

## Hydrogen production by photoreforming of organic compounds

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### ABSTRACT

H<sub>2</sub> is gaining attention as energy vector, particularly if produced from renewable sources. It may be produced through photoreforming of organic compounds that act as hole scavengers to improve hydrogen productivity with respect to direct water photosplitting. Methanol is used here as model molecule to investigate the effect of catalyst composition and of substrate concentration on photocatalytic activity. Simple catalysts formulations were selected, in order to propose an easily scalable technology with a poorly expensive material. TiO<sub>2</sub> with different structure (anatase, rutile and a mixture of them) was used as semiconductor, doped with a small amount of Au (0.1 wt%) to improve the lifetime of photogenerated charges.

A new photoreactor was set up, with external irradiation that improves the scale up feasibility and possible future application with solar energy. Methanol conversion and hydrogen productivity increased with increasing methanol concentration up to 15 wt%. Rutile led to the highest conversion, but TiO<sub>2</sub> P25 showed the highest hydrogen productivity.

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The best result was achieved by treating a 15 wt% methanol solution with 0.1 wt% Au/TiO<sub>2</sub> P25, which led to 0.276 mol H<sub>2</sub> h<sup>-1</sup> kg<sub>cat</sub><sup>-1</sup>.

*Keywords:* Hydrogen production; Photocatalytic water splitting; Photocatalytic reforming; Titanium dioxide.

## 1 - INTRODUCTION

H<sub>2</sub> is raising attention as energy vector to feed combustors or fuel cells. In order to improve its sustainability, different processes are investigated to produce it from renewable sources. On one hand it may be produced by electrolysis of water. This system now is limited to the production of very high purity H<sub>2</sub>, due to the huge cost of electrical power with respect to competing technologies, but it can raise further interest if inexpensive and renewable electricity should be available. Nowadays, hydrogen is mainly produced through thermocatalytic processes, such as the steam reforming of hydrocarbons, thus one relatively direct way to turn to renewables is the adaptation of such processes to new substrates, such as ethanol or glycerol [1-3]. Additionally, other routes, such as the gasification or pyrolysis of biomass are in a demonstrative stage [4,5].

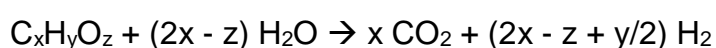
The direct water splitting is an attractive route because it would bring to pure hydrogen and oxygen without byproducts. However, despite being exothermal, it is a highly endoergonic process, which needs 237.18 kJ/mol of water ( $-\Delta G^0_{\text{formation}}$  at 298K). This energy should be supplied either in form of electrical power, as in electrolysis, or as thermal energy, but in such a case the temperature exceeds 2000 °C. Some thermal cycles have been developed to limit the decomposition temperature, but at least 800-1000°C are needed in the most favourable cases.

An alternative route could be the use of solar energy, coupled with the choice of appropriate materials, to accomplish the process photocatalytically. Many examples are proposed in the

literature [6]. The photocatalytic process is mediated by a semiconductor material, which absorbs the fraction of incident radiation with energy higher than its band gap, allowing the promotion of an electron from the valence band to the conduction one. The electron can be used to reduce a compound that has appropriate redox potential to fit the conduction band energy. Accordingly, the hole, left in the valence band upon photoexcitation, is available to oxidise any available substrate whose redox potential fits its band energy. To sum up, a redox reaction can occur between two redox couples that have potentials included in the semiconductor band gap.

Unfortunately, in the direct water splitting the water oxidation half reaction is a multi-electronic process and it is by far too slow to achieve practically relevant results. However, if more reactive compounds should be available in solution, they could improve significantly the overall reaction rate, possibly leading to a feasible process.

For instance, hydrogen production can be carried out using methanol as sacrificial agent. This process may be called photoreforming and occurs through the following general scheme [7]:



The organic compound acts as hole scavenger, by consuming holes faster than  $OH^-$  ions and being progressively oxidised (mineralised) to  $CO_2$  and  $H_2O$ . In case of complex organic molecules, many different intermediates are expected. This process can be useful also to convert organic compounds present in waste water, for water cleaning and depuration purposes. In this sense, the photoreforming of organic compounds can be seen as a virtuous process to produce hydrogen while depurating water from contaminants or wastes. Many examples of organic compounds have been summarised by Christoforidis and Fornasiero [8].

Methanol has been used in this work as model molecule. Au doped TiO<sub>2</sub> with different polymorph structures have been compared, together with different methanol concentrations. Indeed, despite many attempts to develop complex catalysts to improve productivity, titanium dioxide still represents a good choice due to commercial availability at moderate cost, stability and appropriate band potentials for the proposed reaction. One major drawback is that all its polymorphs (anatase, rutile or brookite) have quite big band gap (3.0-3.2 eV) and thus it can absorb only the UV portion of the spectrum. This limits the possibility to exploit efficiently solar light. The addition of metals on its surface may improve the absorption in the visible range [9-13]. Furthermore, the metal can entrap the photogenerated electron by forming a Schottky barrier, so preventing its recombination with the valence band holes [14]. In addition, TiO<sub>2</sub> has a high overpotential for H<sub>2</sub>, which is substantially decreased by adding an appropriate metal which is more suitable for hydrogen evolution [15]. The amount of metal should be limited and optimised, because too high loading can act as a recombination centre for electrons and holes [13,16].

In the literature, annular reactor configurations are often proposed. On one hand this allows lower optical path and more efficient exposure to light. On the other hand, the scale up possibilities are lower. Therefore, a photoreactor with external irradiation has been here employed, less efficient than comparative models with annular configuration, but more suitable to scale up and adaptable to solar light, for a more realistic prevision of system performances. The results obtained have been compared with similar catalytic systems, but tested with different photoreactor configurations.

## **2 – EXPERIMENTAL**

### *2.1 – Photocatalysts*

TiO<sub>2</sub> P25 (Evonik) has been used as semiconductor, constituted by *ca.* 80% anatase and 20% rutile. The photocatalyst was loaded with 0.1 wt% Au by deposition-precipitation in

nanostructured form. Comparative samples were prepared by depositing the same amount of Au on pure rutile (R) and pure anatase (A). The samples were labelled P25, A and R based on the three different supports.

All the details on catalyst preparation and characterisation are reported elsewhere [9,17,18].

## 2.2 – Photoreactor

A cylindrical glass photoreactor was used, with a jacket to flow cooling water and a quartz window to guarantee UV transparency during external irradiation. The overall volume was 500 mL, filled with 200 mL of solution and allowing for gas accumulation for 300 mL. A Jelosil 250 W lamp was used, with maximum of emission at 365 nm and mean measured irradiance 113 W/m<sup>2</sup>.

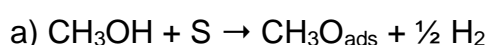
Methanol was used as hole scavenger, in variable concentration in water. The photocatalyst was added in 0.2 g amount. Before switching on the lamp, the solution was outgassed by flushing with 200 NL/h of N<sub>2</sub> for 10 min.

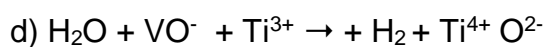
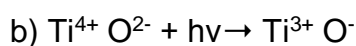
The liquid phase was analysed by means of an Agilent 6890 gaschromatograph, with a FID detector. The gas phase was analysed with an Agilent 7890 gaschromatograph, furnished with a TCD detector and calibrated to quantify H<sub>2</sub>, CO and CO<sub>2</sub>.

Sampling of the liquid phase was periodically (every 30 min at the beginning of the reaction, every 1-2 hours later. Sampling of the gas phase was carried out every 2-3 h by collecting 10 mL of gas to avoid excessive dilution of the sample.

## 3 – RESULTS AND DISCUSSION

When using methanol as sacrificial agent the following steps can be postulated to describe the reaction, which can compete with H<sub>2</sub> production from water (step d):





Methanol oxidation occurs through consecutive steps (formally lumped in reaction c), leading to HCHO and HCOOH as possible intermediates, which cannot be easily quantified using gaschromatography, because the FID detector is insufficiently sensitive and the TCD does not resolve with respect to water. Formaldehyde is also difficult to detect due to oligomers formation. HPLC was used when needed to highlight these intermediates.

The effect of methanol concentration has been assessed at first on 0.1 wt%/TiO<sub>2</sub> P25. The maximum methanol conversion achieved was 5.6 % after 7 h, starting from a 6 wt% methanol solution and increased to 8.5 % for a 15 wt% solution. The productivities of H<sub>2</sub>, CO<sub>2</sub> and CO are reported in Fig. 1 depending on the initial methanol concentration.

The higher the starting methanol concentration, the higher H<sub>2</sub> productivity. This confirms the strong dependence of methanol photoreforming on substrate concentration, as already reviewed recently [7,8]. The amount of hydrogen produced exceeded the stoichiometric expectations with CO and CO<sub>2</sub>. Besides the formation of intermediates (HCHO and HCOOH) remaining in solution, the possible contribution of direct water splitting was also hypothesised and it was checked by testing oxygen formation. Sampling of the gas after outgassing at time 0 revealed negligible oxygen content. Sampling at different reaction time was carried out to monitor oxygen formation as ratio between the chromatographic areas of oxygen and nitrogen. Qualitatively increasing oxygen amount was observed with time, supporting a contribution from direct water splitting, though not determinant.

Formic acid was also monitored by HPLC as possible reaction intermediate (Fig. 2). Its time evolution is compatible with the trend expected for a reaction intermediate, which

accumulates and then converts to the final product ( $\text{CO}_2$ ), with a maximum between 250-350 min.

The performance of the different catalysts was compared with a 15 wt% starting concentration of methanol and summarised in Fig. 3 and 4.

According to the results the highest methanol conversion was achieved for the rutile-based sample, whereas anatase and P25 performed similarly, with *ca.* halved conversion with respect to rutile. However, when looking at the productivity of  $\text{H}_2$  the highest value was attained for the P25-supported sample (Fig. 4).

The anatase-supported sample confirmed indeed less active than rutile as for hydrogen productivity, but both samples were by far less active than P25.

Rutile is characterised by a slightly lower band gap (3.0 eV) with respect to anatase and P25 (*ca.* 3.2 eV). Therefore, upon light absorption a higher methanol conversion is expected with rutile. Nevertheless, the overall reaction to produce hydrogen is based on the multistep mechanism mentioned above, which needs multiple electron transfer. P25 is typically reported as an efficient photocatalyst because the phase junction between rutile and anatase allows more efficient electron-hole separation and thus an improvement of the lifetime of the photogenerated charges. On this basis, methanol conversion was less efficient with P25 than for rutile due to lower light harvesting, but the consecutive conversion of the surface intermediates was the opposite due to more effective use of the photogenerated charges with P25.

Higher  $\text{H}_2$  yield is reported in the literature. For instance, Beltram et al. [19] investigated Pt 0.2 wt% over various  $\text{TiO}_2$  polymorphs for the photoreforming of ethanol (50 wt%) and glycerol (1 M) aqueous solutions. At difference with the present results very small  $\text{H}_2$  productivity was obtained with rutile (*ca.* 0.25 or 0.5 mol/h  $\text{kg}_{\text{cat}}$ , respectively for ethanol and glycerol), the highest one being ascribed to anatase (*ca.* 1.8 or 1.25 mol/h  $\text{kg}_{\text{cat}}$ , respectively

for ethanol and glycerol). 15 mol/h kg<sub>cat</sub> of H<sub>2</sub> were obtained by using a 0.5 wt% Au/TiO<sub>2</sub> by glycerol photoreforming [20], while 2 mol/h kg<sub>cat</sub> of H<sub>2</sub> were obtained with bare P25 TiO<sub>2</sub>, raising to 6.7 when adding Cu and using a 7.9 wt% methanol solution [21].

The higher hydrogen productivity achieved in the above reported examples is mainly ascribed to the configuration of the reactor. Indeed, all these experiments were carried out with annular photoreactors where the lamp is immersed in the solution and/or with more intense irradiation. For instance, more than double irradiance with respect to the present case is reported in [19] and one order of magnitude higher in [20]. Nevertheless, our reactor configuration was here selected in spite of the lower light harvesting because the design proposed here is more adapt to scale up and for the future exploitation of solar light.

#### **4 – CONCLUSIONS**

The photoreforming process can be proposed as an effective route to convert organic compounds into hydrogen. The reaction converted in ca. 7 h up to ca. 17 % of a 15 wt% starting methanol solution, the conversion increasing with initial methanol concentration. Furthermore, there is a strong dependence of conversion and hydrogen productivity from the titania polymorph selected. Rutile was the most efficient in light harvesting, due to the smallest band gap. This led to higher methanol conversion. However, P25, though characterised by lower methanol conversion, was overall more efficient than the other polymorphs to achieve full mineralisation of the intermediates. The phase junction between rutile and anatase allows to prevent electron-hole recombination and thus higher charge utilisation. This led to higher hydrogen productivity in spite of the lower conversion of methanol, likely due to more efficient conversion of reaction intermediates.

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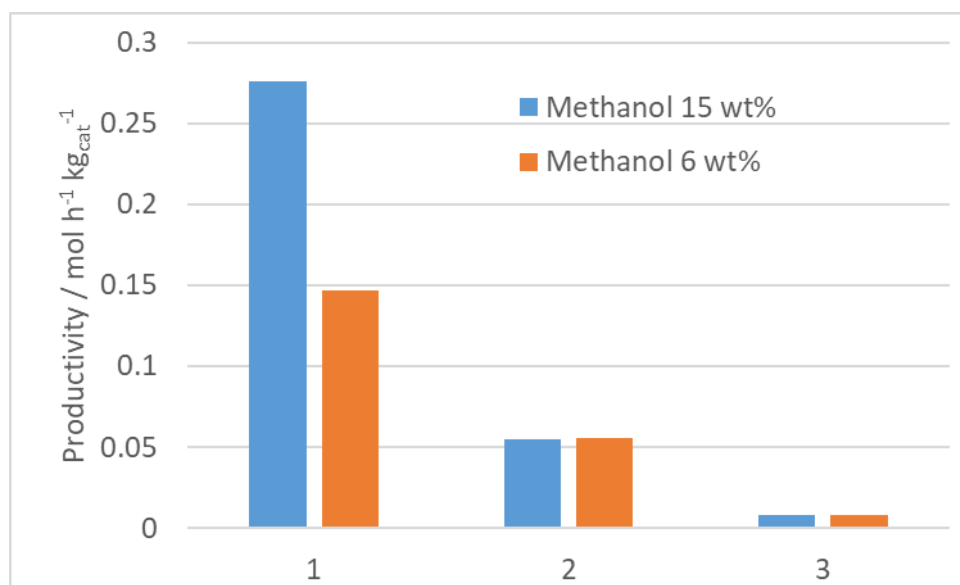
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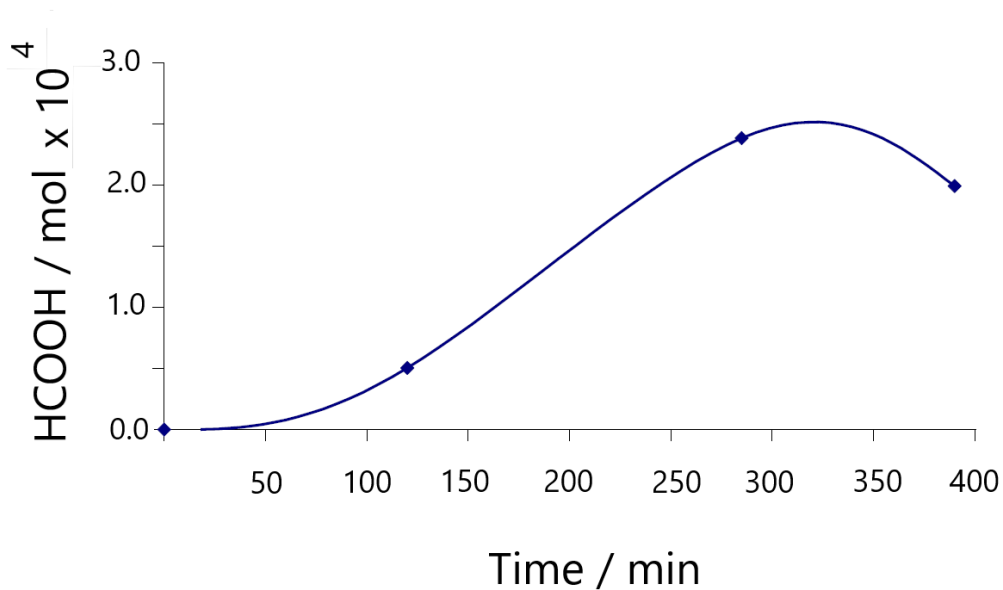
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## FIGURES

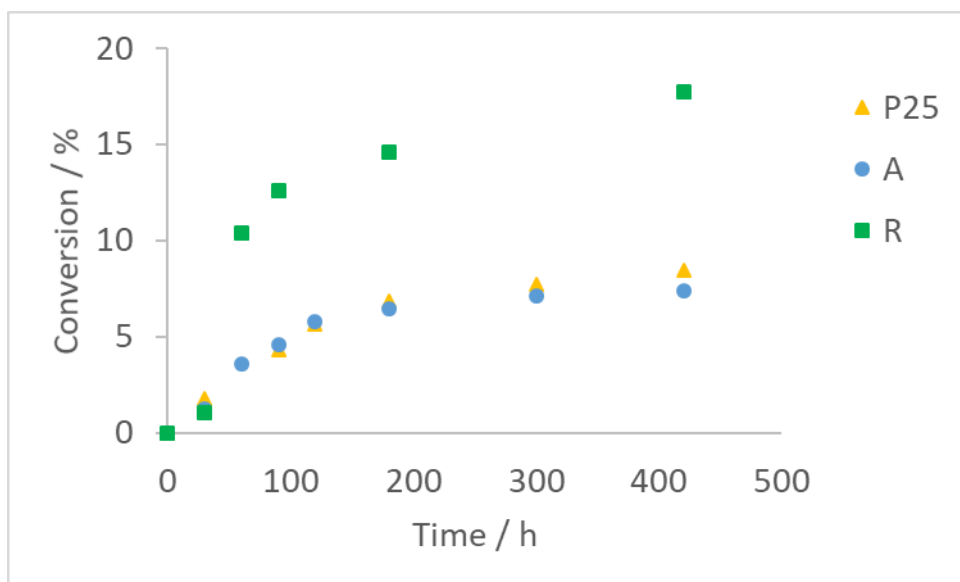
**Fig. 1:** Effect of methanol concentration on productivity. Catalyst 0.1 wt%/TiO<sub>2</sub> P25. 1 = H<sub>2</sub>; 2 = CO<sub>2</sub>; 3 = CO.



**Fig. 2:** HCOOH evolution with reaction time as determined by HPLC.



**Fig. 3:** Conversion vs. time for catalyst 0.1 wt%/TiO<sub>2</sub> prepared with different titania polymorphs. Initial methanol concentration = 15 wt%.



**Fig. 4:** Effect of the titania polymorph on productivity. 1 = H<sub>2</sub>; 2 = CO<sub>2</sub>; 3 = CO.

