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Catalytic and Photocatalytic water gas shift reaction (WGSR) using a continuous flow, gas phase reactor.

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Abstract

A series of different M/TiO₂ catalysts are prepared, where M = Au, Pt, Pd and Ag, with a 0.2 wt% loading, and tested for activity as catalysts and photocatalysts for the water gas shift reaction, WGSR, using a continuous flow, gas phase reactor. For both the thermal (dark) and photocatalytic (UV irradiated) WGSR the best catalyst/photocatalyst is Au/TiO₂. The kinetics of the WGSR is studied as a function of reactor temperature, Au loading and concentrations of CO and H₂O. Langmuir-Hinshelwood kinetics are observed for the photocatalytic WGSR with non-competitive adsorption of the CO and H₂O, whereas those for the thermal WGSR fit a slightly more complex, previously reported, reaction mechanism. At 125 °C, with a 0.2 wt% loading, the Au/TiO₂ photocatalysis of the WGSR is very efficient, with a formal quantum efficiency for 1/2H₂ production of 57%. The potential scale up of the relatively efficient photocatalytic WGSR is discussed briefly.

Key words: water gas shift; carbon monoxide; catalysis; photocatalysis; titanium dioxide; gold.

1. Introduction

Hydrogen is a much needed chemical feedstock, especially for ammonia production, which is an essential component in the industrial manufacture of fertilizers [1]. In addition, hydrogen is emerging as an important potential fuel for the future, in which a hydrogen economy is established, i.e. one in which hydrogen, rather than hydrocarbons, is used to provide power for transport and homes [2, 3]. Much of the world's hydrogen is produced *via* steam reforming of natural gas [3], with additional hydrogen being generated from the reaction of water and CO, i.e. the water-gas shift reaction (WGSR), [4]:

Almost all ammonia and oil refinery hydrogen plants have a low temperature stage (150-250 °C) for driving the above reaction, usually using a Cu/ZnO catalyst [5]. Noble metals can also be used as catalysts for reaction (1), although Pt is rather low in activity, due to the formation of a passivating surface layer of oxide, at these low temperatures. In contrast, and perhaps not surprisingly, under these same conditions, Au is the most active of the noble metals, and much more active than the traditional Cu/ZnO catalyst noted above, especially when deposited on a TiO₂ support [6]. Although a Au/TiO₂ catalyst for reaction (1) deactivates over time, its activity can be readily restored by flowing air over the catalyst at elevated temperatures [6].

Semiconductor photocatalysis can be used to effect a wide range of different reactions at low temperatures, with TiO₂ being the semiconductor of choice, as it is abundant, inexpensive and photocatalytically very active [7]. One such reaction is the WGSR, although a metal co-catalyst also needs to be present, i.e. M/TiO₂, where M is usually a noble metal [8-13], i.e.

In the 1980's, work carried out by the various research groups [8-13] on the photocatalytic WGSR, i.e. reaction (2), focussed on using M/TiO₂, where M = Pt or Pd, usually using a batch reactor with a circulating gas phase and run at low temperatures, i.e. between 30-60°C [8-13]. As reported by Sato *et al.* [12] in their study of the photocatalytic WGSR, i.e. reaction (2), no hydrogen is produced with just TiO₂ thereby highlighting the importance of the metal co-catalyst.

Sato and his co-workers have proposed a simple, commonly used, flux-matching model as the basis of the reaction mechanism for the photocatalysed WGSR by their M/TiO₂ photocatalysts, in which an electron-hole pair is formed upon *ultra*-bandgap irradiation [12], i.e.

and the photogenerated electrons are drawn to the metal co-catalyst, which mediates the reduction of H₂O to H₂:

while the photogenerated holes oxidise the CO to CO₂ on the TiO₂ substrate:

Since the 1980's there have been few reports on the photocatalytic WGSR [14] that is until Bowker *et al.* [15] in 2002, studied the activity of Pd/TiO₂ and found the reaction rate peaked at a 0.5 wt% loading and was zero at 2 wt%. The most recent study of the photocatalysed WGSR, i.e. reaction (2), is that of Sastre *et al.* [16], carried out using a batch reactor at room temperature, which showed that an Au/TiO₂ photocatalyst was much more active than Pd/TiO₂ [17].

Table 1 summarises the major features of most of the published reports on the WGSR photocatalysed by M/TiO₂ photocatalysts [8-13, 15, 16], a brief inspection of which reveals no studies of the reaction in a continuous gas flow system, nor at a temperature > 60°C. A continuous gas flow system is more industrially relevant since, for the majority of applications, it usually saves time and energy, and so cost [18], especially as flow systems are more easily scaled up for industrial production than batch systems [19]. To date, little attempt has been made to optimise the performance, or probe the kinetics, of the M/TiO₂ photocatalysed WGSR and this lack of detail is addressed here in a study of reaction (2) using a continuous flow system, where M = the noble metals: Pt, Pd, Au and Ag. In particular, the kinetics exhibited by the best of the photocatalysts tested (i.e. Au/TiO₂) is studied as a function of the key reaction parameters: temperature, metal loading, CO and H₂O concentration.

Table 1: Brief details of previous studies of the WGSR photocatalysed by M/TiO₂

Metal/TiO ₂	Wt.%	TiO ₂	Deposition	Temp (°C)	Reactor	Light Source	* δ (%)	Ref
None, Pt	2	Anatase	Photolysis	0 - 60	0.25 g of catalyst used in a gas phase reactor.	200 W Hg lamp (275 nm, 380 nm and 415 nm cut-off filters used in a wavelength dependence study).	7	[13, 14]
Pt	2 and 10	Anatase	Photodeposition and impregnation	27	0.2 g of catalyst used while water vapour and CO were circulated	200 W Hg lamp (0.21 W cm ⁻² at 100%)	<5	[11]
Pt	1.5	Anatase	Photodeposition	30 - 60	0.2 g of catalysts used in the gas phase and 0.1 g of catalyst used in the liquid phase. Gas phase; recirculation glass device. Liquid phase; agitated suspension.	400 W high pressure Hg lamp.	-	[12]
Pt	1 and 5	TiO ₂ , Anatase and P25	photodeposition	60	0.2 g in a circulating gas phase chamber	200 W Hg lamp (10 mW cm ⁻²)	-	[9, 10]
Pd	0.01, 0.1, 0.5, 1 and 2	P25	Incipient wetness.	35	0.2 g of catalyst and 100 mL deionised water with various amounts of CO injected into the headspace.	400 W Xe arc lamp (Pyrex vessel cut off wavelengths below 300 nm).	-	[16]
Pt, Pd, Cu, Au, Ag	1	P25	Deposition/precipitation and impregnation	42	Pelletized catalyst 1 x 1.5 cm ² covered the surface of the gas phase reactor containing moist saturated N ₂ and CO.	Solar light irradiation using an Oriel solar simulator (1 kW cm ⁻²) with an AM1.5 filter. Visible light irradiation carried out using a 450 nm LED lamp.	-	[17]

* δ = formal quantum efficiency for 1/2H₂ production

2. Experimental

2.1. Materials declaration.

Unless otherwise stated, 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, where M = Au, Pt, Pd, and Ag, were prepared using the incipient wetness method [20-24]. Thus, for a typical photocatalyst Au/TiO₂ (0.2 wt %), 40 mg of the metal salt (HAuCl₄·3H₂O) were dissolved in 80 cm³ of water and the resulting solution added dropwise to 10 g of the P25 TiO₂ powder. This aqueous dispersion was agitated continuously to produce a slurry which was left to dry overnight in an oven at 110 °C. The residual powder was then ground using a pestle and mortar and calcined at 500 °C for 2 h before being sieved to an aggregated particle size between 250 – 400 µm. The Au salt coating the TiO₂ powder particles was then reduced to the metal in a stream of hydrogen (50 cm³ min⁻¹) in a tubular furnace at 200 °C for 2 h thereby yielding a 0.2 wt% Au/TiO₂ photocatalyst. This method was also used to produce other 0.2 wt% M/TiO₂ photocatalysts using the metal salts: H₂PtCl₆·6H₂O, PdCl₂ and AgNO₃. For the Au/TiO₂ photocatalyst, various metal loadings of Au/TiO₂ (0.01, 0.1, 0.2, 0.5, and 1 wt%) were produced by altering the amount of metal salt used (i.e. 2, 20, 40, 101, and 202 mg, respectively).

2.3. Photocatalyst characterisation.

The weight loading of each photocatalyst was 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 crystalline structure of the TiO₂ and (ii) Brunauer-Emmett-Teller, BET, (Micrometrics, Tristar 3020) for surface area assessment. From these studies, the TiO₂ appeared to be an 80:20 mix of anatase and rutile with a specific area of ca. 50 m² g⁻¹, both before and after metal deposition and annealing. Additionally, the samples were analysed using a Transmission Electron Microscopy, TEM, (Jeol, JEM-1400), which revealed an average TiO₂ particle radius for the P25 powder of ca. 15 nm. The Au particle radii for a 0.2 wt%, and 1 wt%, Au/TiO₂ photocatalyst were estimated to be 2.0, and 4 nm, respectively, from many TEM images, such as illustrated in Fig. 1 below.

Fig. 1: Typical TEM micrographs of P25, 0.2 wt% Au/TiO₂ and 1 wt% Au/TiO₂ where the average Au particle sizes (radius) is revealed to be, N/A, 2.0 and 4 nm respectively. Note: The average Au particle size was measured from various particles identified using many TEM micrographs.

Other TEM studies on the 0.2 wt% M/TiO₂ photocatalysts, where M = Pt, Pd and Ag, showed metal particle radii of: 0.5, 3 and 1.5 nm, respectively [24].

As illustrated in Fig. 2(a), digital photographic images were recorded for the Au/TiO₂ photocatalysts and show a transition from light violet to a deep dark blue as the metal loading was increased from 0.01 wt% to 1 wt%. Fig 2(b) shows digital photographic images of Pt, Pd and Ag 0.2 wt% M/TiO₂ photocatalysts which were dark grey, light grey and dark red/brown, respectively.

Fig. 2: (a) Digital images of various Au/TiO₂ photocatalysts with 0 to 1 Wt% Au loading (from left to right; 0, 0.01, 0.1, 0.2, 0.5, and 1 wt%) and (b) Digital images for 0.2 wt% Pt, Pd and Ag/TiO₂ photocatalysts (from left to right).

2.4. Thermal and photocatalytic activity testing in the gas phase.

The kinetics of reactions (1) or (2), catalysed or photocatalysed, respectively, by various M/TiO₂ powders (M = Au, Pd, Pt and Ag), were studied using a continuous flow, gas phase photoreactor system, the details of which have been described elsewhere [18, 23, 24] and an illustration of which is given in the labelled schematic in Fig. S1, in the electronic supplementary information, i.e. ESI, section. In a typical run, 2.4 g of the photocatalyst powder under test were placed into a serpentine 'S-bend' borosilicate glass reactor with internal and external diameters of 3.75 mm and 6 mm, respectively, see Figs. S1 and S2 in the ESI. The catalyst was held in place using two plugs of glass wool at the top and bottom of the serpentine, and the reactor was inserted into the main body of the heated flow reactor. UV irradiation of the serpentine glass reactor was carried out by using a 10 W, 365 nm narrow-band UVA LED (RS Components, LZ1-10UV00) with an irradiance of 9.5 mW cm⁻². Typically, the reaction was run at ca. 125 °C, unless stated otherwise with the reactor temperature set and controlled by a semi-cylindrical ceramic fibre heater.

In a typical run, a stream of Ar, containing: H₂O vapour (10% by volume) and CO (10% by volume), was passed over the catalyst/photocatalyst for 4 h, at a flow rate of 10 cm³ min⁻¹. The initial 1.25 h of a run was carried out in the dark, during which the M/TiO₂ powder under test was assessed as a thermal catalyst of reaction (1), after that the glass reactor was UV irradiated for 1.5 h, thereby testing the M/TiO₂ powder as a photocatalyst of reaction (2), and then, finally, the system was returned to the dark for the final 1.25 h of the run, in order to demonstrate that the photocatalytic response was reversible and that the observed thermal catalytic activity was restorable. The % (v/v) levels of H₂ and CO in the gas stream, [H₂] and [CO], respectively, were determined using gas chromatography, with the gas stream sampled every 0.5 h during the 4 h period of a typical reaction run. The gas chromatograph used was a Perkin Elmer, Clarus Arnel 580 GC fitted with a Porapak D column with a TCD, for analysis of H₂ and an FID-methaniser for the analysis of CO₂. The values of [H₂] and [CO₂] (units: %) measured by GC at any time, *t*, during a run were converted to values for the rate of the WGSR, i.e. *r*(H₂) and the *r*(CO₂), respectively (units: mol h⁻¹) using the following expression:

$$r(\text{H}_2 \text{ or CO}_2) = [\text{H}_2] \text{ (or } [\text{CO}_2]) \cdot f \cdot P / 100RT \quad (6)$$

where, T is the sampled gas temperature (typically 292.5 K) and f is the gas flow rate (typically, $10 \text{ cm}^3 \text{ min}^{-1}$, i.e. $60 \times 10^{-5} \text{ m}^3 \text{ h}^{-1}$). Eqn (6) was used throughout this work to convert the $[\text{H}_2]$ and $[\text{CO}]$ values to $r(\text{H}_2)$ and $r(\text{CO})$ values. A typical resulting plot of $r(\text{H}_2)$ and the $r(\text{CO}_2)$, versus reaction time is illustrated in Fig. 3, and further details as to how this was constructed from the original measured $\% \text{H}_2$ and $\% \text{CO}_2$ values are given in section S3 of the ESI.

A typical example of the observed variation in rate for a 0.2 wt% Au/TiO₂ catalyst/photocatalyst with time profile run at 125 °C, before, during and after UV irradiation, is illustrated in Fig. 3. These results show that, when using a 0.2 wt% Au/TiO₂ catalyst/photocatalyst, both reaction (1) (the dark, thermal catalytic WGSR) and reaction (2) (the UV driven photocatalytic WGSR) produce equal amounts of H₂ and CO₂, as expected. This feature was exhibited by all the catalysts/photocatalysts tested in this work and indicates the major reactions that take place on the M/TiO₂ catalysts/photocatalysts are well described by reactions (1) and/or (2), in the absence and presence of UV illumination, respectively.

Fig. 3: A typical example of light off, light on, light off cycle, carried out at 125°C using a 0.2 wt% Au/TiO₂ catalyst. Here the production of H₂ (white circles) and CO₂ (black circles) with the average $r(\text{H}_2)$ reported for dark and UV conditions, 5.2 and 25.6 ($10^{-5} \text{ mol h}^{-1}$) respectively, are highlighted by broken horizontal lines.

3. Results and discussion

3.1. Au and other metals as M

In an initial study of the thermal reaction (1), and photocatalytic reaction (2), i.e. the two versions of the WGS mediated by M/TiO₂ and studied here, a series of different metals were tested, namely with M = Au, Pt, Pd and Ag, and a loading of 0.2 wt% and a reactor temperature of 125 °C. The results of the study of the variation in the rates of reactions (1) and (2) as a function of metal co-catalyst, M, are illustrated in Fig. 4, in the form of a histogram plot of $r(\text{H}_2)$ vs metal co-catalyst, and reveals that the photocatalytic reaction rate was always much greater (typically 6x's) that of the thermal (i.e. dark) reaction, regardless of the metal, and no thermal or photocatalytic reaction takes place in the absence of M.

Fig. 4: Histogram plot of $r(\text{H}_2)$ vs metal type recorded using a series of different M/TiO₂, 0.2 wt% loading, in the WGS reactor at 125 °C, with UV light off (grey shaded boxes) and on, 365 nm, 9.5 mW cm⁻² (unshaded boxes).

The results illustrated in Fig. 4 show that the trends in activities for the thermal and the photocatalytic WGS reactions as a function of the metal deposited are very similar, if not the same, with Au and Ag the most and least active, respectively, and Pt and Pd similar and of an intermediate activity. This is perhaps not too surprising given the similarities in reaction mechanism for the two processes, reactions (1) and (2). Thus, the reaction mechanism for the photocatalytic WGS, reaction (2), involves adsorbed OH radical formation (via $\text{h}^+ + \text{H}_2\text{O}_{\text{ads}}$

—→ OH_{ads} + H⁺) and the subsequent reaction of OH_{ads} with CO_{ads} to form CO₂, as summarised by reaction (5). Hydrogen formation occurs on the metal *via* the initial formation of adsorbed H radicals (e⁻ + H⁺ —→ H_{ads}) which then combine to form H₂, as summarised by reaction (4). Similar features are present in the reported mechanism for the thermal (dark) WGSR, i.e. reaction (1), which is summarised below [25], i.e.

with reaction (7) occurring on the oxide (at O vacancies), CO adsorption on nearby gold particles and all other steps at the oxide-metal interface [25].

It follows that in both mechanisms, the rate of reaction will depend upon a number of different features of the metal, such as work function, CO heat of adsorption, M-H bond strength, as well as the radius of the metal particles. The values of these different parameters for the metals used here are listed in Table S1 in section S4, in the ESI and only the M-H bond strength appears to show any clear correlation with observed rate, as illustrated by Fig. S5 in section S4. However, little can be taken from this apparent correlation given the concomitant significant variation in all the other parameters, in particular metal particle radius, which will have a significant impact on rate.

Finally, given our knowledge of: the value of $r(\text{H}_2)$ (units: moles of H₂ h⁻¹) for reaction (2) for each M/TiO₂ photocatalyst, the irradiance (9.5 mW cm⁻², 365 nm), the irradiation area (of the serpentine reactor, $A = 8.9 \text{ cm}^2$), then the formal quantum efficiency for each of the M/TiO₂ photocatalysts for the generation of ½H₂, i.e. δ , can be calculated, using the following expression,

$$\delta = 2xr(\text{H}_2) \times N_A / (9.5 \times 1.84 \times 10^{15} \times A \times 3600) \quad (10)$$

given 1 mW cm⁻² of 365 nm radiation $\equiv 1.84 \times 10^{15}$ photons cm⁻² s⁻¹ and N_A = Avogadro's constant. Using the rate data contained in Fig. 4 and eqn (10) the following values of δ were calculated for the M/TiO₂ photocatalysed WGSR, of 0.57, 0.35, 0.32 and 0.17, where M = Au, Pt, Pd and Ag, respectively. These values reveal that the WGSR photocatalysed by Au/TiO₂ in particular is a very efficient process (57%) which is ca. 10 times greater than that reported

previously [11,13,14], although in the latter work $M = \text{Pt}$ and the reaction was conducted at a much lower temperature, see Table 1. The rate data reported by Sastre *et al* [16] in their study of the same system but carried out in a batch reactor at room temperature, when treated in the same way, reveals δ values of 0.36, 0.14, 0.14 and 0.06 for $M = \text{Au}$, Pt , Pd and Ag , respectively. In both cases it seems likely a component (ca. 20% in the case of the Au/TiO_2 photocatalyst/catalyst used here; see Fig. 4) of the overall measured rate of H_2 generation used in the above calculation is due to thermal catalysis, i.e. reaction (1), but, even if this is taken into account, the formal quantum efficiency for the Au/TiO_2 photocatalyst is still very high ($\delta = \text{ca. } 0.46$ here).

3.2. Temperature

The rates of reaction, $r(\text{H}_2)$, were determined for the thermal and photocatalytic versions of the WGSR using the Au/TiO_2 powder over the temperature range 75- 175 °C and the results of this work are illustrated in Fig. 5.

Fig. 5: Plot of $r(\text{H}_2)$ vs temperature for the WGSR thermal (dark) catalysed reaction (open circles) and the photocatalysed reaction (closed circles) by Au/TiO_2 . The broken lines represent kinetic model best fits to the data, see Table S2 in S5 in the ESI for fitting constants.

A simple reaction mechanism can be used to interpret these results, in which it is assumed that unoccupied, un-excited reaction sites, S , can mediate reaction (1), *via*

where, k_D is the dark (thermal) rate constant, whereas the electronically excited unoccupied sites, S^* , can mediate reaction (2), *via*

where, k_1 and k_{-1} are the rate constants for the electronic excitation of S (to S^*) and the thermal back reaction, respectively, and k_{UV} is the rate constant for the subsequent reaction of S^* with the reactants. If θ is taken as the fraction of S^* sites, which obviously will have a very small value, then the individual rates of the thermal and photocatalytic reactions are $r_D = k_D(1-\theta)$ and $r_{UV} = k_{UV}\theta$, respectively, where,

$$\theta = 1/(1 + k_b + k_{UV}') \quad (13)$$

and $k_b = k_{-1}/k_1$ and $k_{UV}' = k_{UV}/k_1$; see section S5 in the ESI, for the derivation of eqn (13). In the absence of UV irradiation, the rate of H_2 evolution, *i.e.* r_D , will be equal to k_D , since $\theta = 0$. The measured variation of k_D as a function of temperature is illustrated in Fig. 5, and an Arrhenius best line fit to the data, represented by the broken line, reveals values of: 74 kJ mol^{-1} and $3.0 \times 10^5 \text{ mol h}^{-1}$ for the activation energy (E_a) and the pre-Arrhenius factor (A), respectively. For the same system, but under UV irradiation, the overall (*i.e.* Total) rate of H_2 evolution, r_T , is given by the expression:

$$r_T = r_D + r_{UV} \quad (14)$$

where $r_D = k_D(1-\theta)$, $r_{UV} = k_{UV}\theta$, and θ is defined by eqn (13). If it is assumed that the temperature sensitivities of the rate constants k_b , k_{UV}' and k_{UV} are, like k_D , also described by the Arrhenius equation, then it is possible to produce the excellent (solid line) fit to the measured variation of r_T vs T , as illustrated in Fig. 5, using optimised fit values of E_a and A for k_b , k_{UV}' and k_{UV} , as well as the calculated values for E_a and A reported above for k_D . Table S2 in the ESI section lists the optimised values of E_a and A used to produce this solid line fit which appear worthy of brief comment. For example, as noted earlier, it seems likely that θ , the fraction of sites that are UV activated will be very small and this appears to be confirmed by the values of θ calculated as a function of temperature, using eqn (13) and the optimised E_a

(and A) values for k_b and k_{UV}' given in Table S2, a plot of which is illustrated in Fig. 6 and reveals a maximum value of θ of ca. 10^{-6} .

Fig. 6: Plot of θ vs T , where the values of θ were calculated using eqn (13) and the optimised E_a (and A) values for in Table S2 (5 parameters).

The values of E_a and A for the various model rate constants, given in Table S2, allow not only the calculation of the variation of r_T as a function of T , illustrated by the solid line in Fig. 5, but also the model predicted variations of the component rates r_{UV} and r_D with temperature, the results of which are illustrated in Fig. 7, and show that a significant decrease in θ above ca. 398 K, illustrated in Fig. 6, produces a marked decrease in r_{UV} , which is not surprising given $r_{UV} = k_{UV} \cdot \theta$. As a consequence, by ca. 448 K there is little difference between the rate for the WGSR using Au/TiO₂ in the dark and that when illuminated with UV, because at and above 448 K the overall rate is dominated by the thermal WGSR.

Fig. 7: Plot of r_T vs T data points and optimised fits for r_T (solid line), r_{UV} (broken dot and dash line) and r_D (dashed line) as a function of T . These optimised fits were calculated using the optimised Arrhenius data for the rate constants k_b , $k_{UV'}$, k_{UV} and k_D , given in Table S2, in the ESI and eqns (13) and (14).

Indeed, the plots of the modelled r_T , r_{UV} and r_D data suggest that at 348K, over 98% of the observed rate for the illuminated Au/TiO₂ system is due to photocatalysis whereas at 448 K it is < 10%. Figure 7 shows that the *peak* of the photocatalytic activity is ca. 398 K, i.e. 125 °C, with the rate decreasing at temperatures below and above this temperature, as illustrated by the broken-dotted line. Consequently, 398 K, i.e. 125 °C, was used as the reactor temperature in the studies of the photocatalysed WGS, i.e. reaction (2), as a function of Au loading and concentrations of CO and H₂O, which are described below.

3.3. Au Loading

The rates of the catalysed and photocatalysed WGS reaction were measured for different Au wt % loadings, from 0.01 wt% to 1 wt%, and the results of this work are illustrated in Fig. 8(a). These results show that the ratio of the total photocatalytic rate, r_T , to that of the dark catalytic rate, r_D , decreases from 27.7 to 1.2 as the wt% Au is increased from 0.01 to 1 wt%. These results indicate that increasing the loading of Au on the TiO₂ enhances the rate of the thermal WGS significantly; indeed, a plot of r_D vs wt%, illustrated in Fig. 8(b), reveals a good straight line, which suggests that r_D is proportional to volume of the Au particles, i.e.

proportional to r^3 , assuming that the number of Au particles, N_p , is constant with increasing wt% Au, although it would appear more likely that r_D would be proportional to $(\text{wt\% Au})^{2/3}$, if r_D was proportional r^2 . Note also that, not surprisingly, TiO_2 on its own is not able to mediate the WGSR either catalytically or photocatalytically.

(a)

(b)

Fig.8: (a) histogram plot of the measured variation in $r(\text{H}_2)$, $= r_T$, for the thermal (filled columns; $r_T = r_D$) and photocatalysed WGSR (unfilled columns; $r_T = r_D + r_{UV}$) as a function of wt% of Au and (b) subsequent plot of the $r(\text{H}_2)$, $= r_D$, data in (a) vs wt% Au.

Assuming that r_{UV} is the difference between r_T and r_D , as indicated by eqn (14), then the data in Fig. 8(a) for the photocatalysed WGSR can be used to construct the plot of $\Delta r(H_2) = r_{UV}$, vs wt% Au, illustrated in Fig. 9, where $\Delta r(H_2) = r_T - r_D = r_{UV}$.

Fig. 9: Plot of $\Delta r(H_2)$, i.e. r_{UV} , vs wt% Au constructed using the data illustrated in Fig. 8(a). The solid line plot is the best fit to the data based on the EPAO model, using experimentally determined values of the wt% Au when r of 0.2 and 2 nm, respectively, and a and b optimised fit model constant values of 4 nm and 22.2, respectively. See S6 in ESI for more model details.

The plot of r_{UV} vs wt% Au for the photocatalysed WGSR is similar in shape to that generated by Millard and Bowker [15] for the same reaction, but using Pd instead of Au deposited on P25 TiO₂. As noted earlier, in the latter work, conducted at room temperature, in aqueous solution and in a *batch* reactor, the rate peaked at a loading of ca. 0.5 wt% Pd and was zero at 2 wt% Pd. As noted by Millard and Bowker [15], the complete lack of photocatalytic activity observed at 2 wt% Pd is not due to the UV screening of the TiO₂ surface by the Pd hemispherical particles (with $r = 1$ nm), since a simple calculation shows that a loading of 26.5 wt%(and not 2 wt% as found) of such particles as hemispheres would be required to completely cover, and so screen, the surface of the TiO₂ through hexagonal packing. Millard and Bowker [15] rationalised this feature, and their measured profile of r vs % wt Pd, using a model in which each Pd particle is active over a circular boundary region of radius, r_z , which is much greater (ca. 7 times) than that of the Pd hemisphere particle at its centre, radius, r . In this model, the rate is proportional to the number of Pd particles, N_p , and the circumference of the boundary. The value of N_p is assumed to be a constant, regardless of the wt% Pd, so

that as the metal loading is increased so too is the value of r and r_z until a maximum rate is reached, when the value of r_z is sufficiently large that the boundaries touch. The value of the metal loading at this high point in rate is defined as the **wt%(max)** and increasing the metal loading above **wt%(max)** results in an increasing degree of boundary overlap, and so loss of boundary perimeter length and a rapid loss in activity.

More recently a revised model of has been reported which appears to better describe the variations in rate observed by Millar and Bowker [15] for the photocatalysed WGSR and those observed by others for the photocatalysed reforming of methanol [23, 24]. In this photocatalytic area and overlap (EPAO) kinetic model [23], the overall rate of reaction is assumed to be proportional to the circular, photocatalytic extended *area* that surrounds each metal hemisphere, as well as the number of particles, N_p . The radius of this extended area (or boundary region) is, as before, r_z , and increases with increasing metal loading. As before, the model predicts a maximum rate will be achieved when the circular areas of activation touch. However, when the metal loading exceeds the value of **wt%(max)**, the areas of activation overlap and produce a loss in photocatalytic activity due to a loss in *area* of activation. In the EPAO model, the radius of the *area* of activation, r_z , depends directly upon the value of r via the following expression,

$$r_z = a + br \quad (15)$$

where, a and b are two system-dependent constants.

In order to fit the EPAO model to a set of measured rate vs %wt of M data, knowledge of just one value of the metal wt% and its associated value of r (this combination is called a paired data set) is required, since it allows the calculation of the value of N_p , from which optimised fit to the data values of a and b can be derived. The solid line in Fig. 9 illustrates the EPAO kinetic model optimised fit to the r_{UV} vs wt% Au data set reported in this study, with the values used to generate this optimised fit given in Table S3 in S6 in the ESI. The model fit to the data illustrated in Fig. 9 appears reasonable, especially at high %wt% Au loadings given the likely error in calculating a true value for r_{UV} using eqn (14) since, at these high metal loadings, the value of r_T is close to that of r_D .

3.5. Variation in CO and H₂O concentrations

In all of the work described so far the concentrations of CO and H₂O were fixed at 10 vol% and in the final part of this study the variation in the photocatalytic rate of the WGSR, i.e. r_{UV} ,

where $r_{UV} = \Delta r(H_2) = r_T - r_D$, and the thermal rate, i.e. r_D , were studied both as a function of $[CO]$ (with $[H_2O]$ fixed at 10 vol%) and $[H_2O]$, (with $[CO]$ fixed at 10 vol%). The results of this work for the photocatalysed WGSr are illustrated in Fig. 10 and reveal that r_{UV} increases sharply as the $[CO]$ is increased from zero to 10 vol % of CO and levels off as the $[CO]$ is increased further, whereas, in contrast, over the range 5-20 vol % of H_2O at least, r_{UV} is largely independent of $[H_2O]$.

Fig. 10: Plot of $\Delta r(H_2) = r_T - r_D = r_{UV}$ for the photocatalysed WGSr, i.e. reaction (2) with M = 0.2 wt% Au, as a function of $[CO]$ (with $[H_2O] = 10 \text{ vol\%}$) and, in the case of the insert diagram, $[H_2O]$, (with $[CO] = 10 \text{ vol\%}$). As usual the total flow rate was $10 \text{ cm}^3 \text{ min}^{-1}$, and reactor temperature 125°C .

Like many photocatalytic processes [26], the above observed kinetics appear to fit Langmuir-Hinshelwood kinetics in which the CO and H_2O are non-competitively adsorbed, i.e.

$$r_{UV} = \frac{k^* K^*(CO) [CO]}{1 + K^*(CO) [CO]} \times \frac{K^*(H_2O) [H_2O]}{1 + K^*(H_2O) [H_2O]} \quad (16)$$

where k^* is the maximum rate and $K^*(CO)$ and $K^*(H_2O)$, the apparent Langmuir adsorption constants for CO and H_2O , respectively; note the * prefix is used here in order to stress that these constants refer to the photocatalysed WGSr, i.e. reaction (2). The solid lines illustrated in Fig. 10 are the lines of best fit to eqn (16) calculated using values for k^* , $K^*(CO)$ and $K^*(H_2O)$, of $34.7 \times 10^{-5} \text{ mol h}^{-1}$, $0.21 (\text{vol\%})^{-1}$ and $2 (\text{vol\%})^{-1}$, respectively. It is well known that although most photocatalytic reactions exhibit apparent Langmuir-Hinshelwood kinetics, the mechanism is likely to be much more complex, especially since the Langmuir adsorption

constants associated with such apparent fits to Langmuir-Hinshelwood kinetics are usually found to be strongly dependent upon irradiance [27-30]. Many of the mechanisms that have been proposed to provide a rationale for the apparent Langmuir-Hinshelwood type kinetics exhibited by photocatalytic systems have been reviewed recently [31], although, as yet, no one mechanism has found universal approval [32].

To our knowledge this is the first study of the kinetics of the photocatalysed WGS as a function of $[\text{CO}]$ and $[\text{H}_2\text{O}]$ and the apparent good fit of the kinetic data illustrated in Fig. 10 to eqn (16), based on non-competitive adsorption Langmuir-Hinshelwood kinetics suggests that the oxidation of the CO and the reduction of the water occur at two different sites, namely the metal co-catalyst and TiO_2 substrate, respectively, which, in turn, is consistent with the flux-matching model of the photocatalytic process described earlier and summarised by reactions (3)-(5).

The kinetics of the thermal (dark) WGS reaction, i.e. reaction (2), was also studied, i.e. the value of r_D measured under the same reaction conditions as above and the results of this work are illustrated in Fig. 11.

Fig. 11: Plot of $r(\text{H}_2) = r_D$ for the thermal WGS, i.e. reaction (1) with $M = 0.2 \text{ wt\% Au}$, as a function of $[\text{CO}]$ (with $[\text{H}_2\text{O}] = 10 \text{ vol\%}$) and, in the case of the insert diagram, $[\text{H}_2\text{O}]$, (with $[\text{CO}] = 10 \text{ vol\%}$). As usual the total flow rate was $10 \text{ cm}^3 \text{ min}^{-1}$, and reactor temperature 125°C .

An initial inspection of these results suggests that, like the photocatalytic reaction, the kinetics might be well described by an apparent Langmuir-Hinshelwood rate equation along

the lines of eqn (16). However, unlike the photocatalytic WGSR, no common set of values for k , $K(\text{CO})$ and $K(\text{H}_2\text{O})$ could be found that provided a good fit to the observed variations in r_D as a function of $[\text{CO}]$ and $[\text{H}_2\text{O}]$, illustrated in Fig. 11, based on a Langmuir-Hinshelwood kinetic model either with and without competitive adsorption. Not surprisingly, many studies of the kinetics of the thermal WGSR have been carried out previously [32] and several different reaction mechanisms and associated kinetic equations reported, of which the best fit to the kinetic data illustrated in Fig. 11 was found based on kinetic equation derived from a relatively complex reaction mechanism involving intermediate formic acid formation and water adsorption on the supporting substrate and CO and water dissociative adsorption on the metal, with each adsorption described by a Langmuir type isotherm [33]. Despite its relative complexity, the overall reaction rate equation associated with the model is quite simple, i.e.

$$r_{UV} = \frac{kK(\text{CO})[\text{CO}]K(\text{H}_2\text{O})[\text{H}_2\text{O}]}{(1+K(\text{CO})[\text{CO}]+\sqrt{K(\text{H}_2\text{O})[\text{H}_2\text{O}]})^2} \quad (17)$$

where k is the maximum rate and $K(\text{CO})$ and $K(\text{H}_2\text{O})$, are the apparent Langmuir adsorption constants for CO and H_2O dissociative adsorption on the metal, respectively. Thus, the solid lines used to fit the data illustrated in Fig. 11 were based on eqn (17) and calculated using values for $K(\text{CO})$ and $K(\text{H}_2\text{O})$, of $0.125 \text{ (vol\%)}^{-1}$ and $2.8 \text{ (vol\%)}^{-1}$, respectively. Although the values of $K(\text{CO})$ and $K(\text{H}_2\text{O})$ are common for both the main and insert plots illustrated in Fig. 11, the optimised fit values of k were slight different namely, $8.0 \times 10^{-5} \text{ mol h}^{-1}$ and $9.4 \times 10^{-5} \text{ mol h}^{-1}$, respectively. A summary of the results and calculations reported in this paper is given in Table S4 in section S7 in the ESI.

4. Conclusions

Au/TiO_2 is the best of the M/TiO_2 catalysts tested in a gas phase flow system with $[\text{CO}]$ and $[\text{H}_2\text{O}]$ at 10 vol%, where $\text{M} = \text{Au, Pt, Pd and Ag}$, for the thermal (dark) and photocatalytic (UV irradiated) WGSR. Using Au/TiO_2 in the photocatalytic WGSR, the optimum temperature and metal loading are $125 \text{ }^\circ\text{C}$ and 0.2 wt%, respectively, whereas in the thermal WGSR, the rate simply increases with increasing temperature and metal loading. The two processes (i.e. the light and dark WGSRs, reactions (1) and (2) respectively, appear competitive, probably due to the utilisation of the same reaction site, with the latter reaction largely suppressing the former at high metal loading ($> 1 \text{ wt\%}$) and reaction temperatures ($> 448 \text{ K}$). At $125 \text{ }^\circ\text{C}$, with a 0.2 wt% loading, the Au/TiO_2 photocatalyst is very efficient, exhibiting a formal quantum

efficiency for $1/2\text{H}_2$ production of 57%. The kinetics of photocatalytic (UV irradiated) WGS for the Au/TiO_2 photocatalyst, appear to be those typical for a photocatalytic reaction, exhibiting apparent Langmuir-Hinshelwood kinetics, with the non-competitive adsorption of the CO and H_2O . The latter feature suggests that the oxidation of the CO and reduction of the water occur at two different sites, namely the metal co-catalyst and TiO_2 substrate, respectively, which in turn is consistent with a flux matching model of the photocatalytic process. The kinetics of thermal WGS fit the reported [33] rate equation for a more complicated reaction mechanism, involving intermediate formation of formic acid and the adsorption and the dissociative adsorption of CO and water on the metal, respectively. The use of relatively low temperatures and high photonic efficiencies suggest that a photocatalytic approach to the WGS may have promise commercially and is worth investigating as such as a scaled-up process. The advantage of the system described here is that it is already of a form (a continuous flow) that is used in industry. In addition, continuous flow industrial photoreactors are not uncommon, particularly in the water purification industry [34] and in industrial organic synthesis (promoting reactions such as chlorinations, sulfonations, sulfoxidations or nitrosylations [35]). The low temperature used in this work (125°C) also favours its ready scale up, as most industrial photocatalytic reactors are not designed to work at high temperatures. The major problem with scaling-up this system is the cost of the most effective co-catalyst (Au). Thus, further work is required to probe the longevity and recyclability of the TiO_2/Au photocatalyst and to explore the possible use of Earth-abundant co-catalysts. The fact that Cu/ZnO is one of the best low temperature, thermal catalysts for the WGS is particularly intriguing as ZnO is a very effective semiconductor photocatalyst. Thus, an investigation of the efficacy of Cu/TiO_2 and Cu/ZnO as photocatalysts for the WGS is an obvious direction of research that should be followed.

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