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Sustainable H_2 gas production by photocatalysis

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ABSTRACT

The photocatalytic, ambient temperature, reforming of oxy-hydrocarbons, used to generate hydrogen gas, has been studied in some detail over Pd-titania systems and a general mechanism is developed. In the case of water–methanol mixtures, methanol adsorption on the metal surface results in hydrogen gas evolution and the formation of adsorbed CO. The latter is subsequently oxidised by an oxygen species (O^-) generated in the semiconductor by UV light. Desorption of the resulting CO_2 enables another methanol molecule to adsorb, restarting the cycle. Water is reduced at the titania hole replacing the lost anion and generating further hydrogen. We will discuss the evidence for this mechanism and extend it to consider the photocatalysis of higher alcohols including ethanol, butanol and glycerol.

1. Introduction

The use of fossil fuels as the main energy source in modern society not only brings benefits of convenience and an established technology, but also has the well-known disadvantage of CO_2 release. This gas which is produced by most combustion processes is believed to be the main culprit involved in global warming and shows a significant percentage increase since global industrialisation [1]. An attractive alternative to fossil fuels as an energy source is H_2 which is widely considered to be the most promising clean energy carrier for the future and its use is being explored in many areas of technology [2]. The fundamental problem that underlies this approach however is finding an environmentally friendly source of hydrogen.

Water is an obvious source for both hydrogen and oxygen and there is therefore a great deal of interest in methods by which the individual components might be economically obtained. The use of photocatalysis for water splitting to generate H_2 has risen in interest over the past few decades. Previously we [3], and others [4], have reported on hydrogen production using ambient temperature reforming of methanol and glycerol on a variety of titania-supported catalysts. A mechanism for methanol reforming over Pd modified TiO_2 catalysts was reported earlier [5] in which the precious metal provides the active site for alcohol dehydrogenation whilst the titania acts as a photon absorber creating an active oxidising species. The dehydrogenation of alcohols on Pd surfaces involves O–H bond cleavage leaving an alkoxy group on the surface. This is further dehydrogenated to CO and gas phase hydrogen. The aim of this paper is to explore this proposed mechanism in more detail by comparing the photocatalytic reactivity of a number of primary, secondary and tertiary alcohols: ethanol, 1-propanol, 1-butanol, cyclohexanol and glycerol and glucose. From the observed activity of these molecules we deduce further details of the mechanism.

2. Experimental

The reaction vessel consists of a Pyrex reaction flask with a purge line and a septum for sampling. The catalyst was prepared using the incipient wetness impregnation method in which the 0.01 g of $PdCl_2$ (99.9%, Sigma–Aldrich) dissolved in 1.5 ml of distilled water acidified with one drop of HNO_3 was added drop wise into the 2 g of titania (P25, Degussa) and thoroughly grind. This was heated at 200 °C for 2 h followed by calcination at 500 °C in air oven for 3 h. The catalysts used here had a loading of 0.5 wt% Pd with respect to the support, this loading being shown previously to give optimum photocatalytic yields [5]. The as-prepared catalyst was ground in a pestle and mortar and sieved to an aggregate size of less than 53 μm. The reaction mixture, consisting of 0.2 g catalysts and 100 ml deionised water, were placed in the flask and purged with Ar for 30 min to evacuate dissolved gases. 100 μl of alcohols – methanol (Sigma–Aldrich 99.8%), ethanol, 1-propanol, 1-butanol, 2-butanol, 3-butanol and glycerol (Fisher Scientific, 99%) 2-propanol (Acros Organic 99%), and 0.5 g of D-glucose (Analar) and 0.5 g sucrose (FSA Laboratory Supplies) were added respectively, and the mixture was stirred with a magnetic stirrer and illuminated with a 400 W Xe arc lamp (Oriel model 66084) from the side of the flask. Samples of 0.2 ml gas were extracted by syringe and

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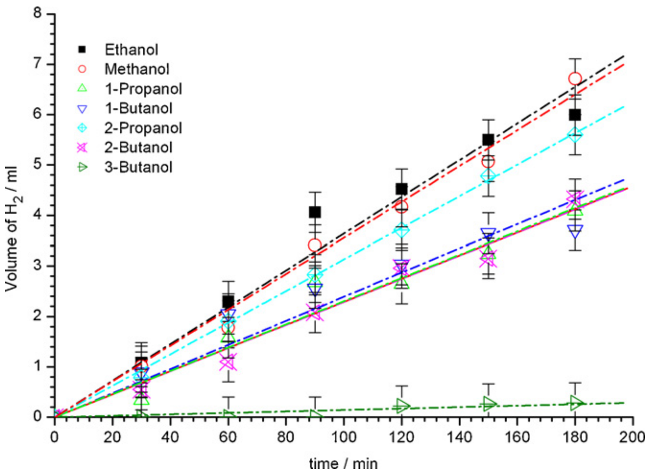

Fig. 1. A plot of H_2 production from the photocatalytic reforming of alcohols: primary alcohol (methanol, ethanol, 1-propanol and 1-butanol), secondary alcohol (2-propanol and 2-butanol) and tertiary alcohol (3-butanol).

analysed using a Varian 3300 gas chromatograph with a thermal conductivity detector and MS 13X column, 2 m long. Calibration of the hydrogen gas volume measurement within the photoreactor showed an error of approximately ±0.8 ml. For identification of the by-products, 0.2 ml of gas samples after 3 h of reaction respectively were analysed by injection into a sampling system attached to a Hiden Analytical quadrupole Hal 201 mass spectrometer.

3. Results and discussion

Fig. 1 shows H_2 production from a series of primary alcohols (C1–C4), secondary alcohols (2-propanol and 2-butanol) and a tertiary alcohol (3-butanol) over a 0.5% Pd/TiO_2 photocatalyst. The hydrogen production rate from the primary and secondary alcohols is fairly similar over 3 h of reaction. Note that in the absence of a photocatalyst or UV light irradiation, no hydrogen was produced. Further analysis of the gas phase was carried out after 3 h of reaction using mass spectrometry. This showed that ethanol produces methane as the only major by-product, 1-propanol produces ethane and 2-propanol produces methane. 1-Butanol and 2-butanol produce propane and ethane respectively. However for the C3 and C4 alcohols, the alkane derivative of its parent alcohol was also observed with propane being obtained from both 1-propanol and 2-propanol and butane from both 1-butanol and 2-butanol. A summary of the products obtained from each reaction is given in Table 1. The dehydration of alcohols, and in particular propanol, is frequently used as a probe of the acid–base properties of metal oxide surfaces: acid sites catalysing dehydration to produce propene whereas basic sites lead to acetone formation. With titania, propene is the dominant product of propanol reaction at 400 K [6]. In the photocatalytic reforming reaction only trace quantities of propene were observed indicating that the production of propane is due to further hydrogenation at the metal sites. Pd is an excellent hydrogenation catalyst and can carry out such reactions at low temperature [7]. We suggest here that the dehydration reaction is possibly driven by photo-stimulated reaction followed by hydrogenation of the alkene, due to the availability of hydrogen in the reactor from the photo-driven reforming reaction.

Table 1
Products of the photocatalytic reactions of different alcohols over 0.5 wt% Pd TiO_2 catalysts determined by mass spectrometry.

Alcohol	Products
Methanol	H_2, CO_2
Ethanol	H_2, CO_2, CH_4
1-Propanol	H_2, CO_2, C_2H_6, C_3H_8
2-Propanol	H_2, CO_2, CH_4, C_3H_8
1-Butanol	H_2, CO_2, C_3H_8, C_4H_{10}
2-Butanol	H_2, CO_2, C_2H_6, C_4H_{10}

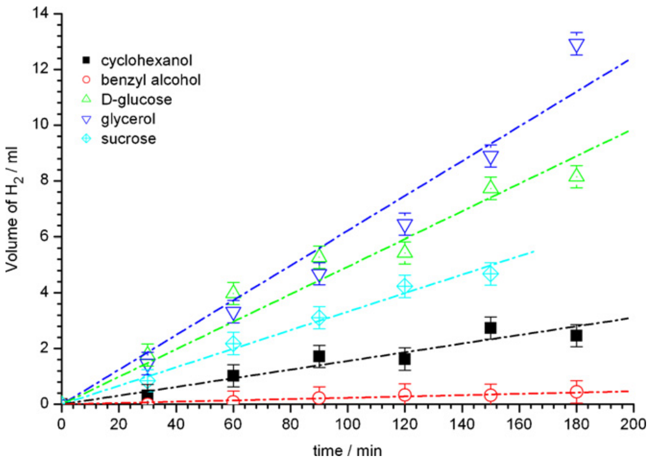

Fig. 2. A plot of H_2 production from the photocatalytic reforming of related molecules with alcohol functional group: ring alcohol (cyclohexanol), aromatic alcohol (benzyl alcohol), and sugar (D-glucose, sucrose and glycerol).

H_2 production from molecules with a hydroxyl group on the structure and somewhat more complex alcohols (cyclohexanol, benzyl alcohol, glycerol, D-glucose and sucrose) are shown in Fig. 2. 3-Butanol and benzyl alcohol produce very little hydrogen, whilst cyclohexanol gives 2 ml of hydrogen after 3 h of reaction. Sugar-type alcohols D-glucose and sucrose show good reactivity in producing hydrogen with 8 ml and 4 ml in 3 h respectively and glycerol gives 12 ml in 3 h. From all of these data there is evidence to suggest that an important linking factor is the presence of hydrogen atoms in the molecule at the alpha carbon (α) position but the absence of any significant hydrogen from benzyl alcohol indicates that whilst the presence of an α-hydrogen may be a necessary condition for reaction it is not sufficient. We return to this point below.

That the rate of hydrogen production does not increase when long chain alcohols were employed implies that the hydrogen generated does not come from the liberation of all the hydrogen atoms in the alcohol. Instead, the amount of H_2 produced can be estimated by the number of α-hydrogen atoms present. In methanol and glycerol reforming, for example, where all the carbon atoms possess α-hydrogens, complete dehydrogenation occurs on the Pd, leaving absorbed CO on the surface, and converting all the hydrogen atoms into gas phase molecular hydrogen; the rate of hydrogen production from glycerol reforming is therefore approximately twice that for methanol [8]. D-Glucose follows the prediction with 8 ml of hydrogen produce in 3 h. However, the rate does not depend solely on the number of α-hydrogens since sucrose with approximately twice the number of α-hydrogens as D-glucose produces only 5 ml of hydrogen in 3 h. Ethanol has β-hydrogens, but these are not lost in the photocatalysis, instead C–C bond-breaking occurs as evidenced by the production of methane during the reaction, together with the CO_2 and H_2. Based on the number of α-hydrogens in ethanol and the presence of methane in the products, we estimate that 2 moles of H_2 should be produced from the photoreforming of ethanol–water mixtures as written in Eq. (1). However, Fig. 1 shows that the rate is not significantly different from that of methanol (3 mol of H_2, Eq. (2))

$$C_2H_5OH + H_2O \rightarrow CO_2 + 2H_2 + CH_4 \tag{1}$$

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2 \tag{2}$$

Adsorption of organic on Pd

$RCH_2CH_2OH(l) \rightarrow RCH_2CH_2OH(a)$ 3

Dehydrogenation of alcohol

$RCH_2CH_2OH(a) \rightarrow RCH_2CH_2O(a) + H(a)$ 4

Recombinative desorption of hydrogen

$2H(a) \rightarrow H_2(g)$ 5

Dissociation of alkoxide

$RCH_2CH_2O(a) \rightarrow RCH_2(a) + CO(a) + 2H(a)$ 6

Formation of alkane

$RCH_2(a) + H(a) \rightarrow RCH_3(g)$ 7

Photoactivation

$Ti^{4+} + O^{2-} + h\nu \rightarrow Ti^{3+} + O^{-}$ 8

CO oxidation and oxygen vacancy formation

$O^{-} + CO(a) \rightarrow CO_2(g) + V_o^{-}$ 9

Polaron de-excitation

$Ti^{3+} + V_o^{-} \rightarrow Ti^{4+} + V_o^{2-}$ 10

Water reduction

$V_o^{2-} + H_2O \rightarrow O^{2-} + H_2(g)$ 11

Scheme 1. Proposed mechanism for the photoreforming of primary alcohols.

According to Gates et al., the rate determining step in alkoxide decomposition on palladium surfaces is the elimination of the β-hydrogen in the alkoxide [9] (where "β" refers to the position relative to the palladium and is therefore equivalent to the α-hydrogens discussed above). This may account for the similar rate in methanol and ethanol decomposition on Pd surface and hence similar H_2 production rate. Further identification of the by-products from the primary alcohol reactions indicates the presence of alkane groups with the loss of one carbon from the parent alcohol (for example, ethane from 1-propanol, propane from 1-butanol). The tertiary alcohol has no α-hydrogen and therefore shows little hydrogen production. However, although benzyl alcohol possesses two α-hydrogens, it shows no reactivity in 3 h; this apparent contradiction is discussed further below.

Based on the detailed mechanism previously reported for methanol and glycerol on Pd/TiO_2 catalysts [3,8], the present findings are used to generalise the mechanism for longer chain primary alcohols as summarised in Scheme 1.

The first step in ethanol photocatalytic reforming involves the dissociation of the hydroxyl on the palladium leaving an ethoxy group and an adsorbed H. Studies previously carried out on ethanol oxidation on Pd surfaces at room temperature, have shown that the major pathway for ethanol decomposition is via surface ethoxy followed by C–C bond-breakage to produce a methyl group, carbon monoxide and hydrogen adatoms [10]. The methyl groups produce methane by recombination with hydrogen atoms absorbed on the Pd surface. This however leaves a surface poisoned by a strongly adsorbed CO which is only removed with light irradiation. Electrophilic O^- species generated on titania migrate to oxidise the CO to CO_2. The vacant site on the metal is then replaced by another alcohol molecule liberating another mole of hydrogen gas. The oxygen vacancy on the titania is filled by an oxygen supplied by the decomposition of a water molecule since the experiment was carried out under anaerobic conditions. Longer chain primary alcohols, 1-propanol and 1-butanol have been studied and produce mainly ethane and propane respectively as by-products alongside CO_2 and H_2. Studies carried out by Davis and Barteau on primary alcohol decomposition on Pd surface showed that the decomposition occurs by the elimination of CO to form a hydrocarbon one carbon atom shorter than the parent alcohol chain [11]. These primary alcohols undergo stoichiometric decarbonylation on the Pd surface which involves α C–C bond scission [12,13]. The TiO_2 semiconductor facilitates this process by providing energy and an oxidiser species for restarting the cycle. There is some evidence, in the case of the longer primary alcohols that the Pd surface is poisoned by C species [11]; this might explain the decreasing H_2 production rate in the present results as the number of carbons in the chain increases (ethanol – 6.08×10^{-4} ml s^{-1}, 1-butanol – 3.49×10^{-4} ml s^{-1}).

Dehydrogenation of alcohol on Pd

$CH_3CH(OH)CH_3(a) \rightarrow CH_3CH(O)CH_3(a) + H(a)(g)$ 12

Non-selective dissociation of the adsorbed alkoxide

$CH_3CH(O)CH_3(a) \rightarrow CO(a) + 2CH_3(a) + H(a)$ 13-a

Dehydrogenating via beta-hydride elimination

$CH_3CH(O)CH_3(a) \rightarrow CH_3C(O)CH_3(a) + H(a)$ 13-b(i)

Decarbonylation of ketone

$CH_3C(O)CH_3(a) \rightarrow 2CH_3(a) + CO(a)$ 13-b(ii)

Formation of alkane

$CH_3(a) + H(a) \rightarrow CH_4(g)$ 14

Scheme 2. Proposed mechanistic steps for secondary alcohol photoreforming via beta-hydride elimination.

Secondary alcohols can produce H_2 by two possible mechanistic pathways. The absorbed alkoxide could decompose via non-selective decomposition yielding (in the case of 2-propanol) two molecules of methane, H_2 and CO_2 (step (13-a), Scheme 2). Alternatively, the molecule could decompose by a beta-hydride elimination mechanism involving a ketone intermediate to get similar products [14]. Shekhar and coworkers showed that 2-propanol decomposes on palladium to produce CO, methane, hydrogen and surface carbon. However, methane desorption from 2-propanol was observed to start at 345 K, nearly 50 K higher than for ethanol decomposition, suggesting that C–C scission in the secondary alcohol exhibits a higher activation barrier than that for a primary alcohol [12]. The importance of α C–C bond scission in longer chain alcohol reactions is further emphasised by the reaction of benzyl alcohol which failed to give significant quantities of hydrogen. Although the benzyl alcohol possesses two α hydrogen atoms, the α C–C bond is attached to an aromatic ring and is expected to have much higher dissociation barrier (~427 kJ mol^{-1}) than that of aliphatic C–C bonds (350–370 kJ/mol) [15].

The second mechanistic pathway by which 2-propanol decomposition might occur is beta-hydride elimination (Scheme 2); after dehydration of the alcohol the resulting 2-propoxide eliminates a second hydrogen atom (step (13-b(i))) to form adsorbed acetone. No acetone was observed as a product of 2-propanol in the present experiments. However, in a study to be published separately we have observed the photocatalysed decomposition of acetone into CO_2 and methane on palladium (steps (13-b(ii)) and (14)).

It was stated above that the critical factor for generating hydrogen from water in the presence of alcohol is the availability of a strongly bonded CO molecule on the Pd surface which facilitates reduction on the titania. The CO on the Pd surface acts as a hole scavenger and prevents recombination of the photogenerated electron–hole pairs. Once the electrophilic oxygen species is consumed in oxidising the CO, the resulting oxygen vacancy on the titania acts as a reducing agent, decomposing water into hydrogen. Therefore, the rate of alcohol dissociation on metal surfaces at ambient temperature can be used to determine the reactivity in producing hydrogen gas as well as the reaction rate.

4. Conclusion

Photocatalytic reforming of alcohols can offer sustainable hydrogen gas production at ambient temperatures when bio-fuels are used as sacrificial reductants. The main characteristic of an alcohol that determines its reactivity is the availability of α-hydrogens and the ease of dissociation of the α C–C bond. The decomposition mechanism for alcohols on the Pd surface is similar for primary and secondary alcohol involving O–H bond scission and α C–C bond cleavage. Branched alcohol decomposition probably involves a ketone intermediate before it reforms into an alkane, H_2 and absorbed CO on the Pd surface. The adsorbed CO effectively undergoes a photocatalytic water-gas-shift reaction, splitting water and producing more hydrogen.

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