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The photocatalytic reforming of methanol

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Abstract

Sustainable hydrogen production systems are of great importance to the future of mankind, and photocatalysis represents one of the technologies currently showing promise as a method for hydrogen production. Understanding how such catalysis proceeds is important, and here we report some of our work on the anaerobic photocatalytic reforming of methanol at ambient temperatures. This utilises a metal-titania catalyst, but only a very limited range of metals are suitable, the best being Pd, Pt and Au. The reaction requires both surface titania and metal to be present, and shows a very strong dependence on the loading of the metal. A model for the reaction is presented.

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1. Introduction

With mounting concern over climate change there is pressure for the increased use of renewable resources and in particular, for finding ways of harnessing solar energy. Photocatalysis is an attractive tool in this respect and is becoming important in applications ranging from the decomposition of aqueous pollutants to the photochemical splitting of water to generate hydrogen. Approximately 95% of present hydrogen needs are sourced from the steam reforming of methane, a non-renewable source, and so the possibility of using sunlight to generate hydrogen as a renewable green fuel is an enticing prospect.

Photocatalytic substrates are generally semiconductors which interact with the incident radiation by electron-hole pair separation and these are then employed in reduction and oxidation steps. The field was pioneered by the work of Fujishima and Honda with TiO_2 [1], although the large band gap of TiO_2 (3.2 eV) means that it is only active under UV illumination, a relatively small component of solar radiation. However, semiconductors with smaller band gaps than TiO_2 are generally less stable under irradiation and photocatalytic research has therefore concentrated on TiO_2 [2]. As well as the poor response to sunlight, however, TiO_2 catalysts also show poor catalytic efficiency due to recombination of the electron-hole pair and recombination of the dissociated molecules at the surface. One approach to resolving these problems is the addition of nanoclusters of a transition metals. These metal clusters can trap electrons, preventing recombination, the hole is then free to migrate to the surface of the TiO_2 where it can catalyse oxidation, whilst the electron enables reduction on the metal, producing a physical separation of reaction products.

It is in this area that we have focused our attention, in parallel with studies of adsorption and reaction with metal clusters supported on semiconductor surfaces in the absence of light activation. Because hydrogen production rates are low in these systems we have studied mainly photochemical reforming of methanol over TiO_2 catalysts loaded with metal nanoparticles present. Previous work on such systems has been rather limited, but others have shown that methanol reforming is possible at ambient temperature with the use of photocatalysis [3–6], and that hydrogen production rates are generally much higher than those observed for direct water-splitting. Our objective is to understand the detailed mechanism and kinetics of this reaction, and to develop more efficient catalysts for the process.

2. Experimental

The reaction vessel consists of a ~100 ml pyrex flask with a purge line and a septum for sampling. The Pyrex glass cuts off

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all wavelengths below 300 nm. The catalyst was prepared using the incipient wetness method in which the appropriate mass of metal salt (usually $PdCl_2$, $HAuCl_4 \cdot 3H_2O$ or $H_2PtCl_6 \cdot 6H_2O$) was dissolved in acidified water. A volume just sufficient to fill the pores of the photoactive support, P25 titania (Degussa) was added to the catalyst and allowed to dry in an oven at ~380 K for 2 h. After drying the catalyst was calcined at 780 K for 2 h, ground in a pestle and mortar and sieved to an aggregate size of less than 53 μm. Typically 0.2 g catalyst and 100 ml deionised water were placed in the flask and purged with Ar for 1 h in order to remove dissolved gases. The appropriate volume of methanol was added and the mixture was stirred with a magnetic stirrer, and was illuminated by a 400 W Xe arc lamp (Oriel model 66084) from the side of the flask. Samples of 0.2 ml were taken periodically from the gas phase 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}. Peak areas were determined by integration with an LDC Milton Roy CI-10 integrator.

3. Results and discussion

3.1. Photocatalysis on metal/titania

Fig. 1a shows the results for anaerobic photocatalysis on titania, with various metals added. Titania alone is almost inactive for hydrogen production, whereas with the addition of certain metals it exhibits reasonably good performance for this reaction. The best metal appears to be Pd in Fig. 1a, but a few other metals also exhibit reasonable activity. These include Pt, Ir, and perhaps most surprisingly, Au. Rh and Ru exhibit definite activity, but it is significantly lower than that of Pd, while the other metals investigated exhibit essentially no activity at all. This probably relates to the ease of reducibility of the surface layers of the metal, with the precious metals which are most noble existing as the pure metal (at least at the surface), whereas the others may remain as oxides. The metal component is likely to be necessary for the initial dehydrogenation of the methanol, as outlined in the mechanism below. Note that, although Pd appears to be best when comparing similar loadings, if we replot Fig. 1a in terms of molar loading of the metal (Fig. 1b), then Pt appears to be a little better than Pd. The overall reaction corresponds with the ambient temperature reforming of methanol with water.

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

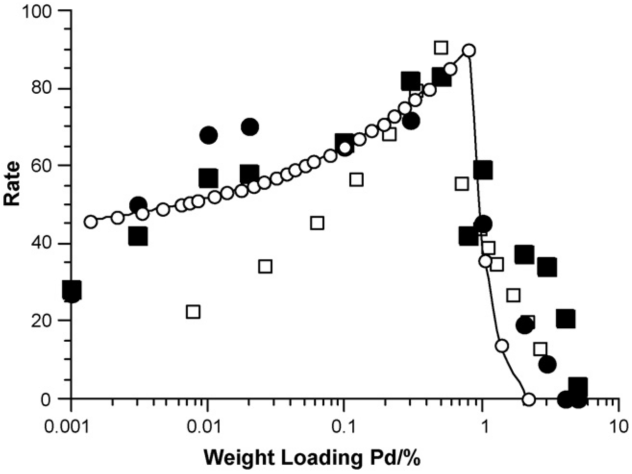

Fig. 2. The dependence of the rate of hydrogen evolution on weight loading of Pd on the TiO_2 support for two sets of catalysts, showing the level of reproducibility of repeat preparations/experiments (solid data points). Also shown is the mathematical form of the rate dependence upon loading from two treatments; the simple particle perimeter model (open squares) and the extended perimeter model (fitted line and open circles). For the simple model the loading for the maximum rate has been arbitrarily fitted, but this is not so for the extended model. The parameters used for the latter were an extended perimeter 15 nm beyond the edge of the particle and a particle density of 4×10^{11} particles cm^{-2}, with hexagonal particle packing [7].

3.2. The active site: metal loading dependence

As shown in Fig. 2, there is a very unusual and marked dependence of the reaction rate on the metal loading, showing a maximum at low loadings of Pd, at ~0.5 wt.%. However, other features are also apparent in Fig. 2, most notably that very low loadings of Pd produce a marked increase in reaction rate, while the rate of hydrogen evolution is zero for loadings above 4%. A model has been developed to explain such data [7,8], and this is based on the assumption that the active site for the reaction (that

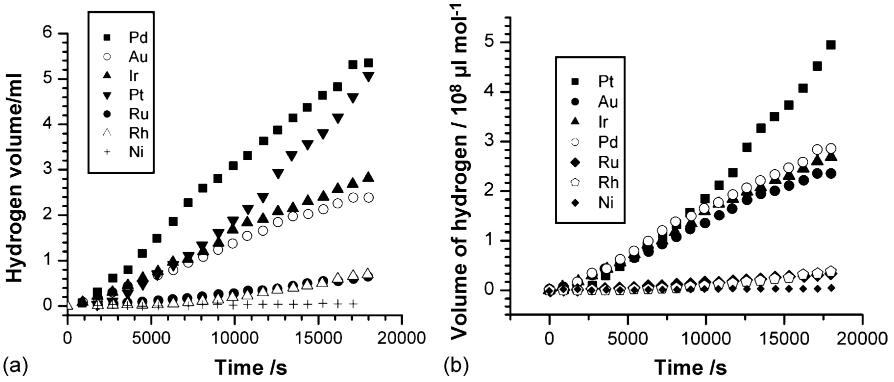

Fig. 1. (a) (left panel) shows the hydrogen production for the same weight loading (1%) of a variety of group 8–11 elements while (b) (right panel) shows the production per mole of metal loaded.

is, the site involved in the rate determining step) is located at the periphery of the metal particle. The simple explanation for the *shape* of the curve in Fig. 2, then, is that, as the metal loading increases, so does the extent of the perimeter (in fact it is a $W^{1/3}$ dependence where W is the wt.% loading [7]). However, above a certain loading, the metal particles begin to touch and overlap. With an idealised model of perfectly ordered, mono-sized hemispheres, this is the point of maximum perimeter; as loading further increases, so the amount of perimeter decreases, and hence the rate diminishes (the dependence on weight loading in this range is inverse cosine of reciprocal loading [7]). In fact, we have shown that this model, though conceptually correct, does not quantitatively fit the data in one important respect, that is, it cannot fit the low loading of the maximum rate. For normal situations (and even for rafts of monolayer particles) the maximum occurs theoretically at higher loadings. A possible explanation for this is that the active sites are located near, but remote from the metal particles, this then provides a model which fits the data more exactly. In particular it fits the maximum better, because perimeters begin to overlap at much lower loadings, hence reducing the loading for maximum rate. However, the exact reason why the sites are located in this position is not certain but is considered in more detail in Section 3.4.

3.3. The effect of methanol concentration on the rate of hydrogen evolution

To probe the proposed mechanism of methanol oxidation further, the rate of hydrogen production over palladium modified TiO_2 in the presence of UV light was studied as a function of methanol concentration. Fig. 3 shows the evolution of hydrogen with time for different volumes of methanol added to 0.2 g of 0.5 wt.% of Pd/TiO_2 and 100 ml of deionised water. In all the experiments the conversion is low and thus the rate of hydrogen formation is not affected by reactant concentration changes during the time of the experiment. Above ~30 μl the methanol volume has little effect on the rate of hydrogen evolution but at lower volumes a significant decrease in hydrogen production is evident, that is a typical kind of Langmuirian catalytic behaviour, as also manifested in Fig. 4. Fig. 4 is a plot of the rate of hydrogen production as a function of methanol concentration. The specific surface area of the TiO_2 catalyst was 59 m^2/g. Assuming 1.5×10^{19} sites per m^2 (which is variable, depending on the surface planes exposed, but which is the surface atom density of the [0 0 1] plane of rutile titania) this corresponds to about 1.8×10^{20} surface sites in our sample. By extrapolation of the rates at low methanol concentration, the rate appears to be maximised at ~10 μl of methanol as shown in Fig. 4 corresponding to $\sim 1.4 \times 10^{20}$ methanol molecules, which, within the approximations and accuracy involved, implies that the catalyst maximises in reaction rate when ~1 monolayer is adsorbed on the catalyst surface. This corresponds with saturation of methanol on the surface, and thus that adsorbed methanol is a crucial part of the reaction mechanism. We have shown in earlier molecular beam work that methanol is unstable on Pd surfaces at ambient temperature [9], decomposing to give gas phase hydrogen and leave a Pd surface poisoned for further reaction by CO. On the other hand, methanol adsorbs to a monolayer coverage on titania at ambient temperature to leave a very unreactive layer, which does not dehydrogenate until ~500 K [10,11]. Note such reactions have been shown by us previously to be first order in the light intensity, so that the maximum rate of hydrogen evolution in Figs. 3 and 4 can be increased by increasing the light level, which would result in faster removal of poisoning CO from the system.

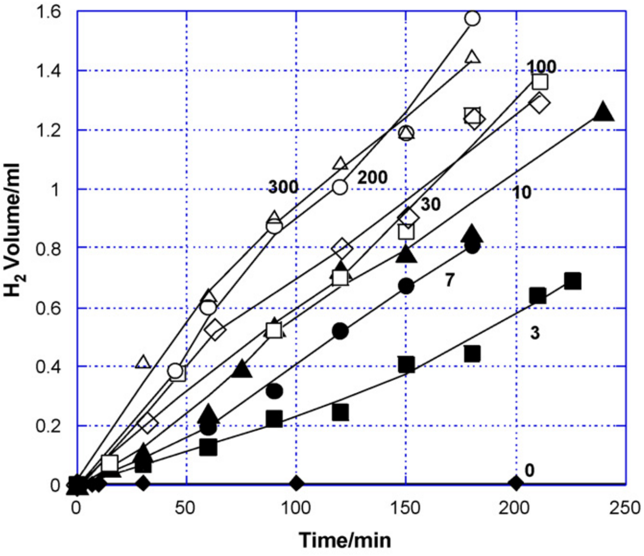

Fig. 3. The effect of methanol concentration on hydrogen production. The lines represent smoothed fits passing through the origin, and the numbers in the figure are the number of microlitres of methanol present in the reacting solution.

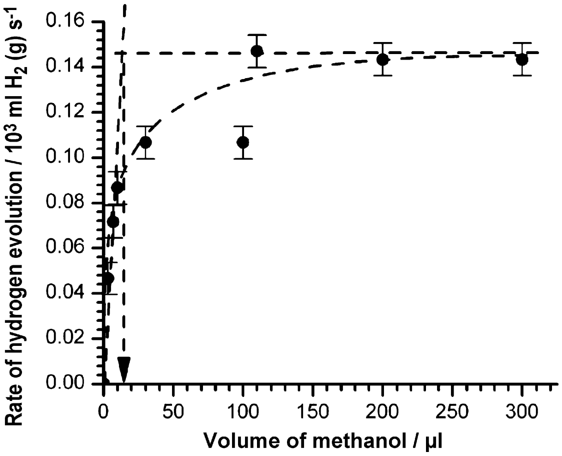

Fig. 4. The rate of hydrogen production vs. methanol concentration. The line is drawn to give an approximate idea of the point of concentration at which the rate is maximised and this amount corresponds with about a monolayer equivalent of methanol.

3.4. The reaction mechanism

The mechanism of the reaction is illustrated in Fig. 5 as a catalytic cycle. The important dehydrogenation reactions take

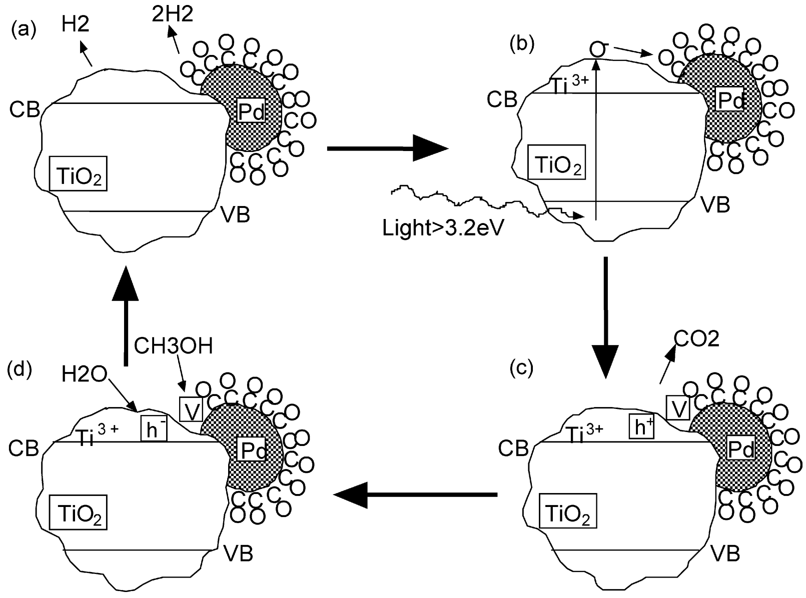

Fig. 5. The proposed model for the photocatalytic reforming of methanol on Pd/TiO_2.

place on the metal component, as shown by molecular beam work (Fig. 5a) and, in the absence of light, the reaction would stop at this point, with the metal sites blocked by CO. CO is strongly held on precious metals (desorption temperature ~450 K [12]), with a long lifetime at ambient temperature. Others report that hydrogen evolution occurs due to a photocatalytic process (photoreduction of H^+ [13]), but we feel this is extremely unlikely; adsorbed hydrogen is unstable on metals at this temperature and will evolve naturally, without the need for photoreduction. Light is required to activate the sample for steady-state hydrogen evolution by band-gap excitation to produce highly activated oxygen species (possibly O^- species) on the titania (Fig. 5b). We have shown that the wavelength threshold for the reaction is at ~3.2 eV, the measured gap energy for titania. The electrophilic species attacks the CO at the periphery of the particle and removes CO as CO_2 (Fig. 5c), enabling another methanol molecule to adsorb and produce hydrogen (Fig. 5d) and so restart the cycle. It is proposed that water is reduced at the titania hole, replacing the lost anion. Since the CO is relatively strongly held, the rate determining step is likely to be that involving adsorbed CO, which is also the most stable species present in the system.

Exactly how the reaction proceeds at the molecular scale is not clear. The implication of the mathematical relationships above is that the boundary appears to be somewhat remote from the metal particle periphery. If so, then there has to be net diffusion of species away from the metal particle to the active site. It is likely that this diffusing species is adsorbed CO, which must find the active oxygen species where it is oxidised to CO_2. Diffusion on titania should be facile, since CO is very weakly held on titania. Indeed the lifetime there must be short, but nonetheless, it is quite possible for such weakly held species to diffuse over a significant number of sites in that short lifetime, as described elsewhere [14].

3.5. The reaction on gold

It is somewhat surprising that an element as inactive as gold can show activity for photocatalysis, but, as shown above, it is one of the most active metals for the reaction. Haruta et al. [15,16] and Hutchings et al. [17,18] have shown that gold in nanoparticulate form is, in fact, active for a variety of catalytic reactions, and is one of the most active metals, in combination with the correct support, for the oxidation of CO, showing 100% conversion at ambient temperature [8]. There are also some limited reports of activity for photocatalytic degradation of ethanol in aqueous solution [19,20]. In our work on photocatalysis with gold [20], its behaviour is broadly similar to that of Pd, as described above, but there are some differences. First of all, the activity shows two maxima, at about 0.2% and 2% weight loading. We do not know the reason for this, but it may be related to different morphologies of the Au at the two loadings. A similar dual maximum has been reported by Sermon et al. for the hydrogenation of pent-1-ene [21]. Overall though, like Pd, the rate is low at low loading and drops to zero at high loadings, presumably for the reasons outlined in Section 3.4. Secondly, we could not find significant activity for the WGS reaction, unlike Pd. We propose that this is due to a somewhat different mechanism for the reaction; the surface is no longer blocked by CO, but is instead blocked by another intermediate. It is possible that this is the methoxy group, but we have recently shown by TPD that a formate species is produced on gold [22], and decomposes to produce CO_2 and hydrogen at elevated temperature. Whether this or the methoxy is the species present at room temperature is uncertain. Thus, without light, the reaction stops at a partially dehydrogenated species, and so does not form adsorbed CO. CO is also weakly bound on gold and this explains why the WGS reaction does not proceed well. The situation is reversed on Pd; CO is strongly bound, whereas methoxy and formate are unstable at ambient temperature on that metal.

4. Conclusions

Hydrogen can be produced by the anaerobic photocatalytic reforming of methanol at ambient temperatures. The reaction requires a combination of a metal which is active for dehydrogenation and a photoactive support (in this case titania). The support provides the centre for storing the energy to drive the reaction (by band-gap excitation), and an activated oxidising species. The active site for the reaction appears to be at the periphery of the metal particles, resulting in a severe reduction in rate at high metal loading, when the periphery sites are limited in number. The catalysis is bi-functional in nature, requiring both titania and metal to be available *at the surface*.

Although this process is of interest in terms of environmental protection and the reduction in use of fossil fuels, methanol itself is a fossil fuel-derived chemical (by steam-reforming of methane). Thus, a cleaner and more sustainable route must involve water splitting. Considerable work is proceeding in this direction around the world, including that in our laboratory, and Anpo et al. [22] have elegantly demonstrated relatively efficient water-splitting systems with product gas separation. We look forward to further developments in this area, with the aim of sustainability, even if at slow production rate, of useful, natural hydrogen production systems.

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