Photocatalytic reforming of alcohols over Pd doped TiO_2

At present, more than 90% of the hydrogen produced commercially comes from the steam reforming of fossil fuels; if the environmental benefits of the "hydrogen economy" are to be realised, a renewable and cost effective source of hydrogen is required. Replacing fossil fuels with biomass is a possible solution but the low hydrogen content of biomass (~6.5% compared to ~25% in natural gas) makes reforming uneconomic. However, current reforming methods are energy intensive; steam methane reforming for example, (Equation 1) operates at temperatures of up to 1000°C and pressures of up to 25 bar generating several kg of greenhouse gasses per kg of hydrogen. Photocatalytic reforming on the other hand, operates near to ambient condition and could therefore, provide an economically competitive approach to reforming biomass.

$$CH_4(g) + H_2O(g) \xrightarrow[25\ bar]{1200\ K,} CO(g) + 3H_2(g)$$

Equation 1. Steam reforming of methane

Noble metal doped TiO_2 is the most effective and widely studied photocatalyst for the reforming reaction but there remains considerable controversy over the mechanism, and in particular, over the role of metal nanoparticles: do they act simply as electron acceptors thereby prolonging the lifetime of the core-hole pair or, are they intimately involved in the decomposition reactions? Our aim was to elucidate the reforming mechanism over metal doped TiO_2 by studying the effect of the molecular structure of alcohols on the kinetics and products of the reaction. The rate of hydrogen production was determined by GC and the gas phase products determined using a Hiden Analytical QIC-20 Gas Analysis System, Figure 1.

The different alcohols studied gave very widely varying rates of reaction but as Figure 2 shows, these can be rationalized with the following 4 rules:

1. The alcohol must have a hydrogen in the α-position;
2. Primary alcohols undergo decarbonylation yielding a single molecule of CO_2 (by further reaction with water) and hydrogen plus an alkane (the exception being methanol which produces no alkane);
3. Methylene groups produced in the reaction undergo complete oxidation to yield carbon dioxide;
4. The dominant pathway for methyl groups produced at the surface from the photo-reforming process is recombination with hydrogen and desorption. However, in the case of secondary alcohols, where there is competition for hydrogen between alkyl groups, oxidation of the methyl group becomes probable.

The rules derived here correspond closely to the expected chemistry of the alcohols over palladium surface rather than that seen over TiO_2. We deduce that the facile kinetics of the reactions at the palladium surface result in it dominating the reaction, but the titania is crucial for light absorption and the production of an adsorbed CO oxidant.

HIDEN ANALYTICAL LTD
420 Europa Boulevard, Warrington, WA5 7UN, England
t: +44 (0) 1925 445225 f: +44 (0) 1925 416518
e: info@hiden.co.uk **w: www.HidenAnalytical.com**

Figure 1. Dr Bahruji (left) & Dr Davies next to the Hiden QIC-20 Gas Analysis System

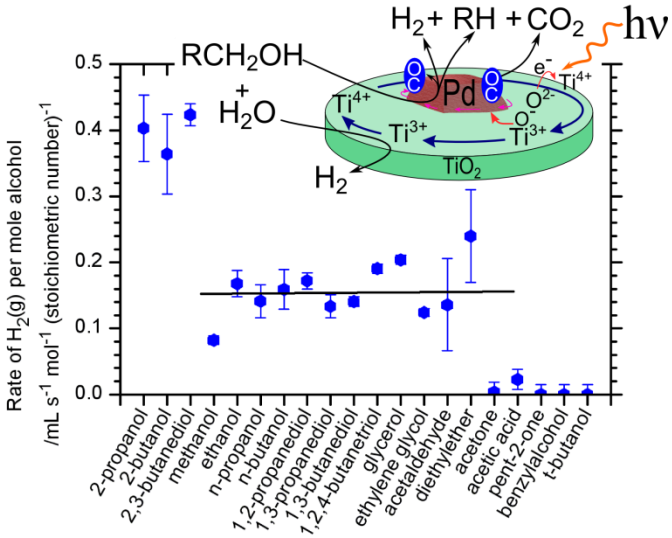

Figure 2. The chart compares the rates of hydrogen evolution from the photoreforming of a number of different oxygenates calculated per mole of alcohol reformed on the basis of the predicted H_2 gas stoichiometric number predicted by rules 1-3 above. The first three outlying points are secondary alcohols where there is evidence for the decomposition of the methyl groups (rule 4.). Inset is a pictorial representation of the proposed photocatalytic reforming mechanism.

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t: +44 (0) 1925 445225 f: +44 (0) 1925 416518
e: info@hiden.co.uk **w: www.HidenAnalytical.com**

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Project Summary by:
Hasliza Bahruji, Michael Bowker, Philip R. Davies & Fabien Pedrono
Cardiff Catalysis Institute, School of Chemistry
Cardiff University
Main Building, Park Place
Cardiff CF10 3AT
UK

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Hiden Product:
QIC-20 Atmospheric Gas Analysis System
(QIC-20 System now updated with the New QGA Atmospheric Gas Analysis System)

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