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Photonic efficiency and selectivity study of M (M = Pt, Pd, Au and Ag)/TiO₂ photocatalysts for methanol reforming in the gas phase

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Abstract

A number of different M/TiO₂ photocatalysts, where M (the co-catalyst) = Pt, Pd, Au and Ag, are used to drive the steam reforming of methanol (MeOH) in a gas phase *continuous* flow reactor operated at 100 °C. The rate of H₂ production is: Pt > Pd > Au > Ag >> no metal. The photonic efficiency of Pt/TiO₂ photocatalyst is ca. 120% which suggests some of the hydrogen derives from a current-doubling reaction mechanism. The Pt/TiO₂ photocatalyst drives the steam reforming of MeOH, which generates H₂ and CO₂, with an apparent selectivity of 100% over a wide UV irradiance range (i.e. 1-9.5 mW cm⁻² at 365 nm). In contrast, in the dark, the decomposition of MeOH, which generates H₂ and CO, dominates with a selectivity of ca. 79%. In contrast to Pt, the Pd/TiO₂ photocatalyst is non-selective to either MeOH reforming or its decomposition, so that CO₂ and CO are generated with equal rates. The Au and Ag photocatalysts are less active than either the Pt or Pd co-catalysts and exhibit a variation in selectivity with UV irradiance which is intermediate between that of Pt and Pd. The possible use of photocatalysis as a means to generate H₂ from alcohol-based biofuels is briefly discussed.

Key words: metal;, titanium dioxide; efficiency; selectivity; methanol; reforming; photocatalysis

1. Introduction

There is a growing interest in a hydrogen economy in which hydrogen, rather than hydrocarbons, is the fuel for transport and homes [1]. Unfortunately, although hydrogen is a very versatile fuel, an economic way to store it on a large scale has still to be identified. As a consequence, a great deal of research has been directed towards other, easier to store, fuels, like alcohols, many of which can be produced from biomass and are envisaged to be the major target fuels generated by future bio-refineries [1]. These bio-alcohols are renewable, CO₂ neutral, energy rich and have the same handling advantages as gasoline. Although all alcohols can yield hydrogen *via* steam reforming, the simplest of the alcohols, methanol, MeOH, has attracted particular attention since the steam reforming reaction is straightforward and generates a very simple set of products, i.e.

In the thermal catalysis of reaction (1), most catalysts are only effective above 200 °C [2, 3] and the need for such an elevated temperature reduces the overall energy efficiency of the system. In contrast, reaction (1) can be promoted *via* semiconductor photocatalysis at ambient temperatures and so numerous photocatalytic studies of reaction (1) have been carried out in recent years. Most of these studies have been conducted in *aqueous* solution and in a *batch* reactor, 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 [4-12]. In these studies it is believed 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 [13, 14]. Such *batch* photocatalytic reactions require a photocatalyst powder recovery step, which makes it a less attractive process when it comes to scaling up.

In contrast to the above, many industrial catalytic processes are run as *continuous* gas phase flow operations for reasons of time, energy and cost. Interestingly, there have been few studies of the semiconductor photocatalysed reaction (1) in a gas flow system and, of those, most have been conducted using a less industrially relevant closed recirculating system [14-22]. As an alternative, this group has more recently used a *continuous* gas phase flow system to study reaction (1) over a range of temperatures, i.e. 100-200 °C, using a Pt/TiO₂

photocatalyst [23]. This work revealed that the photocatalysed rate of reaction decreased markedly with increasing temperature and, at all temperatures, a significant level of CO was produced *via* the thermal (i.e. dark) decomposition of MeOH:

The latter reaction is highly undesirable in that CO is a well-recognised poison of electrochemical cells and its presence in H₂ would limit severely the latter's use in producing electricity using a fuel cell [24]. Following on from this work [23], this paper explores the photonic efficiency and selectivity of a number of different M/TiO₂ photocatalysts, where M (the co-catalyst) is Pt, Pd, Au and Ag, for reaction (1) at 100 °C in a *continuous* gas phase flow reactor.

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 M/TiO₂ photocatalysts, whereby M = Pt, Pd, Au and Ag, were prepared using the incipient wetness method [9, 23, 25, 26]. 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 resulting 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 and then sieved to an aggregated particle size between 250-400 µm. The powder was subsequently reduced at 200 °C for 2 h in a tubular furnace under a steady flow of pure H₂ (50 cm³ min⁻¹), thereby yielding the 0.2 wt% Pt/TiO₂ photocatalyst. Note: the incipient wetness method, with its final reduction step, is often used by the catalyst community to produce nanoparticulate metal dispersions on a wide variety of inert substrates [23, 26-29]. In this work, as noted elsewhere, the conversion of the cream colour PtO₂ coated TiO₂ powder particles by the hydrogen produces a striking and rapid colour change to a grey powder, commonly assumed to be due to the reduction of the metal oxide to the metal, as illustrated by the before and after photographic images illustrated in the figure S2 in the SI section; no further colour change is effected by increasing the temperature of reduction reactor temperature even to 500 °C. Temperature programme reduction studies of the Pt/TiO₂ catalyst produced using this technique show that the reduction is readily effected at 200 °C [27, 29].

The above method was also used to prepare the other M/TiO₂ photocatalysts, where M = Pd, Au and Ag, at 0.2 wt%, using the following metal salts: PdCl₂, HAuCl₄·3H₂O and AgNO₃, respectively, which produced coloured products consistent with the generation of nanometre sized metal particles [14]. The prompt generation of H₂ observed upon

illumination of any of the M/TiO₂ photocatalysts suggest little or no oxide layer exists on these pre-reduced metal particles.

2.3 Photocatalyst Characterisation

The weight loadings of each prepared catalyst were confirmed using an Inductively Coupled Plasma-Optical Emission Spectrometer, ICP-OES, (Agilent, 5110). The photocatalyst powders were also analysed using: (i) X-ray powder diffraction (XRD) (Panalytical, X'Pert) to confirm the crystal structure of the TiO₂ and (ii) Brunauer-Emmett-Teller (BET) (Micromeritics, Tristar 3020) 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 of ca. 50 m² g⁻¹, before and after metal deposition and annealing.

A digital photographic image was obtained of each of the M/TiO₂ photocatalysts as well as images and the results are illustrated in Figure 1. Thus, the 0.2 wt% M/TiO₂ photocatalyst powders were: dark grey, light grey, blue and dark red/brown for the Pt, Pd, Au and Ag metals deposited powders, respectively.

Figure 1: A series of digital images of the 0.2 wt% metal deposited TiO₂ photocatalyst powders.

The same powders were analysed using Transmission Electron Microscopy, TEM, (Jeol, JEM-1400) and typical micrographs were obtained for each 0.2 wt% M/TiO₂ photocatalysts using a JEM-1400 plus TEM (Jeol) and the results are illustrated in figure 2, with examples of the metal islands highlighted by a red ring. All the images obtained by TEM reveal an average TiO₂ particle diameter of ca. 30 nm, which is consistent with a measured BET surface area of ca. 50 m² g⁻¹. In contrast, the size of the metal particles, although largely consistent for each metal, varied significantly from metal to metal. Thus, from the TEMs, the average metal particle diameter for the 0.2 wt% M/TiO₂ photocatalysts were: 1 nm, 6 nm, 4 nm and 3 nm

for M = Pt, Pd, Au and Ag, respectively. The TEMs of the photocatalysts before and after use showed no obvious change, with the metal particle sizes remaining unchanged.

Figure 2: TEM images for the 0.2 wt% M/TiO₂ photocatalysts, where M is (from left to right): nothing, Pt, Pd, Au and Ag. Examples of the metal islands are highlighted by the red ring and the average metal particle diameter determined from this and other images were: 1, 6, 4 and 3 nm for M = Pt, Pd, Au and Ag, respectively.

Note that in a previous paper [23], using ostensibly the same Pt/TiO₂ photocatalyst, aggregated Pt particles of 2-3 nm were observed using HAADF STEM and this might appear to suggest some lack or reliability in the method of production, the incipient wetness method – which would be surprising given its widespread use [23, 26-29]. However, a closer inspection of the HAADF STEM image reveals that whilst some aggregated particles were present, the bulk of the Pt particles appeared to be ca. 0.8 nm in diameter, which is reasonably consistent with our measured value of 1 nm, especially given the slight differences in preparation methods, such as level of H₂ used in the reduction step, i.e. 5% in [23] cf. 100% here.

2.3 Photocatalytic activity testing: in the gaseous phase

In the study of reactions (1) and (2) in the *gas* phase, using different metal/TiO₂ photocatalyst samples, a serpentine ‘S-bend’ borosilicate glass reactor with internal and external diameters 3.75 mm and 6 mm, respectively, was loaded with ca. 2.4 g ($\pm$ 2%) of each 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. Once loaded the ‘S-bend’ reactor was inserted into the center of the heated flow reactor. The heated flow reactor [23, 26] consisted of a semi-cylindrical ceramic fiber heater (diameter: 14.7 cm; height: 35.7 cm) surrounded by a quartz cylinder (diameter: 19.7 cm; 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 center of the flow reactor, with 365 nm UV light from a 10 W 365 nm narrow band UV LED (RS Components, LZ1-10UV00). Unless stated otherwise, the irradiance was fixed at 9.5 mW cm⁻², generated using an applied voltage of 0.7 V, and placed 10 cm from the reactor. Here, and in all this work, the UV irradiance was confirmed using a calibrated spectroradiometer (Gooch & Housego, OL 756). In experiments where the irradiance of the UV LED was varied, this was achieved by varying the applied voltage. Further details concerning the photoreactor have been reported elsewhere [26].

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 powder in the 'S' glass reactor, for 4 hours, at a flow rate of 5 cm³ min⁻¹. After the first 1.25 h, the Pt/TiO₂ photocatalyst sample under test was irradiated for 1.5 hours, and then returned to the dark for the remaining 1.25 h. The gas stream was sampled every 0.5 h during this 4 h period and subjected to analysis using a gas chromatograph (Perkin Elmer, Clarus Arnel 580 GC) fitted with a Porapak D column with a TCD, for the analysis of H₂ and an FID-methaniser for the analysis of CO and CO₂. 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: 39.6 s, given the volume of the serpentine reactor was 3.3 cm³ and the flow rate 5 cm³ min⁻¹. For each photocatalyst tested using this system, the average concentrations of H₂, CO₂ and CO in the gas stream were measured periodically with UV illumination (i.e. under photocatalytic conditions) and without UV illumination, i.e. under dark or thermal conditions. These concentration values, measured at different reaction times, coupled with the knowledge that the reactor's residence time (39.6 s), allowed the calculation of the associated rates of the photocatalytic or thermal: H₂, CO₂ and CO generation, i.e. $r(\text{H}_2)$, $r(\text{CO}_2)$ and $r(\text{CO})$, respectively. A typical example of the $r(\text{H}_2)$, $r(\text{CO}_2)$ and $r(\text{CO})$ profiles recorded for a series of three light-on, light-off cycles for the Pt/TiO₂ photocatalyst under standard conditions (100°C, 9.5 mW cm⁻²) are illustrated in figure S1 in the Supplementary Information (SI) file. In this data set example, as in all this work, the calculated average rates determined for $r(\text{H}_2)$, $r(\text{CO}_2)$ and $r(\text{CO})$ had an error of ca. 10%.

Note that recently the early-stage deactivation of Pt/TiO₂ photocatalysts has been reported for reaction (1) carried out in the liquid phase due to the interplay between oxygen vacancies and active Pt sites which was most strikingly apparent at low Pt loadings and high UV irradiances [30]. In contrast, in this gas phase study, no deactivation of any of the M/TiO₂ photocatalysts was observed, nor any physical change, such as metal particle size, after use.

All irradiations were carried out at 100 °C; (1) to ensure that in the reactor, the MeOH and H₂O were in the gas phase, and in particular that water condensation was not an issue, and (2) to be consistent with a previous study which examined in detail the effect of Pt metal loading on the kinetics of the TiO₂ photocatalysed reaction (1) and (2) [26]. In addition, other work, carried out < 100°C by other [18], suggests production of formic acid and formaldehyde production is an issue, which does not appear to be the case at 100 °C, *vide infra*.

3. Results and Discussion

3.1 Photonic efficiencies (δ) of the M/TiO₂ photocatalysts

In an initial set of experiments the rates, r , of H₂, CO₂ and CO by the 0.2 wt% M/TiO₂ photocatalysts of reaction (1) and (2) were determined and the results are illustrated in figure 3. As observed by others [14, 17, 31], a small amount of H₂ is generated by TiO₂ alone, but the concomitant levels of CO₂ and/or CO production were too small to measure. This low level production of hydrogen was accompanied by the TiO₂ photocatalyst turning a light blue colour, indicating the presence of Ti(III) [32, 33], although this didn't appear to impede the very low production of H₂. The original brilliant white colouration of the irradiated P25 TiO₂ could be subsequently restored by exposing the slightly blue used TiO₂ photocatalyst to air, as has been observed by others [32, 33] and is consistent with the known reactivity of Ti(III) with O₂. Given the key role played by the photodeposited metal in the evolution of H₂ in this system, and in most mechanistic interpretations of the photocatalysed version of reaction (1) and (2), it remains unclear why any H₂ is photo-generated at all by plain P25 TiO₂, although it is worthwhile noting that its origin is not due to the thermally driven versions of reactions (1) and (2), since no H₂ is generated in the dark.

Figure 3: Average rates of H₂ (no shading), CO₂ (diagonal shading) and CO (vertical shading) production determined for the 0.2 wt% M/TiO₂ photocatalysts, where M is (from left to right): nothing, Pt, Pd, Au and Ag. All rates measured at 100°C under 365 nm irradiation (9.5 mW cm⁻²).

In contrast to the results for plain TiO₂, when a metal is present, the rate of photocatalysed hydrogen production, $r(\text{H}_2)$, is significant, i.e. 13-57 times greater, depending on the metal, compared to that of TiO₂. From the rates of hydrogen evolution the order of the efficacy of the different metals appears to be: Pt > Pd > Au > Ag >> none.

Photonic efficiency values for this system for hydrogen production, $\delta(\frac{1}{2}\text{H}_2)$, were calculated using the following expression:

$$\delta(\frac{1}{2}\text{H}_2) = 200 \cdot r(\text{H}_2) \text{ \{unit: moles h}^{-1}\} / [\text{incident UV intensity, } I, \text{ \{units: moles of photons h}^{-1}\}}] \quad (3)$$

As such, the parameter $\delta(\frac{1}{2}\text{H}_2)$ is effectively a measure of the percentage reacted photogenerated electrons to the number of incident photons and helps highlight the 'current-doubling' feature this system can exhibit, *vide infra*. Thus, values of $r(\text{H}_2)$ for each metal were taken from figure 3, in which the 365 nm UV irradiance was 9.5 mW cm⁻² and the illuminated area was 8.9 cm², so that $I = 9.3 \times 10^{-4}$ moles of photons h⁻¹, and the following values for $\delta(\frac{1}{2}\text{H}_2)$ were calculated for the M/TiO₂ photocatalysts: 128, 96, 74, 28 and 2%, where M = Pt, Pd, Au, Ag and none respectively.

If a simple photoelectrochemical mechanism is assumed, where two photogenerated electrons are responsible for the formation of one H₂ molecule, then the maximum value that $\delta(\frac{1}{2}\text{H}_2)$, could be is 100%, thus the value of 128% calculated for the Pt/TiO₂ photocatalyst raises an obvious concern. However, it should be noted that the values of $r(\text{H}_2)$ from figure 3, use to calculate the values of $\delta(\frac{1}{2}\text{H}_2)$ reported above, comprise a small contribution due to the dark rate, i.e. the thermally driven version of reactions (1) and (2). If the latter contribution is subtracted, then $\delta(\frac{1}{2}\text{H}_2)$ values of: 120, 118, 70, 26 and 2 %, for the M/TiO₂ photocatalysts, where M = Pt, Pd, Au, Ag and none respectively, can be calculated.

The latter results suggest that, for Pt and Pd at least, there is a possibility that the overall generation of H₂ *via* photocatalysed reactions (1) and (2), is not simple, and that some additional route to hydrogen evolution is involved. In fact, the photoelectrochemical oxidation of MeOH is well known to exhibit the feature of apparent super photonic efficiencies (i.e. $\delta(\frac{1}{2}\text{H}_2) > 1$), due to 'current-doubling', although rarely, if at all [34, 35] is the photocurrent actually doubled. Current doubling is usually ascribed to the direct hole oxidation of MeOH producing an α -hydroxyalkyl radical which is a strong reducing agent and able to inject an electron into the conduction band of the TiO₂ and/or the metal catalyst in

photocatalyst powder studies [35]. Obviously, if this latter process was 100% efficient the overall effect would be that one photon would generate two electrons, i.e. 'current doubling', and the process would exhibit a quantum yield of 2 for hydrogen evolution, and not the expected maximum value of 1. Thus, like many studies of the photocatalysed reaction (1) in solution, it follows that in this continuous, gas phase photocatalytic study, the $\delta(\frac{1}{2}\text{H}_2)$ values of: 120 and 118% observed here for the Pt and Pd M/TiO₂ photocatalysts suggest some degree of current doubling. However, as an alternative explanation, it is also possible that the measured higher than unity values for $\delta(\frac{1}{2}\text{H}_2)$ noted above are due to a synergistic effect between the thermo (dark) catalytic activity and the photo-catalytic activity.

Given $\delta(\frac{1}{2}\text{H}_2)$ values of: 120, 118, 70, 26 and 2 %, for the M/TiO₂ photocatalysts, where M = Pt, Pd, Au, Ag and none, respectively, it follows that an important feature of the Pt/TiO₂ gas phase system, for photocatalysing reactions (1) and (2), is its high photon efficiency, i.e. effectively over 100%, since one incident photon appears to generate more than one conductance band electron.

As noted earlier, in the photocatalysed reforming of MeOH, by M/TiO₂, the role of the metal co-catalyst is believed to be 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 [13, 14, 36]. This model provides a simple explanation for the observed efficacy for H₂ production of the different metal co-catalysts deposited on TiO₂, namely: Pt > Pd > Au > Ag >> none, given their work functions (in eV) are: (5.12-5.93), (5.22-5.60), (5.10-5.47) and (4.26-4.74) [37], respectively, and that of TiO₂ is 4.6-4.7 eV for TiO₂ [38], and silver has a high overpotential for hydrogen evolution (i.e. 220 mV) compared to that of the other metals (70 (Pt and Pd) - 90 (Au) mV) [39].

Alternatively, Bowker *et al* [28], in their study of the photocatalysed reforming of MeOH in aqueous solution, report the same trend in activities and suggest that it is related to the ease of reducing the corresponding oxide that will reside initially on the surface of the metal. Although both rationales may be valid and apply here apply here, each assumes that the average metal particle size is the same, when in practice it is not, as illustrated by the

TEMs in figure 2 and so the latter's influence on rate cannot be discounted nor easily assessed.

A brief inspection of reactions (1) and (2) suggests that, in this work, if these two reactions were the only photocatalytic processes responsible for the *observed* overall rate of H₂ evolution, $r(\text{H}_2)$, then for each of the metals, the latter should be equal to the *calculated* rate of H₂ evolution, $r(\text{H}_2)_{\text{calc}}$, i.e.

$$r(\text{H}_2)_{\text{calc}} = 3.r(\text{CO}_2) + 2.r(\text{CO}) \quad (4)$$

where $r(\text{CO}_2)$ and $r(\text{CO})$ are the rates of concomitant CO₂ and CO production. This assumption appears to be confirmed by a plot of rate of H₂ evolution, *calculated* using the data in figure 3 and eqn (4), i.e. $r(\text{H}_2)_{\text{calc}}$, vs. the *observed* rate of photocatalytic H₂ production, $r(\text{H}_2)$, illustrated in figure 4, which gives a reasonable fit to the illustrated straight broken line with unity gradient. The one notable exception appears to be Pd/TiO₂ and this may be due in part to the much greater heat of adsorption of CO on Pd, compared to the other metals, including Pt, where for example $\Delta H_{\text{ads}}(\text{CO})$ on the 110 plane is 167 kJ mol⁻¹ for Pd and only 134 kJ mol⁻¹ for Pt and, as a consequence, the CO uptake on M/SiO₂ is 85 μmol g⁻¹ for Pd, but only 23 μmol g⁻¹ for Pt [40]. This strong adsorption may result in a lower than expected level of CO in the gas phase and thus a lower value for $r(\text{CO})$ and so, *via* eqn (4), a lower than expected value for $r(\text{H}_2)_{\text{calc}}$. In addition, as we shall see, it appears likely that this strong adsorption is responsible for the significant observed difference in selectivity between the photocatalytic reactions (1) and (2) when Pd is used, *vide infra*.

Figure 4: Plot of $r(\text{H}_2)_{\text{calc}}$, calculated using eqn (4) and the data in figure 3, vs. the observed rate of H_2 photocatalytic generation, $r(\text{H}_2)$. All rates measured at 100°C under 365 nm irradiation (9.5 mW cm^{-2}).

An alternative explanation for the deviation from eqn (4) exhibited by Pd, illustrated in figure 4, is the generation of intermediate species, most notably formaldehyde (HCHO) and formic acid (HCOOH), as observed by others in a study of reaction (1) at a much lower temperature, 55°C [18]. However, the analytical system used here, i.e. GC with FID and methaniser, although very able to measure very low levels of HCHO and HCOOH [41], was unable to detect the presence of either species in all this work. This doesn't mean that such species were not generated and indeed, an earlier study involving a DRIFTS study of the Pt/TiO_2 photocatalyst in the gas phase reforming of MeOH revealed the presence of surface-bound formate [23]. Rather it suggests that the high temperature, irradiance and long residence time (39.6 s) associated with this study aid in their effective photocatalytic breakdown to CO_2 and H_2 .

3.2 Selectivities (S) of the M/TiO_2 photocatalysts

In one set of experiments the rates, r , of H_2 , CO_2 and CO by the $0.2 \text{ wt\% } M/\text{TiO}_2$ photocatalysts of reaction (1) and (2) were determined as a function of irradiance, I . Figure 5 illustrates the observed variation in $r(\text{H}_2)$ vs I , for the different metals. For each metal, the data arising from this work was used to plot $r(\text{H}_2)_{\text{calc}}$ vs. $r(\text{H}_2)$ and each yielded a good straight line with unity gradient, except Pd, which, although a good straight line, had a gradient < 1 .

These results suggest that, for each metal, the H_2 derives primarily from reactions (1) and (2), which prompts the question: how does the selectivity for the steam reforming of MeOH, i.e. reaction (1), vary with M? Here, selectivity, S , refers to the rate of reaction (1) over the overall rate of removal of MeOH, and is defined by the expression:

$$S = r(CO_2) / \{r(CO_2) + r(CO)\} \quad (5)$$

Figure 5: Plots of $r(H_2)$ vs irradiance, I , for the 0.2 wt% M/TiO₂ photocatalysts, where M is (from top to bottom): Pt, Pd, Au and Ag. Note: for each metal this work also generated $r(CO_2)$ and $r(CO)$ values associated with each $r(H_2)$ value, i.e. a ' $r(CO_2)$, $r(CO)$ and $r(H_2)$ ' data set, for each irradiance. All rates measured at 100°C under 365 nm irradiation.

The data sets of $r(CO_2)$, $r(CO)$ and $r(H_2)$ as a function of UV irradiance, I , generated in this study for each metal enabled plots of $r(CO_2)$ and $r(CO)$ vs. $r(H_2)$ to be constructed for each metal, three of which are illustrated in figure 6(a), (b) and (c), for Pt, Au and Pd respectively. From the red data points illustrated in figure 6(a) for Pt/TiO₂ it is clear that the thermal (dark) reaction favours CO production, i.e. reaction (2), over that of CO₂, i.e. reaction (1), with a calculated value for S of 0.21. However, as the rate of the photocatalytic process is increased, by irradiating the Pt/TiO₂ and with increasing irradiance, reaction (1) increasingly dominates reaction (2). The approximate invariance of $r(CO)$ with I illustrated in figure 6(a), suggests that when the co-catalyst is Pt, CO is only generated by the thermal (dark)

decomposition of MeOH, i.e. reaction (2) and that photocatalysis using Pt/TiO₂, *selectively* drives reaction (1), i.e. $S = 1$ for the purely photocatalytic process with Pt/TiO₂.

In contrast to the above, from the red data points illustrated in figure 6(b), for Pd/TiO₂ it appears that the thermal (dark) reaction favours *neither* reactions (1) or (2) and that this situation prevails when the process is driven photocatalytically, at all irradiance values, i.e. at all $r(\text{H}_2)$ values *observed* in this work. When Au (or Ag) is used as the co-catalyst an intermediate behaviour is exhibited in which both $r(\text{CO}_2)$ and $r(\text{CO})$ increase linearly with increasing I and therefore $r(\text{H}_2)$, as illustrated in figure 6(c), with $r(\text{CO}_2)$ always $\gg r(\text{CO})$.

Figure 6: Plots of $r(\text{CO}_2)$ (filled circles) and $r(\text{CO})$ (open circles) vs. overall rate, $r(\text{H}_2)$, constructed from the data sets referred to in figure 5, for 0.2 wt% M/TiO₂, where M is (a) Pt, (b) Pd and (c) Au, respectively. In each figure the red points are those recorded in the absence of light, i.e. the dark (thermal) rates. All photocatalytic rates measured at 100°C under 365 nm irradiation and the variation in $r(\text{H}_2)$, was achieved by varying the irradiance from 0 – 9.5 mW cm⁻² (as illustrated in figure 5).

The rate data illustrated in figure 6 shows that for all the metals tested the rates of CO₂ and CO generation can be expressed as a linear function of the overall rate of H₂ production, $r(H_2)$, i.e. $r(CO_2) = \alpha \cdot \Delta r(H_2) + c(CO_2)$ and $r(CO) = \beta \cdot \Delta r(H_2) + c(CO)$, where: $\Delta r(H_2) = r(H_2) - r(H_2)_{\text{dark}}$ (i.e. the latter being the measured rate of H₂ evolution in the dark) and where $c(CO_2)$ and $c(CO)$ are the dark (thermal) rates of CO₂ and CO generation. It follows that the variation in selectivity, S , can be described as follows:

$$S = \{\alpha \cdot \Delta r(H_2) + c(CO_2)\} / \{(\alpha + \beta) \cdot \Delta r(H_2) + c(CO_2) + c(CO)\} \quad (6)$$

The values of α , β , $r(H_2)_{\text{dark}}$, $c(CO)$ and $c(CO_2)$ derived for each of the metals from the lines of best fit to the $r(CO_2)$ and $r(CO)$ vs $r(H_2)$ data sets illustrated in figure 6 are listed in Table S1 in the Supplementary Information file. These values coupled with eqn (6) allowed the variation of the selectivity, S , for each metal to be calculated as a function of $r(H_2)$, the results of which are illustrated in figure 7.

In the case of the Pt/TiO₂, given $\beta = 0$, since $r(CO)$ is independent of $r(H_2)$, i.e. irradiance, so that $S = \{\alpha \cdot \Delta r(H_2) + c(CO_2)\} / \{\alpha \cdot \Delta r(H_2) + c(CO_2) + c(CO)\}$ it follows from eqn (6) that S will increase with increasing $r(H_2)$ and tend to 1 at high $r(H_2)$, when $\alpha \cdot \Delta r(H_2) \gg \{c(CO_2) + c(CO)\}$. Increasing $r(H_2)$ in this system may appear fairly simple to achieve, given that in all this work, $r(H_2)$ is increased by increasing the incident irradiance, ρ . However, in most photocatalytic processes, the rate is found to depend upon ρ^θ , where $\theta = 1$ at low ρ , when the probability of photogenerated electron-hole recombination is low, but $\theta = 0.5$ at high ρ , where recombination dominates. A review describing many of the mechanisms used to provide more detailed explanations for this dependence has been reported recently [42].

Given all of the above, it is not surprising to note, therefore, that in practice for most photocatalytic systems, including the ones reported here, the rate is found to depend upon ρ^θ , where $\theta = 0.7-0.8$, and to exhibit a $r(H_2)$ vs ρ profiles similar to those illustrated in figure 5 for the M/TiO₂ photocatalysts. Thus, the solid line of best fit to the rate vs ρ data for Pt/TiO₂ illustrated in figure 5, was generated using a value for $\theta = 0.73$, which suggests a high, but not impossible UV irradiance of 43.5 mW cm⁻², would treble the rate observed at 9.5 mW cm⁻² (ca. 60 x10⁻⁵ mol h⁻¹, see figure 5) and, assuming the selectivity is described by

eqn (6), increase the selectivity from the measured value of 79.1 %, illustrated by the highest point in figure 7, to 91.6 %.

In the case of Pd/TiO₂, and in striking contrast to Pt/TiO₂, $\alpha = \beta$ and $c(\text{CO}_2) = c(\text{CO})$ (see Table S1), and so, according to eqn(6), S remains invariant with $r(\text{H}_2)$ in the absence and presence of UV irradiation, and has an approximate value of 0.5, i.e. this photocatalyst exhibits little or no selectivity with regard reactions (1) and (2).

Figure 7: Plot of S , calculated using eqn (6) and the lines of best fit to the data sets illustrated in figure 6, as a function of overall rate, $r(\text{H}_2)$ for 0.2 wt% M/TiO₂ photocatalysts, where M is: Pt (black broken line), Pd (blue broken line), Au (pink broken line) and Ag (orange broken line). The start of each line identifies the S dark (thermal) values.

Finally, and as noted previously, the trends in $r(\text{CO}_2)$ and $r(\text{CO})$ vs. $r(\text{H}_2)$ for Au/TiO₂, illustrated in figure 6, are similar to those for Ag/TiO₂, with $c(\text{CO}) \approx c(\text{CO}_2)$ and both quite small (i.e. $< 1 \times 10^{-5} \text{ mol h}^{-1}$). As a consequence, the calculated S vs $r(\text{H}_2)$ profiles for both these photocatalysts, illustrated in figure 7, are very similar in that they both increase markedly upon irradiance, but, in contrast to Pt, quickly reach a maximum value of ca. 0.75 -

0.85 which cannot be improved much upon with increasing irradiance, i.e. they do not tend to a value of unity (see Table S1 for values of α and β for Au and Ag). This feature follows from eqn (6), since at high irradiance, when $(\alpha+\beta).r(H_2) \gg c(CO)$ or $c(CO_2)$, then S in eqn (6) reduces to $= \alpha/(\alpha+\beta)$, i.e. a fixed value $<$ unity. Both Au/TiO₂ and Ag/TiO₂ photocatalysts will attain this limiting selectivity level (of ca. 0.75 for Au and 0.85 for Ag) at much lower irradiances than the Pt/TiO₂ photocatalyst because the condition $(\alpha+\beta).r(H_2) \gg \{c(CO) + c(CO_2)\}$ is less exacting than the condition $\alpha.r(H_2) \gg \{c(CO) + c(CO_2)\}$, since the parameters $c(CO_2)$ and $c(CO)$ are much smaller ($< 1 \times 10^{-5} \text{ mol h}^{-1}$), for Au (and Ag), than for Pt (ca. $3.9 \times 10^{-5} \text{ mol h}^{-1}$).

The trends in selectivity illustrated in figure 7 arise from a combination of a number of factors, such as: (i) the dark (thermal) activity of the metal deposits to catalyse reactions (1) and/or (2), a measure of which is $r(H_2)_{\text{dark}}$, see table S1, (ii) the adsorption of H₂ and, most importantly CO, on the metal deposits, (iii) the work functions and overpotentials for H₂ evolution of the metals, and (iv) almost certainly a photocatalytic and thermal rate dependence upon particle size. The Pt/TiO₂ photocatalyst is the most selective as it appears to only promote the photocatalysis of reaction (1), with reaction (2) appearing to be mainly a dark, and not insignificant, reaction. In contrast the Pd/TiO₂ photocatalyst appears to photocatalyse both reactions (1) and (2) equally well, for reasons which are unclear although its strong tendency to adsorb CO noted earlier is likely to play a role. Finally, the Au/TiO₂ and Ag/TiO₂ photocatalysts appear to exhibit an intermediate behaviour, photocatalysing reaction (1) more so than (2) and exhibiting a low dark activity (see Table S1), which allows a maximum, non-unity, selectivity value to be achieved at relatively low irradiance values compared to the Pt/TiO₂ photocatalyst.

Conclusions

A number of different M/TiO₂ photocatalysts, where M = Pt, Pd, Au and Ag, were used to drive the steam reforming of MeOH in a gas phase *continuous* flow reactor operated at 100 °C. The Pt/TiO₂ photocatalyst is the most active, with a photonic efficiency of 120% that suggests some of the hydrogen derives from a current-doubling reaction mechanism. In terms of rate of H₂ production, the order of photocatalytic activity is: Pt > Pd > Au > Ag $\gg$ no metal. In addition to its high efficiency, the Pt/TiO₂ photocatalyst differs markedly from the

other photocatalysts in that it appears to drive exclusively the steam reforming of MeOH, which generates H_2 and CO_2 , rather than the decomposition of MeOH, which generates H_2 and CO; although in the dark, the latter process dominates with a ca. 79% efficiency. In striking contrast to Pt, the Pd/TiO₂ photocatalyst appears to favour equally the MeOH steam reforming and decomposition reactions. The Au and Ag photocatalysts are less active than either the Pt or Pd co-catalysts and exhibit a very similar variation in selectivity with increasing UV irradiance which is intermediate between that of Pt and Pd. If, in the future, MeOH is to be generated as a potential source of hydrogen, then photocatalysis using Pt/TiO₂, carried out at a high UVA irradiance in a *continuous* flow gas reactor should be considered as a possible method, since it is very efficient and generates no CO in the photocatalytic process, although some is generated thermally. Further work is in progress to see if the latter can be further reduced by operating the reactor at a lower temperature than used in this work, i.e. < 100 °C, since the absence of CO is highly desirable, not least if the H_2 generated is eventually to be used in a fuel cell. However, at these lower temperatures, water condensation and more the stabilisation of intermediates such as formic acid and formaldehyde may prove an issue as has been found by others [17].

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