Catal Lett (2009) 128:253–255
DOI 10.1007/s10562-008-9781-1

Photocatalytic Reforming of Glycerol over Gold and Palladium as an Alternative Fuel Source

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Received: 26 September 2008 / Accepted: 12 November 2008 / Published online: 13 December 2008

Abstract The photocatalytic reforming of glycerol to hydrogen over palladium and gold modified TiO_2 catalysts is reported. The rate of hydrogen production exceeds that measured for the photoreforming of methanol over both catalysts with the palladium catalyst performing approximately four times better than the gold. The reaction occurs under ambient conditions and neither system suffered from poisoning after extensive testing. This therefore offers a potentially attractive route by which one of the major waste products from the manufacture of biodiesel can be converted into a useful product.

Keywords Photocatalysis · Glycerol · Photoreforming · TiO_2 · Gold · Palladium

1 Introduction

Since the energy crisis in 1970 there has been considerable interest in the production of biodiesel from the transesterification of oils from plants such as rape, soya and palm as a replacement for petroleum diesel. Current concerns over finite natural oil reserves and the impending consequences of global warming have led to a considerable increase in the attention given to this area. Biodiesel appears to offer a means of reducing both net carbon dioxide emissions and air pollution. However, one of the issues with this technology is that for every tonne of biodiesel generated 100 kg of glycerol is produced which has an adverse effect on biodiesel economics [1]. There is therefore a need to identify new routes by which the glycerol side product can be converted into useful materials. One possibility, recently studied [2] by Douette et al. [2] is the conversion of glycerol to hydrogen. Douette et al.'s approach was to use a nickel reforming catalyst at ca. 800 °C, generating hydrogen and carbon dioxide. Whilst the lab experiment came close to generating the expected seven moles of hydrogen for each mole of glycerol (Eq. 1 in Scheme 1) the high temperatures involved are far from ideal and catalyst poisoning was also an issue.

Photocatalysis is an alternative approach to the conversion of glycerol which overcomes the issue of high temperatures and appears to avoid catalyst poisoning. In a very thorough recent paper, Kondarides reported hydrogen production by photo-reforming biomass components over Pt promoted TiO_2 catalyst [3]. In the present paper we examine the potential of the photocatalysed reforming of glycerol over palladium and gold promoted catalysts. Photocatalysis is known to be an efficient method for reforming methanol and other alcohols in the presence of water under ambient temperatures [4–9]. Bowker and co-workers have studied many factors which affect the photocatalytic production of hydrogen from methanol/water mixtures [4, 7, 10, 11]. The present model for the system is that the precious metal provides an efficient means of dehydrogenating the alcohol whilst the titania acts as photon absorber creating an active oxidising species.

$$C_3H_8O_3 + H_2O \rightarrow 7H_2 + 3CO_2 \qquad (1)$$

$$CH_3OH + H_2O \rightarrow 3H_2 + CO_2 \qquad (2)$$

Scheme 1 Stoichiometric equation for the steam reforming of (1) glycerol and (2) methanol

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2 Experimental

Experiments were carried out in a Pyrex reaction flask equipped with a rubber septum through which samples could be extracted with a calibrated syringe. The flask and reaction mixture was purged for 30 min with argon before illumination with UV light. The promoted P25 titania catalysts were prepared by incipient wetness using $PdCl_2$ or $HAuCl_4 \cdot 3H_2O$ dissolved in acidified water, followed by a two stage drying and calcining process involving heating at 110 °C for 2 h and then at 500 °C for 2 h. After cooling, samples were ground and sieved to an aggregate size of less than 53 μm. A volume of 0.2 g of catalyst was stirred with 100 mL of deionised water and 100 μL of glycerol or methanol in the reaction flask and illuminated by a 400 W Xe arc lamp (Oriel model 66921). Samples were taken every 30 min and analyzed by GC (Varian 3900).

3 Results and Discussion

In Fig. 1, we compare the rate of photocatalytic reforming of glycerol to hydrogen over a 0.5% Pd/TiO_2 photocatalyst with that of methanol reforming and the maximum rate reported by Kondarides et al. [3] for glycerol reforming over a Pt catalyst. The hydrogen production rate from both glycerol and methanol is fairly constant with irradiation time, with the hydrogen production rate from glycerol approximately double that of methanol. In the absence of the photocatalyst no hydrogen was produced.

Methanol contains one hydroxyl group and is oxidised according to Eq. 2 in Scheme 1 [8, 12]. The greater reaction rate of glycerol is consistent with the stoichiometry of the two proposed reaction schemes suggesting that the reforming reaction goes to completion in both cases.

No hydrogen production was observed, under similar conditions, from alkanes or alkenes but we have identified hydrogen production from higher alcohols [4] and glucose [13]. The present experiment confirms that the most important factor for hydrogen production from such molecules is the presence of an alcohol group which is readily oxidised by the photocatalytically excited oxygen state. Effectively, glycerol is like three methanol groups in this respect.

Gold is also an effective metal in photocatalysts [4, 7]. Figure 2 shows data for 2.0% Au/TiO_2 in the presence of methanol and glycerol. In this case, photocatalytic reforming of glycerol produces three times more hydrogen than methanol. Clearly gold is also efficient for the photocatalytic reforming reactions, though the hydrogen production rate from glycerol is 1.7 times slower than over the 0.5% Pd/TiO_2 catalyst.

A similar mechanism to that described in detail previously for methanol [14] can be applied in the case of the photoreforming of glycerol. Mechanistically, it can be summarised in Scheme 2.

In the absence if light, the reaction stops at Step (4) in Scheme 2 due to the blockage of palladium sites by strongly adsorbed CO [15]. It is at this point that the light plays the pivotal role; photoactivation of the TiO_2 results in charge separation and the formation of an extremely reactive, electrophilic oxygen. The latter migrates to the metal surface leaving a polaron vacancy (V_o^-) on the oxide.

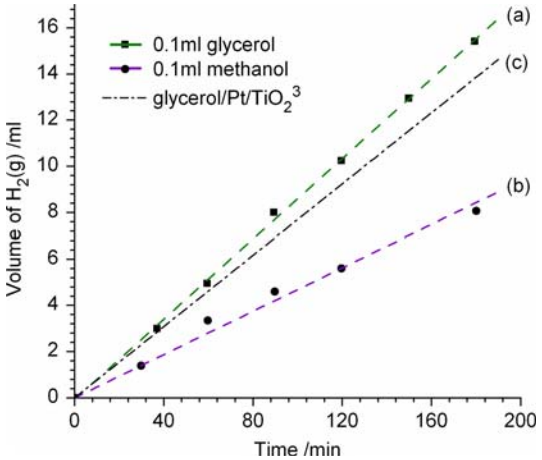

Fig. 1 A comparison of the rates of hydrogen production from the photocatalytic reforming of (*a*) glycerol and (*b*) methanol over a 0.5% Pd/TiO_2 catalyst at ambient temperatures. Line (*c*) represents the maximum rate of H_2 evolution reported by Kondarides et al. for glycerol photoreforming over a 0.5% Pt/TiO_2 catalyst under similar conditions (adjusted to allow for mass of catalyst & volume) [3]

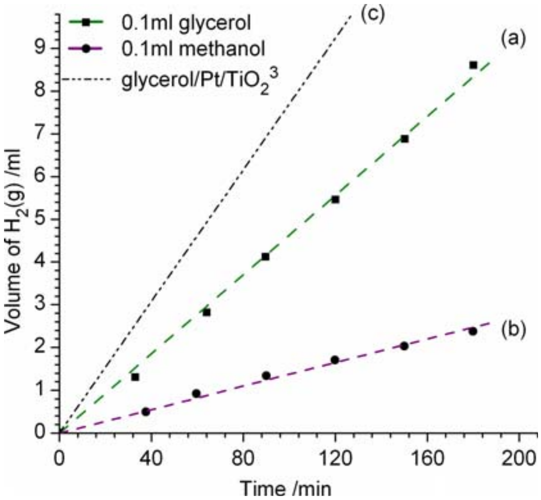

Fig. 2 Comparison between the photo-reforming of (*a*) glycerol and (*b*) methanol for hydrogen production in the case of a 2.0% Au/TiO_2 catalyst. Line (*c*) represents the maximum rate of H_2 production reported by Kondarides et al. [3] for glycerol reforming over a 0.5% Pt/TiO_2 catalyst under similar conditions (adjusted to allow for mass of catalyst and volume)

Adsorption of organic

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

Dissociation of adsorbate

$$RCH_2CH_2OH\,(a) \rightarrow RCH_2(a) + CO(a) + \tfrac{1}{2}H_2(g) \quad (4)$$

Photoactivation

$$Ti^{4+} + O^{2-} + h\nu \rightarrow Ti^{3+} + O^{-} \quad (5)$$

CO oxidation and oxygen vacancy formation

$$O^{-} + CO(a) \rightarrow CO_2(g) + V_o \quad (6)$$

Polaron de-excitation

$$Ti^{3+} + V_o^{-} \rightarrow Ti^{4+} + V_o^{2-} \quad (7)$$

Water reduction

$$V_o^{2-} + H_2O \rightarrow O^{2-} + H_2 \quad (8)$$

Scheme 2 Proposed mechanism for the photoreforming of an alcohol

At the metal surface the radical oxygen reacts with CO removing it as CO_2, freeing up sites for further adsorption of the alcohol. The vacancy is expected to revert to the normal state by de-excitation (step 7 in Scheme 2) and under the anaerobic conditions of our experiment the oxygen vacancy is then filled by a water molecule, so the last step in the catalytic cycle involves anion vacancy healing and the reduction of water. On gold an alkoxy intermediate has been proposed for the photocatalytic reforming of methanol [7] and it is likely that a similar mechanism is involved in the oxidation of glycerol. Carbon dioxide is the eventual fate of the carbon product.

This kind of reactivity seems to be available to any organic with functional groups which give it the ability adsorb reasonably strongly on the metal component. We have previously investigated photocatalysis on other noble metal surfaces [10, 14]. Glycerol is one such molecule, and work is in progress in our laboratory to enhance the rate at which hydrogen is formed from such reactions.

Acknowledgments We are grateful to the Saudi Arabian government for the provision of a studentship to LSAl-M.

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