Solar hydrogen production from aqueous solutions of ethanol

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Abstract

In this work, photo-catalytic hydrogen production from water is studied, using ethanol as sacrificial agent. Titania was used as a base catalyst due to its stability and corrosion resistance as well as its environmental friendliness and low cost. The need to decrease the electron-hole recombination rate was accounted for by metal doping and also by using the ethanol molecule as a hole trap. Hydrogen production was achieved using own synthesised sol-gel metal doped titania, with production rate values being larger than published literature data.

Keywords: *hydrogen production, titania, water splitting, photo-catalytic materials*

1 Introduction

The generation of hydrogen from water splitting using photo-catalytic surfaces of oxide materials has been recognised since the early seventies with the work of Fujishima and Honda [1].

In the last decades interest in semiconductor photo-catalysis has grown significantly with works mostly referring to uses in water/air purification.

The photo-catalytic production of hydrogen by means of irradiation of a suspension of semiconductor oxides, presents attractive features over other methods with higher cost such as water electrolysis.
In order to increase efficiency in the use of semiconductor electrodes in electrochemical photolysis, integrated systems including semi-conductor / redox couples interfaces, deposition of metallic co-catalyst, sensitizers, etc. have been studied [2,3].

In this work, nanostructured multi-functionalised semi-conductor materials based on titanium dioxide, were synthesized using sol-gel technology and found effective, for the production of hydrogen, under UV illumination.

2 Experimental

A photochemical reactor with a total volume of 4.40 litters distributed between an internal (irradiated) reactor and an external reactor (fluid reservoir) was used, sensing pH and ion-selective electrodes were allowed for as well as facilities for titration of H^+, in order to keep pH constant when required. The internal reactor is contained in a black box and used a 450 W Hg immersion lamp (A.C.E. Glass Incorporated, NJ) as a radiation source. The emission spectrum of the lamp indicated that the UV radiation is mainly situated between 313 and 366 nm. Circulation between reactors was ensured by a peristaltic pump, according to the required recirculation rate. Agitation by magnetic stirrers in both reactors was also used.
Platinised TiO_2 catalyst (at 1.5 wt.% Pt) was prepared using hexachloroplatinic acid (Riedel-de Haen) as the precursor. A pre-determined amount of TiO_2 was first suspended in hot water and the hexachloroplatinic acid previously dissolved in an aliquot of fresh distilled water was added, with continuous nitrogen purging (15 min.) inside the photo-reactor. The mixture was irradiated for 60 min, at constant temperature (30-40ºC), to ensure that all the platinum in the suspension was reduced and deposited onto the surface of TiO_2. The TiO_2 / Pt catalyst was subsequently recovered by filtration and washed repeatedly with water to remove adsorbed chemicals. Finally the particles were dried at 70ºC and stored under vacuum in a desicator.

Characterisation of the powders was done by X-Ray diffraction using a Rigaku, model D-Max IIIC and by scanning electron microscopy (SEM) using a Phillips model XL 30 FEG microscope coupled to EDS.

3 Results

In this work, nanostructured semi-conductor materials based on titanium dioxide, with effective photo-catalytic properties under UV illumination, were synthesized using sol-gel technology. X-Ray diffraction data indicated the presence of anatase and rutile and a crystallite size of 6 nm. Typical morphology of the powder is shown in figure 1.

Aqueous suspensions of the semiconductor powders, with noble metal loadings (Pt) up to 1.5 % were used and the effect of solution pH and temperature (20-70ºC) as well as the effect of concentration of ethanol on hydrogen production were studied, for fixed concentrations of the catalyst. Comparison is made with doped Degussa-P25 TiO_2.

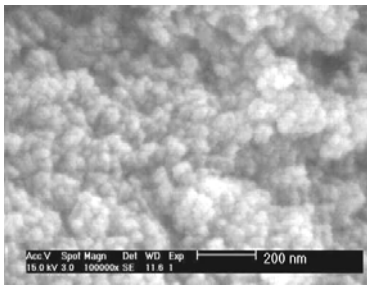

Fig. 1 SEM view of synthesized titania based catalyst powder.

Hydrogen production rates were found to be linear with exposure time with production rate values being larger than published literature data [2]. Particle size, reactive surface area, structure and crystallinity were found to be determinant in the production of highly photoactive titanium dioxide.

Preliminary data obtained using gas chromatography indicated the presence of large amounts of hydrogen in the reaction products, CO_2 and CH_4 were also found in smaller amounts.

Possible reactions are:

$$C_2H_5OH + H_2O \xrightarrow[TiO2]{hv} CH_4 + CO_2 + 2H_2 \quad (1)$$

$$e^-(Me) + H^+_{sol} \rightarrow H_{ads} \quad (2)$$

$$H_{2ads} \rightarrow H_{2\ gas} \quad (3)$$

$$2h + C_2H_5OH \rightarrow 2H^+ + CH_3CHO \quad (4)$$

$$2h + CH_3CHO + H_2O \rightarrow 2\ H^+ + CH_3COOH \quad (5)$$

Me - Metal (Pt); h- hole

Methane and CO_2 may be produced by decomposition of acetic acid. Marked pH variations during the reaction indicated acid production. Another pathway possible is CH_4 formation by hydrogenation of CO_2 (photoreaction).

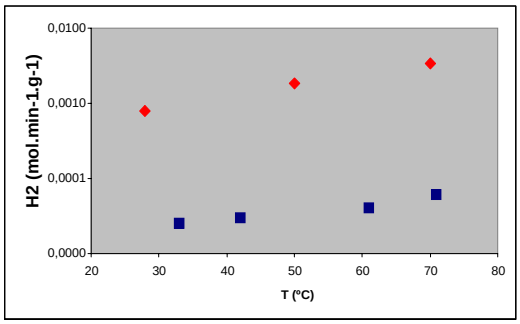

Fig. 2 Volume of produced gas as a function of temperature, from a 5 M aqueous solution at pH 11, using metal doped titania. Results are compared with literature data from [2] (♦ own synthesized sol-gel catalyst data; ■ literature data).

Further work is needed to identify low cost metal loading materials with acceptable enhancement for hydrogen production, as well as modified catalysts that allow effective utilization of visible light**.**

References

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