

Photocatalytic water-gas shift reaction at ambient temperature

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Abstract

Present environmental concerns indicate that hydrogen would be suitable as a future fuel. Photocatalytic production of hydrogen is a valuable technology as a clean method of hydrogen production which can use sunlight as the energy input. The role of the photocatalyst is to absorb sunlight which can then be used to produce hydrogen. In the work reported here, catalysts of palladium on titania have been used for hydrogen production by the ambient temperature reforming of methanol, or by using CO in the water-gas shift reaction. Photocatalysis enables both to take place at ambient temperature. Water is the oxidant under these anaerobic conditions. The reaction appears to take place at the boundary between metal nanoparticles and the support, TiO₂. A complete mechanism for the reaction is proposed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photocatalysis; Titania; Hydrogen production

1. Introduction

Photocatalysis is currently attracting a wide range of interest. These include the photocatalytic production of hydrogen from water (based on the work of Fujishima and Honda [1]), organic synthesis [2], and more direct environmental concerns such as the removal of pollutants from water [3,4].

Previous work in this group [5–7] has involved the study of the photocatalytic production of hydrogen from various reactant mixtures, especially those containing methanol, water, and a photocatalyst (Pd/TiO₂) under anaerobic conditions. Methanol was chosen as a small molecule with only one functional group, making it suitable as a model for more complex reactions. A mechanism was proposed (Fig. 1) in which the titania, palladium and water play important roles [5–7]. The palladium adsorbs methanol onto its surface (a). It then dissociates at the hydroxyl group to give an adsorbed methoxy species. This further decomposes to give one molecule of adsorbed carbon monoxide and two molecules of gaseous hydrogen. At this point the reaction ceases because the surface sites become poisoned with strongly held adsorbed CO. Upon switching on the light a steady-state reaction then occurs. The carbon monoxide is then oxidised by a photogenerated species to give carbon dioxide. The titania absorbs light to provide e⁻/h⁺ pairs

(b), and the energy in the excited titania generates an oxidising species, proposed to be O⁻. There is no reaction in the absence of light, implying a photogenerated species is the oxidant. Water is the net oxidant, determined from the stoichiometry of the reaction. The oxidant cannot come from the normal lattice species because it would simply react with the hydrogen to make water in the absence of light. This oxidant O⁻ reacts at the interface between palladium and titania, where the CO is oxidised (c), and so the particle interface is thought to be the location of the active sites. The vacancy left on the titania is filled by water (d), which liberates hydrogen (e). The hole on palladium is filled by another molecule of methanol. In this way a catalytic cycle is formed, and it can repeat itself as long as methanol and water are available (f). For every mole of methanol reacted, three moles of hydrogen are generated.

This present work concerns the role of carbon monoxide, carried out mainly to examine the validity of the proposed mechanism. Previous work [8] shows that when methanol is introduced onto the surface of a Pd(1 1 0) single crystal, hydrogen is evolved, but adsorption and reaction is stopped once a monolayer of carbon monoxide builds up and poisons the surface. Titania is known to be photoactive so it is not unreasonable to suggest that an oxidant may be generated by the surface of the titania in the presence of light, preventing poisoning. Carbon monoxide is an intermediate in the proposed mechanism, and so it should be possible to use CO as a reactant if the model shown in Fig. 1 is correct.

The reaction with CO is the water-gas shift reaction (albeit with liquid water) and can be written as:

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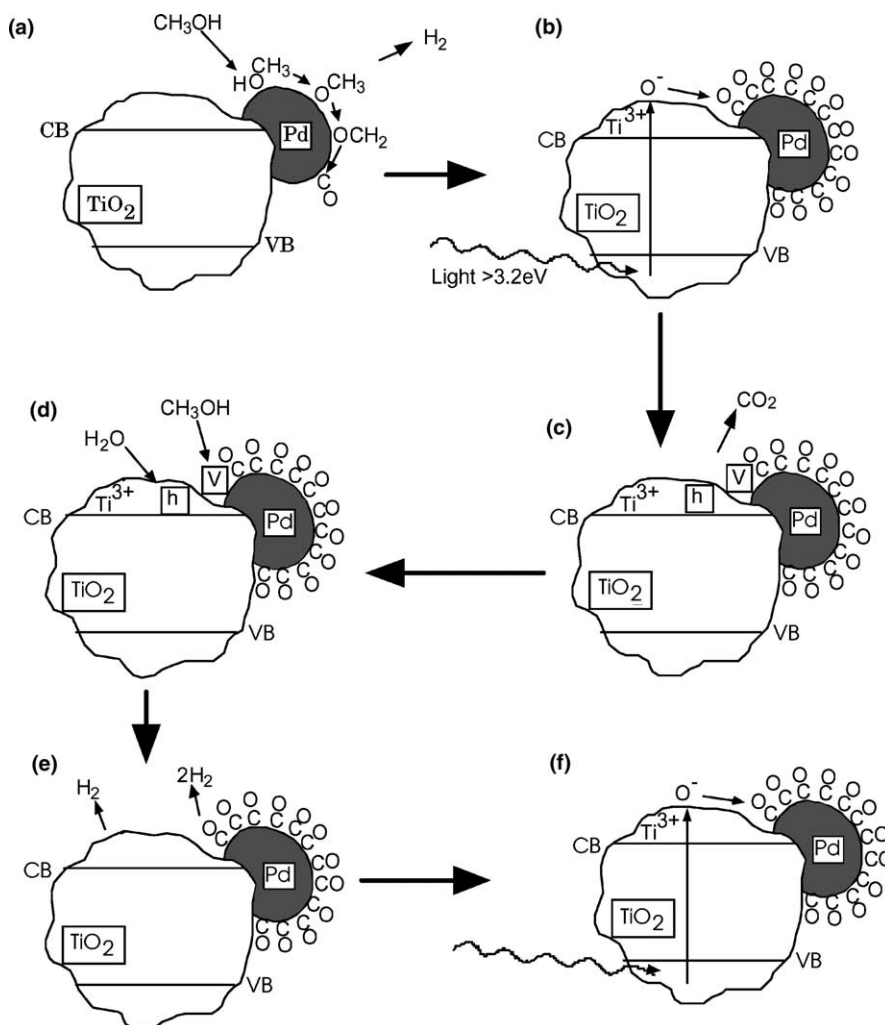
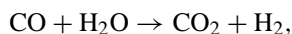


Fig. 1. Schematic representation of the proposed mechanism of hydrogen production from a methanol solution with Pd/TiO₂ photocatalyst, from [5].



$$\Delta H \sim 0 \text{ kJ mol}^{-1} \text{ (for liquid water)}$$

$$= -42 \text{ kJ mol}^{-1} \text{ (for gaseous water),}$$

$$\Delta G = -20 \text{ kJ mol}^{-1} \text{ (for liquid water)}$$

$$= -28 \text{ kJ mol}^{-1} \text{ (for gaseous water)}$$

The reaction is entropically favourable because the number of moles of gaseous product is greater than that of reactants, and the products are gaseous. However, the reaction does not proceed at low temperatures because of kinetic limitations, even in the presence of a catalyst. It must be noted that this reaction differs in hydrogen yield from the reaction with methanol, as only one mole of hydrogen is generated per mole of CO.

2. Equipment

The equipment used in this work is similar to that described by others [9]. It consists of a Pyrex reaction flask,

with a purge line and a septum for sampling. The Pyrex vessel does not absorb a significant amount of light, although it does effectively cut off all wavelengths of less than 300 nm. The reaction mixture (typically 0.2 g catalyst and 100 ml deionised water) was placed in the flask and purged with Ar for 1 h in order to remove dissolved gases. The appropriate amount of CO was injected into the vessel after purging. 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. Samples of 0.2 ml 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 MS 13X column, 2 m long. The retention time for hydrogen was approximately 90 s with an argon carrier gas flowing at 21 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 this method [7].

Catalyst preparation was carried out using the incipient wetness method. The work concentrates on Pd/TiO₂, since this proved to be one of the most efficient catalysts for the reaction. Typically, the preparation procedure was as follows. The appropriate mass of metal salt (PdCl₂) 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 photoactive support, P25 titania (Degussa). The impregnated support was then dried in an oven at 110 °C for 2 h, after which it was ground in a pestle and mortar and calcined at 500 °C for 2 h. It was sieved to an aggregate size of less than 53 μm before use.

3. Results and discussion

3.1. Effect of CO on the system

When carbon monoxide is injected into a reactor which contains water and a photocatalyst, hydrogen is produced (Fig. 2), but only after illumination begins. The catalyst used was 0.2 g of 0.5 wt.% Pd/TiO₂. This goes some way to validating the proposed mechanism, with adsorbed CO as an intermediate.

The rate increases with increasing volume of carbon monoxide. It reaches a maximum at 1 ml CO, then reaction rate falls with increasing volume of CO, until it is approximately zero at 10 ml CO.

The rate of hydrogen evolution for the CO reaction is a factor of 12 smaller than that for the corresponding methanol reaction, that is, four times smaller than might be expected if the turnover were the same as for methanol. The CO reaction

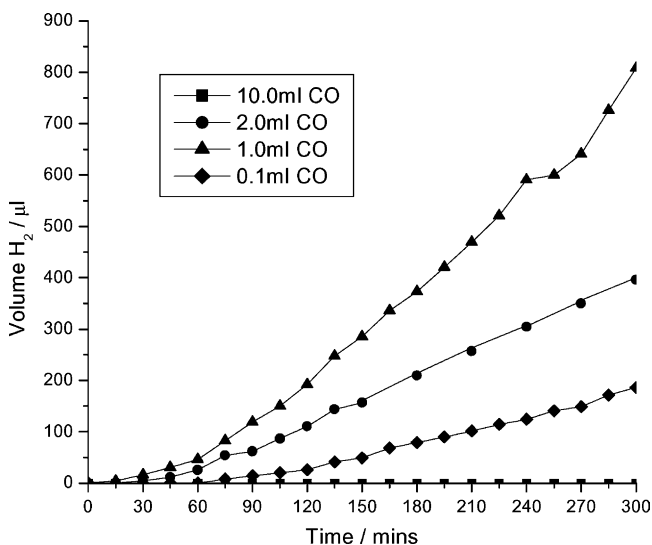
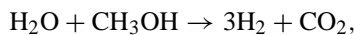
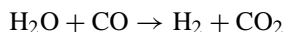


Fig. 2. Volume of hydrogen evolved against time for various volumes of carbon monoxide added to the reaction vessel.

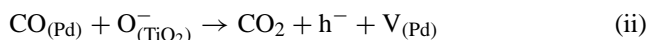
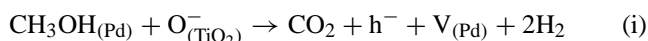
should generate one-third of the amount of hydrogen than the methanol reaction, according to the equations:



$$\Delta H = +131 \text{ kJ mol}^{-1}, \Delta G = +10 \text{ kJ mol}^{-1}$$



The further factor of four differences in rates may indicate several things. It is possible that the rate determining step is different for the two reactions (note that the latter reaction is favoured thermodynamically, but we are well away from equilibrium here). In our proposed mechanism, methanol adsorbs onto the surface and quickly decomposes to give a layer of carbon monoxide. This is then oxidised to give carbon dioxide and the holes and vacancies necessary for the continuation of the cycle.



The first step (i) is not available to the carbon monoxide reaction. It could be that this step is rate determining for methanol (for instance, methoxy decomposition), whilst the second step (ii) is rate determining for carbon monoxide. This would affect the dominant surface intermediate and the rate constant.

3.2. Effect of palladium loading

In order to study the effect on reaction rate, a series of catalysts of different weight loading of palladium on titania were made. These were tested in a standard liquid phase reaction, into which 1 ml CO was injected.

A maximum in rate is found for 0.5 wt.% Pd/TiO₂ (Fig. 3), as for the reaction with methanol [3]. The rate increases

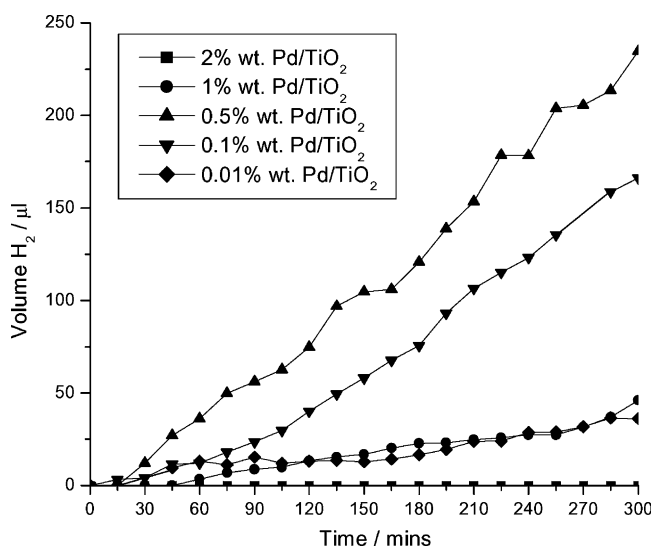


Fig. 3. The effect of palladium loading on the CO reaction.

with increasing loading to a maximum, after this, the rate decreases sharply—there is effectively no reaction (or possibly, a very long induction time) at 2 wt.% Pd/TiO₂. The rate at a very low loading of palladium is high, even though titania alone shows a very low rate of reaction.

This reactivity pattern can be related to the boundary of palladium, as reactivity is postulated by the proposed mechanism to take place at the titania–palladium interface. Boundary length would increase with particle size, which would increase with weight loading. It would reach a maximum rate when the palladium particles are big enough to almost touch, where a maximum perimeter is reached. Any greater loading would give a decrease in rate of hydrogen evolution as the perimeter decreases due to agglomeration of particles. However, there is an inconsistency here, because the reaction rate increases with loading up to 0.5% weight loading, then it decreases, and at a loading of 2 wt.% Pd, the rate is zero. A simple calculation of the coverage by palladium and the point at which particles overlap indicates that the reduction in permitted sites should not happen until a loading of ~10 wt.% Pd. This inconsistency between the optimum loading of the palladium experimentally and by calculation has been explained elsewhere [5] by invoking an active site which is at a boundary somewhat remote from the particle.

From previous work using TEM [7], the particles have an average radius of approximately 10 Å and are hemispherical. Using this information, the density of palladium (~10 g cm⁻³), and the surface area of TiO₂ (~50 m² g⁻¹), the area of a particle is calculated to be about 19,000 Å². From this information, and the loading for maximum rate, we can deduce that the radius of this boundary region is about 70 Å.

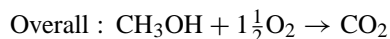
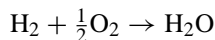
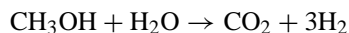
The nature of the boundary region is unclear but appears to be the location of the active sites for the reaction. It is possible that there could be a spillover and build-up of intermediates at the metal–support interface, so that the reactions take place at a site slightly remote from the metal

surface. For example, when the metal surface is saturated with CO, some could be displaced onto the support, or that the oxidising species is depleted around the particles so that CO builds up there. On the other hand, it could be that, due to band-bending in the vicinity of that palladium particles, the appropriate energetics only apply at this point somewhat remote from the metal nanoparticle.

3.3. Effect of oxygen

Immediately after the injection of oxygen into the methanol reaction, it can be seen (Fig. 4) that the reaction rate is retarded, implying another reaction is promoted by the presence of oxygen. The difference between the peak where oxygen is injected and a line continuous with the production thereafter is in the order of 2 ml. The evolution of hydrogen was resumed at its original rate after this volume of hydrogen had been removed from the system.

This implies that the water is probably reformed in the following manner. When carbon monoxide alone is injected, it is sufficient to carry out such a reaction.



In contrast, the injection of nitrogen has no effect whatsoever on the reaction rate, proving that this is not merely a dilution effect. In order to check whether this reaction was photocatalytic or not, the reaction was repeated, but this time with the light switched off as the oxygen was injected. When oxygen was added, the hydrogen was consumed entirely (Fig. 5). There was no reversible effect as seen before, when the light was on. All the hydrogen was consumed, and no more was produced during the time of darkness. No hydrogen was produced when the light was switched on again,

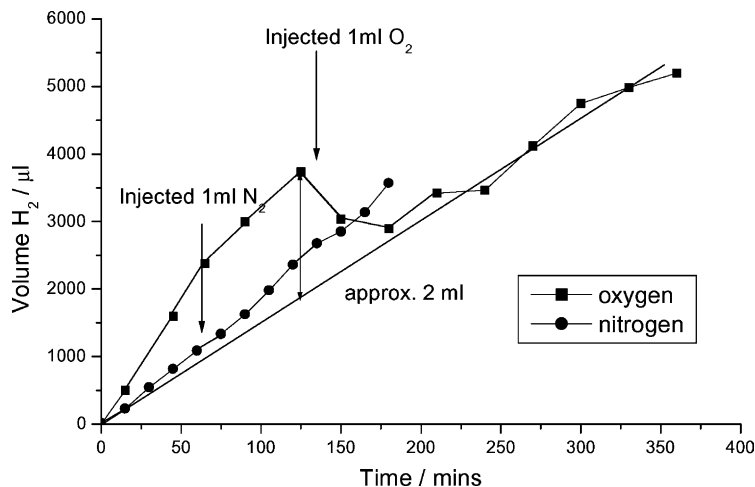


Fig. 4. Effect of oxygen on an established methanol reaction.

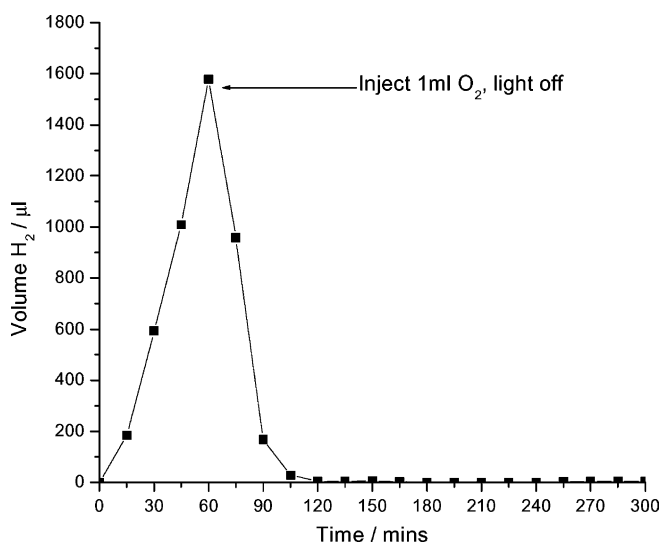


Fig. 5. Effect of injecting oxygen into a methanol reaction in the absence of light.

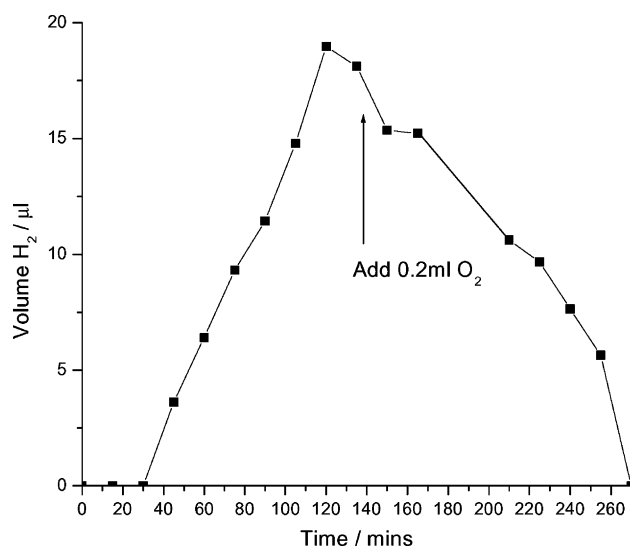


Fig. 6. The effect of injecting oxygen into the carbon monoxide reaction.

presumably because oxygen is still consuming any hydrogen produced. The addition of oxygen to the carbon monoxide also caused this retardation, but as the total volume of hydrogen was low, all hydrogen was consumed (Fig. 6). This

could not be explained as the oxygen poisoning the catalyst, because that would lead to the volume of hydrogen in the flask remaining constant.

4. Conclusions

The introduction of carbon monoxide into a reactor containing a photoactive catalyst (0.5 wt.% Pd/TiO₂) and water leads to the production of hydrogen. This supports a mechanism involving carbon monoxide adsorbed on the palladium components as a key step in methanol photocatalytic reformation. Carbon monoxide adsorbs onto the palladium and then reacts with an oxidant which is photogenerated on titania. Hydrogen is generated by reaction of water with the photogenerated hole on the titania. The rate is one quarter of that for methanol. This may be due to variations in the rate determining step. The effects of palladium loading on the titania support are very similar to those observed for the methanol reaction. Hydrogen production is retarded by the presence of oxygen, due to a scavenging of hydrogen by catalytic reaction with oxygen on the palladium.

Acknowledgements

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