The photocatalytic reforming of methanol

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Abstract

The anaerobic photocatalytic decomposition of methanol in aqueous solution has been investigated using a Pd/TiO_2 catalyst. The rate is near zero order in methanol over most of the range of reaction, but has a complicated dependence on the loading of Pd on the photoactive support. This dependence is explained by assigning the active site for the rate determining step to be at the interface between the Pd and the TiO_2. In the absence of light, the methanol does not decompose at steady state on the catalyst, probably due to poisoning of the Pd surface with adsorbed CO. Light of greater energy than the TiO_2 band gap (~ 3.2 eV) causes photoexcitation of electrons into the conduction band; this produces an oxidant which reacts with adsorbed CO to produce CO_2 and hence maintains a steady state rate of methanol decomposition. The overall oxidant is water. A detailed model for the reaction is proposed. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, photocatalysis has become the focus of a considerable amount of effort. The interests range from the photoelectrocatalytic production of hydrogen from water, first reported by Fujishima and Honda [1] to the clean up of organic pollutants in aqueous effluents, much of the latter being carried out under aerobic, oxidising conditions.

In this paper, we have focused our efforts on a rather fundamental study of what could be considered to be a model organic compound, namely methanol; it is a model for more complex reactions because it is a small, simple molecule with one reactive functional group. If we cannot understand how this molecule reacts, we cannot begin to understand the reactivity of more complex systems, such as sugars, for instance. Further, the work is carried out under anaerobic conditions, thus avoiding direct oxidation mechanisms.

Some work has already been carried out on the anaerobic degradation of this molecule and other alcohols on a variety of catalysts, but with similar overall rates of hydrogen production (Table 1) [2–6]. Various proposals for the mechanisms of the reaction have been given, including dehydrogenation to the aldehyde by Ait-Ichou et al. [7] and Pichat et al. [2], and oxidation by water suggested by Kawai and Sakata [8] and Sakata and Kawai [9].

The aim of the current work was to gain a more fundamental understanding of this reaction and is part of a wider programme of work investigating the water splitting reaction, and the degradation of more complex molecules in water. It is hoped that a better fundamental

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Table 1
Hydrogen production from alcohols using UV light and a photocatalyst under an inert atmosphere

Catalyst	Alcohol	Initial H_2 production rate		Conditions
		$\mu mol/h$	$\mu mol\ h^{-1}\ g^{-1}$	
Pt/TiO$_2$ [8]	Methanol	460	1533	10 ml MeOH, 10 ml H_2O. Pyrex flask
Pd/TiO$_2$ [8]	Methanol	220	733	10 ml MeOH, 10 ml H_2O. Pyrex flask
Pt/TiO$_2$ [9]	Ethanol	508	1693	15 ml EtOH, 15 ml H_2O. Pyrex flask
Pt/TiO$_2$ [2]	Methanol	400	570	10 ml MeOH. Pyrex flask
NiO/TiO$_2$ [6]	Methanol	30	30	H_2O:MeOH = 30:1 (vol = 300 ml). Quartz reactor
Pt/TiO$_2$ [11]	Propan-2-ol	175	700	10 vol.% PrOH in H_2O

understanding will lead to identification of the active sites for the reaction and for photocatalysis more generally, and will help us to understand the possibilities and limitations of this technology.

2. Experimental

The equipment used in this work is similar to that described by others [10]. It consists of a Pyrex reaction flask, with a purge line, a septum for sampling, and a port for a thermometer. The reaction mixture (0.2 g of catalyst, 100 ml of deionised water and the appropriate amount of methanol) was placed in the flask and purged with Ar for 30 min in order to remove dissolved gases. The mixture was stirred with a magnetic stirrer and light from the 400 W Xe arc lamp (Oriel model 66084) entered the vessel from the side. Some 0.2-ml samples were taken periodically from the gas phase both prior to, and after, switching on the lamp. The samples were analysed using a Varian 3300 gas chromatograph, with a thermal conductivity detector and an MS13X column, 2 m long. The retention time for hydrogen was 44 s with an argon carrier gas flowing at 17 ml min^{-1}: integration was carried out with an LDC Milton Roy CI-10 integrator. It was found that, for such a static system (a 'stirred pot' reactor), manual sampling with a gas tight syringe was far more reliable than using an on-line sampling valve due to diffusion limitations down the small bore tubing of the valve, which results in a significant time lag between hydrogen production and detection by that method.

Catalyst preparation was generally by the incipient wetness method. The catalysts were all made with P25 titania (Degussa) as the photoactive support, although other supports have been used, but are not reported here. The work very much concentrates on one type of catalyst, namely Pd/TiO$_2$, since this proved to be one of the most efficient catalysts for the degradation. Typically, the preparation procedure was as follows. The appropriate mass of metal salt (PdCl$_2$) was dissolved in water acidified with a few drops of concentrated HCl to give the desired concentration of metal. The volume added to the catalyst was just sufficient to fill the pores of the support. The impregnated support was then dried in an oven at 110°C for 2 h, was ground in a pestle and mortar and was calcined at 500°C for 2 h. It was then sieved to < 53 μm before use.

3. Results

3.1. The Reaction on Pd / P25 TiO$_2$

Fig. 1a and b show the reaction of methanol on a 1 wt.% Pd catalyst after the light is switched on. The rate of reaction changes at short times (the rate is the slope of the curve in Fig. 1), but after this initial change, it appears essentially
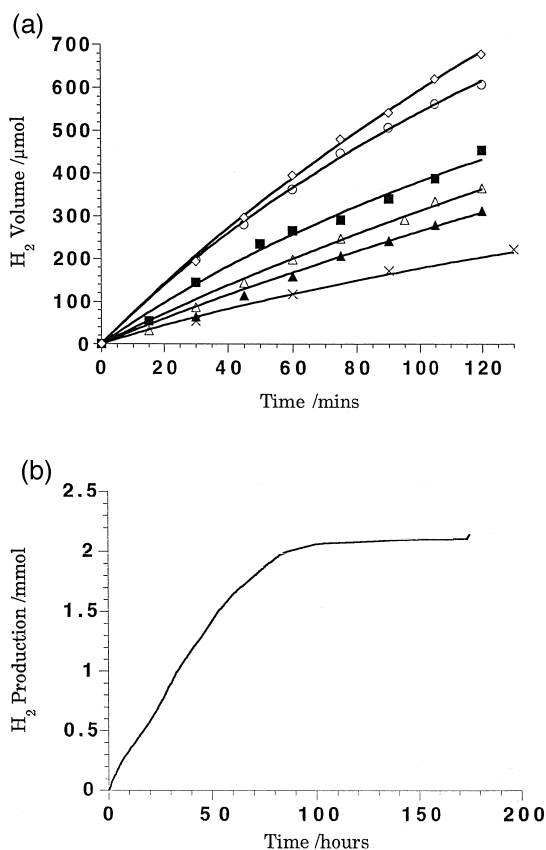
Fig. 1. (a) Time dependence of hydrogen evolution from the degradation of methanol on the Pd/P25 titania catalyst. As a function of increasing rate, the methanol concentration was 0.1 M (crosses), 1.24 M (filled triangles), 2.5 M (open triangles), 6.2 M (squares), 12.4 M (circles), 18.6 M (diamonds). (b) An extended run of the reaction to completion with 0.01 M solution and 0.05 g of catalyst.

which might remain irreversibly held on the titania (a monolayer on the titania is approximately 0.2 mmol of methanol). If more methanol were added to the flask at this point, the reaction again proceeded as before indicating that the catalyst was not poisoned and that the reason for the drop in H_2 production was the complete removal of methanol from the reaction mixture.

Although CO_2 was not followed during every run, samples of the gas phase were analysed by mass spectrometry and this showed that CO_2 was present in the gas phase. Further, the gas phase was analysed by gas chromatography on a separate instrument, and again showed the presence of CO_2. These showed the approximate level of CO_2 evolution to be in a 1:3 ratio with the hydrogen.

3.2. Effect of initial methanol concentration

The rate of hydrogen evolution from different initial concentrations of methanol is given in Figs. 1 and 2. Like Fig. 1b, this indicates only a weak dependence of the rate on methanol concentration, except at the lowest methanol level when there is a sharp increase in H_2 evolution rate from the zero methanol value. This shows

invariant up until approximately 60% of reaction extent (~ 1.5 mmol of H_2 evolved in Fig. 1b). Then the H_2 evolution begins to diminish and appears essentially complete after ~ 100 h reaction time. The total amount of H_2 evolved is 2.5 mmol (including estimated losses due to dissolved hydrogen and sampling), which compares with 1 mmol of methanol originally in the solution. Thus, the stoichiometry of the reaction is greater than 2:1 hydrogen evolved per methanol reacted. This is also a lowest level estimate since we have ignored any possible loss of methanol from the mix during the Ar purge to remove any dissolved gases, and any
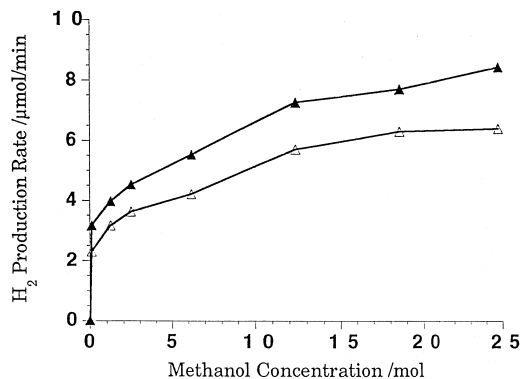

Fig. 2. The dependence of the rate of hydrogen evolution on methanol concentration, showing a sharp effect at very low methanol concentrations, where the filled triangles represent the rate at 60 min and the open triangles the rate at 120 min.
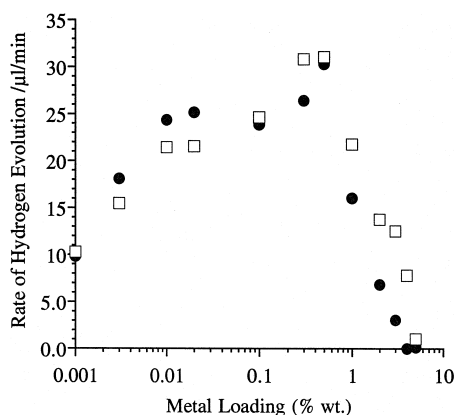
Fig. 3. The dependence of hydrogen evolution rate upon the metal loading on the catalyst, showing a clear maximum at ∼ 0.5 wt.%, and a near zero rate above 5 wt.%. The average reaction rates for individual metal loadings after 2 h (circles) and 5 h (squares) are shown.

that even traces of an organic pollutant in water have a big effect on hydrogen evolution rate, a fact of importance for some other studies in this field, for example, in photocatalytic water splitting, which generally takes place at a much lower rate and has a shorter wavelength threshold.

These data all indicate a near zero order dependence of the reaction on the reactant concentration. Of course, in reality the reaction is slightly positive in order since from 2 to 20 molarity the rate increases from ∼ 4 to ∼ 7 μmol min^{-1}, but this dependence is weak. This is an adsorption system, so the order dependence of the reaction in methanol is a more complex one than the treatment above implies, and this is considered further in the discussion below (Section 4.3).

3.3. Effect of metal loading

The effect of varying the loading of metal on the rate of the reaction was measured and the results are shown in Fig. 3. This is a compilation of results and shows fairly consistent data at high loadings, but, as might be expected, more variable results at very low loadings. There

is a very sharp increase of hydrogen production at low loadings of palladium and a maximum in production at ∼ 0.5 wt.%. The rate declines at higher loadings until little hydrogen is produced at all at 5% Pd. This is quite a remarkable dependence which gives some clues to the active site for the reaction as discussed further below.

3.4. Wavelength dependence

The wavelength of the light entering the reaction mixture was varied by carrying out reaction runs with different filters in the light path, and confirms that the threshold for this reaction is at ∼ 340 nm (the near UV) and in close agreement with the band gap of titania (∼ 360 nm.).

3.5. Reaction intermediates

Various intermediates could be involved in methanol oxidation and so we investigated the photocatalytic degradation of two of the most likely candidates, namely formaldehyde and formic acid, with the results shown in Fig. 4. In the case of formic acid, this was broken down in the absence of light. The rate is only a little lower than for methanol in the presence of light. Neither methanol nor formaldehyde produced
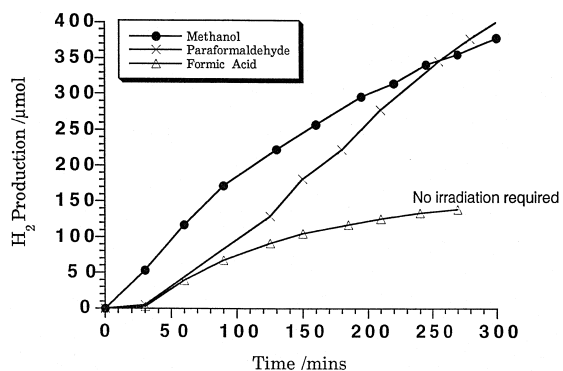

Fig. 4. Comparative degradation of related molecules in aqueous solution. Formic acid decomposed in the absence of light, whereas the other two did not.

hydrogen in the absence of light. The rate for formaldehyde and methanol is similar, though the formaldehyde evolution has a somewhat different profile than that from methanol. Nevertheless, these data imply that large amounts of these intermediates cannot be building up in the reaction solution since they are reacted away as quickly as is methanol. Furthermore, NMR analysis of the solution after 3.5 h runtime showed no evidence of other intermediates or products in solution.

4. Discussion

The results described above beg a number of questions. These can be listed as follows, and will be discussed in sequence below.
1. Why is the reaction rate best for certain metals, and much better than for titania alone?
2. What is the mechanism of the reaction?
3. Why does the rate have such a weak dependence on methanol concentration?
4. Why is there such a complex dependence of decomposition rate on metal loading?

4.1. Metal dependence of rate

It is often the case in photocatalysis that precious metals are good promoters of photocatalytic degradation, and Table 1 shows some comparative sets of data from different workers for methanol anaerobic decomposition, together with rates for some related molecules. It is remarkable that the rates of methanol decomposition are very similar from different labs using different types of equipment. This perhaps relates to the near zero order rate dependence on methanol concentration, and the shallow dependence on metal loading (at least over the range 0.1 to 3% where the rate only varies by a factor of 2 or so). Other metals, however, are rather ineffective for the reaction, perhaps due to irreversible poisoning by the reactants or products.

The reason that the precious metals are effective is probably several-fold and relates to the mechanism of the reaction discussed in more detail below. Titania is the photoactive part of the catalyst, generating usable electrons which, temporarily at least, store the photon energy as potential energy available for use in driving a chemical reaction. It is likely that this involves the generation of an oxidant on its surface, which is used to oxidise methanol (discussed further in Section 4.2 below). It is not likely that methanol adsorbed on titania (if it is adsorbed on titania at all in the presence of excess water) is the species which is decomposed since (i) titania alone is ineffective, and (ii) TPD studies have shown that the methanol is adsorbed very strongly at defect sites which produce mainly methane as the gas phase product (Fig. 5), but only at much higher temperatures, as described earlier by Aas et al. [12]. In contrast, methanol decomposes on pure Pd (or Pd covered with oxygen) at room temperature by complete dehydrogenation to CO and H_2, with the former molecule remaining adsorbed (Fig. 6), eventually poisoning the surface. The reason the precious metals are particularly effective may be their 'nobleness', that is, their ease of reducibility to metal (in contrast to, say, row 1 transition elements), combined with the high dehydrogenation ability of the metal.
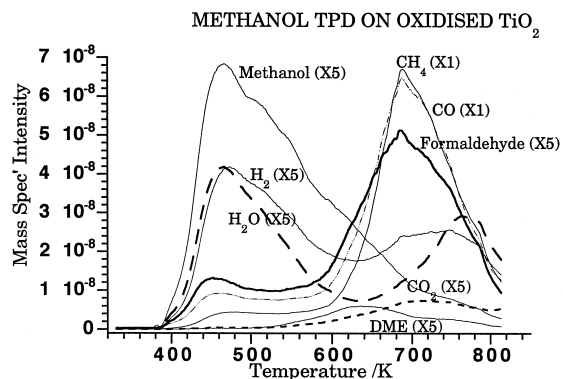

Fig. 5. Temperature programmed desorption from P25 titania after dosing the surface with 0.5 Torr s of methanol at 310 K. The main products are water, hydrogen, methane and CO with small amounts of formaldehyde.

4.2. Reaction mechanism

Here, we should elaborate on the reaction mechanism outlined in Section 4.1 above. The first steps in the reaction, we propose, involve adsorption of methanol on the Pd part of the catalyst (Fig. 7a). These reactions certainly occur on clean Pd(110) at room temperature (Fig. 6), but this activity is quickly lost as the surface becomes poisoned by CO. It is likely that this reaction proceeds through initial dissociation of methanol at the hydroxyl group, to form methoxy, which is then further dehydrogenated to CO and gas phase hydrogen. Even if the Pd surface is initially oxidised, it will quickly reduce by CO_2 and H_2O production [13] after which the clean surface reaction takes over, and once again CO poisons the surface. This reaction probably occurs immediately on exposure of the Pd to methanol, and the hydrogen produced would be purged away in our experiment; in any case, the amount of hydrogen produced would be only the equivalent of the Pd surface reaction extent, that is approximately 3 μmol. Methanol adsorption may take place on the titania pa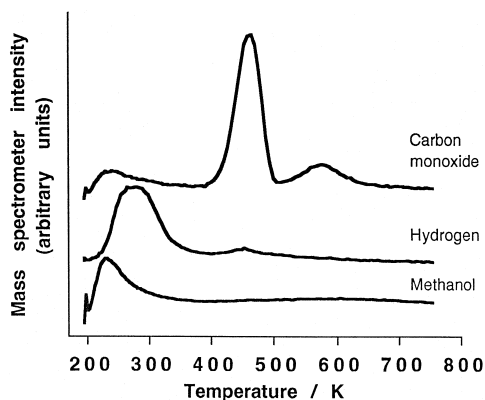rt of the catalyst, but TPD experiments show the formation of a relatively stable surface species, which only decomposes at 450–600 K [12], as shown in Fig. 5. CO_2 is not a major oxidation product in such an experiment.

Under such circumstances, we are left with a CO poisoned Pd surface (Fig. 7b) which requires an oxidant to enable steady state turnover and we propose that this oxidant is produced on the titania. The net oxidant is water (Fig. 7d) since the stoichiometry of the reaction is close to the 3:1 stoichiometry of the reaction below.

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$
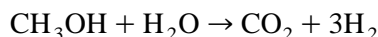
There are therefore several possibilities for the identity of this direct oxidant; it may be
  (i) water itself,
  (ii) hydroxyl groups,
  (iii) oxygen atoms.
Possibility (i) can be quickly eliminated, since it is omnipresent and is available to the Pd, yet the steady state reaction does not go in the absence of light. The importance of TiO_2 is in providing a material for absorption of light energy which is used to enable the reaction to proceed, via the excitation of valence band electrons into the conduction band (i.e., effectively from O^{2-} to Ti^{4+}) as shown in Fig. 7b and Eq. (2) below. Thus, it is possible that an oxygen species (O^-) created in this way may be the oxidant, that is, item (iii) above. Water is then also reduced by annealing of the vacancy left behind (Fig. 7d) and thus becomes the net oxidant of methanol as indicated by the stoichiometric equation above. However, it is also possible that reactive hydroxyl groups (item (ii)) may be the direct oxidant. Here, the absorption of light is important for providing the energy to make available a reactive oxidant. The threshold for the reaction corresponds closely with the band gap of anatase (3.2 eV) being at ~ 360 nm, or 3.4 eV. The oxidant is shown simply as O^- in Fig. 7 and is either formed close to the metal interface by photoexcitement or diffuses to that site across/through the oxide (Fig. 7b). If this is the case, then the hole left by formation of CO_2
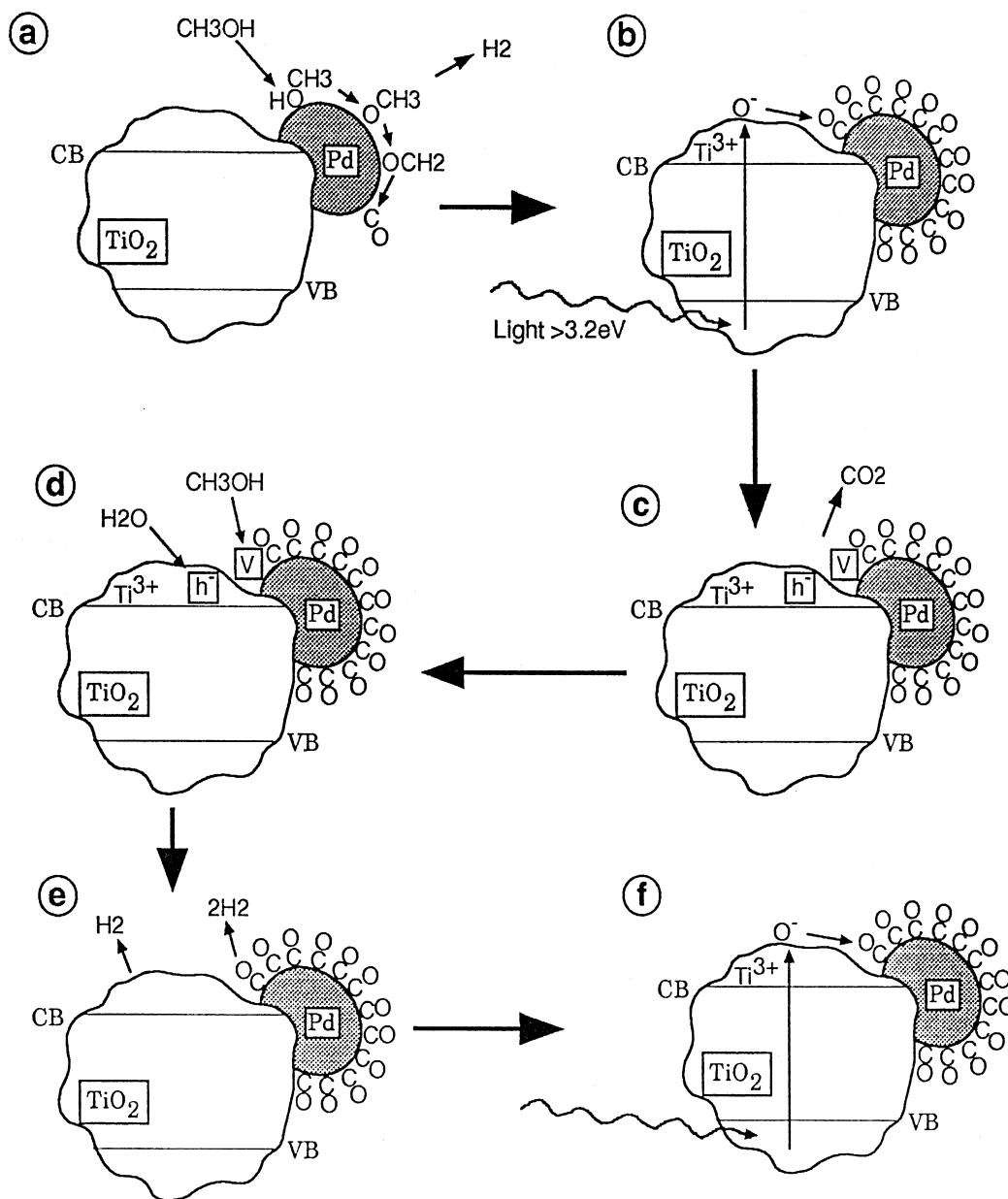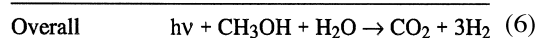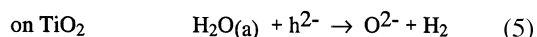

Fig. 6. Temperature programmed desorption from a Pd(110) single crystal after dosing with 2.4×10^{-6} Torr s of methanol at 190 K. The only products are hydrogen and CO, but note that CO is strongly held and does not begin to desorb until 400 K. In a molecular beam reactor, steady state reaction is not achieved at 310 K; there is transient evolution of hydrogen, which quickly stops after saturation of the surface with CO.
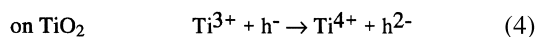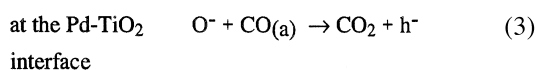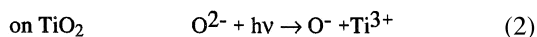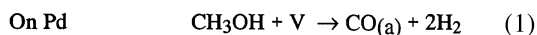
Fig. 7. Schematic models of the photocatalytic degradation of methanol on Pd/P25 titania. (a) Methanol adsorption and decomposition on the Pd particles, proposed to be the beginning of the reaction, before light is admitted. The surface becomes poisoned with strongly held CO (as predicted from Fig. 6 results) and there is a zero steady state rate of methanol degradation. (b) Light excites electrons across the bandgap to produce highly reactive oxidising species, shown here as O^-, though it may be an activated water species. (c) CO_2 is produced from the reaction, leaving a vacant metal site at the periphery of the metal particle, and an anion vacancy (hole) in the oxide, also at the interface. (d/e) Methanol adsorbs on the metal component, liberating hydrogen, and the hole is filled by water which also yields hydrogen. (f) is the return to the beginning of the cycle (b), though the nature of the MASI (the most abundant surface intermediate) during the steady state is not clear; it may be adsorbed methanol or a methoxy species.

(Eq. (3); Fig. 7c) is healed by reaction with water to produce hydrogen, (Fig. 7d,e; Eq. (5)), and the excited O^- state can then further react, or more likely form O^{2-} again by recombina-

tion. Alternatively, the O^- state may directly react with water in a variety of ways to produce excited oxidants such as OH^- or OH^--radical. It is not clear which of these oxidants prevails. The oxidation in this way then leaves a vacancy (V) on the Pd which is filled with CO, again by dehydrogenation of methanol.
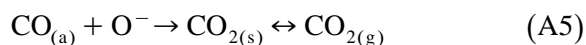
The overall reaction scheme can be written as

On Pd	$CH_3OH + V \rightarrow CO_{(a)} + 2H_2$	(1)
on TiO_2	$O^{2-} + h\nu \rightarrow O^- + Ti^{3+}$	(2)
at the Pd-TiO_2 interface	$O^- + CO_{(a)} \rightarrow CO_2 + h^-$	(3)
on TiO_2	$Ti^{3+} + h^- \rightarrow Ti^{4+} + h^{2-}$	(4)
on TiO_2	$H_2O_{(a)} + h^{2-} \rightarrow O^{2-} + H_2$	(5)

$$\overline{\qquad\qquad\qquad\qquad\qquad\qquad}$$

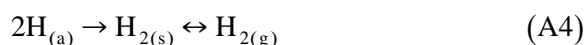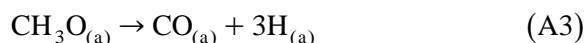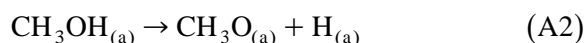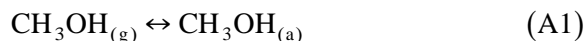| Overall	$h\nu + CH_3OH + H_2O \rightarrow CO_2 + 3H_2$	(6)

with subscript (a) referring to adsorbed species. Here steps 4 and 5, especially, may be a more complicated series of reactions, possibly involving reactive water intermediates, and O^- itself may not be the $CO_{(a)}$ oxidant. Although in the absence of light, it is likely that the surface will be poisoned with CO, it is not certain what is the dominant surface species in the presence of light.

4.3. Methanol concentration dependence

The kinetics of the reaction appear to be Langmuir-like and there is only a weak dependence on methanol concentration in the solution. This is probably because over most of this range the reaction is near the zero order limit of the Langmuir equation (Michaelis–Menten equation), that is, the active centre of the catalyst is near saturated with the reactant (or a

component of the reactant in equilibrium with the reactant). The implication of this is that, at least during the reaction, the surface is near saturated with methanol or with a dissociated form of methanol (perhaps methoxy or CO). This adsorbed form is in equilibrium with methanol in solution and the overall scheme can be written as

$$CH_3OH_{(g)} \leftrightarrow CH_3OH_{(a)} \tag{A1}$$

$$CH_3OH_{(a)} \rightarrow CH_3O_{(a)} + H_{(a)} \tag{A2}$$

$$CH_3O_{(a)} \rightarrow CO_{(a)} + 3H_{(a)} \tag{A3}$$

$$2H_{(a)} \rightarrow H_{2(s)} \leftrightarrow H_{2(g)} \tag{A4}$$

$$CO_{(a)} + O^- \rightarrow CO_{2(s)} \leftrightarrow CO_{2(g)} \tag{A5}$$

where the subscript (s) refers to species in solution.

Step A1 here is methanol adsorption which is likely to be an equilibrium step, as also may be step A2, which is methanol dissociation. In terms of the kinetic analysis given above, either methanol or an intermediate is the dominant surface species during photocatalysis and is near saturation coverage for many of our measurements. Methoxy dehydrogenates through to CO which is then oxidised to produce CO_2 which is in gas–solute equilibrium. Hydrogen is evolved by recombination, again probably on the Pd. The slow step might be step A3 when under photocatalytic conditions, though it could possibly be step A2. The CO oxidant is generated by the light and is proportional to the light flux; the nature of this oxidant was discussed above, and is represented in Eq. (A5) as an oxygen ion; it could be a hydroxide ion.

4.4. Metal loading dependence

The loading dependence shown in Fig. 3 gives support for the proposal regarding the nature of the active site for this photocatalytic reaction in particular, and is also instructive for such reactions generally on these materials.

It is clear that TiO_2 alone has only slight activity for this reaction, and the same applies to Pd/Al_2O_3; it is essential to have both active components together in the solution. Thus, we associate increasing activity at low Pd loadings with the presence of Pd on the photoactive support TiO_2. However, the dependence is very sharp, increasing most at low loadings, then apparently flattening off. Thus, an increase from 0.001 to 0.5% loading only increases the activity approximately three times. It is likely that this is due to the nature of the active site — we propose that it is an edge interface between Pd and TiO_2 particles, Fig. 7d. In this case, and assuming hemispherical Pd particles on the support, the number of active sites (NAS) obeys the following relationship,

$$NAS = Y + Z \tag{III}$$

where Y represents a term during the growth phase of particles, during which the perimeter gets bigger as the particle size increases. However, as the Pd particles get larger, they eventually merge (Fig. 8) which then begins to diminish the perimeter active area, eventually diminishing the activity to zero when no more perimeter exists; then all the TiO_2 surface is covered with Pd. The term Z above describes the variation of active sites during this phase.

Thus, it is essential to have exposed titania and palladium together on the surface. To present Eq. (III) in a full form, then

$$NAS/a = N^{2/3} \cdot \left(12\pi^2 V\right)^{1/3}$$
$$\cdot \left[1 - \left(\cos^{-1}\left\{d/\left[2(3V/2N\pi)^{1/3}\right]\right\}\right.\right.$$
$$\left.\left. /\theta\right)\right] \tag{IV}$$

where V is the volume of metal ($= W/\rho$, the weight to density ratio), d is the interparticle separation, N is the total number of particles in the sample, θ is a geometric factor (30 for a hexagonal close packed arrangement of particles, 45 for a square array with four nearest neighbours) and a is the linear site density (sites per unit length of perimeter). The relationship between perimeter and Pd loading is a cube root at low Pd concentrations, and an inverse cosine at high loadings, thus diminishing as the coverage of Pd increases beyond a critical level (by experiment, Fig. 3, this level is about 0.5% Pd). Thus, in general terms, these functions produce the correct approximate shape for the loading dependence of the photocatalytic rate. In fact Fig. 9 shows a comparison between experiment and theory and the fit between the
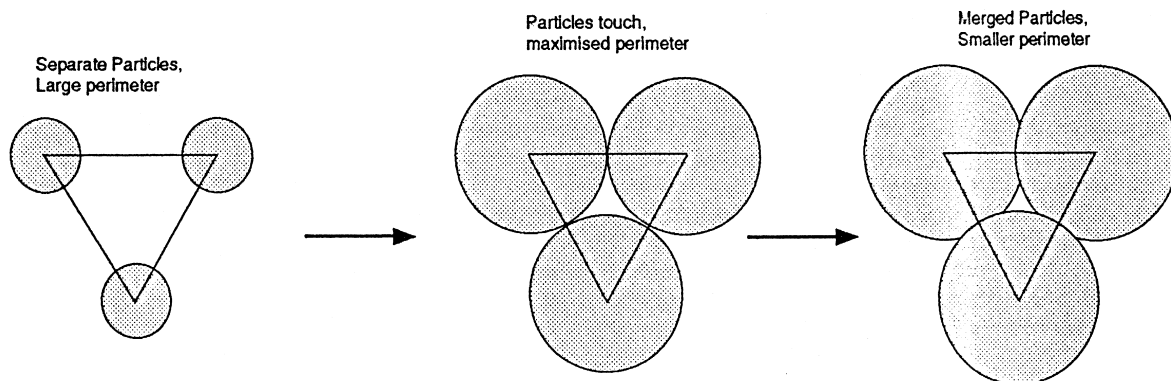

Fig. 8. Schematic illustration of the effect of particle growth on hexagonally arranged particles. On the left, particles do not touch and the perimeter length is relatively large (and is largest when the particles just touch). On the right, the particles have merged and the perimeter length is significantly reduced.
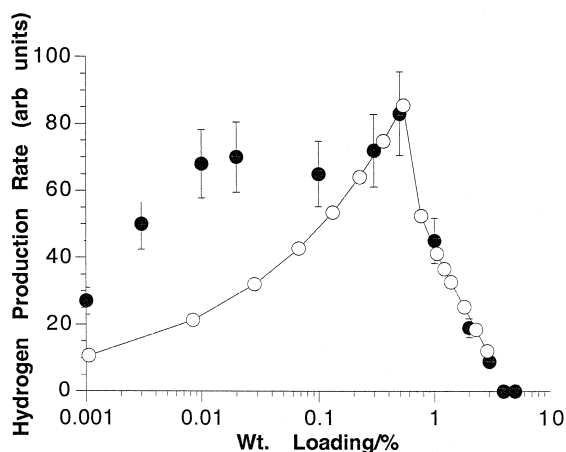
Fig. 9. Comparison of the experimental data for the metal loading dependence of hydrogen yield (filled circles) with the theoretical dependence of the active sites on loading (open circles), from Eq. (IV) which assumes that the active sites are located at the metal–oxide interface.

two is quite good, the main fitting parameter being the density of nucleation sites at which the Pd particles first form. It is not intended that this be a quantitative fit since several factors have been ignored in this treatment. These factors are (i) the real value for the nucleation site density and the fact that not all particles nucleate at the same low Pd loading; (ii) the modelling of equisized particles, which is related to point (i); (iii) hemispherical particles; (iv) as a consequence of the preceding assumptions the particles all touch at exactly the same loading, at which point function Z takes over from function Y, but we have assumed the geometry of this is that particles form a square array on the surface of the titania. We could include all these factors mathematically, but we would then have too many floating parameters, such that a very good fit to the data would be obtained, but from which little additional information would be derived. Suffice it to say that the qualitative fit of Fig. 9. indicates that this simple model approximates to the metal loading dependence of the rate, that is, the rate increases at low loadings due to an increase in active sites due to the extending perimeter of the particles, and this

is a sharp function at low loadings, while at a certain size the perimeter diminishes due to particle coalescence. In reality, TEM shows that at 5% loading the Pd particles apparently do not touch, even though they are inactive. Thus, it may be that there is an active area around each Pd particle which extends significantly beyond the interface (for instance, a depletion zone), but the edge of which is important for the reaction. Such a treatment would give a better fit at low loadings because of the enhanced perimeter. This will be considered in detail in a future publication.

5. Conclusions

We have studied a model, anaerobic photocatalytic degradation reaction, namely, the oxidation of methanol to carbon dioxide and hydrogen. The net oxidant appears to be water, as proposed earlier by Kawai and Sakata [8] and Sakata and Kawai [9]. The reaction occurs by dehydrogenation of methanol on Pd, a reaction which is quickly poisoned in the absence of light by strongly adsorbed CO. Light of wavelengths < 340 nm produces O^- on the titania lattice which acts as the CO oxidant, either directly itself, or by producing an activated state of water. This then maintains a steady state reaction in the presence of light. The dependence of the reaction on Pd loading is particularly illuminating, showing a sharp increase at low loadings, a maximum at $\sim 0.5\%$ Pd, and decreasing to near zero at 5% Pd. This behaviour is explained by assuming that the active site for the reaction is located at the periphery of the Pd particles adjacent to the titania. Thus, both surface titania and surface Pd are essential for the reaction. The main roles of the two components are methanol adsorption and dehydrogenation on the Pd, water adsorption and band gap excitation on the titania, while the active interface site oxidises CO adsorbed on the Pd.

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