the P25 TiO₂ powder which was agitated continuously. The resulting dispersion was dried at 110 °C overnight before being calcined at 500 °C for 2 h, then sieved to an aggregated particle size between 250-400 µm, before being reduced at 200 °C for 2 h in a tubular furnace under a steady flow of H₂ (50 cm³ min⁻¹) thereby yielding the 0.2 wt% Pt/TiO₂ photocatalyst. Samples of Pt/TiO₂ with a range of different loadings of platinum (0.0001- 10 wt% Pt) were also made using the same method, but with different amounts of metal salt. Using the same method of preparation, coupled with high resolution TEM, Bowker et al. [11] showed that the metal particles are mainly round and monodispersed.

2.3 Photocatalyst Characterisation

The weight loadings of each prepared catalyst were confirmed using an Agilent 5110 Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES); the error associated with each weight loading was estimated to be ± 5%. The photocatalyst powders were also analysed using: (i) X-ray powder diffraction (XRD) (Panalytical XRD, Micromeritics Tristar 3020) in order to confirm the crystal structure of the TiO₂ and (ii) Brunauer-Emmett-Teller (BET) surface area of each catalyst. In the cases of both (i) and (ii) the TiO₂ appeared to be an 80:20 mix of anatase and rutile with a specific surface area, SA, of 50 m² g⁻¹, before and after metal deposition and annealing.

A series of digital photographs were taken of the Pt/TiO₂ photocatalysts with different Pt loadings and the results of this work are illustrated in figure 2(a). The latter images show that as the Pt loading is increased the synthesised Pt/TiO₂ photocatalysts appear increasingly dark grey, understandably suggesting significant UV screening of the surface, even though this is NOT borne out by electron microscopy studies, *vide infra*. In addition, the same powders were analysed using Transmission Electron Microscopy (TEM), with a JEM-1400plus TEM (Jeol) and typical micrographs arising from his work are shown in figure 2(b). All three images reveal an average TiO₂ particle radius of 15 nm, which is consistent with a measured BET specific surface area, SA, of ca. 50 m² g⁻¹.

In addition, the Pt particle radius appears about 0.5 and 1.5 nm for the 0.2 and 10 wt% Pt loaded photocatalysts. Note: as we shall see, the former *paired* data set, i.e. 0.5 nm Pt particles for the 0.2 wt% Pt loaded TiO₂ photocatalyst, is the *paired r and wt% metal* value set (always shown in **bold and used** to highlight experimentally determined values) required in the kinetic model presented here, and the MSI kinetic model, to calculate the number of metal sites, N , and subsequently the distance between these sites, R . The electron micrographs illustrated in figure 2(b) show that despite the dark appearance of the 10 wt% Pt/TiO₂ photocatalyst, much of the surface of the TiO₂ remains unoccupied by Pt islands, as noted earlier and as expected based on simple calculations. For example, assuming a Pt hemispherical particle radius of 1.5 nm at 10 wt%, it can be shown that the fraction of the 50 m² g⁻¹ surface occupied is only 4.6 %.

Figure 2: (a) photographs of the Pt/TiO₂ photocatalyst powders with different loadings of Pt, namely: from left to right: 0, 0.001, 0.001, 0.003, 0.01, 0.03, 0.05, 0.1, 0.2, 0.5, 1, 4 and 10 wt% Pt; (b) TEM images of three typical photocatalyst powders with (from left to right) 0, 0.2 and 10 wt% Pt. The red circle highlights a typical Pt particle which had a radius, r , of *ca.* 0.5 and *ca.* 1.5 nm for the 0.2 and 10 wt% loaded Pt/TiO₂ powders, respectively.

Each Pt/TiO₂ photocatalyst made was photographed, see figure 2(a) and tested for activity, with regards to sensitising reaction (1), both in *aqueous* solution and in the *gas* phase.

2.4 Photocatalytic activity testing: in aqueous solution

In *aqueous* solution, 12.5 mg of Pt/TiO₂ under test were dispersed in 25 cm³ solution of a 50:50 v/v mixed solvent of methanol and water, so that [MeOH] = 12.4 M, and placed in a 54 cm³ cylindrical borosilicate glass reactor fitted with a screw on cap containing a suba seal (for sampling the head space). This solution was then argon purged for 20 min and irradiated using a 2.8 W 365 nm narrow band UV LED (20 mW cm⁻²). The headspace (29 cm³) above the reaction solution was sampled periodically during the irradiation and analysed using a GC fitted with a thermal conductivity detector. Some of the [H₂] vs irradiation time profiles generated arising from this work are illustrated in figure 2.

Figure 2: Typical set of [H₂] vs irradiation time profiles generated upon irradiation of a TiO₂ photocatalyst with different loadings of Pt with 365 nm light (20mW cm⁻²). The wt% Pt levels used here were (from top to bottom): 0.2, 1.0, 0.05, 0.01, 10, 0.001 and 0 (TiO₂ P25), respectively. Note that in the absence of light, no H₂ evolution was detected.

2.5 Photocatalytic activity testing: in gaseous phase

In the study of reaction (1) in the *gas* phase, using the different Pt/TiO₂ photocatalyst samples, a serpentine 'S-bend' borosilicate glass reactor [28], shown in figure 3, with internal and external diameters of 3.75 mm and 6 mm, respectively, was loaded with ca. 2.4 g ($\pm$ 2%) of the Pt/TiO₂ photocatalyst powder under test; the powder was held in place with small plugs of glass wool at the

top and bottom of the serpentine reactor, as shown in figure 3. Once loaded, the 'S-bend' reactor was inserted into the centre of the heated flow reactor. The heated flow reactor [28] consisted of a semi-cylindrical ceramic fibre heater (diameter of 14.7 cm and height of 35.7 cm) surrounded by a quartz cylinder (diameter of 19.7 cm and height of 38.5 cm). The remainder of the quartz cylinder was packed with a thermal insulation blanket to ensure a constant reactor temperature (ca. 100 °C), although a small window was left so as to allow the UV radiation, of the serpentine photocatalyst-containing reactor vessel at the centre of the flow reactor, with 365 nm UV light from a 2.8 W 365 nm narrow band UV LED; irradiance = 20 mW cm⁻². A schematic flow diagram of the entire experimental set up for the gas-phase reaction is illustrated in the Supplementary Information in Figures S1 and S2.

Figure 3 – A photograph showing 2.4 g of 0.2 wt% Pt/TiO₂ sealed within a typical serpentine 'S-bend' reactor, with an internal volume of 3.3 cm³.

In a typical reaction run, a stream of Ar containing H₂O (10 % by volume, 4.16 mM) and MeOH (5 % by volume, 2.08 mM) was passed over the photocatalyst bed for 4.5 hours, at a flow rate of 15 cm³ min⁻¹. After the first 1.25 h, the Pt/TiO₂ photocatalyst sample under test was irradiated for 2 hours, and then left in the dark for the remaining 1.25 h. The gas stream was sampled every 0.5 h during this 4.5 h period and subjected to analysis using a gas chromatograph (Perkin Elmer) fitted with a Porapak D column with a TCD, for the analysis of H₂. At the start of each photoreaction, the serpentine reactor was flushed with Ar and thermostatted at 100 °C, before being exposed to the H₂O/MeOH reactant feed and subsequent illumination. The reactant residence time was calculated as: 13.2 s, given the volume of the serpentine reactor was 3.3 cm³ and the flow rate 15 cm³ min⁻¹. Three H₂ vs irradiation time profiles were generated in series for each of the Pt/TiO₂ photocatalysts tested using the above system, and an *average* value for the rate of hydrogen evolution, $r(\text{H}_2)$, was then calculated from the [H₂] vs irradiation time data. For example, the three $r(\text{H}_2)$ vs irradiation

time profiles generated, for a 0.05 wt % Pt loaded TiO_2 catalyst, are illustrated in figure 4, from which a value of $r(\text{H}_2)$, of $142 \mu\text{L min}^{-1}$ was determined.

Figure 4: Typical set of three $r(\text{H}_2)$ vs irradiation time profiles recorded using the *gas phase* photocatalytic system, with a 0.05 wt% Pt/ TiO_2 photocatalyst. The average value of $r(\text{H}_2)$, $142 \mu\text{L min}^{-1}$, determined using this data is illustrated by the broken red horizontal red line.

Note: although the $[\text{MeOH}]$ used in the gas phase study (2.08 mM) was much lower than that used in the aqueous phase study (12.4 M), for practical reasons and to allow comparison with another gas phase study [28], other work by Bowker *et al.* [11, 17] demonstrated that the rate of reaction was largely independent of $[\text{MeOH}]$.

3. The Expanding Photocatalytic Area and Overlap kinetic model (EPAO model)

The **expanding photocatalytic area and overlap**, i.e. EPAO, model developed here to describe the kinetics of reaction (1) photocatalysed by a metal-decorated semiconductor sensitiser is based on a similar set of assumptions made by Bowker *et al.* in their metal support interface model [11, 17], but with *area* replacing *perimeter*. Thus, the main assumptions of the EPAO kinetic model are:

- i. the metal is uniformly distributed as hemispherical islands of radius, r , across the surface of the semiconductor photocatalyst particles, each spaced a distance, R , apart, where the distance depends upon their packing (hexagonal or square packed);
- ii. the rate of hydrogen generation due to the photocatalysed reforming of MeOH, $r(\text{H}_2)$, is proportional to the total photocatalytically active *area*, A_T' , per m^2 ;
- iii. the *area* of the active zone around each metal island has a radius, r_z , where r_z is a simple linear function of r , the radius of the metal island;
- iv. the increase in $r(\text{H}_2)$ with wt% metal (in the increasing rate stage) is due to the increase in r_z and so in A_T' ;
- v. when $r(\text{H}_2)$ is a maximum, $r(\text{H}_2)_{\text{max}}$, so is A_T' , i.e. $A_T'(\text{max})$, i.e. the photocatalytic *area* does not increase any further with r , although a deactivating zone of influence does, and at this point the photocatalytically active *areas* are just touching so that $r_z = r_{\text{touch}} = R/2$. A possible reason for this deactivation zone is suggested later;
- vi. the sudden and striking loss in rate above the wt% metal associated with $r(\text{H}_2)_{\text{max}}$, i.e. above **wt%(max)**, where $r_z > r_{\text{touch}}$, is due overlap of the expanding deactivation zones overlapping with the photocatalytically active *areas*, thereby reducing the value of A_T' , for all metal islands with increasing r_z above r_{touch} ; this is the decreasing rate stage.

Figure 5 provides a schematic illustration of the EPAO kinetic model for two hemispherical metal particle 'islands', a distance R apart, in their increasing rate stage (in which the photocatalytically active zones are expanding – highlighted in red hatching – due to increasing wt% metal loading), up to the maximum rate, at which point they touch and wt% metal = **wt%(max)**, and after, as their deactivation zones expand and overlap (highlighted in grey) with the photocatalytically active zones and so reduce the value of A_T' from its maximum value of $A_T'(\text{max})$.

Figure 5: A pair of metal particles (black dots) radius r , on the surface of a semiconductor photocatalyst, with zones of photocatalytic activity (red hatched) areas or radius r_z , in the following rate of H_2 evolution stages (from left to right): (i) increasing, (ii) maximum and (iii) decreasing. The grey hatched areas identify areas of overlap of the expanding deactivation zones, when $r_z > r_{\text{touch}}$, which reduces the size of the photocatalytic activity (red hatched) areas

Given the above assumptions it follows that:

$$r(H_2) = k A_T' \quad (2)$$

where, in the growing rate stage:

$$A_T' = N \cdot \pi r_z^2 \quad (3)$$

where N is the number of metal islands per m^2 , separated from each other by a distance R and r_z is the radius of the extended zone. The value for N is calculated from a knowledge of the wt% of metal and metal particle size, i.e. a paired set of data: r and **wt% metal**, since:

$$N = \text{wt\% metal} / (100 \cdot SA \cdot \rho) / V_p \quad (4)$$

where SA = the specific surface area of the semiconductor photocatalyst (units: m^2/g), ρ the density of the metal (units: g/m^3) and V_p = volume of the hemi-spherical metal particles, radius r , i.e. $2\pi r^3/3$. For example, Bowker *et al.* [11, 17] report that for 0.5 wt% loading of Pd (on P25 TiO_2 , $SA = 50 m^2/g$) the Pd particles had a radius of 1 nm. Using this paired r , **wt% metal** data set, and eqn (4), a value of $N = 3.97 \times 10^{15}$ metal sites per m^2 can be calculated [11]. Once a value for N has been determined, from a r , **wt% metal** paired data set, it can then be used to calculate a value for R , the distance between metal sites, depending on whether the sites are hexagonal $R = \{2/(N \cdot \sqrt{3})\}^{0.5}$, or square packed ($R = (1/N)^{0.5}$); thus, for the Pd metal hemispheres in the Pd/ TiO_2 system reported by Bowker *et al.* [11, 17], a value of $R = 17.1$ nm, can be derived, assuming they are hexagonally packed and $N = 3.97 \times 10^{15}$ metal sites per m^2 . The calculated values for N and R , are essential parameters used by both the MSI and EAOP models to fit the all $r(H_2)$ vs. wt% metal data reported here; thus, the above values of N and R are used in the model fits of the data illustrated in figure 1.

In this initial *increasing* $r(H_2)$ stage, it is assumed that the value of r_z , $= r_z(\text{incrs})$, is directly related to the metal particle radius, r , by the following simple expression:

$$r_z(\text{incrs}) = a + br \quad (5)$$

where, a and b are constants; this function is similar to that used by Bowker *et al.* [11] to describe the variation in the radius of the extended zone in their *perimeter* model. The active circular area 'a' suggests that even very small metal particles are able to act as a very effective sink for electrons, photogenerated in the surrounding semiconductor area, thereby implying that the electric field that exists between the two, *vide infra*, is largely independent of metal mass.

Eventually the activation zones, which expand with increasing wt% metal, and thus with increasing value of r , touch, as illustrated in figure 5, at which point $r(H_2)$ is a maximum, as is A_T' , i.e. $A_T'(\text{max})$. This point has associated with it a series of values that help characterise the system, namely those for: (i) wt% metal loading, i.e. **%wt(max)** (note: the use of bold highlights the fact that this is an experimentally determined value), (ii) metal particle radius, r^* , a value for which can be readily calculated from the value of **%wt(max)** and (iii) $r_{\text{touch}} = R/2$, where, as noted earlier, the value of R is determined from the paired data set: r and **wt% metal**.

In this model the subsequent decrease in rate with increasing wt% metal above the maximum rate, is due to the decrease in A_T' from its peak value of $A_T'(\text{max})$, when $r_z = R/2$, as the extended zones the neighbouring metal islands overlap and become deactivation zones – as illustrated by the grey zones in figure 5.

It can be shown that [29] for two overlapping circles of radii r_1 (here = $r_z(\text{decrs})$, *vide infra*) and r_2 (here = $r_{\text{touch}} = R/2$), the centres of which are separated by a distance d (here = R), the overlapping area, ΔA , is given by the following expression:

$$\Delta A = r_1^2 \cos^{-1}(d_1/r_1) - d_1(r_1^2 - d_1^2) + r_2^2 \cos^{-1}(d_2/r_2) - d_2(r_2^2 - d_2^2) \quad (6)$$

where $d_1 = (r_1^2 - r_2^2 + d^2)/2d$ and $d_2 = d - d_1$. In this work it is assumed that $r_z(\text{decrs})$'s dependence upon r , although still proportional to r , may less marked than that of $r_z(\text{incrs})$ and so is described by the expression:

$$r_z(\text{decrs}) = R/2 + b'(r - r^*) \quad (7)$$

where b' is a constant.

It follows from the above, that in the decreasing $r(H_2)$ stage, the overall photocatalytic active area available per m^2 of surface is given by:

$$A_T' = \pi N(r_{\text{touch}}^2 - f \cdot \Delta A) \quad (8)$$

Where f is a packing factor (= 4 or 6 for square or hexagonal packing, respectively). This very simple EPAO kinetic model, can then be used to describe the kinetics of the photo-catalysed reaction (1) by a metal/semiconductor photocatalyst.

Table 1 contains the values of: (i) the paired data set **%wt metal, r** , used to calculate N and R and r_{touch} , (ii) **%wt(max)**, used to calculate r^* , and (ii) the fitting parameters: a , b , and b' . These values are used in the above model to create the solid line fits to the various $r(\text{H}_2)$ vs wt% metal plots reported below. It is worth noting that the values of a and b are related to one another *via* the expression:

$$-a = R/2 - br^* \quad (9)$$

where, R and r^* are known constants, derived from the experimental parameters of the system, **%wt metal, r** and **%wt(max)**, the determination of which is described above.

Table 1: Key parameters and data used in the EPAO kinetic model to fit the $r(\text{H}_2)$ vs $\log(\text{wt\% metal})$ data, reported by Bowker et. al. [11, 17] and here, for the photocatalysed reforming of methanol in aqueous solution and the gas phase*

Parameter	Units	Key equation	MeOH(aq), [11, 17]	MeOH(aq),	MeOH + steam
Number of metal island sites per unit area, N	Sites m^{-2}	$N = \text{wt\% metal}/(100 \cdot \text{SA} \cdot \rho(\text{metal}))/V_p$	3.97×10^{15}	7.12×10^{14}	7.12×10^{14}
Distance between metal sites, (hexagonal or square packed), R	m	$R = (2/\sqrt{3} \cdot N)^{0.5}$ or $(1/N)^{0.5}$	1.71×10^{-8} (hex packed)	1.18×10^{-8} (square packed)	1.18×10^{-8} (square packed)
Volume of hemispherical particles, V_p	m^3	$V_p = 2\pi r^3/3$	2.09×10^{-27}	2.62×10^{-28}	2.62×10^{-28}
Particle radius, r	m	Determined from TEM for the wt% metal value below	1×10^{-9}	5.0×10^{-10}	5.0×10^{-10}
% wt loading of metal, wt% metal	%		0.5	0.2	0.2
% wt loading of metal when $r(\text{H}_2)$ is a maximum, %wt(max)	%		0.3	0.2	0.01
$r_z(\text{incrs})$ parameters (a, b)	m	$r_z(\text{incrs}) = a + br$	$5.5 \times 10^{-9}, 3.6$	$1.5 \times 10^{-9}, 8.85$	$1.5 \times 10^{-9}, 24.1$
Radius of metal islands when the extended fields touch, r^*	m	$r^* = (R/2 - a)/b$ or $r^* = \{1.5 \times \text{wt\%}(\text{max})/(100 \cdot \text{SA} \cdot \rho(\text{metal}) \cdot N \cdot \pi)\}^{1/3}$	0.843×10^{-9}	0.5×10^{-9}	0.184×10^{-9}
$r_z(\text{decrs})$ parameter (b')	m	$r_z(\text{decrs}) = R/2 + b'(r - r^*)$	3.6^{**}	2.9	2.8

*: $\rho(\text{Pt})$ and $\rho(\text{Pd}) = 21.5$ and 12.02 g cm^{-3} , respectively; Specific surface area of $\text{TiO}_2 = 50 \text{ m}^2/\text{g}$; values marked in bold are those for the metal particle radius, r , (determined using TEM) at a known **wt% metal**, the paired data set, and the known wt% metal when $r(\text{H}_2)$ is a maximum, **wt%(max)**; **: in this case, it can also be shown that $r_z(\text{incrs}) = r_z(\text{decrs}) = a + br$, i.e. the rate of increase in r_z doesn't change after the zones overlap.

4. Results and discussion

4.1 Model fits to MeOH reformation in aqueous solution

As noted earlier, the paired data set: **%wt metal**, r in Table 1, namely the values of 0.5 wt%, 1 nm, respectively, reported by Bowker et al [11, 17], were used to determine values for N and R , using the equations in Table 1. In the EPAO kinetic model a value of 0.3 wt% for **wt%(max)**, was determined from the plot of the $r(\text{H}_2)$ vs. wt% Pd data reported by Bowker et al [11, 17] and illustrated in figure 6, and used to determine the value for the radius of the Pd particles when the rate was at a maximum, i.e. r^* of 0.843 nm (see Table 1 also for key equation used in this calculation), which – in turn – was used in the calculation of values for $r_z(\text{decrs})$ via eqn (7). The values of **%wt metal**, r , **wt%(max)**, a , b , and b' , used in the *area* model to create the solid line in figure 6, are given in Table 1, along with the other model useful calculated values, R and N .

Figure 6: Plot of rate of hydrogen evolution vs wt% Pd data reported by Bowker et al [11, 17], (open and closed circles refer to measured rates at 2 and 5 h respectively). The solid line has been generated using the EPAO model, and the values of: the wt% metal, r , a , b and b' values reported in Table 1.

A quick comparison between the solid line fits to the data of the *perimeter* model (illustrated in figure 1) and the *area* model, reported here (and illustrated in figure 6) suggests that the latter provides a better description of the $r(\text{H}_2)$ vs wt% metal profile for the Pd/TiO₂/reaction(1) system.

Other work was then carried out to test the EPAO kinetic model further and see if the $r(\text{H}_2)$ vs wt% Pd profile observed by Bowker *et al.* [8, 11, 17], in their study of reaction (1) in aqueous solution sensitised by Pd/TiO₂, also featured when a different metal, such as Pt, was used as the water reduction catalyst, in the same photocatalytic reaction. Thus, as described in the Experimental section, a series of Pt/P25 TiO₂ photocatalyst powders were prepared with loadings that spanned the range 0.0001 to 10 wt%. These powders were then tested as photocatalyst sensitisers of reaction (1) in *aqueous* solution ([MeOH] = 12.4 M; reaction solution volume = 25 cm³; [Pt/TiO₂] = 12.5 mg; irradiance = 20 mW cm⁻²) and involved recording the variation in photogenerated H₂ concentration vs. irradiation time profile for all the Pt/TiO₂ photocatalysts, some of the results for which are illustrated in figure 2. The complete set of these [H₂] vs time profiles allowed the calculation of a series of initial $r(\text{H}_2)$, wt% Pt data points which were then used to construct the plot $r(\text{H}_2)$ vs wt% Pt illustrated in figure 7. Also shown in this figure is the EPAO model solid line fit to the data, based on the experimental (in **bold**) and optimised parameters: **%wt metal**, **r** , **%wt(max)**, **a** , **b** , and **b'** , respectively, in Table 1. The model fit to the data is very good and has a similar shape to the $r(\text{H}_2)$ vs wt% Pd plot illustrated in figure 6. This is possibly not surprising given the similarity of the systems, i.e. the same photocatalysed reforming reaction, although using a different metal, but deposited using the same method (i.e. the incipient wetness method [28]). As a result, key experimental values for the Pd/TiO₂ and Pt/TiO₂ systems, such as **%wt metal**, **r** , **%wt(max)**, are similar, making the key model values: N , R and r^* similar. For example, for the Pd/TiO₂ (and Pt/TiO₂) systems the values of R and r^* are 17.1 (11.8) nm and 0.84 (0.5) nm, respectively.

Figure 7: Plot of rate of hydrogen evolution vs wt% Pt data for the photocatalysed reforming of methanol, i.e. reaction (1). The solid line was generated using the EPAO model, with the values of: the wt% Pt, r , wt% Pt(max), a , b and b' values reported in Table 1.

4.2 Model fits to MeOH reformation in the gas phase

The same Pt/TiO₂ powders were used as photocatalysts to probe the kinetics of H₂ evolution *via* reaction (1) sensitised by Pt/TiO₂ at 100°C in a *gas* stream, comprising a carrier gas of Ar (85 v/v %) with MeOH (5 v/v %) and water (10 v/v %); flow rate = 15 cm³ min⁻¹. Initial work showed that, unlike the *aqueous* solution study, in the *gas* phase study the rate of hydrogen evolution was not negligible in the absence of light, and that this was especially so at very high Pt loadings. Thus, in the *gas* phase study of the Pt/TiO₂ photocatalysed reaction (1), $r(\text{H}_2)$ vs wt% Pt data for reaction (1) with and without (i.e. in the dark) UV irradiation, i.e. $r(\text{H}_2)_{\text{illum}}$ and $r(\text{H}_2)_{\text{dark}}$ values, were determined for each Pt/TiO₂ photocatalyst and the results of this work are illustrated in figure 8.

Figure 8: A bar chart of $r(\text{H}_2)$ vs P wt % Pt loading, recorded using the gas phase photocatalytic system with and without UV irradiation.

A brief inspection of the values of $r(\text{H}_2)$ determined in the dark, due to the thermal catalysis of reaction (1), revealed that they are significant, especially as the metal loading approached 10 wt%. The EPAO model assumes that $r(\text{H}_2)$ is just due to photocatalysis, rather than photo- plus thermal-catalysis, thus, in order to extract out just the *photocatalytic* rate data it is assumed here that for each Pt/TiO₂ photocatalyst, the average value of $r(\text{H}_2)$ determined for the illuminated system is the sum of the $r(\text{H}_2)$ due to photocatalysis and that due to (dark) thermal catalysis, i.e.

$$r(\text{H}_2)_{\text{illum}} = r(\text{H}_2)_{\text{photo}} + r(\text{H}_2)_{\text{dark}} \quad (10)$$

whereas in the dark just $r(\text{H}_2)_{\text{dark}}$ is measured. This assumption allowed the calculation of values for $r(\text{H}_2)_{\text{photo}}$ for each wt% Pt using the data in figure 8 and a plot of the results is illustrated in figure 9.

Figure 9: Plot of the rate of hydrogen evolution due to reaction (1) photocatalysed by Pt/TiO₂ in the *gas* phase (at 100 °C) as a function wt%Pt, where $r(\text{H}_2)_{\text{photo}}$ was calculated using eqn (10) using the values of $r(\text{H}_2)_{\text{illum}}$ and $r(\text{H}_2)_{\text{dark}}$ in figure 8. The solid line was generated using the EPAO kinetic model, with the values of: the wt% Pt, r , wt% Pt(max), a , b and b' values reported in Table 1.

Note that in the EPAO model fit to the *gas* phase data in figure 9, illustrated by the solid line, the paired data set values of: **r , wt% metal** used are the same (thus, so too are the values of N and R) as those used to fit the *aqueous* solution data illustrated in figure 7. What is strikingly different between these two different data sets, however, are the respective values for **wt%(max)**, i.e. in the gas phase study the value is 20 times lower (i.e. 0.01 wt% rather than 0.2 wt%) than that found in aqueous solution, *cf.* figures 7 and 9. Why this should be is not clear, although the model suggests that it is related to the value of b , which controls the fractional increase in the active zone with increasing r , *via* eqn (5). Thus, the model fits to the data in figures 7 and 9 suggest that this

fractional increase, a measure of which is the value of b , is ca. 2.7 x's greater in the *gas* phase compared to the *liquid* phase. However, the many differences between the two systems, such as: diffusion coefficients, reactant concentrations, [photocatalyst] and temperature, makes it impossible at present to identify a specific underlying cause for this factor of 2.7.

4.3 A theoretical rationale

As we have seen, the EPAO model is based on the concept of an extended reaction *area* around Pt and Pd deposits on TiO₂. This can be rationalised in terms of theory if, as is often reported, the Pt metal islands aid the separation of the photogenerated electron-hole pairs by acting as a sink for photogenerated electrons and a catalyst for their subsequent reduction reaction with water to generate H₂ [16]. Interestingly, although many assign the electron 'sink' role to Pt deposits on TiO₂ the theory of metal/semiconductor (i.e. Schottky) junctions actually predicts that the photogenerated holes should flow to the Pt, not the electrons, given that the work function of Pt and electron affinity of TiO₂ are 5.2 and 4.0 eV, respectively [30]. However, the electron sink role of Pt, assumed by so many [15,16] and here in the EPAO model, can be rationalised in terms of a metallised semiconductor model, in which the Pt forms an ohmic junction with TiO₂ [30]. As it is also known that methanol forms a Schottky junction with bare TiO₂ [31], it follows that the EPAO model, in which a large area around each metal deposit is activated by the metal, suggests that the electric field, which must exist between the Pt deposits and the surrounding TiO₂, is sufficiently strong, that – in effect – the Pt 'hoovers' up the conduction band electrons photogenerated by the surrounding, naked, TiO₂, surface over a large ($\gg r$) distance from each metal deposit. At the same time, it can be envisaged that the remaining photogenerated holes migrate to the surface of the naked TiO₂ surrounding each metal 'island' and there oxidise the surface adsorbed methanol to CO₂ and acid. A schematic illustration of this reaction is illustrated in figure 10. The EPAO kinetic model and the theoretical model schematic in figure 10 suggests that the *area* of the photocatalytically active zone associated with a metal island will be a function of the initial metal particle size and limited in size by the surrounding metal islands and the strength of the electric field pulling the photogenerated electrons to the metal island. In addition, the schematic illustrated in figure 10 suggests that when the photocatalytic active zones overlap, as illustrated in figure 5, this may be associated with the metal particles becoming so large that the electric fields associated with their extended zones overlap and interfere with each other so as to reduce markedly the efficacy of separation of photogenerated electron-hole pairs in these areas of overlap, thereby reducing the efficiency of the overall photocatalytic process.

Figure 10: Schematic illustration of the electron scavenging nature of the Pt metal deposits (Ohmic junction) on TiO_2 , which act as a sink for photogenerated electrons in the surrounding naked TiO_2 , and the concomitant hole scavenging nature (Schottky junction) of the methanol.

4.4 Visualisation of the extended zone

If the extended area model is a common feature of Pt (or Pd)/ TiO_2 photocatalysts, or metal/semiconductor photocatalysts in general, then it might be possible to actually observe it *via* a study of the photocatalysed mineralisation of a coloured, solid, but gas permeable, oxidisable pollutant deposited onto a TiO_2 photocatalytic film with just one large (say 2-3 mm) island of Pt. The ideal pollutant has to be coloured, so its destruction can be observed and very gas permeable, i.e. porous, so as to allow ambient O_2 access to the surface of the Pt 'dot', where it can be reduced to water by the photogenerated 'hoovered up' conduction band electrons. In addition, this ideal pollutant must be readily oxidised by the photogenerated holes at the surface of the surrounding, metal free TiO_2 . One possible contender for this role as solid pollutant is soot, which when deposited using a candle, tends to form a brown coloured very porous layer of carbon which is oxidisable by holes photogenerated on TiO_2 [26, 27, 32, 33].

The overall reaction can be summarised as follows:

If the extended zone concept presented here is applicable to reaction (11) and is appropriate on such a macro scale then according to the original *perimeter* MSI kinetic model the soot will be destroyed initially at the edge of the Pt 'dot' and the area of visible soot removal will slowly expand away from the edge of the Pt 'dot' with increasing irradiation time. In contrast, if the extended *area* model is applicable, then the soot in a set area – the extended zone - around the Pt 'dot' will slowly

disappear with irradiation time and the size of the extended zone will be proportional to the size of the Pt 'dot'.

In order to test this hypotheses, a very active anatase sol-gel TiO_2 film ($2\text{ }\mu\text{m}$ thick) was prepared and a small (2.7 mm), but still easily observed Pt 'dot', was deposited onto its surface using an ink containing chloroplatinic acid and glycerol [22]. After Pt deposition the remaining ink was washed off and the Pt 'dot', and surrounding TiO_2 then covered with a $3.5\text{ }\mu\text{m}$ layer of brown-coloured soot, using a candle. The soot formed a candy-floss-like, highly porous layer on top of the TiO_2 film, which was typically ca. $3.5\text{ }\mu\text{m}$ thick. The soot covered film was then irradiated with UV light (365 nm LED, 20 mW cm^{-2}) and photographed at regular intervals and the results of this work are illustrated in figure 11. These images show that with UV irradiation a soot free zone around the Pt 'dot' gradually emerges as expected if reaction (11) is described by the EPAO kinetic model. The results of other work suggest that the eventual size of the soot free, extended zone, even after prolonged irradiation, is directly proportional to the initial size of the Pt 'dot', which again is consistent with the EPAO model. Although the results of this initial study are promising but obviously not conclusive, clearly more work is required to establish beyond doubt the relevance of an EPAO kinetic and the theoretical rationale presented here.

Figure 11 Photographs of a Pt dot ($d = 2.7\text{ mm}$) covered in a layer of soot (ca. $3.5\text{ }\mu\text{m}$ thick) after 0, 24, 48, and 84 h of irradiation under a UVA lamp (2 mW cm^{-2} , 352 nm).

5. Conclusions

The incipient wetness method is used to deposit a fine dispersion of metal (Pd or Pt) nanoparticles (typically 0.5-1 nm in radius) on the surface of P25 TiO₂ powder particles with the size of the metal particles depending on the wt% of metal deposited. However, even at high wt% loadings (up to 10%) much of the TiO₂ remains metal 'island' free. When used to mediate the reforming of MeOH, all the photocatalysts tested exhibited a rate of hydrogen vs wt% metal profile with similar features, namely a smooth if slightly tapering off increase in $r(\text{H}_2)$ with wt% metal until a maximum rate is obtained, at which point any further increase in wt% metal is accompanied by the rapid deactivation of the photocatalyst. An extended *area* and overlap kinetic model provides reasonable fits to the $r(\text{H}_2)$ vs wt% metal profiles determined for the photocatalysed reduction of water and concomitant oxidation of MeOH in *aqueous* solution exhibited by Pd and Pt/TiO₂ photocatalysts in aqueous solution. The model also provides a good fit to the $r(\text{H}_2)$ vs wt% for the same reaction mediated by Pt/TiO₂, but with the reactants in the *gas* phase at 100°C. The kinetic model is rationalised by assuming that each metal island forms an electric field with the surrounding TiO₂ so as to effectively hoover up the photogenerated electrons in the surrounding TiO₂, thereby allowing it to effect the reduction of water at the metal, leaving the remaining photogenerated holes to oxidise the methanol adsorbed on the TiO₂. The efficacy of this process reduces rapidly as the electric fields (i.e. extended zones), associated with each metal deposit, increasingly overlap with increasing loading above a critical level, **wt%(max)**. Support for the simple kinetic model is provided by a study of the oxidation of soot deposited on and around a Pt dot on a sol-gel TiO₂ film. Thus, upon UV irradiation of this system a zone of photocatalytic activity is revealed by the gradual disappearance of the soot around the Pt 'dot', the radius of which appears to be proportional to the radius of the metal 'dot'. Much more work is required to test the validity of the expanding photocatalytic area and overlap (EPAO) model proposed here, but these initial results are encouraging and if found to be a general feature of Pt/TiO₂ systems the EPAO model will provide a better understanding of how catalyst deposits can act on the surface of photocatalyst powders and films.

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