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Photocatalytic Water Splitting using a Modified Pt-TiO2. Kinetic Modeling and Hydrogen Production Efficiency

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Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree in Doctor of Philosophy

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PHOTOCATALYTIC WATER SPLITTING USING A MODIFIED PT-TiO$_2$. KINETIC MODELING AND HYDROGEN PRODUCTION EFFICIENCY

(Thesis format: Monograph)

by

Salvador Escobedo Salas

Graduate Program in Chemical and Biochemical Engineering

A thesis submitted in partial fulfillment of the requirements for the degree of
Doctor of Philosophy

The School of Graduate and Postdoctoral Studies
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London, Ontario, Canada

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Abstract

Nowadays, the world experiences a high energy demand caused by the expansion of the industry sector as well as increasing world population. There is, as a result, a steady depletion of non-renewable fossil fuels. This also leads to significant contaminant emissions such as CO₂, contributing to green house gases and other noxious pollutants such as NOx and SOx. Thus, it is of high importance and interest to promote new alternative and environmental-friendly sources of energy. Heterogeneous photocatalysis as practiced in the present PhD dissertation is a promising alternative, producing hydrogen and simultaneously using a renewable organic scavenger (ethanol) at ambient conditions. In addition, heterogeneous photocatalysis can be, in principle, promoted by the interaction of a semiconductor material and photons in the solar light spectrum (UV-Visible-IR radiation).

The present PhD dissertation demonstrates that hydrogen can be produced photocatalytically using a modified Degussa P25 (TiO₂)-Pt photocatalyst in a slurry medium under near-UV irradiation and having ethanol as a sacrificial reagent (scavenger). The modified DP25-Pt photocatalyst was prepared using the incipient wetness impregnation technique. The Pt modified photocatalyst exhibited a 2.73 eV reduced band gap.

Experiments were performed in a Photo-CREC Water II Reactor (PCW-II Reactor). This novel unit provides both radial and axial symmetrical irradiation profiles. Macroscopic energy balances developed in this unit, showed a 95% LVREA at 0.15 g of photocatalyst per liter of aqueous solution.

Runs in the PCW-II Reactor showed hydrogen formation via H⁺ radicals under oxygen free conditions. The use of 2 v/v% ethanol as sacrificial reagent enabled producing significant hydrogen amounts with the simultaneous formation of CH₄ and C₂H₆ by products. It is proven that hydrogen formation in the presence of ethanol is a function of water solution pH and Pt loading on the TiO₂ photocatalyst.

Regarding the consumption of an ethanol scavenger, experimental findings are supported by an “in series-parallel” reaction network and a kinetic model. Kinetic model parameters were estimated using numerical non-linear regression. These kinetic parameters were determined under rigorous statistical methods. These methods were adapted to give an adequate fit to the
experimental data and to all the by product species resulting from the photocatalytic hydrogen production “in series-parallel” kinetic model. Furthermore, hydrogen production, in the context of the present research, was also described using an “in parallel” reaction network. In this case, once again, kinetic parameters were established using carefully determined statistical methods.

Concerning energy efficiencies, it was observed that the best obtained 7.9% quantum yield for hydrogen production indicates a good degree of photon utilization. This is particularly true in view of the fact that hydrogen production requires two simultaneous or quasi-simultaneous photons interacting with a semiconductor site. It was also proven via the Photochemical Thermodynamic Efficiency Factors (PTEFs) that observed PTEFs are in accordance with the thermodynamics remaining in all cases below 1.

One can thus, conclude, with the result of the present research, the value of a modified DP25-Pt photocatalyst operating in the Photo-CREC Water II Reactor for hydrogen production, via photocatalytic water splitting.

**Keywords**

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Nomenclature

\( a_v \)  Catalyst transference area (cm\(^2\)/cm\(^3\))

C\(_2\)H\(_4\)O  Acetaldehyde

\( c \)  Speed of light (3.0 \times 10^8 \text{ m/s})

\( C \)  Photocatalyst loading (g/l)

\( C_i \)  Concentration of \( i \) component (mol/l)

\( d_p \)  Porous diameter (cm)

\( e^- \)  Electron

\( h^+ \)  electron hole

\( h \)  Planck’s constant (6.63 \times 10^{-34} \text{ J/s})

\( E(\lambda) \)  Energy of a photon at a given wave length (J)

\( E_{bg} \)  Energy band gap (eV)

\( E_{av} \)  Average Energy of a photon (kJ/mol photon)

eV  Electron volts

\( \Delta H \)  Enthalpy (KJ/mol)

H\(_2\)PtCl\(_6\)  Chloroplatinic Acid

H\(^+\)  Hydrogen radical dot

\([H^+]\)  Protons (μmole/cm\(^3\))

\( I(\lambda) \)  Intensity of light (W/cm\(^2\))

\( I_A \)  X-ray anatase peak intensity
$I_R$  X-ray rutile peak intensity

$k_f$  Mass transfer coefficient (cm/s)

$k_i$  Reaction kinetic constant (mol/h)

$K$ or $K_i^A$  Adsorption constant of $i$ component (l/mol)

$k_n$  Kinetic rate constant at $n$ direction on the parallel-series reaction network

$k_r$  Reaction transfer coefficient

$L$  Length of the lamp (cm)

$m$  Number of experimental data points

$M^0$  Basal state metal

$\eta$  Fraction of photon energy

$\text{nm}$  Nanometers

$N_i$  Number of $i$ molecules produce

$p$  Number of model parameters

$P_0$  Rate of photons emitted by the BLB Lamp (einstein/s)

$P_a$  Rate of absorbed photons (einstein/s)

$P_{a-wall}$  Rate of photons absorbed by the inner Pyrex glass (einstein/s)

$P_{bs}$  Rate of backscattered photons exiting the system (einstein/s)

$P_{fs}$  Rate of forward-scattered radiation (einstein/s)

$P_i$  Rate of photons reaching the reactor inner surface (einstein/s)

$P_{ns}$  Rate of transmitted nonscattered radiation (einstein/s)

xx
\( P_t \)    Rate of transmitted photons (einstein/s)

Pt    Platinum

\( q(\theta, z, \lambda, t) \)    Net radiative flux over the lamp emission spectrum (\( \mu W/cm^2 \))

Q    Volumetric flow rate (\( cm^3/h \))

\( Q_{\text{eq, ads}} \)    Equilibrium adsorption of adsorbate on the photocatalyst (\( mol/g_{\text{cat}} \))

\( Q_{\text{eq, max}} \)    Max equilibrium adsorption of the adsorbate on the photocatalyst (\( mol/g_{\text{cat}} \))

R    Radial coordinate

\( r_i \)    Reaction velocity (\( h^{-1} \))

Redox    Reduction Oxidation Reactions

t    Time (h)

TiO\(_2\)    Titanium dioxide

\( V_{\text{reactor}} \)    Total liquid reactor volume (6000 \( cm^3 \))

\( V_g \)    Total volume of the gas chamber (5716 \( cm^3 \))

W    Weight (g)

\( W_{\text{irr}} \)    Photocatalyst powder irradiated (\( g_{\text{cat}} \))

wt\%    Weight percent (\% m/m)

\( x \)    Intensity weight fraction (\%)

\( z \)    Cartesian coordinate (m)

\textit{Greek Symbols}

\( \gamma \)    Stoichiometric coefficient of hydrogen
\( \theta \)  Diffraction angle, also scattering angular angle (°)

\( \lambda \)  Wave length (nm)

\( \rho \)  Density (g/cm³)

\( \tau \)  Stoichiometric coefficient of Acetic Acid

\( \varphi \)  Efficient quantum yield (%)

\( \overline{\varphi} \)  Overall quantum yield (%)

**Acronyms**

AOP  Advance Oxidation Process

BLB  Black Light Blue lamp

BET  Brunauer-Emmett-Teller Surface Area Method

CB  Conduction Band

DOF  Degree of freedom

DP25  Degussa P25 (TiO₂)

EtOH  Ethanol

FIB  Focused Ion Beam

ID  Internal Diameter

LTU  Lamp Testing Unit

LVREA  Local Volumetric Rate of Energy Absorption

LVRPA  Local Volumetric Rate of Photon Absorption

MREB  Macroscopic Radiation Energy Balance
<table>
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<tr>
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<tr>
<td>NTP</td>
<td>Normal Temperature Pressure (298 °K and 1 atm)</td>
</tr>
<tr>
<td>ODEs</td>
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</tr>
<tr>
<td>PCW-II</td>
<td>Photo CREC Water II reactor</td>
</tr>
<tr>
<td>PEC</td>
<td>Photo- Electric- Cell</td>
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<td>PTEF</td>
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<td>RID</td>
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<td>STP</td>
<td>Standard Temperature and Pressure (273 °K and 1 atm)</td>
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<tr>
<td>TCB</td>
<td>Total Carbon Balance</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>VIS</td>
<td>Visible</td>
</tr>
<tr>
<td>VB</td>
<td>Valence Band</td>
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**Subscripts**

<table>
<thead>
<tr>
<th>Subscript</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Adsorption</td>
</tr>
<tr>
<td>ads</td>
<td>Adsorbed</td>
</tr>
<tr>
<td>av</td>
<td>Average</td>
</tr>
<tr>
<td>bg</td>
<td>Band gap</td>
</tr>
<tr>
<td>cat</td>
<td>Photocatalyst</td>
</tr>
<tr>
<td>Exp</td>
<td>Experimental data</td>
</tr>
</tbody>
</table>
$f$  
Formation

gt  
Gas tank

(H$^+$OH$^-$)  
H and OH radicals dots simultaneously formed

$i$  
Any number of reaction path

int  
Intersection

L  
Liquid

max  
Maximum

min  
Minimum

r  
Reactor

theor  
Theoric

T  
Total

*Superscripts*

0  
Basal state

O  
Standard (STP)

*  
Star or excited state
Chapter 1
Introduction

1 General Introduction

Global energy demands together with their potential environmental impact are expected to continue increasing in the coming years. The world’s population growth and the continuous expansion of the manufacturing sector are two main observable contributing factors of this increased energy requirements. It is also expected that these issues will be accompanied by a steady increase in the cost of energy and renewed concerns regarding the security of the energy supply and climate change (Johnston, Mayo, and Khare 2005). In addition, the growth of hydrocarbon feedstocks demands vis-a-vis of available fossil fuel resources shows that the world community is ready for the incorporation of new alternative fuels. Not doing so will make life on the planet unsustainable in the medium and long range (Ball and Wietschel 2009).

A number of recent studies suggest that the direct use of hydrogen as a fuel may provide a much cleaner and far less expensive fuel alternative (Dunn 2002). Almost no pollution is produced by engines that burn hydrogen. Hydrogen is the simplest and most abundant element in the universe. 75% of the universe mass consists of hydrogen, a colorless and odorless gas. Although hydrogen does not occur naturally, it can always be found combined with other elements such as: water and organic compounds (Momirlan and Veziroglu 2005). In addition, hydrogen is high in energy content, and is currently a useful “chemical feedstock” in a diversity of industries. Furthermore, it can be envisioned that hydrogen could be a future energy source for homes, businesses, industries and for transportation (Dunn 2002). Hydrogen can also contribute as an energy carrier or as an energy vector (Ball and Wietschel 2009; Gardner 2009).

Nowadays, hydrogen is being produced in large quantities for industrial and commercial purposes. Most of hydrogen production however, requires fossil fuels. It largely uses steam to reform natural gas, it utilizes electrolysis from electricity which can
be produced from natural gas, coal, petroleum feedstocks or nuclear energy (Gardner 2009; Dunn 2002).

Thus, nowadays challenge is to produce hydrogen from renewable resources (see Table 1). In this respect, hydrogen can be considered as a secondary energy carrier, being produced first from other alternative renewable feedstocks. Table 1 summarizes the several approaches including the advantages and the disadvantages that must be considered to manufacture hydrogen. Most recent reports show, in particular, that hydrogen production has significant opportunities in the following areas: 1) hydrogen from solar or hydrogen produced via photocatalytic water splitting, 2) hydrogen from biomass gasification or hydrogen produced using biological organisms (bacteria or algae) and 3) hydrogen from photovoltaic or hydrogen produced using photo electro chemical cells (Momirlan and Veziroglu 2005).

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Technology</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Abundant</td>
<td>Solar-hydrogen</td>
<td>× Clear sky is required</td>
</tr>
<tr>
<td>✓ Cheap materials</td>
<td></td>
<td>× Conversion efficiency</td>
</tr>
<tr>
<td>✓ Use of water or organic sources</td>
<td></td>
<td></td>
</tr>
<tr>
<td>✓ Sunlight use</td>
<td>Photovoltaic</td>
<td>× Expensive Technology</td>
</tr>
<tr>
<td>✓ Excess energy may be provided</td>
<td></td>
<td>× Requires clear sky</td>
</tr>
<tr>
<td>✓ Operates day/night</td>
<td>Wind power</td>
<td>× High cost</td>
</tr>
<tr>
<td>✓ Provides water/power day/night operation</td>
<td>Hydroelectric</td>
<td>× Exposition to high wind</td>
</tr>
<tr>
<td>✓ Constant operation day/night</td>
<td>Tidal power</td>
<td>× Requires a lot of water</td>
</tr>
<tr>
<td>✓ Geothermal power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>✓ Biomass</td>
<td></td>
<td>× Limited to coasts</td>
</tr>
<tr>
<td>✓ Geothermal activity</td>
<td></td>
<td>× Limited access to site of geothermal activity</td>
</tr>
<tr>
<td>✓ Green gases are emitted</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 reports that hydrogen can be supplied from a diversity of resources including renewable ones, such as important reason why hydrogen is such a promising energy carrier. Also, hydrogen can provide a link between renewable energy and the industrial or public sector, transforming biomass, wind or solar energy as new alternatives for hydrogen production reducing oil dependence as well as excessive CO₂ emissions.
Table 2: Advantages and drawbacks of hydrogen production

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>✓ Use of renewable source of energy.</td>
<td>× Low hydrogen production efficiencies.</td>
</tr>
<tr>
<td>✓ Environmental friendly.</td>
<td>× Current lack of efficient infrastructure to store, transport and distribute hydrogen.</td>
</tr>
<tr>
<td>✓ High energy power.</td>
<td>× Hydrogen production costs.</td>
</tr>
</tbody>
</table>

Heterogeneous photocatalysis represents an ideal technology to produce hydrogen and simultaneously remove a wide range of organic pollutants (Patsoura, Kondarides, and Verykios 2007).

Heterogeneous photocatalysis has been studied for water/air purification (Ortiz-Gomez, Serrano-Rosales, and de Lasa 2008; Ibrahim and de Lasa 2002; Serrano and de Lasa 1999) and in recent years for hydrogen production due to its low cost, environmentally friendly and potentially efficient methods (Escobedo Salas, Serrano Rosales, and de Lasa 2013).

In both cases, during the photocatalytic reaction, the photocatalyst (most commonly TiO$_2$) absorbs irradiated photons. Photons with energy equal to or greater than the semiconductor band gap energy excite electrons from the valence band into the conduction band. The resulting electron (e$^-$)/hole (h$^+$) pairs can then migrate to the surface and initiate redox reactions with adsorbed organic molecules or protons (Hoffmann et al. 1995). Excited electrons interact with hydrogen ions (protons) forming H$^-$ radicals. On the other hand, electron holes contribute by oxidizing water or organic molecules, either directly or through OH$^-$ radical intermediates, to yield final products which are, in most CO$_2$ and H$_2$O (Stratakis et al. 2010). However, photocatalytic reactions are restricted by the recombination of the photogenerated electron-holes, which limit the efficiency of photocatalytic hydrogen production.

Regarding photocatalytic hydrogen production, most of the efforts have been developed to synthesize efficient photocatalysts which are easy to manufacture and are cost effective. Nevertheless, while developing photocatalysts, it is of special importance to
manufacture one with a reduced energy band gap ($E_{bg}$) which will allow the efficient use of solar energy for hydrogen production.

However, to achieve higher hydrogen efficiencies, “sacrificial reagents” such as alcohols, carbohydrates, hydrocarbons and organic pollutants are required. These materials, which are so-called “hole scavengers” can react irreversibly with the holes ($h^+$) on the semiconductor outer surfaces.

Nevertheless, to be able to use them in practice, electron donors must be inexpensive and easily accessible (Y. Li et al. 2006). Sacrificial reagents should not be derived from fossil fuels given that this is against the objective of using hydrogen as an environmentally friendly fuel. Thus, sacrificial reagents should be a renewable resource (M. Zhou et al. 2012; Zheng et al. 2009) or chemical species derived from them such as propanol, ethanol, methanol (C. Zhou et al. 2010; Chavadej et al. 2008; Ikeda et al. 2007). This will make hydrogen production a sustainable process. Otherwise, the main environmental advantage of producing hydrogen via water splitting and solar energy will be loss or partially lost.

Regarding solar light, near-UV light in the 340-388 nm wavelength range corresponds to 4-5% of the complete solar irradiation spectrum (Salaices, Serrano, and de Lasa 2004). Thus, the application of the DP25 ($\text{TiO}_2$) photocatalyst with solar light is limited.

Platinum can, however, delay both charge recombination ($e^-/h^+$) and serve as a temporary electron reservoir. The accumulated electrons on platinum can eventually react with water or protons forming $\text{H}^+$ radicals (Egerton and Mattinson 2008; Higashimoto et al. 2008; Carina et al. 2004). As a result, the electron band gap ($E_{bg}$) and the photocatalytic activity for hydrogen generation can be improved (Riassetto et al. 2009a; Zheng et al. 2009; Blount and Falconer 2002).

In this respect, it is envisioned that a good and low cost “sacrificial reagent” can be ethanol (Strataki et al. 2010) in low concentrations (1-2 vol. %). Low ethanol concentrations can be obtained from the natural fermentation of glucose, fructose, sucrose and even agricultural waste in many farm communities around the world.
However, more work is required to devise reproducible, stable and efficient photosystems for water splitting or photocatalytic hydrogen production. Although this is a major technical challenge, it is a needed path for photocatalysis commercialization of hydrogen production (Hagen 2006).

This PhD dissertation reports hydrogen formation via water splitting using a Photo-CREC Water II Reactor. This novel photocatalytic reactor was adapted in the context of this project, with a specially designed H₂ collector well-mixed tank. This study also takes advantage of a modified semiconductor material (Pt/TiO₂) with a conveniently reduced band gap and 2 vol. % ethanol (EtOH) as a h⁺ holes scavenger. Experiments with near-UV light and Pt modified TiO₂ were performed under the special condition of having “all” irradiated photons with photon energies superseding the semiconductor band gap. Thus, under these conditions, the entire irradiation near-UV lamp spectrum was used for photocatalytic transformation. In addition, using the Photo-CREC Water II Reactor allowed establishing a macroscopic energy balance at different pH’s conditions. Furthermore, the experimental data of this study provides the needed data base to define a kinetic model as well as quantum yields and PTEFs using photocatalysis for hydrogen production.
Chapter 2
Literature Review

2 Introduction

Approximately 88% of the world’s energy supply is derived from fossil fuels. Their combustion brings about severe pollution and contributes to the green house effect. To reduce air noxious gas and CO$_2$ emissions, hydrogen energy is widely considered to be a good alternative for future clean energy. Nevertheless, renewable energy only contributes to about 5% of the commercial hydrogen production via water electrolysis, while the other 95% hydrogen is mainly derived from fossil fuels (Zheng et al. 2009). Hydrogen production using photocatalytic water splitting by modifying TiO$_2$ and renewable raw materials in water offers a promising method for clean, low-cost and environmentally friendly production of hydrogen. This chapter reports fundamentals and applications of photocatalysis as alternatives for photocatalytic hydrogen production.

2.1 Photocatalysis

The word “photocatalysis” has a Greek origin and composes of two parts: the prefix “photo” (phos: light) and the word “catalysis” (katalyo: break apart, decompose) (Kondarides 2005). However, a proper scientific definition is “a change in the rate of a chemical reaction or its initiation under the action of light radiation (ultraviolet, visible or infrared) in the presence of a substance or semiconductor (the photocatalyst) that absorbs light continuously with interactions and regeneration of electron/holes during a photochemical activation”. Moreover, the definition of photocatalysis also includes the photochemical transformations of chemical reagents in the system (IUPAC 2012).

Photocatalysis has become one of the most studied technologies in the last decades. Photocatalysis or Advance Oxidation Process (AOP) as is commonly commercially known is a process that involves photochemical reactions and photocatalytic activation processes. Photocatalytic reactions may occur homogeneously or heterogeneously. While both homogeneous and heterogeneous photocatalysis are promising technologies, heterogeneous photocatalysis has been more extensively studied in latest years because of
its potential use for environmental problems, energy generation and organic syntheses. However, both types of photocatalysis need to be considered and their main differences explain.

2.2 Homogeneous Photocatalysis

The existence of reactants and photocatalysts in the same phase is defined as homogeneous photocatalysis. The interest of homogeneous photocatalysis for researches is to study the degradation of toxic water pollutants. In this respect, we can note that the most effective oxidation of organic contaminants can be obtained with the generation of a powerful oxidizing reagent, such as OH$^-$ or another radical (Cieśla et al. 2004). The most advanced oxidation process (AOP) in homogeneous photocatalysis includes the photodecomposition of hydrogen peroxide ($\text{H}_2\text{O}_2/\text{UV}$), ozone photolysis ($\text{O}_3/\text{UV}$), transition metal oxides and photo-Fenton systems ($\text{Fe}^+ \text{ and Fe}^+/\text{H}_2\text{O}_2$).

2.3 Heterogeneous Photocatalysis

The presence of a photocatalyst (semiconductor material) in a different phase from the reactants is defined as heterogeneous photocatalysis. In this way, semiconductor surfaces provide a path to initiate a light-induced oxidation/reduction process promoting a photochemical reaction. This allows photoconversion of wide range of chemical species either in aqueous solutions or in gaseous phase (Anne and Dulay 1995). Furthermore, the use of this technology is gaining importance in photocatalytic water/air treatment. There is, however a recent interest in alternative methods of energy production from renewable sources.

Since the discovery by Fujishima and Honda (1972), of the photoassisted water electrolysis (water can be photo-electrochemically decomposed into hydrogen and oxygen) using a semiconductor electrode under UV irradiation photocatalysis is gaining importance. Photocatalytic water splitting has been extensively studied in recent years, with a focus on “hydrogen generation”. Photocatalytic hydrogen production involves the use of solar energy, a semiconductor material and an organic hole scavenger to split water.
This is a promising method for the generating of hydrogen from renewable resources (Dunn 2002).

Photocatalytic reactions (see Figure 1) have been classified into two categories: 1) Uphill reactions. In this reaction, a photon energy is converted into chemical energy and 2) Downhill reactions. A large positive change in the Gibbs Free Energy ($\Delta G^\circ = 237$ kJ/mol) accompanies water splitting when $\text{H}_2$ and $\text{O}_2$ are final products (A. Kudo, Kato, and Tsuji 2004).

![Diagram of photocatalytic reactions](image)

**Figure 1:** Types of photocatalytic reactions (A. Kudo, Kato, and Tsuji 2004)

Water splitting or photocatalytic hydrogen production has been studied by researchers in the area of photocatalysis, electrochemistry and photochemistry, and organic and inorganic chemistry. However, the number of reported photocatalysts showing water decomposition into $\text{H}_2$ and $\text{O}_2$, or the ones able to produce hydrogen also using a carbonaceous feedstock as hole scavengers are very limited.

### 2.3.1 Photocatalysts (Photocatalytic Semiconductors)

A photocatalyst is defined as a material (mostly common TiO$_2$) that is not consumed and assists in accelerating a reaction, which takes place in a substance activated by the absorption of a photon. Photocatalyst activity is influenced by several factors including: structure, particle size, surface properties, preparation, spectral activation and resistance to mechanical stresses (Rahman et al. 2011; de Lasa, Salaices, and Serrano 2005).

The usual form of semiconductor photocatalysts is one where the diameter of particles ranges from a micrometer to a nanometer. These particles however can be aggregates of
nano crystals. These particles are used either as dispersed powders or in the layers, forming thin films (Hagen 2006).

Regarding possible photocatalysts, the most suitable photocatalysts due to their photocorrosion resistance, photo-stability and their wide band gap energies (able to utilize near-UV/Visible radiation) are metal oxide semiconductors (see Table 3).

**Table 3: Band gap energies and corresponding radiation wavelength required for the excitation of various semiconductors**

<table>
<thead>
<tr>
<th>Semiconductor</th>
<th>Band Gap Energy (eV)</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond</td>
<td>5.4</td>
<td>230</td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>3.87</td>
<td>320</td>
</tr>
<tr>
<td>ZnS</td>
<td>3.6</td>
<td>344</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>3.5</td>
<td>354</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>3.4</td>
<td>365</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>TiO$_2$ (anatase)</td>
<td>3.2</td>
<td>388</td>
</tr>
<tr>
<td>α-Fe$_2$O$_3$</td>
<td>3.1</td>
<td>400</td>
</tr>
<tr>
<td>TiO$_2$ (rutile)</td>
<td>3.0</td>
<td>413</td>
</tr>
<tr>
<td>SiC</td>
<td>3.0</td>
<td>413</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>2.8</td>
<td>443</td>
</tr>
<tr>
<td>CdS</td>
<td>2.4</td>
<td>517</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.3</td>
<td>539</td>
</tr>
<tr>
<td>GaP</td>
<td>2.3</td>
<td>539</td>
</tr>
<tr>
<td>Cu$_2$O</td>
<td>2.172</td>
<td>571</td>
</tr>
<tr>
<td>CdSe</td>
<td>1.7</td>
<td>729</td>
</tr>
<tr>
<td>GaAs</td>
<td>1.4</td>
<td>886</td>
</tr>
<tr>
<td>WeS$_2$</td>
<td>1.2</td>
<td>1033</td>
</tr>
<tr>
<td>Si</td>
<td>1.17</td>
<td>1060</td>
</tr>
<tr>
<td>PbS</td>
<td>0.286</td>
<td>4336</td>
</tr>
<tr>
<td>PbSe</td>
<td>0.165</td>
<td>7515</td>
</tr>
</tbody>
</table>

The band gap ($E_{bg}$) in semiconductors is the separation between the valence band (VB) and the conduction band (CB) (see Figure 2). The semiconductor band gap determines what type of photons can activate a photocatalyst, by promoting excited electrons to move from the valence band to the conduction band.

Semiconductors can be classified into two categories: 1) intrinsic semiconductors and 2) extrinsic semiconductors. An intrinsic semiconductor is a pure material in which, electron and holes flow in opposite directions in the presence of an electric field (i.e. TiO$_2$). An
An extrinsic semiconductor can be formed through the addition of impurities by doping. This process results in a change of relative concentrations of electron and holes in the material (i.e. Metal-TiO$_2$).

Chemical doping impurities are called donors. Semiconductors doped can be of the $n$-type with $n$ standing for a negative charge. Impurities that take away an electron from the semiconductor are called acceptors, yielding $p$-type semiconductors with $p$ representing a positive charge. There is however, an important parameter to describe the occupancy of electrons in the system, which is the Fermi Energy Level as described by (Kondarides 2005).

**Figure 2: Energy band scheme for a solid semiconductor**

The Fermi Energy Level is defined as the energy at which the probability of electron addition is equal to 0.5 and is related to the number of electrons in the intrinsic semiconductors. This Fermi Level of intrinsic semiconductors is located midway between the conduction and valence bands to represent the equal statistical probability of finding a charge carrier in either of these two energy bands (see Figure 3).

**Figure 3: Fermi Level position for: a) intrinsic, b) $n$-type and c) $p$-type semiconductors**
By shifting the conduction band (n-type) by doping it with an intrinsic semiconductor with donor impurities, “the probability of electron encounters increases”. As well by shifting a valence band (p-type) by doping it with acceptor impurities “the hole encounters augments”. Hence, by displacing the Fermi Level by adding donor or acceptor impurities, some photocatalytic semiconductor properties can be improved (Mete et al. 2009). As a result, the photocatalyst energy band gap can be narrowed and the semiconductor can absorbed the longest wavelength photons from the sunlight spectrum (Yu, Qi, and Jaroniec 2010).

2.3.1.1 Titanium Dioxide (TiO₂)

In last decade, TiO₂ photocatalysts have been extensively studied for environmental applications. Despite its use as a white pigment, TiO₂ is useful for paper, rubber, plastics and cosmetic production. Titanium dioxide is widely used as a photocatalyst since it is not very expensive, has good thermal stability, is chemically and biologically inert, is non-toxic and is able to promote the oxidation of organic compounds, including the inactivation of microorganisms (de Lasa, Salaices, and Serrano 2005). TiO₂ has been regarded as a promising candidate to support the future hydrogen economy because it is stable, abundant, low-cost and environmental friendly (Zheng et al. 2009).

It is well acknowledged that the photoactivity of TiO₂ depends on the structure and microstructure of the semiconductor powder. TiO₂ can be present in various microcrystalline structures, of which the most relevant are rutile, anatase and brokite. The most common physical properties of these types of TiO₂ structures are documented in Table 4.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Crystalline form</th>
<th>Density (g/cm³)</th>
<th>Refractive Index</th>
<th>Mohs’ hardness</th>
<th>Permittivity</th>
<th>Melting point</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rutile</td>
<td>Tetragonal system</td>
<td>4.27</td>
<td>2.72</td>
<td>7.0~7.5</td>
<td>114</td>
<td>1825</td>
</tr>
<tr>
<td>Anatase</td>
<td>Tetragonal system</td>
<td>3.90</td>
<td>2.52</td>
<td>5.5~6.0</td>
<td>48</td>
<td>Transformation to Rutile</td>
</tr>
</tbody>
</table>
Thermodynamic stability of the TiO$_2$ polymorphs is impacted by particle size. In fact, anatase and brookite are stable at small particle sizes, regardless of the fact that they have lower surface enthalpies than Rutile (Weibel, Bouchet, and Knauth 2006). Nevertheless, the surface properties of TiO$_2$ are responsible for, to large extent, its excellent photocatalytic performance. Thus, a high photocatalytic activity is due to both large surface area and small energy band. TiO$_2$ (anatase) can work as a photocatalyst under near-UV Light (365-388 nm) irradiation, as it is shown on Table 3. Nevertheless, TiO$_2$ photo activation is limited under solar light as a result of the fact that 4-5% of near-UV light is contained in the whole sunlight spectrum (Mohapatra et al. 2007).

During photocatalytic oxidation (see Figure 4), the catalyst absorbs near-UV light, which excites electrons from the valence band into the conduction band. The resulting electron (e$^-$)/hole (h$^+$) pairs can then migrate to the surface and initiate redox reactions with adsorbed organics (de Lasa, Salaices, and Serrano 2005; Blount and Falconer 2002).

**Figure 4:** Titanium dioxide particle (TiO$_2$) scheme during photocatalytic light activation reaction process (Oxidation/Reduction)

2.3.2 Photocatalytic Hydrogen Production Techniques

Among the diversity of semiconductors a limited group of materials that covers some of the basic requirements to improve some chemical and physical properties can be selected
for photocatalytic hydrogen generation. These materials must be environmentally friendly, be reliable and be able to endure process conditions (Bard 1979). In this group of potential candidate materials, one could cite, on one hand, some catalyst supports such as oxide materials (i.e. TiO$_2$). Unfortunately, some have low surface area. However, to improve the semiconductor surface area, some materials may be included such as zeolites, aluminas, activated carbon or silicas. On the other hand, the deposition of precursors, such as transition metals or lanthanides on oxide semiconductors is needed to enhance their photocatalytic activity for hydrogen production (Strataki et al. 2010; Yoong, Chong, and Dutta 2009; Hameed, Gondal, and Yamani 2004; N. Wu and Lee 2004). Therefore, under this scenario, an improvement or modification of different existing techniques is needed to develop new types of semiconductors for photocatalytic hydrogen generation (A. Kudo 2006).

2.3.2.1 Metal Loading on TiO$_2$

Nowadays, a great effort is been made to look for new precursors (metals) in order to improve the photocatalytic TiO$_2$ efficiency. One must consider that the activity of the TiO$_2$ powder depends on its bulk and its surface properties. Therefore, TiO$_2$ powders have been modified by different metal particle deposition methods, such as precipitation, doping, impregnation or photodeposition with transition metals (Ni et al. 2007; Emilio et al. 2004). Moreover, it has been shown that the photocatalytic hydrogen production rate can be enhanced by the effects of deposition method and the precursor concentration (F. Wang et al. 2009).

New advances have been reported when noble metals such as platinum (Pt), gold (Au), palladium (Pd), rhodium (Rh), nickel (Ni), copper (Cu) and silver (Ag) have been deposited on the surface of TiO$_2$. These have shown an improvement in the photocatalytic activity by shuttling and storing photogenerated electrons from the photocatalyst to the acceptor (Connelly and Idriss 2012; Maicu et al. 2011; Bahruji et al. 2011; Mogyorósi et al. 2009; Greaves et al. 2006; Megyery-balog 2004). In this respect, different studies have demonstrated that metal ion or metal deposited on semiconductors exhibit shifts in the Fermi Level bringing it to significantly negative energy potentials. This shift improves the interfacial charge transfer process efficiency and enhances the
semiconductor energy bang gap (Kowalska et al. 2008). It must be noted that the Fermi Level of deposited precursors (noble metals) are lower than the levels of TiO₂. Thus, the photo-excited electrons can be transferred from the conduction band (CB) to the noble metal particles deposited on TiO₂ surface. As well the photo generated holes on the valence band (VB) remain unchanged (see Figure 5) (Antony et al. 2012).

![Figure 5: Photocatalytic activation scheme of TiO₂ sensitized by noble metal particles (M⁰)](image)

Metalized TiO₂ particles and colloids are often used as photocatalysts for photocatalytic hydrogen production (Sreethawong, Junbua, and Chavadej 2009) and photodecomposition of organic polluting materials (Teh and Mohamed 2011; Katsumata et al. 2009; Chiang et al. 2004; Sun, Vorontsov, and Smirniotis 2003).

### 2.3.2.1.1 Platinum deposition on TiO₂

The role of noble metals such as Platinum on TiO₂ is then, to provide a site for the more efficient reduction of protons (Egerton and Mattinson 2008). Platinum clusters or nanoparticles loaded on the TiO₂ surface are known to act as an electron sinks. This strongly enhances the photocatalytic activity of titanium dioxide through the formation of a Schottky barrier (retarding the electron/hole recombination) at the TiO₂/Pt interface. This phenomenon appears to promote an efficient separation of holes and electrons charges carriers photo-generated under near-UV light. As a result, the interfacial charge transfer and the efficiency of the photocatalytic reaction are enhanced (Kandiel, Dillert, and Bahnemann 2009; Riassetto et al. 2009b; Patsoura, Kondarides, and Verykios 2006; Emilio et al. 2004; Choi et al. 2003). Nevertheless, this effect depends on the substrate to
be treated (Emilio, Gettar, and Litter 2005), surface conditions, particle size and particle dispersion, as well as on the method of platinum deposition (Abida et al. 2011; Siemon et al. 2002) and platinum loading (Emilio et al. 2004).

Platinum deposits can serve as a temporary electron reservoir (chamber). Electrons are transferred from the TiO$_2$ bulk to the platinum precursor (Uosaki, Yoneda, and Kita 1985). The accumulated electrons onto the Pt eventually react with adsorbed protons on the TiO$_2$ surface (W.-N. Wang et al. 2012; J. Kim, Lee, and Choi 2008). Furthermore, the TiO$_2$ electrode has been reported as a good support for Pt. Therefore, platinized titanium anodes have certainly found applications in electrochemical technology. Moreover, platinization either electrochemically or photocatalytically appears to increase the hydrogen evolution reaction rate not having however a kinetic effect vis-a-vis of oxygen evolution on TiO$_2$ single crystals electrodes. Besides this, platinum doped on titania photocatalysts have shown long term photoelectro-catalytic stability (H. R. Kim et al. 2008).

### 2.3.2.2 Addition of Sacrificial Reagents

Sacrificial reagents or hole scavengers are chemical additives in photocatalytic reaction systems. Furthermore, a sacrificial reagent (electron donor) provides an efficient electron/hole separation due to the fact that it reacts irreversibly with photo generated holes (see Figure 6), resulting in higher quantum efficiencies. Nevertheless, the continued addition of electron donors is required to maintain hydrogen production since sacrificial reagents are consumed during the photocatalytic reaction. Acetic acid, lactic acid, acetaldehyde, formaldehyde, EDTA, methanol and ethanol have been tested and proved to be effective sacrificial reagents to improve hydrogen production (Ni et al. 2007; N.-L. Wu et al. 2004; Dickinson et al. 1999). Both organic pollutants and biomass in aqueous solutions can also act as electron donors (Zielinska, Borowiakpalen, and Kalenczuk 2008; Kondarides et al. 2007).
Figure 6: Schematic representation during a photochemical reaction on TiO$_2$ in presence of a sacrificial reagent ($C_xH_yO_z$)

Other sacrificial reagents for hydrogen evolution are inorganic ions, such as Ce$^{4+}$/Ce$^{3+}$, $S^{2-}$/SO$_3^{2-}$ and IO$_3^-$/I$^-$. Ions in solution are intended to prevent the backward electron/hole recombination over a metal co-catalyst (Abe, Sayama, and Arakawa 2003).

2.4 Photocatalytic Reactor Configuration for H$_2$ production and Light Sources

Although various types of reactor designs have been developed mostly for water/air treatment, there is no mention in the literature with respect to solar hydrogen production reactors (Jing et al. 2010). The current lack of industrial and commercial applications is mainly due to the low photocatalytic efficiency of photocatalytic semiconductors and to the absence of efficient, intermediate and large scale photoreactor configurations (Mukherjee and Ray 1999). Nevertheless, hydrogen production and water/air treatment systems based on heterogeneous photocatalysis are in constant development and change, as researchers look for more environmental friendly photocatalytic processes.

A number of suggestions have been made to improve the photocatalytic process: a) a large catalyst surface area has to be irradiated, b) the irradiated light distribution must be uniform inside the reactor, c) the external and internal diffusion must be minimized, and d) the absorption of light has to be adequate to promote electron and holes scavengers. Nonetheless, not all of the above requirements have been met in a single reactor. Therefore, photocatalytic reactors can be classified according their design features: 1)
type of radiation, 2) Position of irradiation source and 3) state of the catalysts (de Lasa, Salaices, and Serrano 2005).

2.4.1 Type of Radiation or Light Sources

In principle sunlight is the actual energy source considered for commercial applications due to its wide solar spectrum. Measurements of solar light are required to determine the type of energy that can be useful inside the photoreactor for photocatalytic hydrogen production (see Figure 7). Nevertheless, most of the data reported in the literature is obtained by an assortment of solar simulators instead of natural solar energy (J. Nowotny et al. 2007).

![Figure 7: Natural solar energy spectrum distribution](image)

A comparison of the irradiation spectra (output profiles) for different types of lamps is presented below (see Figure 8) for: a) a 150W xenon arc (ozone-free), b) a 150W mercury-xenon (ozone-producing), c) a 15 W black light blue (BLB) lamp and d) a solar simulated radiation with a powerful 300W ceramic xenon lamp. One should notice that, the mercury-xenon lamp and the BLB lamp have strong Hg emission lines over the xenon spectrum. Furthermore, the ceramic xenon lamp has high irradiation, at wavelengths that can be of interest for specific applications such as photocatalytic processes (J. Yang et al. 2012; Aryal et al. 2010). However, the artificial light sources do not have the same spectral distribution as sunlight.
A multivariant research approach to light sources is essential and a very relevant component for photocatalytic processes such as degradation of water/air and hydrogen production. In addition, photocatalytic activity is strongly dependent on the light irradiation or photon flux (energy per unit area) on the surface of the photocatalyst. In this respect, ultraviolet and more specifically near-UV radiation is of relevant to this study. Therefore, more specific radiation light research with respect to our BLB lamp is demonstrated and discussed in further sections of this thesis.

2.4.2 Irradiation Source Position

The irradiation source incidence position is essential in the reactor configuration. Hence, the photocatalytic reactor configuration largely conditions its performance. This demonstrates the importance of the irradiation source location (Imoberdorf et al. 2007).

The most common type of reactor geometry is the tubular type or annular type. This geometry allows one to adapt the light reactor position in three different manners (see Figure 9).
As it is shown above, each case proves to have different irradiation flux patterns to activate the photocatalyst at different geometries throughout the reactor. However, the photocatalyst state needs to be addressed to make the photocatalyst-light contact more efficient.

2.4.3 State of the Photocatalyst

The photocatalyst can be either supported or suspended in the photocatalytic reactor system (de Lasas, Salaices, and Serrano 2005). These two different states permit one to study the advantages and disadvantages of the photocatalyst inside the photocatalytic reactor system. Hence, it is necessary to define and differentiate each state as follows:

a) Photocatalytic slurry (suspended) reactors. The photocatalyst particles are freely dispersed in the fluid phase (water). Therefore, the photocatalyst is fully incorporated in the liquid mobile phase.
Table 5: Advantages and Disadvantages of suspended photocatalyst reactors

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔ Fairly uniform catalyst distribution</td>
<td>× Requires post-process filtration</td>
</tr>
<tr>
<td>✔ High photocatalytic surface area to reactor volume ratio</td>
<td>× Important light scattering and adsorption in the particles suspended medium</td>
</tr>
<tr>
<td>✔ Limited mass transfer</td>
<td></td>
</tr>
<tr>
<td>✔ Minimum catalyst fouling effects due to the possible continuous removal and catalyst replacement</td>
<td></td>
</tr>
<tr>
<td>✔ Well mixed particles suspension</td>
<td></td>
</tr>
<tr>
<td>✔ Low pressure drop through the reactor</td>
<td></td>
</tr>
</tbody>
</table>

b) Photocatalytic reactors with immobilized photocatalyst. The photocatalyst is either anchored to a fixed support or dispersed on the stationary phase.

Table 6: Advantages and Disadvantages of immobilized photocatalyst reactors

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Drawbacks</th>
</tr>
</thead>
<tbody>
<tr>
<td>✔ Continuous operation</td>
<td>× Low light utilization efficiencies due to light scattering by immobilized photocatalyst</td>
</tr>
<tr>
<td>✔ Improved removal of organic material from water phase while using a support with adsorption properties</td>
<td>× Restricted processing capacities due to the mass transfer limitations</td>
</tr>
<tr>
<td>✔ No need for an additional catalyst separation operation</td>
<td>× Possible catalyst deactivation and catalyst wash out</td>
</tr>
</tbody>
</table>

2.5 Photo-CREC Reactors

The novel Photo-CREC Reactors were first introduced by Professor de Lasa’s team at CREC. Photo-CREC Reactors are devices for photocatalytic degradation of water/air via UV-light on slurry or other immobilize conditions (de Lasa, Salaices, and Serrano 2005). Lately, they have been considered for hydrogen production (Escobedo Salas, Serrano Rosales, and de Lasa 2013).

2.5.1 Photo-CREC Water II Reactor (PCW-II)

The Photo-CREC Water II Reactor (PCW-II) is an efficient system for photocatalytic water degradation via UV-light on slurry conditions. It consists of two concentric tubes (or containers) with a UV lamp inside the transparent inner container and a free-flowing
photocatalyst suspension in the concentric channel (Moreira 2011). The reactor operates in a batch mode. Moreover, it is also equipped with a four point flow distributor injector at the reactor entrance to ensure uniform injection and intense mixing. The injection points are located in the top section of the reactor at 90º- radial and 45º- azimuthal positions.

However, the Photo-CREC Water II Reactor with a new hydrogen storage/mixing tank was implemented for photocatalytic hydrogen production as part of the present PhD dissertation. The novel H₂ tank addition to the system has shown outstanding performance to capture and measure hydrogen taking advantage of the advanced radiation emitted by the PCW-II reactor. The details of the PCW-II for hydrogen production are described later on in Section 4.1 of this thesis.

### 2.5.2 Photo CREC Air Reactor

This novel unit was designed by the CREC research group. The objective of the unit design was to implement a highly efficient photocatalytic unit for air treatment. The Photo-CREC Air Reactor operates in a batch mode. The Photo-CREC Air Reactor uses 8 UV lamps held by four aluminum housings with internal reflective walls. The aluminum housings are located outside around a sealed quartz cylinder. In addition, the photocatalyst (TiO₂) is immobilized by a cylindrical stainless steel mesh, which incorporates a cylindrical reaction section with an aerodynamic bullet nose, promoting uniform distribution over the photocatalyst (Garcia 2012).

### 2.6 Photocatalytic Reactor Energy Efficiencies

Several studies have emphasized the importance of energy efficiencies in photochemical reactors as a key factor of the reactor design. Nonetheless, energy efficiencies still present challenges due to the many variables involved, such as: a) reaction rates, b) reaction mechanism, c) OH⁻/H⁺ free radicals, d) kinetic constants, e) adsorption parameters, f) irradiation field, g) photocatalyst absorption, h) photocatalyst loading and i) the type of organic specie to be converted. Consequently, the photocatalytic reactor efficiencies still need to be established (Benito Serrano et al. 2010).
Energy efficiencies have been evaluated using different factors for instance: a) the quantum yield and b) the apparent quantum yield (Emeline et al. 2006; Ishibashi et al. 2000). Later, a photocatalytic thermodynamic efficiency factor (PTEF) based on thermodynamic considerations was proposed (B. Serrano and de Lasa 1997). Thus, energy efficiency estimations using the quantum yields demand the calculation of the incident photons on TiO$_2$, while the quantum efficiencies require the evaluation of the absorbed photons in the reactor media (Cabrera, Alfano, and Cassano 1995).

On this basis, QY and PTEF factors point toward a high degree of photon utilization on Photo CREC reactors for the photocatalytic conversion of organic pollutants in water/air (Benito Serrano et al. 2009) and the photocatalytic generation of hydrogen.

2.6.1 Quantum Yield ($\varphi$)

One can define the quantum yield for any photocatalytic reaction as the number of photoconverted or photoproduced molecules per photon of light absorbed by the photocatalyst (Emeline et al. 2006; Cabrera, Alfano, and Cassano 1994). Quantum yields are useful and valuable efficiency estimators in photocatalysis (Garcia H., Serrano, and de Lasa 2012; Benito Serrano et al. 2009). Therefore, on this basis, it is important to summarize several possible quantum yield definitions as reported in Table 7.

**Table 7: Definition of quantum parameters** (de Lasa, Salaices, and Serrano 2005)

<table>
<thead>
<tr>
<th>No.</th>
<th>Definition</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Cassano et al. (1995); Davydov et al. (1999)</td>
<td># of pollutants molecules degraded from primary process number of photons absorbed</td>
</tr>
<tr>
<td></td>
<td>Primary Quantum Yield (Primary QY)</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>Cassano et al. (1995)</td>
<td># of pollutants molecules degraded from primary and secondary process number of photons absorbed</td>
</tr>
<tr>
<td></td>
<td>Overall Quantum Yield (Overall QY)</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Peil and Hoffmann (1995); Valladares and Bolton (1993); Yamazaki-Nishida et al. (1994)</td>
<td># of pollutants molecules degraded number of photons absorbed</td>
</tr>
<tr>
<td></td>
<td>Quantum Yield (Apparent QY)</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Fox and Dulay (1993); Nimlos et al. (1993); Sczechowski et al. (1995); Zhang et al. (1994)</td>
<td># of pollutants molecules degraded from primary process number of photons entering the reactor</td>
</tr>
<tr>
<td></td>
<td>Global Quantum Yield (QE)</td>
<td></td>
</tr>
</tbody>
</table>
Quantum Yield $(QY \text{ or } \phi)$

The simplest evaluation of the quantum yield is often based on the rate of photoconverted or photo produced molecules throughout the entire irradiation time (de Lasa, Salaices, and Serrano 2005).

In addition, the quantum yield determination calls for the analysis of $(P_a)$, which is the rate of absorbed photons on the photocatalyst surface. $\frac{dN_{i}}{dt}$ denotes the photoconversion rate of $i$ species molecules.

$$\phi = \frac{\frac{dN_{i}}{dt}}{P_a} \quad (2-1)$$

Hence, the proper definition of quantum yield needs a careful analysis to determine the number of photons absorbed by the photocatalyst. The experimental method to evaluate the rate of absorbed photons in slurry reactor conditions is based on a macroscopic radiation energy balance. Macroscopic energy balances involve the use of optoelectric methods with near-UV lamps, spectro-photo-radiometers and collimators (Miguel Salaices, Serrano, and de Lasa 2001a). A more detail description of the macroscopic radiation energy balance is given further in Section 5.3.1 of this thesis.

### 2.6.2 Photochemical Thermodynamic Efficiency Factor ($PTEF$)

The CREC research group has developed research activity in this area in order to be able to assess the quantum yields in photocatalytic reactors. The CREC research group has also shown that thermodynamics can also be valuable in defining efficiencies. More specifically, one can refer to the $PTEF$ or Photochemical Thermodynamic Efficiency Factor suggested initially by Serrano and de Lasa (1997) for photocatalytic water decontamination. $PTEF$ was more recently extended for air treatment (Garcia H., Serrano, and de Lasa 2010).
There is, however, the need for a PTEF factor specially tailored for hydrogen production. In this case, one could describe a PTEF efficiency in a water splitting reactor unit for hydrogen production as follows,

\[
PTEF = \eta = \frac{Q_{used}}{Q_a}
\]

(2-2)

where, \(Q_{used}\) corresponds the irradiation energy used for the desired formation of OH\(^-\) and H\(^-\) radicals, and \(Q_a\) denotes the irradiation energy absorbed.

The \(Q_{used}\) shall encompass the energy required for the formation of both OH\(^-\) and H\(^-\) radical groups simultaneously. This new approach not described in the literature as of today and is later developed further in Section 8.1.2.

### 2.7 Photocatalytic Kinetic Studies for Hydrogen Production

The present section describes the various available kinetic models as reported in the technical literature for hydrogen production.

#### 2.7.1 Photocatalytic Multicomponent Langmuir-Hinshelwood Isotherm

Heterogeneous photocatalytic kinetic processes can be explained by the most commonly used kinetic Langmuir-Hinshelwood (LH) expression (Kumar, Porkodi, and Rocha 2008). The general form of the LH equation for photocatalytic reactions is given by:

\[
r_i = \frac{k_i^k K_i^A C_i}{1 + \sum_{j=1}^{n} K_j^A C_j} \quad \left(\text{mole g}^{-1}\text{cat min}^{-1}\right)
\]

(2-3)

where \(r_i\) represents the reaction rate for \(i\) components, \(k_i^k\) stands for the reaction kinetic constant \(\left(\text{mole g}^{-1}\text{cat min}^{-1}\right)\), \(K_i^A\) denotes the absorption constant \(\left(\frac{L}{\text{mole}}\right)\) and \(C_i\) is the concentration of participating species \(\left(\text{mole L}^{-1}\right)\).

When a photoreactor is operated in a batch mode as is the case of PCW-II, a balance equation for each component “\(i\)” can be expressed as follows:
\[ r_i = \frac{1}{W} \frac{dN_i}{dt} = \frac{V}{W} \frac{dN_i}{dt} = \frac{V}{W} \frac{dc_i}{dt} \]  \hspace{1cm} (2-4)

where \( W \) represents the mass of the solid catalyst (\( g_{\text{cat}} \)), \( V \)=reactor volume (L), \( N \)=number of moles (mole) and \( t \)=time (min).

Replacing eq. (2-3) into eq. (2-4) the reaction rate for the “i” chemical species of the slurry reaction can be attained,

\[ r_i = \frac{dc_i}{dt} = \frac{W k_i k^A c_i}{V 1 + \Sigma_{j=1}^n k^A_j c_j} \]  \hspace{1cm} (2-5)

We can also express the above equation when \( k_i = \frac{W}{V} k^A_i \) as:

\[ \frac{dc_i}{dt} = \frac{k_i c_i}{1 + \Sigma_{j=1}^n k^A_j c_j} \]  \hspace{1cm} (2-6)

Thus, eq. (2-6) can describe any chemical species in the reaction network, obtained during the photocatalytic oxidation/reduction of the sacrificial reagent and the respective chemical intermediate species (de Lasa, Salaices, and Serrano 2005).

The estimation of kinetic and adsorption parameters involved in equation (2-6) can be developed numerically. However, the LH model displays one limitation: it involves the non-linear regression of a large number of kinetic and adsorption parameters. This could lead to models with high cross correlation. Nonetheless, given that adsorption parameters can be calculated independently, this allows decoupling the calculation of the kinetic parameters and adsorption parameters in the LH model. The outcome is a set of kinetic parameters with narrow spans and a good fit for both reactant, intermediate and final product chemical species (Moreira 2011).

The review of the technical literature on this topic shows us that there is a lack of kinetic models to describe photocatalytic hydrogen production using organic scavengers. Thus, it is important to propose such kinetic models for hydrogen production based on competitive site adsorption models and leading to Langmuir-Hinshelwood kinetics.
2.8 Photocatalytic Process Application

In the last decade photocatalysis using semiconductor powders has attracted scientists toward the study of TiO$_2$. This semiconductor has diverse applications due to the versatility and multidisciplinary nature as photocatalyst for different photocatalytic processes (Tennakone 1993). Titanium dioxide is widely used as a photocatalyst since it is not very expensive, has good thermal stability, is chemically and biologically inert, is non-toxic and is able to promote oxidation/reduction of organic compounds, including the inactivation of microorganisms.

Photocatalysis with semiconductor particles have diverse applications. The most extensively applied technologies using TiO$_2$ are devoted to environmental procedures such as: water treatment (Vamathevan et al. 2002), air purification (Ibrahim and de Lasa 2003), self-cleaning/sterilizing surfaces (Kamegawa, Shimizu, and Yamashita 2012; Kühn et al. 2003), metal extraction (Tennakone and Wijayantha 1998), metal corrosion prevention (Park, Kim, and Choi 2002), and water splitting for hydrogen production (Lalitha et al. 2010). In addition, TiO$_2$ is also broadly used within the industry to fabricate white pigment, paper, rubber, plastics and cosmetics (Jaroenworaluck et al. 2006).

The photocatalytic surface reaction principles and low cost are among other aforementioned properties of TiO$_2$ making this semiconductor material a suitable candidate for diverse and new alternative technology applications.

2.9 Conclusions

Photocatalytic processes are an interesting environmental alternative address water pollution, air purification and hydrogen generation. Both photon absorption and semiconductors are needed for photochemical oxidation/reduction reactions to take place.

Chapter 2 provides an overview of photocatalytic processes, photocatalyst synthesis, photocatalytic reactor design and configuration, as relevant to the present PhD dissertation.
This chapter emphasizes the importance of energy efficiency factors such as the quantum yield (\(\phi\)) and the Photochemical Thermodynamic Efficiency Factor (\(PTEF\)) for photocatalytic hydrogen production.

Furthermore, Chapter 2 provides a review of photocatalytic kinetic modeling for model organic chemical species and intermediate species in water. It appears that kinetic modeling using Langmuir-Hinshelwood formulations is a suitable approach for fundamentally based kinetics for hydrogen production assisted with organic OH scavengers.

On the other hand, a photocatalytic kinetic study is presented with a simple approach for the model component (organic pollutant) and the intermediate species involved. Thus, kinetic modeling particularly LH model seems to be a suitable alternative for precursor-TiO\(_2\) loaded during the photocatalytic hydrogen generation.

In all these respect, this PhD dissertation attempts to provide new alternatives for photocatalytic hydrogen production using modified photocatalysts. The PhD dissertation also addresses the key issues of photocatalytic reaction kinetics and energy efficiency.
Chapter 3
Scope of the Research

3 General Objectives

The goal of the present PhD dissertation is to contribute with photocatalytic water splitting for hydrogen production studies.

It was envisioned from the early stages of this research that both the photocatalyst and a renewable organic sacrificial reagent would be selected for studies in a bench-scale photocatalytic reactor “Photo-CREC Water II”. As a result, it was also anticipated that key contributions in this thesis should include: a) photocatalyst synthesis, b) quantification of hydrogen produced, c) determination of a kinetic reaction model and d) evaluation of quantum yields and energy efficiencies.

3.1 Particular Research Objectives

The present PhD dissertation was planned as having several experimental and theoretical particular objectives, which include:

a) The design of an efficient tank connected to the photocatalytic reactor capable of storing hydrogen under well-mixed conditions for both the slurry solution and the gas phase.

b) The synthesis of a photocatalyst suitable for photocatalytic water splitting.

c) The study of the influence of various photocatalyst and operational parameters during the photocatalytic reaction process such as, Pt-TiO$_2$ loading, pH and sacrificial reagent.

d) The study of the radiation spectrum in the Photo-CREC Water II Reactor.

e) The development of a kinetic model able to describe the observed photocatalytic reaction rates for both hydrogen production and the conversion of the sacrificial reagent.
3.1.1 Photocatalyst Preparation and Characterization

Regarding photocatalyst synthesis and characterization, this research was planned to be developed with the following goals:

a) To develop a Pt-modified TiO$_2$ photocatalyst for photocatalytic hydrogen production.

b) To characterize the Pt-modified photocatalyst in terms of physical and chemical properties.

3.1.2 Photocatalytic Reactor Design and Irradiation Study

A modified slurry Photo-CREC Water II reactor was considered for hydrogen production studies. It was envisioned that the available Photo-CREC Water II unit should be equipped with the following key components:

a) A hydrogen storage tank with a self propelled mixing device was considered a requirement for adequate photocatalyst re-suspension and representative samples of hydrogen concentration.

b) A spectro radiometer and quartz wall windows for irradiation measurements in various strategic reactor locations.

c) Pt-TiO$_2$ photocatalyst of adequate sizes and loadings for hydrogen generation in a slurry unit via water splitting.

3.1.3 Photocatalytic Kinetic Study

Regarding kinetics, experiments were planned for photocatalytic hydrogen production using ethanol as a sacrificial reagent. The expectation was that this would allow the following:

a) To identify and quantify intermediate byproducts and reaction products during the photocatalytic activity for hydrogen production, using gas chromatography (GC).

b) To investigate the hydrogen production reaction mechanisms and the reaction network under near-UV irradiation conditions.

c) To evaluate kinetic rate equations from the experimental results.
d) To estimate the kinetic parameters with the help of non-linear regression and a set of ordinary differential equation, using rigorous kinetic parameter estimation.

3.1.4 Energy Efficiencies Evaluation

Concerning the determination of energy utilization for hydrogen production in the Photo-CREC Water II Reactor the following was envisioned:

a) To measure photon absorption during photocatalytic hydrogen production in the Photo-CREC Water II Reactor. This will allow one to perform macroscopic irradiation balances accounting for irradiation absorbed in the photocatalyst.

b) To evaluate the hydrogen production reaction mechanisms and to estimate both quantum yields \((\phi)\) and Photochemical Thermodynamic Efficiency Factors \((PTEF)\).
Chapter 4
Experimental Methods

4 Introduction

This chapter describes an efficient and reliable reactor set up to carry out the photocatalytic generation of hydrogen. This chapter also addresses the experimental procedure to synthesize and modified a commercial photocatalyst for new applications of environmental energy generation. Furthermore, the analytical units and techniques used for identification-quantification of products, intermediates and byproducts are explained in detail.

4.1 Photo-CREC Water II Reactor for Hydrogen Production

A novel Photo-CREC Water II Reactor was used in the present study (Figure 10). This modified Photo-CREC Water II Reactor operates as a “well mixed” batch unit. This unit includes major improvements required for hydrogen production, namely a self-driven mixing stirrer and a hydrogen storage tank.

The modified Photo-CREC Water II Reactor for hydrogen production also includes two concentric tubes to provide a radial and axial symmetrical irradiation field. The first tube is a transparent inner cylinder of pyrex glass, that was used due to the fact it only absorbs 5% of the emitted near-UV Light. The pyrex glass tube display good near-UV light transmission properties and has a relatively low cost.

In the Photo-CREC Water II reactor, a Black Light Blue Lamp of 15W is placed inside this glass tube. This near-UV lamp has an emission range between 340 to 410 nm. The second and outer tube is made out of UV opaque polyethylene to minimize radiation reflection. Moreover, this outer reactor tube facilitates radiometric, spectroradiometric measurements and performance of macroscopic energy balances. Macroscopic energy balances are essential for energy efficiency calculations.
Water II reactor provides a concentric annular channel for the circulation of a free-flowing photocatalyst suspension.

Figure 10: Schematic diagram of the Photo-CREC Water II Reactor with H₂ mixing tank: (1) BLB Lamp, (2) Pyrex glass tube, (3) UV- opaque polyethylene cylinder, (4) Fused-silica windows, (5) Centrifugal pump, (6) H₂ storing/mixing tank, (7) Gas sampling port, (8) Purging gas injector and (9) Draining gas valve

Figure 10 reports a schematic diagram of Photo-CREC Water II reactor and its accessories. This figure shows the overall unit configuration: a sealed stirred tank chamber connected in series with a tubular photocatalytic reactor. The Photo-CREC Water II reactor includes the additional following components: i) a BLB Lamp, ii) a pyrex glass tube, iii) a UV- opaque polyethylene cylinder, iv) fused-silica windows, v) a centrifugal pump, vi) a H₂ storing/mixing tank, vii) a gas sampling port, viii) a purging gas injector and viii) a draining gas valve. Dimensions of the main components of Photo-CREC Water II reactor as adapted for hydrogen production are given in Table 8.

Regarding the sealed well mixed tank, it was designed and equipped to accomplish the following: i) To provide a jet driven mixing for TiO₂-water slurry free of sealing issues and hydrogen losses, ii) To allow taking aliquot samples (gas and liquid) allowing measurements of organic scavengers and hydrogen, ii) To permit adding the
photocatalyst (Pt/TiO<sub>2</sub>), iii) To store H<sub>2</sub>, iv) To feed inert gases (N<sub>2</sub> or Ar) as needed, v) To measure the pH and vi) To monitor the temperature. A centrifugal pump circulates the fluid throughout the system and is used to modify the flow rate.

**Table 8: PCW-II and H<sub>2</sub> Mixing/Storing Tank Dimensions and Characteristics**

<table>
<thead>
<tr>
<th>Component</th>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Length (cm)</td>
<td>41.2</td>
</tr>
<tr>
<td></td>
<td>Radius (cm)</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Nominal Input Power (W)</td>
<td>15</td>
</tr>
<tr>
<td>1. Black Light Blue Lamp (BLB USHIO)</td>
<td>Output Power (W)</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Emission Range (nm)</td>
<td>340-410</td>
</tr>
<tr>
<td></td>
<td>Emission Rate (Einstein/s)</td>
<td>1.14X10&lt;sup&gt;5&lt;/sup&gt;</td>
</tr>
<tr>
<td></td>
<td>Efficiency (%)</td>
<td>25</td>
</tr>
<tr>
<td></td>
<td>Average Energy (KJ/molphoton)</td>
<td>324</td>
</tr>
<tr>
<td>2. Inner cylinder (Pyrex Glass)</td>
<td>Length (cm)</td>
<td>61</td>
</tr>
<tr>
<td></td>
<td>Internal Radius (cm)</td>
<td>1.505</td>
</tr>
<tr>
<td></td>
<td>External Radius (cm)</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>Thickness (cm)</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>Height (cm)</td>
<td>45</td>
</tr>
<tr>
<td>3. Annular Reactor</td>
<td>Internal Radius (cm)</td>
<td>1.75</td>
</tr>
<tr>
<td></td>
<td>External Radius (cm)</td>
<td>4.5</td>
</tr>
<tr>
<td>4. Windows (Fused Silica)</td>
<td>Diameter (cm)</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>Thickness (cm)</td>
<td>0.312</td>
</tr>
<tr>
<td>5. Pump (Little Giant Co.)</td>
<td>Voltage</td>
<td>115</td>
</tr>
<tr>
<td></td>
<td>Amperes</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>Hertz</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>Horse Power</td>
<td>1/20</td>
</tr>
<tr>
<td></td>
<td>RPM</td>
<td>300</td>
</tr>
<tr>
<td>6. H&lt;sub&gt;2&lt;/sub&gt; Mixing/Storing tank</td>
<td>Internal Radius (cm)</td>
<td>22.8</td>
</tr>
<tr>
<td></td>
<td>External Radius (cm)</td>
<td>31</td>
</tr>
<tr>
<td></td>
<td>Height (cm)</td>
<td>21</td>
</tr>
<tr>
<td>* Internal Tank Impeller</td>
<td>Diameter (cm)</td>
<td>4.5</td>
</tr>
<tr>
<td></td>
<td>Height (cm)</td>
<td>16.5</td>
</tr>
<tr>
<td>** Acrylic Lid with Integrated Septum</td>
<td>Radius (cm)</td>
<td>15.5</td>
</tr>
<tr>
<td></td>
<td>Thickness (cm)</td>
<td>1.5</td>
</tr>
</tbody>
</table>
Prior to the experiments, the photocatalyst was sonicated for a 10 min. period to ensure good particle distribution in the slurry solution before being added to the water/ethanol solution in the storage tank.

4.2 Lamp Characterization

The Lamp Testing Unit (LTU) developed by CREC’s members (B. Serrano and de Lasa 1997) was used to calibrate the BLB lamp. The LTU Unit consists as reported in Figure 11, of a UV-opaque chamber, a lamp holder and a spectrometric sensor holder rail. Irradiation spectrum measurements can be performed with the sensor cell facing the lamp. The sensor can be displaced along a rail which is located at a fixed distance from the lamp axis for axial distribution irradiation measurements (Salaices, Serrano, and de Lasa 2001b).

![Figure 11: Representation of the lamp testing unit (LTU)](image)

4.3 Synthesis of Pt/TiO₂ Photocatalyst

DP25 Titanium dioxide (TiO₂) from Evonik Degussa Co. was used as semiconductor “support” to prepare the modified photocatalyst of the present study (Castillo et al. 2003; Yori and Parera 1995). Platinum on DP25 photocatalysts was prepared using incipient wetness impregnation (Regdbuto 2008) achieving 0.0616, 0.103 and 0.23 and 1wt% loadings (Ikuma and Bessho 2007; N. Wu and Lee 2004).

DP25 was dried at 140°C for 6 h before impregnation to desorb water and some other species potentially present on the TiO₂ particles. A 99.9wt% H₂PtCl₆ xH₂O reagent from Sigma- Aldrich Co. was dissolved in distillate water to produce the different impregnating Pt solution concentrations (see Appendix A).
The first Pt impregnation step was carried out at vacuum conditions with continuous mixing of the TiO$_2$ support. A 4ml of the precursor solution was employed. This solution was prepared with different precursor concentrations as required by the desired platinum loading to be used. A 2 ml aliquot of this precursor solution was added to 5g of TiO$_2$ in a drop-by-drop manner. Once the liquid addition was complete, the impregnating solution and the TiO$_2$ were left in contact with each other for 10 minutes. The wet photocatalyst was heated up to 140°C during 30 minutes using a 4.6°C/min temperature ramp.

Furthermore, the photocatalyst was left drying for another 2 hours at 140°C. This allowed water evaporation from the TiO$_2$ support leaving the H$_2$PtCl$_6$ phase on the photocatalyst outer surface. The dried photocatalyst cake was crushed in a mortar until the resulting particles were fine enough, and reached an acceptable size.

Following this, a second impregnation step was carried out using a 2ml of the remaining precursor solution and contacting it with 5g of the TiO$_2$ already impregnated one time. The twice impregnated photocatalyst was now dried at 160°C for 3h following a 5.3°C/min temperature ramp. The resulting photocatalyst cake was crushed and later grinded in a mortar. The finely grinded particles which were obtained displayed a particle size distribution which is shown later in Figure 17.

Furthermore, the resulting particles were heated up to 450°C during 1 hour using a 7.5°C/min temperature ramp and were left in the oven at 450°C for another 3 hours. The 450°C temperature was selected to ensure that chlorine was fully removed (Regdbuto 2008; Ikuma and Bessho 2007; Castillo et al. 2003; Yori and Parera 1995).

Finally, the photocatalyst was placed in a flow reactor unit under a 1cc/s of Ar/H$_2$ (90/10%, Praxair) reducing mixture. Reduction steps involved the following: a) a 6.6°C/min temperature increase during 1h, b) once 400°C reached, this temperature was kept here for another 3 hours.

In summary, and using the preparation procedure described in this section, Platinum (Pt$^0$) particles were formed on the TiO$_2$ particle outer surfaces (see Figure 12) (Khnayzer et al. 2012).
Figure 12: Photocatalyst of TiO$_2$ loaded with Platinum using incipient wetness impregnation technique through calcination-reduction process

4.4 Photocatalyst Characterization Methods

Prepared photocatalysts were characterized using: a) Specific surface area, b) Chemisorption, c) X-ray diffraction, d) Particle size distribution, e) X-ray fluorescence, f) UV-VIS NIR spectra and g) SEM/EDX (scanning electron microscopy/energy dispersion X-ray) for Images and for elemental mapping.

The specific surface areas of all prepared photocatalysts were determined using a BET surface area analyzer (Micrometrics, ASAP 2010) and using nitrogen adsorption. A photocatalyst sample was dried and degassed in a sample tube at 300°C for at least 3h before adsorption. The results were assessed by using the Autosorb ASAP 2010 software, Version 5.02.

Moreover, the active metallic particle size (crystallite size) and metal dispersion were calculated by pulse chemisorption analysis (Micrometrics, AutoChem II 2920 V 4.00). The crystalline phases of the photocatalysts were investigated using a X-ray diffractometer RIGAKU Ultima IV (Multi-Purpose Diffractometer). This instrument features a 3-kW X-ray beam with a high-precision 2θ wide-angle horizontal goniometer.
as well as “Cross Beam Optics”. The particle size distribution of the prepared photocatalyst was measured by using a Malvern Zetasizer Nano-Series.

The elemental composition analysis of the photocatalyst was established by X-ray Fluorescence (Philips PW-1480 Wavelength Dispersive Spectrometer) and quantified by utilizing the Iniquant Software. The band gap of the photocatalyst was determined by employing an UV-VIS NIR Spectrophotometer (UV-3600 Shimadzu).

Images and elemental mapping of the photocatalyst were performed using SEM/EDX (LEO/Zeiss 1540XB FIB/SEM). The ion beam column was utilized for in-situ sectioning of samples which were imaged by SEM. The system was fitted with an Oxford Instruments X-ray system allowing for elemental mapping and analysis of the selected sample milled sections. In this way, samples could be monitored in real time at high resolution with an electron column (selective etching can be achieved with sub-100 nm resolution).

4.5 Analytical Techniques

Two GCs units manufactured by Shimadzu were used. One was a GC-2010 equipped with a Grace Hayesep D packed column 100/120 mesh of 9.1m x 2mm x 2μm nominal SS and was used to separate H₂ from O₂ and N₂ (Air). A second GC-2014 set up with an Altech porapak-Q packed column 80/100 mesh of 1.83 x 3.175mm x 21.59mm nominal SS was implemented for CO₂, CH₄, and C₂H₆ detection. Furthermore, these GCs have a TCD and FID detectors as required for the quantification of various species. Argon and Helium carrier gas ultra high purity (Praxair 99.999%) were used in the GC-2010 and the GC-2014, respectively. The use of argon in the Shimadzu GC-2010 as a carrier allows increasing the sensitivity of the detector towards H₂. The GC was interfaced with a desktop that enables the analysis of the injected samples. The samples of 0.8ml were taken manually (Hamilton CO. gastight valve-syringe of 1ml) from the PCW-II mixing/storage H₂ tank at set times. They were then injected in a GC port for analysis. The calibration of the GC TCD and FID detectors were made using several mixtures of known gas and liquid concentrations. The analytical methods for the two different GCs for the detection of different species are presented in Appendix B and Appendix C.
The UFLC-Shimadzu HPLC with a Supelcogel C-610H column of 30cm x 7.8mm ID was employed to separate both the carboxylic acids and alcohols in water. In addition, a UV (LC-20AB) and a RID-10A detectors were employed for quantitative chemical species analysis at various irradiation times. This was done with the intent of tracking the formation of organic acids (Acetic Acid) and ethanol degradation during hydrogen production. Each sample was filtered using a syringe filter 13mm PTFE GD/X (Whatman, 0.2 μm) before being analyzed (see Appendix D).

### 4.6 Conclusions

Chapter 4 highlights the special features of the Photo-CREC Water II Reactor used during the present PhD dissertation. In addition, a photocatalyst modification using incipient wetness impregnation and its characterization is reported. Furthermore, the analytical methodology used to identify and quantify hydrogen, the sacrificial reagent and the byproducts by HPLC and GC during the photocatalytic reaction are described. Finally, the lamp calibration unit and the methods used for axial lamp radiation distribution are reported. All these techniques and analytical methods are essential for fulfilling the objectives of the present PhD dissertation.
Chapter 5
Results and Discussion Part I: Lamp and Photocatalyst Characterization

5 Introduction

The near-UV lamp radiation characterization is essential for both the evaluation of the lamp spectrum and the radiative axial flux distribution. Radiation absorbed by the modified photocatalyst of Pt-TiO$_2$ was also studied using a macroscopic radiation energy balance (MREB). This macroscopic radiation energy balance was developed in Photo-CREC Water II Reactor (PCW-II) using different photocatalyst concentrations. The purpose of this analysis is to determine the local volumetric radiation energy absorption (LVREA) as the optimal photocatalyst loading inside the PCW-II.

Another important matter considered in this chapter is the detailed characterization and the interpretation of data obtained for the synthesized Pt-TiO$_2$ photocatalyst using different platinum loadings.

5.1 Characterization of the BLB Lamp

The performance of artificially powered photocatalytic reactors is strongly influenced by the lamp irradiation spectra. Furthermore, it is advisable that the lamp to be used is warmed up for a period of 5 min to stabilize the lamp’s emissions, before lamp utilization (de Lasa, Salaices, and Serrano 2005). A StellarNet EPP2000C-25 LT16 Spectrometer was used to determine the energy spectrum of the BLB lamp through the fused silica windows in the Photo-CREC Water II Reactor.

Figure 13 displays a typical near-UV irradiation BLB characteristic spectrum emitted in the range of 340 nm to 410nm. Thus, this BLB polychromatic lamp emits photons having a wavelength in a relatively narrow wavelength.
Figure 13: Near-UV irradiation spectrum of a USHIO BLB lamp in the Photo-CREC Water II Reactor. (a) Violet area describes the region of the spectrum with a wavelength smaller than 388nm (b) Blue area describes the region of the spectrum with a wavelength larger than 388nm and smaller than 455nm

Once the irradiation is defined as in Figure 13, the average emitted photon energy ($E_{av}$) can be calculated using the following relationship (Benito Serrano et al. 2009).

$$E_{av} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)E(\lambda)d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda)d\lambda}$$

(5-1)

In the case of the present study and as shown in Figure 13, all photons had a wavelength with a corresponding energy large enough to supersede the band gap of the Pt modified photocatalyst. Thus, all emitted photons were able in principle to contribute to the photocatalytic transformation. As a result, considering that $E(\lambda) = h\nu/\lambda$ and the numerical integration of Eq. (5-1), the calculated average photon energy was $E_{av} = 324.1$ kJ/photon (see Appendix F).

In this respect, radiation distribution along the reactor axis in the Photo-CREC Reactor was also measured using a Lamp Testing Unit (LTU) (B. Serrano and de Lasa 1997). Figure 14 reports the irradiation axial fluxes. One can notice a symmetric irradiation
distribution (purple line) along the reactor axis for a new lamp. There is however, in Figure 14, a non-symmetric irradiation (yellow line) for the case of a lamp used for more than 250 hours. This last case represents typical near-UV lamp performance decay as observed in lamps after more than one hundred hours of operation. As a result, possible asymmetric irradiation distribution displayed by the lamps were identified and excluded from the experimental runs for hydrogen generation.

![Figure 14: Radiative Axial Flux distribution from an USHIO BLB Lamp and a Lamp Testing Unit](image)

5.2 Characterization of the Modified Pt-TiO₂ Photocatalyst

Different techniques are employed to analyze and determine the physical and chemical properties of the modified photocatalyst.

5.2.1 Surface Area Analysis (BET)

The specific surface areas of all the prepared photocatalysts were determined employing a BET surface area analyzer (Micrometrics, ASAP 2010). This analyzer uses nitrogen adsorption-desorption isotherms.
Figure 15 reports the BET specific surface areas for raw DP25 (as received) and DP25 after thermal treatment at 450°C: Cases A and B, respectively. These cases show specific surface areas of 50.85 and 53.31 m²/g. In addition, Figure 15 reports the specific surface areas for modified TiO₂ loaded with 0.06, 0.1, 0.2 and 1 wt % of platinum. Resulting specific surface areas (cases C, D, E and F) are 53.21, 53.25, 53.97 and 53.91 m²/g respectively as reported in Table 9.

It is thus, possible to notice that Pt addition on DP25 slightly increases the specific surface area. Therefore, platinum loadings on DP25 and calcination seem not to affect the specific surface area. Nonetheless, calcination shows a slightly improvement due to desorption of water, gas or any pollutant adsorbed onto the photocatalyst surface.

### Table 9: BET data for different TiO₂-Pt photocatalysts

<table>
<thead>
<tr>
<th>Cat wt% of Pt</th>
<th>Sa (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) TiO₂ (DP25)</td>
<td>50.85</td>
</tr>
<tr>
<td>B) TiO₂ (DP25) Thermally Treated</td>
<td>53.31</td>
</tr>
<tr>
<td>C) TiO₂-0.06 wt% Pt</td>
<td>53.21</td>
</tr>
<tr>
<td>D) TiO₂-0.1 wt% Pt</td>
<td>53.25</td>
</tr>
<tr>
<td>E) TiO₂-0.2 wt% Pt</td>
<td>53.97</td>
</tr>
<tr>
<td>F) TiO₂-1 wt% Pt</td>
<td>53.91</td>
</tr>
</tbody>
</table>

**Figure 15:** Brunauer- Emmett- Teller (BET) Specific Surface Areas for different photocatalysts samples of TiO₂-Pt
5.2.2 Chemisorption Study

Different DP25-Pt photocatalysts were analyzed using pulse chemisorption as reported in Table 10. Pulse chemisorption is a technique allowing establishing the percent of metal dispersion and the active platinum crystallite size at different metal loadings, as is the case of Pt on DP25. It was observed that at high platinum loadings, the metal dispersion on DP25 was reduced from 42.21% to 22.76%. This means that the platinum modified photocatalysts of this study contains good metal dispersion on DP25. Moreover, platinum crystallite sizes were increased with platinum loading from 2.68 to 4.98 nm. These results are consistent with XRD. The XRD characterization suggests that platinum crystallites are smaller than 5nm with no characteristic 2θ peaks for Pt in the diffractogram chart.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Weight Percent (%) of Pt loaded</th>
<th>Active Particle Diameter (nm)</th>
<th>Metal dispersion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25</td>
<td>0.06</td>
<td>2.68</td>
<td>42.21</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>3.15</td>
<td>35.92</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>3.42</td>
<td>33.15</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>4.98</td>
<td>22.76</td>
</tr>
</tbody>
</table>

Regarding the chemisorption analysis one can assume that the well-dispersed metal particles onto TiO₂ surface may improve the electron surface distribution. Furthermore, the increment of Pt crystallite size may also enhance the utilization of platinum as an efficient electron trap.

Therefore, it is expected that higher platinum loadings on DP25 may improve charge distribution in the water-particle suspension, reducing TiO₂ particle agglomeration, as is shown later in Figure 17. However, higher platinum loadings, if uncontrolled, may also favor e⁻/h⁺ recombinations. Thus, one should expect an optimum platinum loading on DP25 for hydrogen production.
5.2.3  X Ray Fluorescence or XRF Analysis

Table 11 reports the XRF analysis of platinum loadings. It can be noticed that the platinum addition on DP25 using incipient wetness impregnation method was successful. The adopted impregnation technique indeed provides the expected metal loadings on DP25. X Ray Fluorescence determined loadings were 0.0616, 0.103, 0.23 and 1.08 wt%. These loadings were in close agreement with the ones anticipated.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Expected</th>
<th>Determined</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25</td>
<td>0.06</td>
<td>0.0616</td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.103</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1.08</td>
</tr>
</tbody>
</table>

5.2.4  X Ray Diffraction or XRD Analysis

The crystalline phases of the photocatalysts were investigated with an X-Ray Diffractometer RIGAKU Ultima IV which is a multi-purpose diffractometer (This instrument features a 3-kW X-Ray beam with a high-precision $\theta$-$\theta$ wide-angle horizontal goniometer and “Cross Beam Optics”).

Figure 16 reports the crystalline diffractogram patterns for DP25 (bare TiO$_2$) and for other four Pt modified photocatalysts. XRD diffractograms were overlapped for comparison. One can note that the characteristic 2θ diffraction anatase peaks at 25°, 37°, 48°, 54° and 55° were consistently observed. The smaller XRD peaks at 27° and 69° were also present, given the rutile content in DP25. There were no other XRD peaks as one could expect for Platinum at 40° and 46° of 2θ values (H. R. Kim et al. 2008; M Salaices, Serrano, and de Las 2002).

These findings are consistent with the low platinum loadings on DP25 TiO$_2$. It is also confirmed that incipient wetness impregnation yields a highly dispersed metallic phase with smaller than 5 nm platinum crystallites, with these small crystallites passing undetected in the XRD.
Figure 16: XRD Diffractograms for DP25 (TiO$_2$) and Pt/TiO$_2$ photocatalysts

Furthermore, using Eq. (5-2), one can calculate the rutile content of DP25 (TiO$_2$) based on the XRD peak intensities (Arakawa and Sayama 2000).

$$x = (1 + \frac{0.8I_A}{I_R})^{-1}$$

with $x$ being the weight fraction of rutile in the TiO$_2$ powder, $I_A$ and $I_R$ being the XRD intensities for anatase and the rutile peaks respectively.

Thus, with Eq. (5-2), it was possible to establish that the DP25 of the present study contains 87% anatase and 13% rutile and that both phases are present in the commercial DP25 (TiO$_2$) and Pt modified TiO$_2$.

5.2.5 Particle Size Distribution or PSD Study

Figure 17 reports the particle size distribution (PSD) of bare DP25 (TiO$_2$) and the platinum-loaded TiO$_2$. It can be observed from the PSD chart, that Degussa P25 displays a significant fraction of particles in the 1000-3000nm range even after sonication. However, when Degussa P25 was impregnated with Pt at 0.06, 0.1, 0.2 and 1 wt% loadings, there was a noticeable PSD displacement of the peaks towards the smaller particle sizes in the 50-100nm range. Thus, it appears that Pt addition helps to reduce
particle agglomeration, favoring better distribution of charges and as a result, interparticle surface forces (Sahu et al. 2011; Tiwari et al. 2008). While this effect may be in principle favorable in terms of irradiation absorption, it may also provide an enhanced electron/hole recombination reducing the effectiveness of hydrogen production.

![Graph showing particle size distribution](image)

**Figure 17: Particle size distribution of different photocatalyst of Pt and bare TiO<sub>2</sub>**

5.2.6 Scan Electron Microscope Analysis (SEM and EDX)

Images and elemental mapping of the photocatalyst were performed using SEM/EDX (LEO/Zeiss 154XB FIB/SEM). Figure 18 reports SEM images for two samples: a) DP25 (TiO<sub>2</sub>) and b) TiO<sub>2</sub> loaded with Platinum. It can be noticed that individual Pt crystallites are difficult to be observe using SEM (Ikuma and Bessho 2007). It can be seen however, that there is particle agglomeration in DP25 strongly influenced by interparticle surface forces. Image a) reports tighter agglomerates in bare DP25 while Image b) shows looser particle agglomerates for platinum doped TiO<sub>2</sub> (DP25) particles. Thus, SEM confirms PSD observations where Pt addition reduces interparticle surface forces (Sahu et al. 2011).
Figure 18: Scan Electron Microscope Images for DP25 and DP25-Pt loading

Figure 19 reports a comparison analysis of the two photocatalyst samples: a.1) bare TiO$_2$ without Pt addition and b.1) TiO$_2$ photocatalyst with platinum nanoparticles deposited onto the surface. One can thus conclude from this analysis, that the incipient wetness impregnation technique provides a reliable method for metal loading onto the TiO$_2$ surface, particularly when working with platinum.

Figure 19: EDX Images comparison for metal (Pt) detection of a.1) DP25 and b.1) DP25-Pt
5.2.7 Diffuse Reflectance UV-Vis Spectroscopy or DRS

Platinum addition enhances irradiation absorption in the visible range. One can certainly see that there is a color change accompanying platinum addition treated by incipient wetness impregnation followed by calcination and reduction. The photocatalyst turns from light yellow to gray (Higashimoto et al. 2008; Kjellin et al. 2007; Fujishima and Honda 1972).

Figure 20 schematically represents the effect of platinum loading on DP25 band gap energy. It can be hypothesized that platinum doping on DP25 introduces additional electron energy levels (Fermi Level) into the conduction band (G. Yang, Yan, and Xiao 2012; Abida et al. 2011; Navarro et al. 2009; Q. Li and Lu 2008). This leads by yielding a reduction of the energy band gap level, as shown in the ensuing discussion from 3.20 to 2.73 eV.

**Figure 20: Schematic representation of the energy band gap for DP25 (TiO₂) and for the modified TiO₂-Pt**

Figure 21 describes the diffuse reflectance of the UV-Vis spectra for non-doped and platinum doped DP25. This UV-Vis spectra provides both an indication of the UV-Vis light semiconductor absorption, as well as a method for evaluating the band gap energy (Kundu et al. 2012; Colón et al. 2010; Subramanian, Wolf, and Kamat 2004). This method is based on extrapolating the spectrum steepest line of each UV-Vis spectra until the wavelength axis is intersected (x-axis in Figure 21). This intersection wavelength defines the band gap energy for the semiconductor under consideration as $E_{bg} = \frac{hc}{\lambda_{int}}$. 
Figure 21: Optical absorption spectra of DP25 (TiO$_2$) and platinum loaded TiO$_2$ at different conditions. This intersection wavelength defines the band gap energy for the photocatalyst under consideration.

Using this method, one can notice that platinum addition progressively reduces UV-Vis light absorption. In addition, the wavelength resulting from the extrapolation with the steepest line gives a $\lambda_{int}$ of 388 nm or a 3.2 eV for DP25 and a 455 nm or a 2.73 eV for platinum modified DP25 with 1wt% of Pt.

Thus, one can conclude that photon absorption is related to the amount of Pt$^0$ present on the photocatalyst surface (Subramanian, Wolf, and Kamat 2004). Furthermore, platinum addition provides semiconductors with a wider irradiation absorption spectrum, absorbing photons with lower energy (Sahu et al. 2011; Ni et al. 2007). It is expected on this basis, that platinum addition on DP25 will provide an enhanced photocatalytic activity for hydrogen production (Murcia et al. 2012; Sahu et al. 2011; Liu et al. 2002; Fujishima and Honda 1972).

5.3 Local Volumetric Rate of Energy Absorption (LVREA)

LVREA can be determined experimentally through the irradiation intensity macroscopic balance inside the photocatalytic reactor. In this respect, chemical actinometry provides
insufficient assessment of LVREA given that it assumes that photons not reaching the outer reactor wall are absorbed. However, instead of this, a macroscopic radiation balance allows the calculation of the accurate radiation absorbed by the solid photocatalyst (Moreira et al. 2010; M Salaices, Serrano, and de Lasa 2002; Miguel Salaices, Serrano, and de Lasa 2001).

Using this approach one can establish the optimal photocatalyst concentration allowing all forward radiation contained in the slurry photocatalyst phase in the Photo-CREC unit (Moreira et al. 2010).

5.3.1 Macroscopic Radiation Energy Balance (MREB)

A macroscopic energy balance can be applied to a control volume as described in Figure 22. This control volume is established to include the semiconductor slurry phase (M Salaices, Serrano, and de Lasa 2002; Miguel Salaices, Serrano, and de Lasa 2001). It allows the evaluation of the rate of photon absorption as follows:

\[ P_a = P_t - P_{bs} - P_t \] (5-3)

where \( P_a \) is the rate of absorbed photons by the photocatalyst, \( P_t \) is the rate of photons reaching the reactor inner surface, \( P_{bs} \) is the rate of backscattered photons exiting the system, and \( P_t \) is the rate of transmitted photons (all in einsteins s\(^{-1}\)).

The various terms in Eq. (5-3) are calculated as follows:

a) \( P_t \) can be evaluated from the difference between the rate of photons emitted by the lamp \( (P_0) \), and the rate of photons absorbed or back reflected by the inner pyrex glass wall \( (P_{a-wall}) \)

\[ P_t = P_0 - P_{a-wall} \] (5-4)

b) \( P_o \) or the rate of photons emitted by the lamp can be calculated given the lamp BLB emission spectrum and radiometric measurements (refer to Figure 13).

\[ P_0 = \int_{\lambda_1}^{\lambda_2} \lambda \int_0^L \int_0^{2\pi} q(\theta, z, \lambda) r d\theta dz d\lambda \] (5-5)
c) $P_{a-watt}$ can be computed from the transmission measurements through the inner pyrex tube. Figure 13 also displays the very modest change of irradiation spectrum radiation that evolves through the inner pyrex glass. The little energy band gap ($\lambda_{E_{bg}}$) changes introduced by the pyrex glass are reported as well.

<p>| Table 12: Pyrex glass transparency and BLB lamp emission rates |
|----------------|----------------|----------------|</p>
<table>
<thead>
<tr>
<th>Variable</th>
<th>Watts</th>
<th>Einsteins s(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>$P_0$</td>
<td>3.98</td>
<td>1.242x10(^{-5})</td>
</tr>
<tr>
<td>$P_i$</td>
<td>3.66</td>
<td>1.142x10(^{-5})</td>
</tr>
<tr>
<td>$P_{a-watt}$</td>
<td>0.32</td>
<td>9.973x10(^{-7})</td>
</tr>
</tbody>
</table>

d) $P_{bs}$ can be approximated by the difference between $P_i$ and the rate of photons transmitted when the photocatalyst concentration approaches zero.

$$P_{bs} = P_i - P|_{c\rightarrow0}$$ \hspace{1cm} (5-6)

e) $P_t$ can be calculated as the addition of the transmitted non-scattered radiation ($P_{ns}$) and the forward scattering radiation ($P_{fs}$).

$$P_t = P_{ns} + P_{fs}$$ \hspace{1cm} (5-7)

Regarding $P_{ns}$, it can be estimated by using the black collimators for the transmitted non-scattered radiation. $P_{fs}$ can also be evaluated using polished-aluminum tube collimators. These two radiation terms account for the combined transmitted non-scattered radiation and forward-scattering radiation (Moreira et al. 2010; Miguel Salaices, Serrano, and de Lasa 2001).
Figure 22: LVREA in the Photo-CREC Water II Reactor annular channel for various Pt loadings on TiO\textsubscript{2} at pH=7. Standard deviations for repeats at 4 axial positions: 2-4\%.

As a result, when using this approach, one can establish in Figure 22 and Figure 23 that LVREA increases with photocatalyst concentration. As a result an optimum LVREA can
be used with 0.15 g of DP25 or modified DP25 per liter. At these conditions, one can secure 95% of the irradiated absorption. One can notice that this optimum value, as reported in Figure 22 and Figure 23, is independent of both the pH and Pt loading.

5.4 Conclusions

Chapter 5 studies near-UV lamp calibrations, TiO$_2$ and modified TiO$_2$-Pt characterizations as follows:

a) Spectrometer radiometer measurements were used for lamp calibrations. It was shown that both radial and axial symmetric irradiations are obtained in a concentric Photo-CREC Water II reactor.

b) Macroscopic Radiation Energy Balances (MREB) and Local Volumetric Rate of Energy Absorption (LVREA) were determined. An optimum value of 0.15 g of Pt modified DP25 per liter was determined.

c) XRF, Pulse Chemisorption and EDX were employed to calculate platinum loadings and Pt crystallite sizes onto the TiO$_2$ surface.

d) XRD was used to confirm the characteristic TiO$_2$ and modified TiO$_2$-Pt crystalline phases.

e) BET analyses on a bare TiO$_2$ semiconductor and on a modified TiO$_2$-Pt photocatalyst were used to show that platinum addition does not significantly modify the specific surface area.

f) PSD and SEM were employed to show that TiO$_2$-Pt reduces particle agglomeration and presumably favors a better distribution of $e^-/h^+$, limiting charge recombinations.

g) DRS was considered to demonstrate that there is a band gap reduction from 3.20 eV to 2.73 eV when platinum is added to TiO$_2$. 
Chapter 6
Results and Discussion Part II: Hydrogen Production and Intermediate Species Analysis

6 Introduction

Experiments of hydrogen formation via photocatalytic water splitting were performed. The system employed for the photocatalytic hydrogen generation was the Photo-CREC Water II Reactor. This unit was used with a specially designed H₂ collector tank and a BLB Lamp that permits the entire use of the near-UV irradiation spectrum. This research also took advantage of the modified semiconductor material of Pt/TiO₂ with a conveniently reduced band gap and 2 v/v% ethanol (EtOH) as a hole (h⁺) scavenger. Experiments with near-UV light and Pt modified TiO₂ were performed under the special condition of having “all” irradiated photons with photon energies superseding the band gap of the semiconductor. This approach also allowed determining the production of different intermediates and byproducts such as: 1) liquid phase: CH₃COOH and 2) gas phase: CH₄, C₂H₆, and CO₂, which were formed during the photocatalytic hydrogen generation.

6.1 Photocatalytic Reaction Mechanism

Figure 24 reports a schematic description of photocatalytic hydrogen production in the modified Photo-CREC Water II Reactor. Figure 24 also provides representations at three different dimension scales: macro-scale, meso-scale (Zoom 1) and micro-scale (Zoom 2). This schematic representation emphasizes the event that could occur at the level of a Pt doped TiO₂ particle (meso-scale) and on a photocatalyst outer surface where platinum crystallite is laid out (micro-scale). Irradiation of this zone, as described in Zoom 2, leads to charge separation (e⁻ and h⁺ sites). This elementary step is the preamble to H’ and OH’ formation.
Figure 24: Description of the Photocatalytic Reaction Steps taking place in a Photo-CREC Water II Unit for hydrogen production showing views of the (a) Macro-scale, (b) Meso-scale, c) Micro-scale

Thus, in the Photo-CREC Water II Reactor, with suspended and impregnated-TiO$_2$ particles and a water solution containing ethanol as an organic scavenger, the following mechanistic steps can be considered (refer to Figure 25 and Section 6.4): i) A photon reaches the semiconductor surface with an energy greater than the band gap, ii) An electron (e$^-$) and a hole (h$^+$) separate when an electron having an energy content higher than the different of the valence band energy and the conduction band energy, iii) Platinum nanoparticles deposited on the surface of the DP25 (TiO$_2$) help by acting as electron reservoirs, capturing moving electrons on the DP25 (TiO$_2$) surface (M. Zhou et al. 2012; Chavadej et al. 2008; Egerton and Mattinson 2008; Coleman, Chiang, and Amal 2005; Emilio et al. 2004), iv) Stored electrons interact with adsorbed protons which are formed from dissociated water yielding H$^-$ radicals, v) Hydrogen radicals couple themselves forming gas phase hydrogen ($H_2$$_{(g)}$).

On the other hand, the produced h$^+$ holes react with OH$^-$ groups forming OH$^-$ radicals. These hydroxyl radicals (OH$^-$) are highly reactive species, able to convert ethanol
(C₂H₅OH) or other present organic species (refer to Figure 25 and Section 6.4). Regarding the ethanol reaction with OH⁻ species, ethanol can form acetaldehyde (C₂H₄O) in the first reaction step of the reaction network. This reaction step can be followed by further acetaldehyde degradation with another OH⁻ yielding acetic acid (CH₃COOH). Moreover, formed acetic acid can be further converted under the prevalent conditions of the Photo-CREC Water II Reactor into carbon monoxide (CO₂), methane (CH₄) and ethane (C₂H₆), may mainly due to the photo-Kolbe reaction (Muggli and Falconer 1999; Sato 1983).

![Figure 25: Schematic representation of the reaction mechanism for hydrogen production in a Photo-CREC Water II Reactor using C₂H₅OH as sacrificial agent](image)

6.2 Effect of different pHs on the Photocatalytic Hydrogen Production

Photocatalytic hydrogen generation was determined at NTP normal conditions (ambient temperature and close to atmospheric pressure) for different pHs (Y. Li et al. 2006) and different Pt loadings (Higashimoto et al. 2008; Kjellin et al. 2007; Ikuma and Bessho 2007; Ni et al. 2007; Liu et al. 2002). Each experiment was developed as follows: i) Near-UV Lamp off: 30 minute period with argon circulated continuously to remove any remaining oxygen from air and until the ethanol adsorption equilibrium on doped TiO₂ was reached; 2) Near-UV Lamp on: 5.5 hours period where water with a suspended photocatalyst was recalcultated continuously under irradiation. During both lamp off and
lamp on, irradiation periods samples were taken periodically and analyzed in a GC (see Appendix B). This process allows one to establish the influence of Pt loading on the doped TiO$_2$ and the effect of the pH.

6.2.1 Effect of Alkaline pH

A 2M NaOH solution was prepared and 2 ml of this solution were added to 6 L water/2 v/v% ethanol solution. This solution was placed in the Photo-CREC Water II reactor auxiliary mixing tank. The resulting pH before the experiment was approximately 10, and remained essentially unchanged during the complete experimental run.

Figure 26 displays the cumulative hydrogen generation at various irradiation times and at various platinum loadings for a pH of 10. It can be observed that at the alkaline conditions of pH=10, the 1 wt% loading provides the best hydrogen generation performance of the four photocatalysts considered.

All these photocatalysts, as described in Figure 26, display a number of common features in terms of hydrogen production as follows: i) the rates of hydrogen production were consistently higher during the first 1.5 hours of the run, ii) the rates of hydrogen production decreased consistently after the initial 1.5 hour run period. Thus, it appears that the platinum-TiO$_2$ under alkaline pHs still allows hydrogen production under the high OH$^-$ and limited H$^+$ concentrations, as one can expect from water equilibrium dissociation. However, it is also possible to observe that while the run is progressing, this limited availability of H$^+$ becomes even more acute on the photocatalyst surface with this leading to a progressive reduction of hydrogen formation rates.
Figure 26: Hydrogen profiles at different Pt loadings on DP25, pH=10, EtOH 2v/v% and Argon as purging gas. Codes: a) Bars in this graph represent standard deviations for repeats and b) Trend lines (--)

6.2.2 Effect of Neutral pH

Experiments were developed with the various photocatalysts with a pH of 7. The pH remained close to the original value during the entire 5.5 hours of the run.

Figure 27 shows the cumulative hydrogen formation. Hydrogen production was detected as soon as the near-UV lamp was turned on with cumulative hydrogen formed increasingly during the whole run. It can be observed that at a pH=7, there is a consistent increase of hydrogen during the first 1.5 hours, with this increase being more modest for the remaining run period. This trend appears to be similar to the one observed at pH=10.
Figure 27: Hydrogen profiles at different Pt loadings on DP25, pH=7, EtOH 2\text{v/v}\% and Argon as purging gas. Codes: a) Bars in this graph represent standard deviations for repeats and b) Trend lines (--) 

6.2.3 Effect of Acid pH

The influence of acid pH on hydrogen formation rate was studied using H$_2$SO$_4$ [2M]. 1ml of this sulfuric acid solution was added in the 6 L tank containing a water/ethanol solution. Regarding the pH, it was observed that it remained close to 4 for the complete 6 hours of the experiment duration.

Figure 28 reports the cumulative hydrogen production for different Pt loadings on DP25. As soon as the lamp was turned on, hydrogen formation was observed. A common and distinctive trend for the cumulative hydrogen formation curves is that they were consistently linear. In this respect, the linear trend was a major difference vis-a-vis of results obtained with the samples having a pH of 7 and 10. In particular, one can also notice in Figure 28 that 1 wt% Pt loading led to the best hydrogen production under acidic conditions. Moreover, the experimental data presented in Figure 28, particularly that with 1 wt% Pt loading has average values on repeats. The experiments were repeated four times in order to validate the reproducibility of the results.
Figure 28: Hydrogen profiles at different Pt loadings on DP25, pH=4, EtOH 2v/v% and Argon as purging gas. Codes: a) Bars in this graph represent standard deviations for repeats and b) Trend lines (---) 

One can see that at the pH=4, the gas phase achieved a significantly increased hydrogen content during the 6 hours experiment. Therefore, it appears that the high concentration of H⁺ ions in the acid aqueous solution favors water dissociation and the formation of hydronium ions. Additionally, the protons adsorbed on the photocatalyst can easily interact with generated and stored electrons, promoting hydrogen formation (Sadeghi et al. 2012; Sobczynski 1987).

It is interesting to note that the rate of hydrogen formation under acid pH becomes a steady process: H⁺ ions from the solution can be quickly resupplied to the photocatalyst surface (see section 6.2.4). As a result, one can observe that there is no decay in hydrogen formation rates under acidic conditions and that the cumulative hydrogen formation continues to increase without a noticeable decline. This is, in our view, a valuable finding which is in clear contrast with the results obtained in the case of alkaline and neutral pH solutions where the H⁺ ion resupply appears to be limited.

Figure 29 reports the hydrogen produced during photocatalytic water splitting. This figure summarizes data at various Pt loadings and pHs. The volumetric flows reported in this figure were calculated using the ideal gas law at room temperature and atmospheric
pressure. In this respect, temperature only varies from 298 to 303°K, and pressure changes from 1 to 1.05atm in a closed reactor system.

<table>
<thead>
<tr>
<th>%Pt</th>
<th>pH=4</th>
<th>pH=7</th>
<th>pH=10</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25</td>
<td>0.66</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.06</td>
<td>1.71</td>
<td>1.16</td>
<td>0.76</td>
</tr>
<tr>
<td>0.2</td>
<td>3.99</td>
<td>1.45</td>
<td>1.68</td>
</tr>
<tr>
<td>1</td>
<td>7.83</td>
<td>2.11</td>
<td>3.05</td>
</tr>
</tbody>
</table>

**Figure 29: Comparison of volumetric hydrogen flow production rate at both different pHs and different platinum loadings on DP25**

Figure 29 shows that 1 wt% Pt loading at pH=4 provides the best platinum loading at any pH conditions. The steady hydrogen volumetric flow calculated at these conditions is 7.83 cm³/h.

### 6.2.4 Balance of H⁺ Species and pH Influence on Hydrogen Production

To describe the influence of the pH, one can consider the following approach as described in our recent contribution (Escobedo Salas, Serrano Rosales, and de Lasa 2013):

At time $t = 0$ there is no irradiation. Under these conditions the $[H^+]$ and $[H^+]_{ads}$ are at equilibrium as shown in the following equation,
As soon as the lamp is turned on the following applies:

\[ K[H^+] = [H^+]_{ads} \]

\[ k_f a_v \frac{1}{\rho_{cat}} \omega V_L \{ [H^+] - [H^+]^\ast \} = k_r \omega V_L [e^-][H^+]^\ast + V_L \frac{d[H^+]^\ast}{dt} \quad (6-1) \]

With \( \omega = \frac{W_{cat}}{V_L} \)

Thus the transport of \([H^+]\) protons through the film surrounding every single particle aggregate contributes to both the consumption of \([H^+]_{ads}\) cations and to the accumulation/de-accumulation of \([H^+]^\ast\) species as described in Figure 30.

\[ k_f a_v W_{cat} \frac{1}{\rho_{cat} V_L} \{ [H^+] - [H^+]^\ast \} = k_r W_{cat} \frac{1}{V_L} [e^-][H^+]^\ast + \frac{d[H^+]^\ast_{ads}}{dt} \quad (6-2) \]

and

\[ K \frac{d[H^+]_{ads}}{dt} = k_f a_v W_{cat} \frac{1}{\rho_{cat} V_L} \{ [H^+] - [H^+]^\ast \} - \frac{k_r W_{cat} K}{V_L} [e^-][H^+]^\ast \quad (6-3) \]

where,

\[ \alpha = \frac{k_f a_v W_{cat}}{\rho_{cat} V_L} \quad \beta = \frac{k_r W_{cat} K}{V_L} \]

Thus,

\[ K \frac{d[H^+]_{ads}}{dt} = \{ \alpha [H^+] - (\alpha + \beta) [H^+]^\ast \} \quad (6-4) \]

In order for the production of hydrogen to proceed as steady process, the following must apply,

\[ \frac{d[H^+]_{ads}}{dt} \approx 0 \text{ and } [H^+] \text{ very close to } [H^+]^\ast \]

To achieve this \( \alpha \gg \beta \)
\[ \beta_{lt \to 0} = \frac{k_{f} W_{cat} K_{\text{H}^{+}}} {V_{L}} \frac{[\text{H}^{+}]}{\frac{dN_{H_{2}}}{dt}} \ll 1 \quad (6-5) \]

Considering that,

\[ 2H_{ad}^{+} + 2e^{-} \to 2H^{*} \to H_{2} \]

Then, at irradiation times approaching zero, it follows that:

\[ \beta_{lt \to 0} = \frac{2dN_{H_{2}}}{dt} \frac{V_{g}}{V_{L}} \frac{t=0}{\rho_{\text{cat}} V_{L}} \ll 1 \quad (6-6) \]

Moreover and considering that the various parameters involved in the case of our study could be estimated when using a 1 wt% Pt on DP25 semiconductor the following applies:

\[ k_{f} = \frac{2dN_{H_{2}}}{dt} = 0.96 \frac{cm}{s} ; \quad a_{p} = \frac{6}{d_{p}} = 60000 \frac{cm^{2}}{cm^{3}} ; \quad \omega = \frac{W_{\text{cat}}}{V_{L}} = 0.00015 \frac{g}{cm^{3}} , \]

\[ \rho_{\text{cat}} = 4.23 \frac{g}{cm^{3}} ; \quad \frac{2dN_{H_{2}}}{dt} \bigg|_{t=0} = 3.47 \times 10^{-5} \frac{\mu \text{ moles}}{cm^{3}s} ; \quad V_{g} = 5716 \ cm^{3} \ \text{and} \ V_{L} = 6000 \ cm^{3} \]

for all pH’s then,

\[ \beta_{lt \to 0} = \frac{\left(3.47 \times 10^{-5} \frac{\mu \text{ moles}}{cm^{3}s}\right)(5716 \ cm^{3})}{\left(12255 \ \frac{cm^{3}}{s}[\text{H}^{+}]\right)(\frac{\mu \text{ moles}}{cm^{3}})} = \frac{1.62 \times 10^{-5} \frac{\mu \text{ moles}}{L}}{[\text{H}^{+}] \frac{\mu \text{ moles}}{L}} \ll 1 \quad (6-7) \]

\[ \beta_{lt \to 0} = \frac{1.62 \times 10^{-5}}{[\text{H}^{+}]} \ll 1 \quad (6-8) \]

In summary, only for the experiments at pH=4 is the condition of equation (6-8) satisfied. Thus, when the pH=4, the experiment is expected to yield a steady production of hydrogen as \[ \frac{dN_{H_{2}}}{dt} = 0.1984 \frac{\mu \text{ moles}}{s} \]. This is in fact what was obtained experimentally in our research at pH=4 using 1 wt% Pt on DP25. Other pHs however such as a pH=7 or a pH=10 were limited by the supply of [H+] species as is expected from equation (6-8).
Figure 30: Description of the various species on the near photocatalyst particle surface

6.3 Generation of Hydrocarbons and CO₂ as Byproducts during the Photocatalytic Hydrogen Production

The generation of useful hydrocarbons mainly CH₄ and C₂H₆ from organic pollutants in the liquid phase via photocatalytic hydrogen production appears to be an interesting alternative to treat sewage or any other organic-contaminated effluents (Asal et al. 2011). Nevertheless, the generation or emissions of CO₂ from waste water or biofuels is imminent through the photocatalytic hydrogen production or through the photodegradation of organic pollutants. The generation of gaseous hydrocarbons and CO₂ may be due to the photo-Kolbe reaction as explained in Section 6.4 (Muggli and Falconer 1999; Sato 1983).

The photo-Kolbe reaction in the liquid phase occurs during the photo degradation of acetic acid. Acetic acid is one of the main intermediate in the photo decomposition of ethanol. Figure 31 displays a slightly decrease in ethanol concentration during the 6 hours of photocatalytic reaction. Furthermore, Figure 31 reports the photoformation and the photoconversion of acetic acid. This can be explained due to the increase in the concentration of acetic acid after the lamp is turned on. On other hand, a reduction in the concentration of acetic acid after 4 hours of experiment has been noticed. One can assume that this diminishment of concentration is due to the photoconversion of acetic acid (as the main intermediate in the liquid phase) to CH₄, C₂H₆ and CO₂. The photoconversion of acetic acid may originate from the photo-Kolbe reaction for the gaseous hydrocarbon generation during the photocatalytic hydrogen production (Sakata, Kawai, and Hashimoto 1984).
During both lamp off and lamp on irradiated liquid samples were periodically taken and analyzed in an HPLC and GC (see Appendix D). In addition, all the HPLC experimental analyses were repeated four times in order to confirm the reproducibility of the results. The data reported in Figure 31 gives the average values obtained from the four experiments.

![Graph showing Ethanol (C₂H₅OH) photo-decomposition and Acetic Acid (CH₃COOH) photo formation profiles at optimum Pt catalyst loading and optimal photocatalytic hydrogen production conditions. Codes: a) Bars in this graph represent standard deviations for repeats and b) trend lines (→)](image)

**Figure 31:** Ethanol (C₂H₅OH) photo-decomposition and Acetic Acid (CH₃COOH) photo formation profiles at optimum Pt catalyst loading and optimal photocatalytic hydrogen production conditions. Codes: a) Bars in this graph represent standard deviations for repeats and b) trend lines (→)

Figure 32 and Figure 33 describe the byproduct gases obtained during photocatalytic hydrogen production. The formed hydrocarbons (byproducts) during the photocatalytic hydrogen generation were produced by using the DP25-1 wt% Pt photocatalyst and the following conditions: a) catalyst loading 0.15 g_cat/L_soln, b) NTP (Normal Room Temperature and Pressure), c) ethanol at 2 v/v%, d) pH=4 and e) oxygen-free conditions under an argon inert gas.

The operation of a photocatalytic reactor with a free of oxygen atmosphere is critical for H₂ generation. There are two main reasons for this: a) free of oxygen products cannot be combusted and as a consequence the water splitting process does not require H₂/O₂ separation and b) water splitting thermodynamics is more favorable under oxygen-free conditions.
conditions as it will be described in Chapter 8. To accomplish this, an organic OH’ scavenger is required, with both hydrocarbons and CO₂ being formed (Dey and Pushpa 2006). One should mention that gas samples were taken from the PCW-II Reactor auxiliary mixing/storing hydrogen tank periodically from the beginning of the experiment and analyzed using a GC (see Appendix C). Various byproduct gases including CH₄, C₂H₆ and CO₂ were measured. Figure 32 and Figure 33 report the cumulative amounts of methane, ethane and carbon dioxide formed using DP25-1 wt% Pt. When reviewing these figures one can notice that as soon as the lamp was turned on, methane, ethane and carbon dioxide were detected. Moreover, as mentioned above, these by products along with the hydrogen production display a distinctive and consistent cumulative linear trend. All the experiments were repeated four times and this was done in order to confirm the reproducibility of the results. Symbols reported in Figure 32 and Figure 33 represent mean values. Standard deviations for the four experimental repeats are also provided in these figures.

![Hydrocarbon profiles of CH₄ and C₂H₆ at optimum Pt catalyst loading and optimal photocatalytic hydrogen production conditions. Codes: a) Bars in this graph represent standard deviations for repeats and b) trend lines (--)](image)

The photocatalytic hydrogen formation mechanism with an organic sacrificial agent such as ethanol, involves ethanol partial oxidation and complete oxidation to CO₂ (Cagnello et al. 2011).
However, the hydrogen generation mechanism is of the photo-redox type including the formation of intermediates and other reaction byproduct species (see Figure 31 and Figure 32).

CO$_2$ formation is reported in Figure 33. One can see that steady CO$_2$ photogeneration as a result of the oxidation of the sacrificial agent (any organic pollutant). Nevertheless, given that one can trace the CO$_2$ released by a renewable ethanol scavenger produced from agricultural resources, the CO$_2$ emissions in this process can be considered neutral (Ball and Wietschel 2009).

![Graph showing CO$_2$ profile at optimum Pt catalyst loading and optimal photocatalytic hydrogen production conditions. Codes: a) Bars in this graph represent standard deviations for repeats and b) trend lines (→)](image)

**Figure 33:** CO$_2$ profile at optimum Pt catalyst loading and optimal photocatalytic hydrogen production conditions. Codes: a) Bars in this graph represent standard deviations for repeats and b) trend lines (→)

Furthermore, the various amounts of gases produced can be represented as a volumetric flow rate ($Q = \text{Volume of gas/irradiation time}$) as reported in Figure 34. The following was considered in these calculations: a) ideal gas equation, b) NTP conditions, c) $V_g$ which is the volume of the gas chamber representing the total available volume for gas collection. As a result a 0.082, a 0.362 and a 0.271 cm$^3$/h volumetric rates for CH$_4$, C$_2$H$_6$ and CO$_2$ were obtained.
Figure 34: Comparative representation of the volumetric flow of Carbon dioxide, Methane and Ethane at optimal conditions of platinum photocatalyst loading and acid pH. Bars in this graph represent standard deviations on repeats.

6.4 Photocatalytic Hydrogen Production Reaction Mechanism

The reaction mechanism that occurs in the photocatalytic hydrogen generation can be represented by different steps as follows:

i. Common Steps During Photocatalytic Processes

Regarding photocatalytic hydrogen production and the steps described in Figure 35, the following adsorption-reaction steps can be considered:

*Step i.1) Dark Period:* During the period that lights are “off”, adsorption of both organic molecules and water take place on the TiO$_2$ surface as follows,

\[
\text{Organic Molecule}_{(l)} \xrightarrow{T\text{iO}_2\text{-Pt}} \text{Organic Molecule}_{(ads)}
\]  \hspace{1cm} (6-9)

\[
\text{H}_2\text{O}_{(l)} \xrightarrow{T\text{iO}_2\text{-Pt}} \text{H}_2\text{O}_{(ads)}
\]  \hspace{1cm} (6-10)
Step i.2) Irradiation Period- Separation of Charges: Once the light is “on” for an extended period of time photoreactions are initiated. Photons with the adequate energy intensity are able to excite the TiO$_2$ particles as follows,

$$h\nu \xrightarrow{TiO_2-Pt} h^+ + e^-$$  \hspace{1cm} (6-11)

Step i.3) Irradiation Period- Formation of OH$^-$ radicals. There is dissociation of water adsorbed molecules. Furthermore, electron holes react with adsorbed OH$^-$ hydroxyl ions adsorbed on the surface of TiO$_2$ producing hydroxyl radicals as follows:

$$H_2O_{(ads)} \xrightarrow{TiO_2-Pt} H^+_{(ads)} + OH^-_{(ads)}$$  \hspace{1cm} (6-12)

$$OH^-_{(ads)} + h^+ \xrightarrow{TiO_2-Pt} OH^*$$  \hspace{1cm} (6-13)

Step i.4) Irradiation Period- Formation of H$^-$ radicals. Platinum acts as an electron reservoir loaded on TiO$_2$ surfaces. In this respect, protons present on the TiO$_2$ surface form H$^-$ radicals with this leading to hydrogen (H$_2$) formation as follows,

$$H^+_{(ads)} + e^- \xrightarrow{TiO_2-Pt} H^-$$  \hspace{1cm} (6-14)

$$H^- \xrightarrow{TiO_2-Pt} \frac{1}{2}H_2(g)$$  \hspace{1cm} (6-15)

Furthermore and on the basis of the experimental observed chemical species the following subsequent “in series-parallel” reaction network can be described as in the below Figure,
Figure 35: Detailed “in series-parallel” model for hydrogen production when using ethanol as an organic scavenger. $\gamma_i$ and $\tau_i$ refer to the stoichiometric coefficients refer to steps “i” in the reaction network (Escobedo Salas, Serrano Rosales, and de Lasa 2013)

Details for these steps are provided in the upcoming sections as follows:

ii. Ethanol Conversion into Acetaldehyde

*Step ii.1) Irradiation Period- Hydroxyl radicals are consumed by the organic scavenger (ethanol) producing acetaldehyde.*

\[
C_2H_5OH_{(ads)} + OH^* \xrightarrow{TiO_2-Pt} C_2H_5O^-_{(ads)} + H_2O_{(ads)} \tag{6-16}
\]

\[
h_\nu + H_2O_{(ads)} + C_2H_5O^-_{(ads)} \xrightarrow{TiO_2-Pt} \frac{1}{2} H_2(g) + C_2H_4O_{(ads)} + H_2O_{(l)} \tag{6-17}
\]

Addition of Equations (6-10) to (6-17) yields the following overall stoichiometric equation,

\[
2h_\nu + C_2H_5OH_{(l)} \xrightarrow{TiO_2-Pt} H_2(g) + C_2H_4O_{(ads)} \tag{6-18}
\]

iii. Acetaldehyde Conversion into Acetic Acid
Step iii.1) Irradiation Period- Hydroxyl radicals are consumed by the acetaldehyde producing acetic acid.

OH$^\cdot$ radicals attack the adsorbed acetaldehyde molecules resulting in the formation of adsorbed enolate anions as follows,

$$C_2H_4O_{(ads)} + OH^* \xrightarrow{T^0_{O_2-Pt}} C_2H_3O^-_{(ads)} + H_2O_{(ads)} \quad (6-19)$$

The formed enolate reacts further with water yielding acetic acid,

$$h\nu + H_2O_{(ads)} + C_2H_3O^-_{(ads)} \xrightarrow{T^0_{O_2-Pt}} \frac{1}{2}H_2(g) + CH_3COOH_{(ads)} \quad (6-20)$$

The algebraic addition of equations (6-10) to (6-15), (6-19) and (6-20) gives the following overall stoichiometric equation,

$$2h\nu + C_2H_4O_{(ads)} + H_2O_{(l)} \xrightarrow{T^0_{O_2-Pt}} H_2(g) + CH_3COOH_{(ads)} \quad (6-21)$$

iv. Ethanol Conversion into Acetic Acid

Step iv.1) Irradiation Period- Hydroxyl radicals are consumed by the organic scavenger (ethanol) producing acetic acid.

The overall reaction assuming total mineralization of acetaldehyde can be reported as a summation of the reactions (6-18) and (6-21). This leads us to the overall stoichiometric expression as follows:

$$4h\nu + C_2H_5OH_{(l)} + H_2O_{(l)} \xrightarrow{T^0_{O_2-Pt}} 2H_2(g) + CH_3COOH_{(ads)} \quad (6-22)$$

v. Acetic Acid Conversion into Methane and Carbon Dioxide

Step v.1) Formed hydroxyl radicals react with adsorbed unimolecular acetic acid forming CO$_2$.

Formed OH$^\cdot$ radicals react with the adsorbed acetic acid to form the acetate anion as follows (Muggli and Falconer 1999; Sato 1983).
\[ \text{CH}_3\text{COOH}_{(ads)} + \text{OH}^* \xrightarrow{T_iO_2-Pt} \text{C}_2\text{H}_3\text{O}_2^-_{(ads)} \]  \hspace{1cm} (6-23)

The formed H\(^\cdot\) radicals react with the acetate anion yielding methane and CO\(_2\),

\[ \text{C}_2\text{H}_3\text{O}_2^-_{(ads)} + \text{H}^* \xrightarrow{T_iO_2-Pt} \text{CH}_4(g) + \text{CO}_2(g) \]  \hspace{1cm} (6-24)

The algebraic addition of equations (6-10) to (6-14), (6-22) and (6-24), leads to the following stoichiometric equation,

\[ h\nu + \text{CH}_3\text{COOH}_{(ads)} \xrightarrow{T_iO_2-Pt} \text{CH}_4(g) + \text{CO}_2(g) \]  \hspace{1cm} (6-25)

vi. Acetic Acid Conversion into Ethane and Carbon Dioxide

Step vi.1) Formed hydroxyl radicals react with adsorbed bimolecular acetic acid forming C\(_2\)H\(_6\) and CO\(_2\).

Formed OH\(^\cdot\) radicals react with the adsorbed bimolecular acetic acid to generate formate anions and methyl radicals as follows (Muggli and Falconer 1999; Sato 1983),

\[ 2\text{CH}_3\text{COOH}_{(ads)} + 2\text{OH}^* \xrightarrow{T_iO_2-Pt} 2\text{CH}_3^*_{(ads)} + 2\text{HCO}_2^-_{(ads)} \]  \hspace{1cm} (6-26)

The formed methyl radicals react between them yielding ethane. The formate anions are broken down into hydrogen and carbon dioxide,

\[ 2\text{CH}_3^*_{(ads)} + 2\text{HCO}_2^-_{(ads)} \xrightarrow{T_iO_2-Pt} \text{H}_2(g) + \text{C}_2\text{H}_6(g) + 2\text{CO}_2(g) \]  \hspace{1cm} (6-27)

The algebraic addition of equations (6-10) to (6-15), (6-26) and (6-27), leads to the following stoichiometric equation,

\[ 2h\nu + 2\text{CH}_3\text{COOH}_{(ads)} \xrightarrow{T_iO_2-Pt} \text{H}_2(g) + \text{C}_2\text{H}_6(g) + 2\text{CO}_2(g) \]  \hspace{1cm} (6-28)

vii. Total Mineralization of Ethanol, Acetaldehyde and Acetic Acid

Step vii.1) Formed hydroxyl radicals react with adsorbed acetic acid forming CO\(_2\).
The overall reaction assuming that total mineralization of ethanol can be reported as a summation of reactions with these being (6-18), (6-21) and (6-25) leading us to the overall stoichiometric expression,

$$5hv + C_2H_5OH_{(l)} + H_2O_{(l)} \xrightarrow{T_iO_2-Pt} 2H_2(g) + CH_4(g) + CO_2(g) \quad (6-29)$$

**Step vii.2) Formed hydroxyl radicals react with adsorbed acetaldehyde forming CO₂**

The overall reaction considering that total mineralization of acetaldehyde can be reported as a summation of the reactions (6-21) and (6-25). This leads us to the overall stoichiometric expression as follows:

$$3hv + C_2H_4O(g) + H_2O_{(l)} \xrightarrow{T_iO_2-Pt} H_2(g) + CH_4(g) + CO_2(g) \quad (6-30)$$

In competition with the above described reaction steps, there is a possible e⁻ and h⁺ site recombination. This electron and hole recombination does not accomplish any useful photocatalytic conversion, and as a consequence contributes to the overall photocatalytic process inefficiency. Thus, e⁻/h⁺ recombination must be limited as much as possible.

Therefore, a proposed “in series-parallel” reaction network is introduced as a short reaction pathway from the previous reaction mechanism. This suggested reaction network will help us to describe the overall process of the photocatalytic hydrogen generation in the presence of a hole (h⁺) scavenger such as ethanol. The scheme is presented in Figure 35. Thus, it provides a detailed overview of the explained reaction mechanism.

### 6.5 Adsorption Isotherm of Ethanol on DP25-1 wt% Pt Photocatalyst

As described in the previous sections, in the case of hydrogen production using ethanol as a hole scavenger, hydrogen, CH₄, C₂H₆ and CO₂ species were produced in the gas phase and acetaldehyde and acetic acid in the water phase.

Quantification of water phase intermediates and their evaluation is critical for a kinetic modeling to be developed. In this respect, adsorption constants of the different chemical
species need to be considered in Langmuir-Hinshelwood kinetics. To accomplish this, a Langmuir isotherm, equation (6-31) was considered for these chemical species as recommended in the technical literature (Kumar, Porkodi, and Rocha 2008).

\[
\theta_A = \frac{Q_{eq,ads}}{Q_{eq,max}} = \frac{K_{eq}^A C_{eq}}{(1+K_{eq}^A C_{eq})}
\]  

In the present study, a photocatalytic hydrogen production reaction requires 2 v/v% of ethanol (as a hole scavenger). An excess of ethanol is present in the liquid phase in comparison with the other species produced. Thus, primarily the experimental measurements of this section focus on calculating the adsorption constant of ethanol on DP25-1 wt% Pt.

To accomplish this, the slurry recirculation rate in the PCW-II Reactor to measure the equilibrium adsorption of ethanol was set at the same one as the one used during the photocatalytic hydrogen generation runs.

Figure 36 reports the ethanol equilibrium concentration reached after 60 minutes. One can observed from this figure that the adsorption equilibrium is reached in 40-50 minutes. From the previous results, a conservative total conservative time of 60 minutes was only used for the adsorption equilibrium constant calculations.

**Figure 36: Ethanol 2 v/v% adsorbed in a modified photocatalyst of DP25-1 wt% Pt as a function of time (T=25 °C and pH=4)**
Figure 37 describes the linearization of the Langmuir equation as given by equation (6-32). This mathematical form of the Langmuir isotherm permit the calculation of both the adsorption constant and the maximum amount of adsorbate adsorbed on the photocatalyst (Moreira et al. 2012).

\[
\frac{1}{Q_{eq,ads}} = \frac{1}{Q_{eq,max}K_A^A} \frac{1}{C_{eq}} + \frac{1}{Q_{eq,max}}
\]  

(6-32)

Results obtained from Figure 37 and equation (6-32) are \(K_{EtOH}^A = 1.427\) L/mol and \(Q_{eq,max} = 0.163\) mol/g\(_{cat}\).

\[y = 4.2992x + 6.1368\]
\[R^2 = 0.998\]

**Figure 37: Representation of the Langmuir Isotherm linear regression of ethanol on DP25-1 wt% Pt**

Figure 38 reports the Langmuir adsorption isotherms calculated values and experimental data points showing the adequacy of the data fitting. Table 13 shows the adsorption parameters determined by using equation (6-32).
Figure 38: Langmuir adsorption isotherm comparison of (o) experimental data of ethanol 2 v/v% (pH=4) and (—) Langmuir model

Table 13: The adsorption constant and maximum adsorption of ethanol 2 v/v% at pH=4 on DP25-1 wt% Pt

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Adsorption Constants</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$K_{EtOH}$ (l/mol)</td>
</tr>
<tr>
<td>DP25-1 wt%Pt</td>
<td>1.427</td>
</tr>
</tbody>
</table>

The adsorption parameters reported in Table 13 were established under dark conditions (near-UV light turned off). One should notice that under dark conditions, the photocatalyst is inactive and adsorption properties could be somewhat differ from those under irradiation (Moreira 2011). Xu and Langford (2000) reported $K^A$ as being inversely proportional to light intensity. Nonetheless, the same authors mentioned that over an irradiation intensity of $2.14 \times 10^{-7}$ (einstein/s), there was no considerable change of $K^A$. In the case of this dissertation study, where the emission rate was $1.14 \times 10^{-5}$ (einstein/s), using a 15 W BLB lamp. Thus, one can conclude that adsorption parameters established without irradiation were still adequate for the irradiation period.

6.6 Photocatalytic Hydrogen Production Carbon Balance

The overall carbon balance provides a determination of carbon conservation closure of the experiments developed. This is a necessary condition to establish the adequacy of a
chemical reaction study with quantification of all chemical species involved. More specifically, during the photocatalytic hydrogen production to establish carbon conservation, one must account for all the carbon containing species including: a) the sacrificial agent (ethanol), b) intermediate species (acetic acid, acetaldehyde) and c) products (methane, ethane and carbon dioxide). As a result, the carbon balance can be presented as follows,

$$Carbon\ Balance\ \% = \left( \frac{Carbon_{Ethanol\ t=0} - Carbon_{all\ produced\ species}}{Carbon_{Ethanol\ t=0}} \right) \times 100$$ (6-33)

Figure 39 reports the carbon balance with a ±2% closure. It was judged that this error variation is in the range of expected errors when using a combined HPLC analysis for ethanol and acetic acid and a GC analysis for methane, ethane and carbon dioxide.

Figure 39: Carbon balance at different irradiation times during photocatalytic hydrogen generation. The shaded area represents the carbon balance error

6.7 Conclusions

a) DP25 loaded with platinum in the presence of sacrificial agents such as ethanol, favors the oxygen-free hydrogen formation.

b) An acidic pH of approximately 4 with a 1 wt% of platinum onto DP25 is found to be the best conditions for the photocatalytic hydrogen production.
c) A water dissociation based model explains the influence of the pH on hydrogen production. Protons under acidic conditions appear to have a strong influence in our photocatalytic hydrogen generation system.

d) Photocatalytic water splitting in the presence of ethanol favors hydrogen formation, as well as other carbon containing species such as CH$_4$ and C$_2$H$_6$ along with CO$_2$, as part of the byproduct gases of the photocatalytic reaction.

e) Ethanol adsorption onto the photocatalyst of DP25-Pt at slurry conditions and at pH of 4 is successfully described by using the Langmuir adsorption isotherm.

f) Carbon balances involving all carbon containing chemical species are developed at various irradiation times showing a maximum ±2% deviations.

g) Observed chemical species allows postulating an “in Series-Parallel” reaction network for the photocatalytic hydrogen production using a DP25-Pt photocatalyst and ethanol as sacrificial reagent (hole scavenger).
Chapter 7
Results and Discussion Part III: Kinetic Modeling for Hydrogen Evolution and its Intermediate Species

7 Introduction

The current chapter reports the kinetic modeling of the photocatalytic water splitting reaction for hydrogen production. This section also provides a new valuable kinetic approach based on an in series-parallel reaction network. The in series-parallel reaction network (RN) describes, as shown in Figure 40, the photocatalytic conversion of ethanol (the organic scavenger), the photocatalytic formation of hydrogen and other carbon containing byproduct species.

The proposed RN for the DP25-1 wt% Pt photocatalyst, as applicable to water splitting, is based on the various observable chemical species. This RN leads to a kinetic model involving a set of ordinary differential equations. The proposed kinetic model may be most valuable in assisting with photo reactor scale up, design, and optimization of the process operating parameters.

A Langmuir-Hinshelwood approximation is adopted for both the adsorption and photoreaction process of various chemical species. Moreover, it is important to use in this analysis as well, reliable and rigorous statistical techniques. Among these techniques, one can account for cross-correlation, optimized regressed parameters and 95% confidence intervals. These approaches may provide adequate values for kinetic rate constant estimation, as well as for meaningful phenomenological based kinetic constants.

It is also observed that hydrogen production using an organic scavenger requires the additive contribution (in parallel-network) of the following: a) the scavenger assisted hydrogen formation and b) the direct electron addition to protons.
7.1 A Kinetic Model Approach by Langmuir-Hinshelwood Equation

The Langmuir-Hinshelwood rate equation can be used to model the rate of formation and disappearance of different chemical species. The LH equation evaluates the reaction kinetic constants, taking into account both the adsorption of chemical species on the photocatalyst surface as well as the gas phase species concentration. Therefore, a general expression of the Langmuir-Hinshelwood equation for this system (Moreira et al. 2012; Ortiz-Gomez et al. 2007; M. Salaices, Serrano, and de Lasa 2004) can be given as follows:

\[ r_i = LVRPA \cdot f[H^+] \cdot \frac{k_i^f K_i^A c_i}{1 + \sum_{j=1}^{n} k_j^A c_j} = \frac{k_i^f k_i^A c_i}{1 + \sum_{j=1}^{n} k_j^A c_j} \]  \hspace{1cm} (7-1)

where \( LVRPA \) is the local volumetric rate of photon absorption, \( f[H^+] \) represents the influence of the pH on the photocatalytic reaction, \( k_i^f \) stands for the intrinsic reaction kinetic constant (mol/g\textsubscript{cat} h), \( K_i^A \) denotes the adsorption constant (l/mol), and \( C_i \) represents the concentration of chemical species (mol/l). In equation (7-1) one can define an apparent kinetic constant \( k_i^* = LVRPA \cdot f[H^+] \cdot k_i^f k_i^A \). Furthermore, the “\( j \)” subscript refers to every component of the \( n \) chemical species present. The subscript \( i \) denotes the “\( i \)” species involved in the \( r_i \) reaction (mol/g\textsubscript{cat} h).

On the other hand, an equation balance for each component “\( i \)”, for a photocatalytic reactor as in PCW-II operated in the batch mode is given by the equation below (Moreira et al. 2012; Ortiz-Gomez et al. 2007; de Lasa, Salaices, and Serrano 2005; M. Salaices, Serrano, and de Lasa 2004) and can be represented as follows,

\[ r_i = \frac{1}{W_{irr}} \frac{dN_i}{dt} = \frac{V_L}{W_{irr}} \frac{dN_i/V_L}{dt} = \frac{V_L}{W_{irr}} \frac{dC_i}{dt} \]  \hspace{1cm} (7-2)

where, \( W_{irr} \) is the irradiated photocatalyst powder (g\textsubscript{cat}), \( V_L \) stands for the reactor volume filled with liquid slurry phase (l), \( N_i \) denotes the number of \( i \) moles (mol) and \( t \) represents the time (h).
Thus, replacing equation (7-2) into equation (7-1), one can obtain the following reaction velocity for individual chemical species in slurry reaction systems,

\[
\frac{dc_i}{dt} = \frac{(\frac{W_{irr}}{V_L})k_i^c K_i^A c_i}{1+\sum_{j=1}^{n} K_j^A c_j}
\]  

(7-3)

Furthermore, equation (7-3) can be presented as:

\[
\frac{dc_i}{dt} = \frac{k_i c_i}{1+\sum_{j=1}^{n} K_j^A c_j}
\]  

(7-4)

When,

\[
k_i = \left(\frac{W_{irr}}{V_L}\right) k_i^c K_i^A
\]  

(7-5)

It is important to note that apparent kinetic constants in equation (7-4) are reported with units in h\(^{-1}\).

One can conclude from the aforementioned equations that, one can obtain an expression with the form of equation (7-4) for every one of the observable chemical species. In fact, this expression represents both photocatalytic oxidation and reduction of chemical species (model compounds and their intermediates) participating in the reaction network scheme. Thus, a set of ordinary differential equations for these chemical species can be established to express the photocatalytic production of hydrogen. This set of differential equations is reported in Section 7.2.1 of this chapter.

The estimation of the LH parameters needs to be calculated numerically. However, a limitation of the LH model is that a high cross-correlation coefficients may result between adsorption and kinetic parameters, if that occurs they need to be determined experimentally (Moreira et al. 2012). This problem can be addressed by determining independently the adsorption constants of the species taking part in the photocatalytic hydrogen formation.
7.2 A Series-Parallel Kinetic Model Development for Photocatalytic Hydrogen Production Using an Optimized Photocatalyst of DP25-Pt

A description of the conversion of the hole scavenger ethanol into \( H_2, CH_4, C_2H_6, \) and \( CO_2 \) and other intermediates such as \( CH_3COOH \) in the liquid phase, can be modeled using a Langmuir-Hinshelwood (LH) rate equation (Moreira et al. 2012; Kumar, Porkodi, and Rocha 2008; Konstantinou and Albanis 2004). It is expected that the modified DP25-1 wt\% Pt behaves in terms of adsorption phenomena as pure DP25 with no interference of Pt species on adsorption phenomenon (Ohtani et al. 1997).

Regarding the kinetic modeling of hydrogen production assisted with an ethanol scavenger, there are specific assumptions that are considered applicable: i) ethanol as well as the various intermediate species can be adsorbed on the photocatalytic surface, ii) adsorption is a dynamic equilibrium process, and iii) ethanol and various intermediate species are not affected by photolysis.

The proposed kinetic model leads to a set of ordinary differential equations (ODEs). These ODEs are based on an *in series-parallel* reaction network (RN) described in Figure 40. This RN represents a simplified version of the one reported in Figure 35, which accounts for the quantifiable chemical species only.

Figure 40: Representation of a simplified proposed *in series-parallel* reaction network for photocatalytic hydrogen production based on observable species. Intend for the kinetic modeling approach. Note: \( \gamma_i \) assumes the values of 2 and 0 for steps 1 and 3.
This “in series-parallel” reaction model (RN) is based on the following assumptions:

a) The photocatalytic reaction takes place in a PCW-II reactor with a slurried 1 wt% Pt-DP25 photocatalyst in a water-ethanol solution.

b) Near-UV photons reach the photocatalyst surface with energy intensities smaller than 410nm, thus allowing electron/hole pair separation. This promotes both oxidation and reduction steps as described in Figure 40.

c) Produced electron holes react with the OH− groups forming OH• radicals. At the same time, electrons produced favor the formation of H• radicals. OH• radicals convert ethanol as described in the above reported RN, following reaction steps 1, 2, 4 and 5.

d) Acetic acid intermediates are generated and consumed through steps 2 and 3.

e) Methane (CH4) and ethane (C2H6) end product species are produced via steps 1, 3, 4 and 5.

f) Carbon dioxide (CO2) is formed via steps 1, 3 and 4.

g) Hydrogen is formed via steps 2, 3 and 4.

Regarding the reaction parameters, they were calculated using statistical based methods. As a result, major indicators of the adequacy of the selected kinetic network (see above) were the cross correlation coefficients in the cross-correlation matrix, the spans for the 95% confidence intervals and the R² regression coefficient.

7.2.1 Development of Ordinary Differential Equations based on LH Equations and on the Proposed In Series-Parallel Reaction Network

The Langmuir-Hinshelwood (LH) rate equation can be considered applicable for each one of the reaction steps involved in the in series-parallel reaction network describing the ethanol rate of change as follows:

\[
\tau_{\text{EtOH}} V_L = \frac{dN_{\text{EtOH}}}{dt} = V_L \frac{dC_{\text{EtOH}}}{dt} = \frac{-V_L C_{\text{EtOH}} (k_1 + k_2 + k_4 + k_5)}{1 + K_{\text{EtOH}}^{A} C_{\text{EtOH}} + K_{\text{AA}}^{A} C_{AA} + K_{\text{EtOH}}^{A} C_{\text{EtOH}} + K_{H_2}^{A} C_{H_2} + K_{CO_2}^{A} C_{CO_2} + K_{C}^{E} C_{E} + K_{M}^{A} C_{M}} \tag{7-6}
\]
However, due to the fact that ethanol is in excess during the experiments, the ethanol concentration does not decrease significantly after 6 hours of irradiation (see Figure 31). Therefore, it can be assumed that ethanol concentrations remain close to $C_{\text{EtOH}} \approx 0.45$ mol/l. Hence, the dominant adsorbed species at all times is the ethanol and as a result one can consider the following inequality:

$$K_{\text{EtOH}}^{A} C_{\text{EtOH}} \gg K_{H_{2}}^{A} C_{H_{2}} + K_{\text{CO}_{2}}^{A} C_{\text{CO}_{2}} + K_{E}^{A} C_{E} + K_{M}^{A} C_{M}$$

It is important to mention that the ethanol adsorption constant on the DP25-1 wt% Pt photocatalyst was determined previously in Section 6.5.

On this basis, one can conclude that ODEs for various chemical species can be described as follows:

a) For acetic acid (AA),

$$\frac{dN_{AA}}{dt} = \frac{V_{L} (k_{2} C_{\text{EtOH}} - k_{3} C_{AA})}{1 + K_{\text{EtOH}}^{A} C_{\text{EtOH}}} \quad (7-7)$$

b) For carbon dioxide (CO$_{2}$),

$$\frac{dN_{\text{CO}_{2}}}{dt} = \frac{V_{L} [(k_{1} + k_{4}) C_{\text{EtOH}} + k_{3} C_{AA}]}{1 + K_{\text{EtOH}}^{A} C_{\text{EtOH}}} \quad (7-8)$$

c) For ethane (E),

$$\frac{dN_{E}}{dt} = \frac{V_{L} C_{\text{EtOH}} (1/2k_{4} + k_{6})}{1 + K_{\text{EtOH}}^{A} C_{\text{EtOH}}} \quad (7-9)$$

d) For methane (M),

$$\frac{dN_{M}}{dt} = \frac{V_{L} (k_{5} C_{\text{EtOH}} + k_{3} C_{AA})}{1 + K_{\text{EtOH}}^{A} C_{\text{EtOH}}} \quad (7-10)$$

e) For hydrogen (H$_{2}$),

$$\frac{dN_{H_{2}}}{dt} = \frac{V_{L} C_{\text{EtOH}} (2k_{1} + 2k_{2} + 2.5k_{4})}{1 + K_{\text{EtOH}}^{A} C_{\text{EtOH}}} \quad (7-11)$$
7.2.2 Kinetic Parameters Estimation for the Proposed In Series-Parallel Reaction Network

The kinetic parameters of the proposed model were determined by using MATLAB® subroutines. The objective function employed was `lsqcurvefit` a non-linear least square fit. This method considers that the adjustment of parameters is obtained with a minimum value for the sum of the square residuals (difference between the modeled data and the experimental data). This objective function involved the minimization of the moles of acetic acid, methane, ethane and CO$_2$ as follows,

$$\min = \sum_{i=1}^{n}(N_{i,exp} - N_{i,model})^2 \quad (7-12)$$

With: $N_{i,exp}$ being the experimental observed moles for the “i” species and $N_{i,model}$ standing for the calculated moles of the “i” species using the proposed kinetic model.

For the estimation of the numerical integration of the ordinary differential equations an `Ode45` was used. This method implements fourth/fifth order Runge-Kutta methods.

The kinetic model parameter evaluation was implemented using experimental data obtained under pH=4, 2 v/v% ethanol and DP25-1 wt% Pt. The kinetic rates involved in each of the steps were modeled using LH expressions as described in Section 7.2.1. On this basis, each kinetic rate was considered as a function of the $k_n$ the intrinsic rate constant, the $C_i$ concentration of chemical species “i” and the adsorption constant $K_{Ai}$ for the “i” component.

Results of the in series-parallel model predictions for photocatalytic hydrogen production using equations from (7-7) to (7-11) are reported in the upcoming figures. The estimation of kinetic parameters is developed using the adsorption constant determined in Section 6.5.

The DOF (degree-of-freedom) for the model analysis was calculated as follows,

$$DOF = m - p \quad (7-13)$$
Where, $m$ is the number of experimental data points and $p$ denotes the number of model parameters. One should note that the degree of freedom (DOF) for the 5 model parameters was 235. This included the four repeats per every run. Thus, the DOF was well in excess of zero and the experimental data points are valuable to estimate the kinetic parameters.

Figure 41 displays the good fit achieved for acetic acid concentrations using the in series-parallel kinetics described in Figure 40.

Figure 41: Change of moles with irradiation time. Experimentally observed (o) and estimated model (—) for acetic acid. Photocatalyst: DP25-1 wt% Pt, ethanol initial concentration of 2 v/v% and pH of 4

Furthermore, Figure 42 reports the methane concentration and its changes with irradiation time both measured and modeled. One can conclude that the proposed kinetic network having methane as an end product describes the experimental data well.
Figure 42: Change of moles with irradiation time. Experimentally observed (o) and estimated model (—) for methane. Photocatalyst: DP25-1 wt% Pt, ethanol initial concentration of 2 v/v% and pH of 4.

Figure 43 shows that ethane concentration changes with irradiation time with a close to linear pattern. It can also be observed that the fit of the suggested kinetics for ethane formation, with ethane being another end product of the photocatalytic reaction, is again very adequate.

Figure 43: Change of moles with irradiation time. Experimentally observed (o) and estimated model (—) for ethane. Photocatalyst: DP25-1 wt% Pt, ethanol initial concentration of 2 v/v% and pH of 4.
Figure 44 reports the steady increase of carbon dioxide with irradiation time. Carbon dioxide is an end product that represents the total mineralization of the organic scavenger. CO₂ is produced along with hydrogen, methane and ethane under the conditions set for the photocatalytic H₂ production using 1 wt% Pt on TiO₂ and pH=4. It is important to note that again, the prediction of the proposed reaction network described the CO₂ data points well.

![Carbon Dioxide Graph](image)

Figure 44: Change of moles with irradiation time. Experimentally observed (o) and estimated model (—) for carbon dioxide. Photocatalyst: DP25-1 wt% Pt, ethanol initial concentration of 2 v/v% and pH of 4

Table 14 reports photocatalytic hydrogen production with five kinetic constants. The five (5) optimized kinetic constants along with the values of the 95% confidence intervals (CI) and the standard deviations (STD). As one can see in the values reported in Table 14, the narrow 95% confidence intervals and the small STD confirm the adequacy of the kinetic parameters obtained.
Table 14: Kinetic parameters calculated via regression of experimental data and model predictions for photocatalytic hydrogen production. Ethanol initial concentration: 2 v/v%, pH=4 and Photocatalyst: 1 wt% Pt on TiO₂

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (h⁻¹)</th>
<th>95% CI</th>
<th>STD (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
<td>2.0097E-06</td>
<td>4.3402E-07</td>
<td>2.3177E-07</td>
</tr>
<tr>
<td>k₂</td>
<td>2.2252E-06</td>
<td>5.2208E-07</td>
<td>2.3154E-07</td>
</tr>
<tr>
<td>k₃</td>
<td>1.6300E-02</td>
<td>7.5359E-04</td>
<td>1.3528E-02</td>
</tr>
<tr>
<td>k₄</td>
<td>5.1865E-06</td>
<td>2.0478E-07</td>
<td>1.2097E-07</td>
</tr>
<tr>
<td>k₅</td>
<td>6.6329E-06</td>
<td>2.8919E-06</td>
<td>1.4815E-07</td>
</tr>
</tbody>
</table>

Furthermore, Table 15, reports the cross-correlation coefficients matrix. Cross-correlation coefficients are a very useful approach to predict the similarity between independent variables. As stated by El Solh et al., if one or more parameters were not significant or were highly correlated, the correlation would have been close to ±1.0, meaning that multiple solutions for the kinetic constant can be obtained (Solh, Jarosch, and de Lasa 2003). Therefore, it can be noticed the acceptable low levels of interaction between kinetic constants with all cross-correlation coefficients being lower than ±0.93.

Table 15: Cross-Correlation coefficients for the optimization of experimental repeats for photocatalytic hydrogen production. Ethanol initial concentration: 2 v/v%, pH=4 and Photocatalyst: 1 wt% Pt on TiO₂

<table>
<thead>
<tr>
<th></th>
<th>k₁</th>
<th>k₂</th>
<th>k₃</th>
<th>k₄</th>
<th>k₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>k₁</td>
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<td>k₂</td>
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<tr>
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<td>k₅</td>
<td>0.1500</td>
<td>0.0000</td>
<td>0.0000</td>
<td>-0.5774</td>
<td>1.0000</td>
</tr>
</tbody>
</table>

Regarding the reconciliation plot reported below, a data quality analysis can be made. The observed in Figure 45 describes a randomly distributed experimental and modeled data points, as well an adequate correlation with a coefficient R² of 0.9977. In addition, Figure 45 shows that the data reported is not clustered in horizontal or vertical bands. On one hand, horizontal bands may be the result of changes in the observed conversion caused by an independent variable which is not included in the kinetic model. On the other hand, vertical bands may be an indication of the kinetic model over-
parameterization (Al-Bogami and de Lasa 2013; Moreira et al. 2012; Solh, Jarosch, and de Lasa 2003). Therefore, it is proven in Figure 45 that the suggested kinetic model acceptably fits the experimental data within the ±5% limit of the experimental error. As a result, one can conclude that the model estimates the experimental data parameters properly.

The reconciliation plot reported of Figure 45 describes in detail what was observed for species concentrations of $2 \times 10^{-5}$ mol and lower with a good prediction of the experimental data.

**Figure 45: Reconciliation plot for the experimental results and predictions using a five (5) kinetic parameters model using a DP25-1 wt% Pt: a) The smaller plot describes the fitting of the chemical species resulting for the 0 to $2 \times 10^{-5}$ mole range and b) The larger graph reports the chemical species fitting for the $2 \times 10^{-5}$ to $1 \times 10^{-4}$ mole range**

Figure 46 reports the residuals for the “in series parallel” model with five (5) kinetic constants following the parameter optimization. As one can see, the “in series parallel” model provides random error prediction between the experimental and the modeled data.
Figure 46: Residuals plot of the estimation of five (5) kinetic parameters for the photocatalytic hydrogen generation on DP25-1 wt% Pt

7.2.2.1 Issues with Kinetic Model Development and Kinetic of Hydrogen Production

Regarding hydrogen production one can notice from Figure 47 that the proposed reaction network does not predict well the experimental data. These model predictions are much lower than experimental values. Model predictions are based on explaining hydrogen production as a result of oxidation-reduction steps associated with ethanol organic scavenger consumption equations (7-7) to (7-11). As a result it was decided to exclude hydrogen from the data regression analysis reported in Table 14 and Table 15.

However, from the reported results in Figure 47 it appears that hydrogen production also takes place via direct electron addition to H⁺. This path is enhanced in particular at acidic conditions (pH=4) with high concentration of protons in the liquid phase. These available protons may react with the accessible electrons on the photocatalyst surface forming extra H⁺ radicals precursors of hydrogen formation (see Figure 48). Platinum may also contribute given its capability to act as an electron reservoir (Pelaez et al. 2012; Ding et al. 2008).
Figure 47: Change of moles of hydrogen with irradiation time: (o) experimental values, (—) model predictions. Photocatalyst: DP25-1 wt% Pt, ethanol initial concentration of 2 v/v% and pH of 4

In any event and in order to establish a kinetic model explaining the total hydrogen produced from direct electron addition to H\(^+\) and from the oxidation-reduction scavenger conversion the following is postulated:

\[
\frac{dN_{H_2}}{dt} = r_{H_2} W_{irr}
\]  

(7-14)

In this equation \(r_{H_2}' = r_{H_2} W_{irr}\), being the hydrogen reaction rate (mol/h).

Thus, the following “in parallel” competitive path for hydrogen production is proposed,

\[
C_2H_5OH_{(l)} + H_2O_{(l)} \rightleftharpoons [H^+] \leftarrow [H^+]/f(\text{scavenger})
\]

Figure 48: Representation of a proposed “in parallel” reaction network for photocatalytic hydrogen production based on the influence of Acid pH. Intend for the kinetic modeling approach

\[
r_{H_2}' = LVRPA f[H^+] [k_{H_2}] + \frac{V_L \cdot C_{ETOH}(2k_1 + 2k_2 + 2.5k_4)}{1 + k_{ETOH}^A C_{ETOH}}
\]  

(7-15)
where, $k_{H_2}$ denotes the hydrogen kinetic rate constant (l/h), $f[H^+]$ stands as a function of pH, thus $[H^+] = \text{antilog} - \text{pH}$ being the number of protons presented in the liquid solution (mol/l), $W_{\text{irr}}$ is the irradiated photocatalyst powder ($g_{\text{cat}}$), $V_L$ stands for the reactor volume filled with liquid slurry phase (l), $N_{H_2}$ denotes the number of moles of hydrogen (mol) and $t$ represents the time (h).

At constant or quasi-constant acidic pH and set LVRPA conditions equation (7-15) becomes,

$$ r'_{H_2} = k'_{H_2} + \frac{V_L C_{\text{Ethanol}} (2k_1 + 2k_2 + 2.5k_4)}{1 + k_{\text{Ethanol}}^2 C_{\text{Ethanol}}} $$

(7-16)

Where $k'_{H_2} = LVRPA \ f[H^+] \ [k_{H_2}] = (0.0003t - 0.0002)[k_{H_2}]$

Linear regression of equation (7-14) and of the $k_{H_2}$ constant leads to a $3.1 \times 10^{-4}$ (l/h) value with an excellent fitting of the H$_2$ production as described in Figure 49.

![Figure 49](image_url)

**Figure 49: Addition of the moles of hydrogen produced with irradiation time:** (o) experimental values, (—) model predictions. Photocatalyst: DP25-1 wt% Pt, ethanol initial concentration of 2 v/v% and pH of 4

On the basis of the data obtained during the first 6 hours of irradiation, it is speculated that H$_2$ production via direct electron addition to protons plays major role in hydrogen production. This path is likely going to lead to OH$^-$ radicals increasing on the
photocatalyst surface. Thus, it is anticipated that following this initial 6 hours hydrogen production period, the consumption of ethanol scavenger will considerably increase. Under these conditions the role of oxidation-reduction scavenger consumption on hydrogen production augments considerably.

7.3 Conclusions

This chapter reports kinetic modeling and the statistical parameters for both ethanol scavenger consumption and hydrogen production performing water splitting using a TiO$_2$-1 wt% Pt photocatalyst, 2 v/v% ethanol scavenger and pH=4. The following conclusions can be stated:

a) Langmuir-Hinshelwood rates are valuable for an in series-parallel reaction network describing the ethanol consumption. This model can be used successfully to describe CH$_3$COOH, CH$_4$, C$_2$H$_6$ and CO$_2$ byproducts.

b) The kinetic constant parameters are predicted in MATLAB$^\text{®}$ using a non-linear square fit lsqcurvefit and an Ode45 numerical estimation for the numerical integration of differential equations.

c) The suggested kinetic model is established with 235 DOF, a small 95% CI with low cross-correlation, low residuals and a correlation coefficient ($R^2$) of 0.9977. These rigorous statistical methods are adopted to adequately predict the experimental data from the proposed “in series-parallel” reaction network.

d) The proposed kinetic model and reaction network are suitable to fit the experimental concentrations of all byproduct species resulting from the scavenger consumption during the photocatalytic hydrogen production.

e) The proposed “in series-parallel” kinetic model is however incapable to describe the much larger hydrogen production levels as observed experimentally. It is speculated that this is the result of the significant influence of electron direct addition to H$^+$, favoring H$^-$ radicals formation, the precursors of H$_2$ are hypothesized.
f) Hydrogen formation rates is satisfactorily modeled instead using a reaction rate additive model (in parallel path) with roles assigned to both hydrogen production via direct electron addition to protons and hydrogen produced via redox ethanol photocatalytic consumption reactions.
Chapter 8
Results and Discussion Part IV: Energy Efficiencies Calculation in the Photo-CREC Water II Reactor for Hydrogen Generation

8 Introduction

Quantum Yields ($\phi$) and Photochemical Thermodynamic Efficiency Factors ($PTEFs$) are important energy efficiency estimators in photochemical reactors. They are used to calculate the energy efficiency during the photocatalytic photoconversion or photocatalytic photodegradation of organic pollutants in photocatalytic processes. The significance of energy efficiencies has been stressed in recent years in scientific technical literature by the CREC research group (Garcia 2012; Garcia H., Serrano, and de Lasa 2012; Moreira 2011; Benito Serrano et al. 2009; de Lasa, Salaices, and Serrano 2005; Ibrahim and de Lasa 2003; Miguel Salaices, Serrano, and de Lasa 2001b; Cassano et al. 1995).

The applications and calculations of both Quantum Yields ($\phi$) and Photochemical Thermodynamic Efficiency Factors ($PTEFs$) to hydrogen production are important contributions to this chapter. The data reported is the result of a significant number of experiments specifically developed to assess the photocatalytic hydrogen production efficiency using a particular type of reactor configuration: the Photo-CREC Water II Reactor.

Regarding energy efficiencies, their evaluation is always a challenge due to the diversity of variables involved. These variables are the following: a) the irradiation absorbed by the photocatalyst, b) the kinetic parameters, c) the heterogeneous reactions mechanism and c) the adsorption constants. One should emphasize that the study and knowledge of efficiency factor allow us to establish reliable criteria to delimit the capabilities of photocatalytic water splitting reactors as an alternative for hydrogen production.
8.1 The Energy Efficient Factors in Photocatalytic Processes

Energy efficiency criteria in a photochemical process such as the Quantum Yield ($\phi$) and the Photochemical Thermodynamic Efficiency Factor (PTEF) are critical indicators in establishing irradiation utilization (Garcia H., Serrano, and De Las 2012; Benito Serrano et al. 2009; Miguel Salaices, Serrano, and de Lasa 2001b). However, to ascertain these parameters in the context of hydrogen production, critical assumptions are required. For instance, it can be assumed that the entire photon energy content contribute to the formation of H’ and OH’ groups. Applicability of this hypothesis is reviewed in the upcoming sections of this chapter.

8.1.1 Quantum Yield for Photocatalytic Hydrogen Production ($\phi$)

The Quantum Yield ($\phi$) definition is modified in the present PhD dissertation to provide an adequate energy efficiency definition (see equation 8-1). The new definition accounts for hydrogen production as a number ratio. This ratio results from determining the rate of H’ molecules produced over the number of photons absorbed in the platinum impregnated TiO$_2$ (Escobedo Salas, Serrano Rosales, and de Lasa 2013; de Lasa, Salaices, and Serrano 2005; Cassano et al. 1995).

$$\phi = \frac{\text{number of H’ molecules produced}}{\text{number of photons absorbed by the photocatalyst } \lambda \leq 455 \text{nm}}$$  \hspace{1cm} (8-1)

Thus, the Quantum Yield can be represented on a percentual basis ($\% \phi$) as follows,

$$\% \phi = \frac{dN_1}{dt} \times 100$$  \hspace{1cm} (8-2)

Regarding Quantum Yields using equation (8-2) for the photocatalytic hydrogen production, calculations are described in the present sections. The calculations require an applicable reaction network for the photocatalytic reaction.

Figure 35 describes an "in series-parallel" model postulated for the photoconversion of organic pollutants in water in a Photo-CREC Water II reactor (Escobedo Salas, Serrano Rosales, and de Lasa 2013; de Lasa, Salaices, and Serrano 2005). This reaction network
is shown to be adequate producing hydrogen and having ethanol as the "organic scavenger".

This mechanism (Figure 35) is expected, given the likely variability of axial and radial photon density in a Photo-CREC Water II reactor. In addition, given the consideration of Chapter 7, one can also expect the direct addition of an electron to H\(^+\) forming H\(^-\) directly, under acidic conditions.

Thus, one can define the "Theoretical Quantum Yields" based on the photon stoichiometric requirements for H\(^-\) radical production as follows,

\[
\phi_{\text{theor}} = \frac{\text{moles of } H^-}{\text{moles of Photons}}
\]  

(8-3)

Therefore, by using equation (8-3), one can determine the values of the "Theoretical Quantum Yield" as reported in Table 16. A detailed description in these theoretical Quantum Yield evaluations is also reported in the Appendix E of this PhD dissertation.

For instance, one can notice that in the case of H\(^+\) converted into H\(^-\) the "Theoretical Quantum Yield" equals 1. Furthermore, in the case of the complete conversion of ethanol, this "Theoretical Quantum Yield" is 0.8. However, considering the possible influence of various reaction steps at any time during the irradiation process, with these steps involving both the scavenger and the intermediates, a reasonable average estimate for this theoretical QY is 0.8 or 80%. It should be emphasized that this theoretical QY value can be used as a reference only, and represents the QY that one can expect when assuming that there is no electron-hole recombination.
Table 16: Description of theoretical quantum yields for the various steps involved in the conversion of ethanol as the organic scavenger for hydrogen production

<table>
<thead>
<tr>
<th>Reaction Path</th>
<th>Reactant</th>
<th>Product</th>
<th>Photons (hv)</th>
<th>H₂ formed</th>
<th>( \varphi )_{theor} = \text{H}^\cdot/\text{Photons}</th>
<th>Refer to the following equation in Appendix</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H⁺</td>
<td>H₂</td>
<td>1</td>
<td>0.5</td>
<td>1</td>
<td>E.2</td>
</tr>
<tr>
<td>2</td>
<td>C₂H₅OH</td>
<td>C₂H₄, CO₂</td>
<td>5</td>
<td>2</td>
<td>0.8</td>
<td>E.14</td>
</tr>
<tr>
<td>3</td>
<td>C₂H₅OH</td>
<td>C₂H₄O</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>E.4</td>
</tr>
<tr>
<td>4</td>
<td>C₂H₅OH</td>
<td>C₂H₃OOH</td>
<td>4</td>
<td>2</td>
<td>1</td>
<td>E.8</td>
</tr>
<tr>
<td>5</td>
<td>C₂H₄O</td>
<td>C₂H₂OOH</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>E.6</td>
</tr>
<tr>
<td>6</td>
<td>CH₃COOH</td>
<td>CH₄, CO₂</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>E.10</td>
</tr>
<tr>
<td>7</td>
<td>C₂H₄O</td>
<td>CH₄, CO₂</td>
<td>3</td>
<td>1</td>
<td>0.666</td>
<td>E.16</td>
</tr>
<tr>
<td>8</td>
<td>2CH₃COOH</td>
<td>C₂H₆, CO₂</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>E.12</td>
</tr>
</tbody>
</table>

8.1.1.1 Effect of the pH on the Quantum Yields (\( \varphi \))

Energy efficiency (% \( \varphi \)) was determined in the context of the present study, at ambient temperature and close to atmospheric pressure (NTP). This experimental study was performed in a PCW-II reactor at different pHs and different platinum loadings (Escobedo Salas, Serrano Rosales, and de Lasa 2013). More detailed information regarding the PCW-II reactor is Section 6.2 of this thesis.

This process allows one to establish the influence of Pt loading on the doped TiO₂ and the effect of pH parameter on quantum yields.

8.1.1.1.1 Effect of Alkaline pH on Quantum Yields

A pH of approximately 10 was set for a water/ethanol solution. The selected pH remained essentially unchanged during the complete experiment. A 2 Molar NaOH solution was prepared and 2 ml of this solution were added to a 6 L water / 2 v/v% ethanol solution. The solution was place in the PCW-II reactor mixing tank.

Figure 50 reports the Quantum Yield for a pH=10. QYs were determined using equation (5-3) and (8-3), and the respective values of hydrogen formation rates. It is important to notice that the reported QYs are based on H⁺ generation rates. Furthermore, it is observed
that there are two characteristic periods for QYs as follows: i) QYs increase reaching a maximum value in between 1-2 hours of irradiation, ii) QYs steadily decline during the remaining period of the run.

![Figure 50: Overall QY calculations at different Pt loadings on DP25, pH=10, EtOH 2 v/v% and Argon as purging gas]

Table 17 describes the hydrogen formation rates and Quantum Yields ($\phi$) for three of the photocatalysts of this study using a Photo-CREC Water II reactor at pH=10. One can see that whole set of platinum impregnated Degussa P25 photocatalysts display a higher hydrogen production than the bare Degussa P25. Thus, it is shown that platinum addition on DP25 having ethanol as the organic scavenger has a positive effect on hydrogen production with hydrogen generation rates reaching a maximum during the 1-2 hour irradiation period. The maximum quantum yield observed under these conditions was 5.7%.
Table 17: Reaction rates at different loadings of Pt on TiO$_2$ and pH=10 in the Photo-CREC Water II Reactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate $^a$ (mol h$^{-1}$ g$_{cat}^{-1}$)</th>
<th>Quantum Yield (% $\varphi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25 0.06wt% Pt</td>
<td>73</td>
<td>1.5</td>
</tr>
<tr>
<td>DP25 0.2wt% Pt</td>
<td>132</td>
<td>2.7</td>
</tr>
<tr>
<td>DP25 1wt% Pt</td>
<td>280</td>
<td>5.7</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 298 K, 1 atm

8.1.1.1.2 Effect of Neutral pH on Quantum Yields

To consider the conditions of hydrogen production at neutral pH, a pH of 7 was established in the PCW-II reactor. These experiments were performed with various photocatalysts of DP25-Pt. The pH value was tracked during the entire 5.5 hours of the experiment and remained very close to the original value of 7.

Figure 51 reports the QYs for the various photocatalysts at pHs of 7. One can notice that similar QY trends as the ones observed at pH=10 are obtained. In fact, in all the studies, photocatalysts display a common trend: i) a QY increase during the first 1.5 hours, and then ii) a QY reduction for the rest of the run.

Figure 51: Overall QY calculations at different platinum loading on DP25, pH=7, EtOH 2 v/v% and using Argon as purging gas
Table 18 reports hydrogen reaction rates and Quantum Yields ($\phi$) in a Photo-CREC Water II reactor for four different photocatalysts at pH=7. It is proven that platinum impregnated DP25 in the presence of the ethanol scavenger allows hydrogen production. Furthermore, it is also noticed that the 1wt% Pt addition yields a maximum hydrogen formation rate of $\frac{mol}{h \times g_{cat}}$ with a 4.6 QY. This QY is close to the best value of 5.7%, with this value being comparable to the one observed under alkaline conditions.

Table 18: Reaction rates at different loadings of Pt on TiO$_2$ and a pH=7 in the Photo-CREC Water II Reactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate $^a$ (mol h$^{-1}$ g$_{cat}^{-1}$)</th>
<th>Quantum Yield (% $\phi$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25 0.06wt% Pt</td>
<td>188</td>
<td>3.8</td>
</tr>
<tr>
<td>DP25 0.2wt% Pt</td>
<td>193</td>
<td>3.9</td>
</tr>
<tr>
<td>DP25 1wt% Pt</td>
<td>226</td>
<td>4.6</td>
</tr>
</tbody>
</table>

$^a$ Reaction conditions: 298 K, 1 atm

8.1.1.1.3 Effect of Acid pH on Quantum Yields

Moreover and in order to further analyze the effect of the pH, a pH of 4 was studied using H$_2$SO$_4$ [2M]. 1 ml of this sulfuric acid solution was added in the 6 L tank containing a water/ethanol 2 v/v % solution. Results of these experiments showed the positive influence of acid conditions in the solution for hydrogen formation. It was also noticed that the pH remained close to the value of 4 for the complete 6 hrs of the experiment.

Figure 52 describes the QY for the pH of 4. Distinctive trends for the QYs were identified once the near UV lamp was turned on: i) First, there is a progressive increase of hydrogen formation rate and as a result of the QYs during the first half an hour of irradiation, ii) Following this, there is a steady hydrogen formation rate during 6 hours with ethanol. The overall ethanol conversion was under these conditions less than 1%. As a result QYs reach maximum values after 0.5 hours and remain at those levels for the rest of the run.

In addition and as described in Figure 52, four different samples of DP25 loaded with platinum were considered in the experimental runs at a pH of 4. The photocatalysts
studied, all showed steady hydrogen formation rates (see Figure 28) after the first half an hour of irradiation, with all of them surpassing the QYs of the bare Degussa D25.

Figure 52: Overall QY calculations at different platinum loadings on DP25, pH=4, EtOH 2 v/v% and using Argon as purging gas

Table 19 reports hydrogen formation rates and Quantum Yields (φ) in the Photo-CREC Water II reactor for the four different Pt modified photocatalysts at pH=4. It can be observed that a hydrogen formation rate is obtained in between 1-2 hours of irradiation with a corresponding 7.9 % Quantum Yield. This value remains steady during the 6 hours of the run.

Table 19: Reaction rates at different loadings of platinum on TiO₂ and pH=4 in the Photo-CREC Water II Reactor

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Reaction rate a (mol h⁻¹ g⁻¹cat⁻¹)</th>
<th>Quantum Yield (% φ) H₂ Production</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP25</td>
<td>36</td>
<td>0.7</td>
</tr>
<tr>
<td>DP25 0.06wt% Pt</td>
<td>89</td>
<td>1.8</td>
</tr>
<tr>
<td>DP25 0.1wt% Pt</td>
<td>142</td>
<td>2.9</td>
</tr>
<tr>
<td>DP25 0.2wt% Pt</td>
<td>200</td>
<td>4.1</td>
</tr>
<tr>
<td>DP25 1wt% Pt</td>
<td>383</td>
<td>7.9</td>
</tr>
</tbody>
</table>

a. Reaction conditions: 298 K, 1 atm
Furthermore, one should note that the 7.9% QYs using Pt impregnated DP25 in a Photo-CREC Water II reactor under acidic conditions, are most valuable. This is the case in spite of being smaller than the expected theoretical 80% QY for hydrogen production (refer to section 8.1.1). These experimentally observed QY values, lower than the theoretical ones, can be justified given that the H’ radical formation via photocatalysis using organic scavengers is likely a 2 photon-photocatalyst site simultaneous or quasi-simultaneous interaction process (Escobedo Salas, Serrano Rosales, and de Lasa 2013; Akihiko Kudo and Miseki 2009).

8.1.2 The Photochemical Thermodynamic Efficiency Factor (PTEF) for Photocatalytic Hydrogen Production

The definition of the photochemical thermodynamic efficiency factor (PTEF) was considered to be the product of $QY_{Exp}$ or $\varphi_{Exp}$ and $\eta_{[H' + OH']}^t$ (Garcia H., Serrano, and de Lasa 2012) expressed in an equation as follows,

$$PTEF = \varphi_{Exp} \times \eta_{[H' + OH']}$$

(8-4)

with $\varphi_{Exp}$ being the experimental quantum yield for hydrogen production and $\eta_{[H' + OH']}^t$ standing for the fraction of photon energy employed to form both the H’ and the OH’ radicals. The equation can be given by,

$$\eta_{[H' + OH']} = \frac{\Delta H_{[H' + OH']}^\circ}{(\text{# of photons interacting in the formation of } H' + OH')(E_{av})}$$

(8-5)

where $\Delta H_{[H' + OH']}^\circ$ is the enthalpy of formation of the H’ and the OH’ radicals (KJ/mol), and $E_{av}$ stands for the average emitted photon energy (Appendix F).

On the other hand, one can expect a $PTEF_{max}$ for combined oxidation-reduction processes (de Lasa, Salaices, and Serrano 2005). This maximum theoretical $PTEF$ or $PTEF_{max}$ can be determined by the following equation,

$$PTEF_{max} = \varphi_{theor} \times \eta_{[H' + OH']}$$

(8-6)
This *PTEF* is defined as the maximum possible thermodynamic value reached during the photocatalytic hydrogen production within the PCW-II reactor.

### 8.1.2.1 Enthalpies and Fraction Energy Required for Simultaneously Hydrogen and Hydroxyl Radicals Formation during Photocatalytic Water Splitting in a Photo-CREC Water II Reactor

While CREC researcher developed significant efforts in assessing the quantum yields and *PTEF* in photocatalysis for water decontamination (Benito Serrano et al. 2009), there is no information as of today on how to extend these concepts to photocatalytic water splitting. In order to accomplish this, the following has to be considered:

**Step 1) Dark Period:** During this period, adsorption of both organic molecules and water take place on the TiO$_2$ surface as follows,

\[
\text{Organic Molecule}_{(l)} \xrightarrow{T\text{TiO}_2-Pt} \text{Organic Molecule}_{(ads)} \tag{8-7}
\]

\[
H_2O_{(l)} \xrightarrow{T\text{TiO}_2-Pt} H_2O_{(ads)} \tag{8-8}
\]

**Step 2) Irradiation Period- Separation of Charges:** It is during the irradiation period when the near-UV lamp is turned “on”. Under these conditions various photoreactions taking place as a result. Photons with the adequate energy content excite the TiO$_2$ particles as follows,

\[
h\nu \xrightarrow{T\text{TiO}_2-Pt} h^+ + e^- \tag{8-9}
\]

**Step 3) Irradiation Period- Formation of OH$^-$ radicals:** Water dissociation forming adsorbed protons and adsorbed hydroxyl species. Irradiation leads to separation of charges (electrons and holes vacant sites). Electron/hole formed reacts with the adsorbed hydroxyl ions (OH$^-$) producing hydroxyl radicals as follows,

\[
H_2O_{(ads)} \xrightarrow{T\text{TiO}_2-Pt} H^+_{(ads)} + OH^-_{(ads)} \tag{8-10}
\]
Step 4) Irradiation Period- Formation of H' radicals. Platinum loaded on the semiconductor surface acts as an electron reservoir. As a result, protons (\(H^+\)) presented on the photocatalyst surface form H' radicals, with this leading to hydrogen (H\(_2\)) formation as follows,

\[
OH^-_{(ads)} + h^+ \xrightarrow{T_{O_2-Pt}} OH^-
\]  

(8-11)

As a result, the previous described reaction mechanism can be summarized as follows:

1. **Path Way 1.** Near-UV photon interacts with TiO\(_2\) surface yielding (h\(^+\)) and (e\(^-\)). First, the holes (h\(^+\)) interact with the adsorbed hydroxyl (OH\(^-\)) group. Following this the formed electron interacts with adsorbed oxygen, leading to the formation of H\(_2\)O\(_2\). Another photon is thus required to yield two additional OH' radicals. In summary two photons interacting sequentially with semiconductor sites, form three OH' radicals (Garcia H., Serrano, and de Lasa 2012; Moreira et al. 2012; Benito Serrano et al. 2010). As a result, the adsorbed organic molecules on TiO\(_2\) react with OH' radicals, being converted later into CO\(_2\) and H\(_2\)O (de Lasa, Salaices, and Serrano 2005). Figure 53 reports the photon requirements to form OH' radicals.

\[
H^+_{(ads)} + e^- \xrightarrow{T_{O_2-Pt}} H^-
\]  

(8-12)

\[
H^+ \xrightarrow{T_{O_2-Pt}} \frac{1}{2} H_2(g)
\]  

(8-13)

2. **Path Way 2.** This is an alternative photoconversion path much more dominant when TiO\(_2\) is loaded with platinum under acidic conditions. Following this pathway, both OH' and H' radicals are formed. Figure 53 also reports the needed energy requirements for this path to happen: Two near-UV photon with an energy content of 648 KJ/mole gives an OH' and H' radicals requiring 504 KJ/mole.
\( \eta_{(OH^*+H^*)} = 0.77 \) or 77\% of energy utilization is expected under these conditions.

\[
\begin{align*}
H_2O + TiO_2 \cdot Pt & \xrightarrow{h\nu} (OH)^*_{act} \xrightarrow{h\nu} OH^* \\
(H^*_{act} & \xrightarrow{Q^{-}} H^*)
\end{align*}
\]

Thus, the findings of this study show that hydrogen production via photocatalytic water splitting is allowed once TiO\(_2\) is doped with Pt. A necessary condition for this reaction to take place is to have two photons interacting simultaneously or quasi-simultaneously with the photocatalyst as described in Figure 53.

Figure 53 shows that the combined energy of two consecutive photons with an average estimated energy content of 648 KJ/mole supersedes the required 504 KJ/mole for the simultaneous formation of H\(^-\) and OH\(^-\) radicals. This allows, as a result, water splitting to take place.

**Figure 53:** Representation of energy levels for photocatalytic water splitting under near-UV light using Pt impregnated TiO\(_2\) photocatalyst
In summary, one can conclude that the data of the present study is relevant as it provides a thermodynamic and mechanistic framework under which photocatalytic hydrogen production can occur.

### 8.1.2.1.1 Calculations for the Enthalpy of Formation of $H^\cdot$ and OH$^\cdot$ Radicals

The excitation of TiO$_2$ and/or other semiconductors is related with to the basic mechanism of a photon being absorbed in the heterogeneous photocatalyst (either from the sunlight or an artificial source). The electron/hole pairs are generated by the excitation of a promoted electron from the valence band to the conduction band of the semiconductors. This process is sketched in Figure 4.

Therefore, the enthalpy of formation of OH$^\cdot$ radicals, is a thermodynamic non-path dependent state function, which is only affected by the initial and final conditions of the experiments. It can be calculated from equation (8-13) as follows,

$$H_2O_{(ads)} + h\nu \xrightarrow{TiO_2-Pt} OH^\cdot + H^\cdot$$  \hspace{1cm} (8-16)

Assuming for equation (8-13) that, $H_2O_{(ads=\ell)}$ and OH$^\cdot_{(ads=\ell)}$ then,

$$H_2O_{(ads)} + h\nu \xrightarrow{TiO_2-Pt} OH^\cdot_{(\ell)} + H^\cdot_{(\ell)}$$  \hspace{1cm} (8-17)

$$\Delta H^\circ_{[H^\cdot + OH^\cdot]_{(\ell)}} = \Delta H^\circ_{f,OH_{(\ell)}} + \Delta H^\circ_{f,H^\cdot_{(\ell)}} - \Delta H^\circ_{f,H_2O_{(\ell)}}$$  \hspace{1cm} (8-18)

The enthalpy of formation of the chemical species involved can be estimated as reported (Benito Serrano et al. 2009).

$$\Delta H^\circ_{f,H^\cdot_{(\ell)}} = 217.97 \frac{KJ}{mol}$$

$$\Delta H^\circ_{f,OH_{(\ell)}} = \Delta H^\circ_{f,OH_{(v)}} + \Delta H^\circ_{condensation,OH^\cdot}$$  \hspace{1cm} (8-19)
Given that $\Delta H_{f,OH^*}^\circ$ is defined in liquid phase reactions rather than in the gas phase $\Delta H_{f,OH^*}^\circ$, this parameter has to be modified using a OH$^*$ radical condensation enthalpy as follows,

$$\Delta H_{f,OH^*}^\circ = 38.95 \frac{KJ}{mol}$$

Considering the limited information available for assessing the condensation enthalpy of the OH$^*$ radical, a possible approach is to consider the condensation enthalpy for the OH$^-$ ion species given the analogous expected condensation properties as follows,

$$\Delta H_{\text{condensation,OH}^*}^\circ = \Delta H_{f,OH^-}^\circ - \Delta H_{f,OH^*}^\circ$$

(8-20)

$$\Delta H_{f,OH^-}^\circ = -229.994 \frac{KJ}{mol}$$

$$\Delta H_{f,OH^*}^\circ = -143.5 \frac{KJ}{mol}$$

$$\Delta H_{\text{condensation,OH}^*}^\circ = -86.49 \frac{KJ}{mol}$$

Then, the enthalpy of formation for the radical OH$^*$ in the liquid phase can be estimated as,

$$\Delta H_{f,OH^*}^\circ = \Delta H_{f,OH^*}^\circ + \Delta H_{\text{condensation,OH}^*}^\circ = -47.544 \frac{KJ}{mol}$$

On this basis, the heat of formation of $\Delta H_{(OH^*+H^*)}^\circ$ for photocatalytic water splitting is calculated from equation (8-18) as follows,

$$\Delta H_{(H^*+OH^*)}^\circ = \left[ -47.54 \frac{KJ}{mol} + 217.97 \frac{KJ}{mol} \right] - \left[ -285.83 \frac{KJ}{mol} \right]$$

$$\Delta H_{(H^*+OH^*)}^\circ = 504 \frac{KJ}{mol}$$
Therefore, the enthalpy of formation of the formed radicals in the Pt-TiO$_2$ can be compared with that of irradiated photons as reported in Figure 54.

**Figure 54: Enthalpy of formation for $\Delta H_{n^+ + OH^*}$ versus the energy content of 1 and 2 photons**

The above Figure shows the energy requirements to form both H$^*$ and OH$^*$ radicals. One can see that only two near-UV photons (purple bar) interacting simultaneously or quasi-simultaneously with the photocatalyst site are able to provide the energy required for H$^*$ and OH$^*$ simultaneous formation.

**8.1.2.1.2 Determination of the Fraction of Photon Energy Required to form OH$^*$ and H$^*$ Radicals**

Using a spectro photo-radiometer, a light spectrum was established to determine the fraction of photons (1 Einstein) emitted by a near-UV lamp generating 1 mol of free radicals of OH$^*$ and H$^*$. Using this spectrum, the average emitted photon energy ($E_{av}$) as proposed by Serrano et al. 2009 was calculated as 324 KJ/mole (see Appendix F).

Thus, the fraction of energy of two consecutive photons required to form simultaneous OH$^*$ and H$^*$ radicals (Escobedo Salas, Serrano Rosales, and de Lasa 2013; Akihiko Kudo and Miseki 2009), can be calculated using equation (8-6) as,
Therefore, the 0.77 represents the fraction of two consecutive photons of energy used to form OH’ and H’ groups achieving the photocatalytic water splitting with hydrogen production in the PCW-II reactor.

### 8.1.2.2 Evaluation of the PTEF at Different pH Conditions

PTEFs can be calculated assuming that the produced H’ and OH’ radicals are the ones leading to both the hydrogen production and ethanol conversion. These PTEFs values are evaluated in this section at different pHs using equations (8-4) and (8-6).

As a result a maximum PTEF can be calculated using the Theoretical Quantum Yield ($\bar{\varphi}_{\text{theor}}$) reported in Table 16 and the $\eta_{[H' + OH']} \times 324$ determined with equation (8-5). Thus, a $PTEF_{\text{max}}$ of 0.6 can be calculated using equations (8-6) as follows,

$$ PTEF_{\text{max}} = 0.78 \times 0.77 = 0.6 $$

Thus, the highest possible PTEF for the ideal condition is 0.6. This means that 60% of the energy absorbed by the photocatalyst is employed in the simultaneous oxidation-reduction process for hydrogen generation. Moreover, it can also be noticed that in agreement with thermodynamic requirements, the $PTEF_{\text{max}}$ as reported above, remains below 1 ($PTEF_{\text{max}} \leq 1$) (Garcia 2012; de Lasas, Salaices, and Serrano 2005).

### 8.1.2.2.1 Effect of Basic pH on the PTEF

Figure 55 reports the PTEFs values using experimental data. One can see that for a basic pH (pH=10), the PTEFs remain in a relatively low range below 0.046.
Figure 55: $PTEF$ and $PTEF_{max}$ for photocatalytic hydrogen production using different photocatalyst-platinum loadings, basic or pH=10 and ethanol as sacrificial reagent.

8.1.2.2.2 Effect of Neutral pH on the $PTEF$

Figure 56 shows the $PTEF$ data for neutral pH or a pH=7. $PTEF$s in this case also remain in a low range below 0.04.
Finally, Figure 57 reports the PTEF at an acid pH or pH=4. In this case, one can notice higher and steadier PTEFs values achieved after 30 minutes of irradiation. In the case of the 1 wt% Pt on TiO$_2$, these PTEFs remain in the 6% level when the photocatalyst is exposed to more than 5.5 hours of irradiation.

One should notice that the 6% PTEF is equivalent to 10% of the maximum PTEF calculated as described in Section 8.1.2. This smaller experimental PTEF versus the maximum value as calculated using thermodynamics is an expected outcome for hydrogen production. This is true given the relatively low probability that two near-UV photons reach simultaneously or quasi-simultaneously a photocatalyst surface site.
Figure 57: PTEF and $PTEF_{\text{max}}$ for photocatalytic hydrogen production using different photocatalyst-platinum loadings, acid or pH=4 and ethanol as sacrificial reagent

8.2 Conclusions

From the data and efficiency values reported in this chapter the following can be concluded:

a) QY and $PTEF$s are calculated to determine the energy efficiencies inside the PCW-II reactor for hydrogen production via water splitting and utilizing different pHs.

b) QYs are established at various irradiation times during the photocatalytic hydrogen production. QY at acid conditions using a 1 wt% Pt-TiO$_2$ a photocatalyst yielded a highest value of 8% or 0.8.

c) A $PTEF_{\text{max}}$ of 0.6 or 60% was calculated based on the theoretical analysis. Best experimentally observed PTEF values were close 10% of this maximum value.

d) A $PTEF$ parameter for hydrogen production is reported. This $PTEF$ involves the fraction of photon energy used for H$^-$ and OH$^-$ radical groups formation. The
obtained results are consistent with two photons interacting simultaneously or quasi-simultaneously with the photocatalyst surface sites.

e) The QYs and PTEFs reported show good energy utilization level for hydrogen production. This is an excellent PCW-II Reactor feature, the result of uniform irradiation, important platinum on DP25 loading and intimate photocatalyst and ethanol-water solution contact.
Chapter 9
Conclusions and Recommendations

9 Introduction
Main findings and contributions of this PhD dissertation are described in the present chapter. In addition, recommendations and suggestions for future work in the area of photocatalytic hydrogen production are also reported.

9.1 Main Conclusions and Contributions

A) An Efficient Upgraded PCW-II Reactor for Hydrogen Production. The new Photo-CREC Water II Reactor was implemented with a self-driven mixing stirrer and a well mixed hydrogen storage tank. This essential addition is shown to provide a suitable manner to collect and mix both gases and slurry solutions. This hydrogen storage tank allows the sampling of both of gas/liquid phases as well as the measuring of pH and temperature during the photocatalytic hydrogen production.

B) Analytical Methods: Gas-Chromatography (GC) and High Performance Liquid Chromatography (HPLC). These analytical techniques were optimized and implemented to identify and quantify species during the photocatalytic hydrogen production using ethanol as an organic scavenger, various chemical species such as ethanol, acetaldehyde, acetic acid, CH$_4$, C$_2$H$_6$ and CO$_2$.

C) Synthesis and Characterization of a Photocatalyst for Hydrogen Production. A novel photocatalyst of DP25-Pt was prepared for hydrogen production. The synthesis of the photocatalysts was developed using the incipient wetness impregnation. Photocatalyst characterization was carried out using XRD, XRF, BET, PSD, SEM, EDX, and DRS in order to establish its physical and chemical properties.

D) Macroscopic Irradiation Balances. Development of a Macroscopic Energy Balance involved a calibration of the BLB UV-Lamp with the determination of radial and axial radiation distribution. Furthermore, LVREA and MREB were
determined to find the desired loading of DP25-Pt per liter in the slurry solution to secure 95% radiation absorption.

E) **Hydrogen Production using a Modified DP25-Pt Photocatalyst.** It was found that DP25-1 wt% Pt under acid conditions produces hydrogen steadily during the 6 hours of irradiation. It was found that methane and ethane together with carbon dioxide were useful reaction co-products.

F) **In Series-Parallel Reaction Network and Langmuir-Hinshelwood Kinetics for the Organic Scavenger Consumption.** A reaction network was proposed for photocatalytic hydrogen production. Furthermore, the role of ethanol adsorption onto DP25-Pt and the Langmuir-Hinshelwood kinetics were considered. Kinetic parameters were determined with a 235 degree of freedom, small 95% confidence intervals, a low cross-correlation, low residuals and a high correlation coefficient $R^2$ of 0.9977. The determined kinetic parameters allowed predicting carbon containing intermediates and end products formed during the photocatalytic hydrogen production.

G) **Kinetic Modeling for Hydrogen Production.** Regarding the hydrogen production rate, an additive “in parallel model” was proposed to account for both “direct” hydrogen formation and “scavenger assisted” hydrogen formation. It appears that both mechanisms play an important role in the overall process of hydrogen production using the DP25-Pt photocatalyst.

H) **Energy Efficiency Factors.** Energy efficiencies were calculated for the photocatalytic hydrogen production in PCW-II reactor. It was proven that results obtained provide a fair approach for a future reactor scale up of the PCW-II reactor unit.

### 9.2 Future Work Recommendations

I) **Light Source.** It is proposed to study the effect of changes of irradiation on photocatalytic hydrogen generation. It is also suggested to equip the PCW-II with lamps with significant emission in the visible range.

II) **Photocatalyst Development.** It is recommended to impregnate DP25 with other suitable metal ions such as Ni, Pd, Co, Rh, Cu, Ag, or Au with high photo activity
in the visible range. This will allow the demonstration of the applicability of the PCW-II reactor powered with solar energy for the production of hydrogen.

III) Analysis of Species. It is suggested to measure the presence of \( \text{H}_2\text{O}_2 \) in the slurry solution for better understanding to the proposed “in series-parallel” kinetic reaction network.
References


Kim, Hong Rok, Jayeeta Chattopadhyay, Jae Ik Son, and Daewon Pak. 2008. “Preparation of Platinum-doped Hollow Spheres and Their Electrocatalytic Activity


Appendices

Appendix A: Calculation of the Percentage of Desired Reagent into the TiO$_2$ Support

A solution of chloroplatinic acid mono-hydrate (H$_2$PtCl$_6$ xH$_2$O) was prepared. The reagent of chloroplatinic acid in granulate shape was dissolved in water. 0.4 ml of water was used for every gram of TiO$_2$ support. The amount of reagent added into both the solution and the TiO$_2$ support was determined by the following formula:

$$m_R = \frac{m_m}{X_M} = \frac{(%M \times m_s)}{X_M(100 - %M)} * (RP) * (SF)$$

$$X_M = \frac{MW_M}{MW_R} \quad \text{and} \quad SF = \frac{(100 + EE)\%}{100\%}$$

Where:

$m_R$= mass of reagent (H$_2$PtCl$_6$ xH$_2$O) (g)

$m_m$= mass of metal (Pt) (g)

$m_s$= mass of support (TiO$_2$) (g)

$X_M$= fraction mol of metal (Pt)

$%M$= Metal loading percentage desired

$MW_M$= Molecular Weight of metal (Pt) (mol/g)

$MW_R$= Molecular Weight of reagent (H$_2$PtCl$_6$ xH$_2$O) (mol/g)

$RP$= Reagent Purity

$SF$= Safety Factor

$EE$= Experimental Error (most common 5%)
Appendix B: Detection of H₂ by a Shimadzu GC 2010

A gas chromatographer unit (Shimadzu 2010) was employed as analytical technique to determine the photocatalytic hydrogen generated. In this study, an analytical method to separate hydrogen (H₂) and air (N₂ and O₂) from an argon (Ar) mixture was developed. Furthermore, retention times and corresponding areas of different species were quantified to determine their corresponding concentrations (see Figure 58). The Shimadzu GC 2010 is equipped with a TCD (Thermal Conductivity Detector) and a FID (Flame ionization detector). The GC detectors are connected in series, respectively. Also, the GC is equipped with a Grace Hayesep D pack column 100/120 mesh of 9.1m x 2mm x 2μm nominal SS.

The target analyte for quantification was hydrogen (H₂). Thus, Argon (Ar) gas was used as carrier gas due to its thermal conductivity and its analytical sensibility. The analysis of this chemical specie took place employing a programmed temperature method. On this basis, one can achieve the best separation for hydrogen (H₂), nitrogen and oxygen (Air). The GC method utilized for this analysis can be described as follows:

1. Injection Port (programmed temperature)

<table>
<thead>
<tr>
<th>Temperature: 200°C</th>
<th>Rate</th>
<th>Flow</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Injection Mode: Direct</td>
<td>0</td>
<td>------</td>
<td>8</td>
</tr>
<tr>
<td>Carrier Gas: Argon</td>
<td>1</td>
<td>120</td>
<td>31</td>
</tr>
<tr>
<td>Flow Control Mode: Flow</td>
<td></td>
<td></td>
<td>Total Flow: 8</td>
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<tr>
<td>Total Flow: 8</td>
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<td></td>
<td>Total time</td>
</tr>
<tr>
<td>Purge Flow: 0</td>
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2. GC Packed Column (programmed temperature)

<table>
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<th>Rate</th>
<th>Flow</th>
<th>Hold time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Equilibrium time: 0.2</td>
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<td>30</td>
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<tr>
<td>Carrier Gas: Argon</td>
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<td>250</td>
<td>210</td>
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<td></td>
<td></td>
<td></td>
<td>Total time</td>
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</table>

3. TCD

<table>
<thead>
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<th>Temperature: 210°C</th>
<th>Current: 15 mA</th>
<th>Make up gas: Argon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample rate: 40</td>
<td>Polarity: (●) Negative</td>
<td>Make up flow: 6 ml/min</td>
</tr>
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</table>
Figure 58: Retention times and corresponding areas of different species: a) Hydrogen, b) Nitrogen and c) Oxygen

The calibration curves of H₂, N₂ and O₂ that correlates the concentrations with the TCD response are quantified by using: a) Hydrogen certified standard gas mixture (10% H₂ and 90% He Praxair), b) Nitrogen grade 5.0 (99.999% Azote Praxair) and c) Oxygen grade 4.3 (99.993% Praxair). The gas samples were taken at different known volumes, hydrogen (0.8, 0.5, 0.2 and 0.1 ml), N₂ and O₂ (0.8, 0.5 and 0.2 ml) respectively (see Figure 59). The different sample volumes taken then were injected into the GC at room temperature and pressure conditions (25°C and 1 atm).

Figure 59: Calibration Curves at the Shimadzu 2010 for different components: a) Hydrogen, b) Nitrogen and c) Oxygen
Appendix C: Detection of CO₂, CH₄ and C₂H₆ by a Shimadzu GC 2014

A GC Analysis was made to identify the intermediates of CO₂, CH₄ and C₂H₆ during the photocatalytic hydrogen production (see Figure 60). In this study, a programmed separation method was created to determine the retention times and corresponding areas of CO₂, CH₄, and C₂H₆. These byproduct gases were quantified to calculate their concentration. The byproduct gases were found in a mix of Hydrogen (H₂), Air (N₂ and O₂) and Helium (He). The Shimadzu GC 2014 was equipped with two detectors a TCD (Thermal Conductivity Detector) and a FID (Flame ionization detector) and both connected in series. Also, the GC employed an Altech porapak Q pack column 80/100 mesh of 1.83 x 3.175mm x 21.59mm nominal SS for the analysis of the byproducts.

The target analyte for quantification were the byproducts generated from the photocatalytic reaction. Helium (He) was used as carried gas due to its analytical sensibility. The analysis of these chemical species was performed using a programmed temperature method to achieve a fair separation of the identify species. The programmed GC method can be described as follows:

1. Injection Port or DING

<table>
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<tr>
<th>Temperature: 200°C</th>
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</tr>
</thead>
<tbody>
<tr>
<td>Injection Mode: Direct</td>
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</tbody>
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2. GC Packed Column (programmed temperature)

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<th>Rate</th>
<th>Temp</th>
<th>Hold time (min)</th>
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<tr>
<td>Equilibrium time: 0.2</td>
<td>1</td>
<td>------</td>
<td>75</td>
</tr>
<tr>
<td>Carrier Gas: Helium</td>
<td>2</td>
<td>55</td>
<td>150</td>
</tr>
<tr>
<td>Eq. time: 0.1</td>
<td>3</td>
<td>20</td>
<td>185</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Total time</td>
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</tbody>
</table>

3. TCD

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<th>Temperature: 125°C</th>
<th>Current: 70 mA</th>
<th>Make up gas: Helium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample rate: 40 msec</td>
<td>Polarity: (●) Positive</td>
<td></td>
</tr>
</tbody>
</table>

4. DFID

<table>
<thead>
<tr>
<th>Temperature: 125°C</th>
<th>Sample rate: 40 msec</th>
<th>Make up gas: Helium</th>
</tr>
</thead>
</table>

5. Methanizer

| Temperature: 380°C | | |
|-------------------| | |
It was correlated the concentration of different chemical species with their respective FID response. Thus, a calibration curve for CH$_4$, CO$_2$, C$_2$H$_6$, CH$_2$O, C$_2$H$_4$O and C$_2$H$_5$OH was performed. The calibrations were prepared using the following pure reactants: 1) CH$_4$ certified standard CP 2 (99.9% Praxair), 2) CO$_2$ grade Instrument 4.0 (99.9% Praxair), 3) C$_2$H$_6$ grade UHP 17 (Air Liquid), 4) CH$_2$O Liquid Reagent (36.5% Sigma-Aldrich), 5) C$_2$H$_4$O Liquid Reagent Plus (99% Sigma-Aldrich) and 6) C$_2$H$_5$OH Anhydrous Ethyl Alcohol grade USP (Commercial alcohols).

The gas and liquid samples were taken at different known volumes. Gas samples of CH$_4$, CO$_2$ and C$_2$H$_6$ (0.8, 0.5, 0.3, 0.2 and 0.1 ml), and Liquid samples of CH$_2$O, C$_2$H$_4$O and C$_2$H$_5$OH (0.0008, 0.0005, 0.0003, 0.0002 and 0.0001 ml) were injected, respectively (see Figure 61 and Figure 62). The GC samples were analyzed at room temperature and pressure conditions (25°C and 1 atm).
Figure 61: Calibration curves at the Shimadzu 2014 for different components: 1) Methane, 2) Carbon Dioxide and 3) Ethane

Figure 62: Calibration curves at the Shimadzu 2014 for different components: 4) Formaldehyde, 5) Acetaldehyde and 6) Ethanol
Appendix D: Detection of CH$_3$OOH and C$_2$H$_5$OH by a Shimadzu HPLC

The UFLC-Shimadzu HPLC with a Supelcogel C-610H column of 30cm x 7.8mm ID was employed to separate both the carboxylic acids and alcohols in water (see Figure 63). In addition, a UV (LC-20AB) and a RID-10A, detectors were utilized to analyze and quantify chemical species at various irradiation times. This was accomplished with the intent of tracking the formation of acetic acid, and the ethanol degradation during the photocatalytic hydrogen production.

The analysis for tracking chemical species was established developing a programmed method. This method employed two in series-connected detectors (UV and RID). As a result of that, one can achieve the best peak separation for the analyzed species. The method can be described as follows:

1. UV and RI detectors
   Column: Supelcogel C-610H, 30cm x 7.8mm ID
   Mobile phase: 0.1% H$_3$PO$_4$ (HPLC grade), low pH for best analysis performance
   Column Temperature: 30°C
   Flow rate: 0.7 ml/min
   Injection of sample: 10 µL

---

Figure 63: Retention times and corresponding areas of different species: 1) Acetic Acid and 2) Ethanol
The calibration curves of CH$_3$COOH and C$_2$H$_5$OH are correlated to the concentration and detector response (UV (LC-20AB) and a RID-10A). The data obtained to determine the calibrations for the chemical species, employed the following pure reactants: 1) CH$_3$COOH Glacial (99.7% Caledon Chemicals) and 2) C$_2$H$_5$OH Anhydrous Ethyl Alcohol grade USP (Commercial alcohols). Liquid samples were taken at different known concentrations as follows: a) CH$_3$COOH (0.00109, 0.00437, 0.00875, 0.0175 and 0.035) mol/l and b) C$_2$H$_5$OH (0.513, 0.256, 0.128, 0.064 and 0.032) mol/l. Figure 64 represents the calibration curves for each chemical species.

**Figure 64: Calibration curves at the Shimadzu HPLC for different components: 1) Acetic Acid and 2) Ethanol**
Appendix E: Calculation of the Theoretical Quantum Yield for the Photocatalytic Hydrogen Production

A reaction mechanism can be established based on the photocatalytic reaction steps as adapted for hydrogen production, a detailed reaction mechanism steps are in Section 6.4 of this dissertation.

The theoretical quantum yields for hydrogen production are determined from the reaction steps presented in Figure 35 as follows,

**Protons Conversion into Hydrogen**

\[ 1h\nu + H^+ \xrightarrow{TlO_2-Pt} H^+ \xrightarrow{TlO_2-Pt} 1/2H_2(g) \]  

(E-1)

Thus, one can conclude that 1 photon is required to produce half of \( H_2 \) molecule or one \( H^\prime \) radical. As a result, the maximum theoretical quantum efficiency based on the \( H^\prime \) formed is 1 as follows:

\[ Q_{theor} = \frac{\text{moles of } H^\prime}{\text{moles of photons}} = 1 \]  

(E-2)

**Ethanol Conversion into Acetaldehyde**

\[ 2h\nu + C_2H_5OH_{(l)} \xrightarrow{TlO_2-Pt} H_2(g) + C_2H_4O_{(ads)} \]  

(E-3)

Thus, one can conclude that 2 photons are required to produce one \( H_2 \) molecule or two \( H^\prime \) radicals. As a result, the maximum theoretical quantum efficiency based on the \( H^\prime \) formed is 1 as follows:

\[ Q_{theor} = \frac{\text{moles of } H^\prime}{\text{moles of photons}} = 1 \]  

(E-4)

**Acetaldehyde Conversion into Acetic Acid**

\[ 2h\nu + C_2H_4O_{(ads)} + H_2O_{(l)} \xrightarrow{TlO_2-Pt} H_2(g) + C_2H_3OOH_{(ads)} \]  

(E-5)
Thus, one can conclude that 2 photons are required to produce one H₂ molecule or 2 H⁺ radicals. As a result, the maximum theoretical quantum efficiency based on the H⁺ formed is 1 as follows:

\[ \varphi_{\text{theor}} = \frac{\text{moles of } H^+}{\text{moles of Photons}} = 1 \] (E-6)

**Ethanol Conversion into Acetic Acid**

\[ 4h\nu + C_2H_5OH(l) + H_2O(l) \xrightarrow{TiO_2-Pt} 2H_2(g) + C_2H_3OOH \] (E-7)

Thus, one can conclude that for the formation of two H₂ molecules requires four photons. As a result, the theoretical quantum efficiency for this step based on the H⁺ formed is 1 as follows:

\[ \varphi_{\text{theor}} = \frac{\text{moles of } H^+}{\text{moles of Photons}} = 1 \] (E-8)

**Acetic Acid Conversion into Methane and Carbon Dioxide**

\[ h\nu + C_2H_3OOH_{(ads)} \xrightarrow{TiO_2-Pt} CH_4(g) + CO_2(g) \] (E-9)

Thus, one can conclude that the photons required do not lead to H₂ formation. As a result, the theoretical quantum efficiency for this step based on the H⁺ formed is 0 as follows:

\[ \varphi_{\text{theor}} = \frac{\text{moles of } H^+}{\text{moles of Photons}} = 0 \] (E-10)

**Acetic Acid Conversion into Ethane and Carbon Dioxide**

\[ 2h\nu + 2C_2H_3OOH_{(ads)} \xrightarrow{TiO_2-Pt} H_2(g) + C_2H_6(g) + 2CO_2(g) \] (E-11)

Thus, one can conclude that 2 photons are required to produce one H₂ molecule or 2 H⁺ radicals. As a result, the theoretical quantum efficiency for this step based on the H⁺ formed is 1 as follows:
\[ \Phi_{\text{theor}} = \frac{\text{moles of } H^\ast}{\text{moles of photons}} = 1 \]  

(E.12)

viii. Total mineralization of Ethanol, Acetaldehyde and Acetic Acid

\[ 5h\nu + C_2H_5OH(l) + H_2O(l) \xrightarrow{T\text{io}_2-Pt} 2H_2(g) + CH_4(g) + CO_2(g) \]  

(E.13)

Thus, one can conclude that for the formation of two H\textsubscript{2} requires 5 photons. As a result, the theoretical quantum efficiency for this step, based in the H\textsuperscript{•} formed, is 0.8 as follows:

\[ \Phi_{\text{theor}} = \frac{\text{moles of } H^\ast}{\text{moles of photons}} = 0.8 \]  

(E.14)

The overall reaction is assuming total mineralization of acetaldehyde. This leads us to the overall stoichiometric expression as follows:

\[ 3h\nu + C_2H_4O(g) + H_2O(l) \xrightarrow{T\text{io}_2-Pt} H_2(g) + CH_4(g) + CO_2(g) \]  

(E.15)

Thus, one can conclude that for the formation of two H\textsubscript{2} molecules requires three photons. As a result, the theoretical quantum efficiency for this step based on the H\textsuperscript{•} formed, is 1 as follows:

\[ \Phi_{\text{theor}} = \frac{\text{moles of } H^\ast}{\text{moles of photons}} = 0.666 \]  

(E.16)
Appendix F: Calculation of the Average Emitted Photon Energy ($E_{av}$)

Using a spectro photo-radiometer a light spectrum was determined for a BLB UV Lamp. As a result of that, one can calculate the fraction of photons (1 Einstein) emitted by the near UV lamp. These photons generate one mol of free radicals of OH’ and H’.

The average emitted photon energy ($E_{av}$) can be calculated, once the irradiation spectrum is defined for the following relationship (Benito Serrano et al. 2009),

$$E_{av} = \frac{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda) E(\lambda) d\lambda}{\int_{\lambda_{min}}^{\lambda_{max}} I(\lambda) d\lambda}$$  \hspace{1cm} (F.1)

In the case of spectra under consideration, the numerical integration of eq. (F.1) is restricted to the $\lambda_{max}$=410 nm upper wavelength. Photons with larger wavelengths do not have enough energy to supersede the TiO$_2$ band gap and as a result to contribute to the photocatalytic transformation. Considering $E(\lambda) = hc/\lambda$.

$$E_{av} = \frac{hc \int_{\lambda_{min}=310 \text{ nm}}^{\lambda_{max}=410 \text{ nm}} I(\lambda) \frac{d\lambda}{\lambda}}{\int_{\lambda_{min}=310 \text{ nm}}^{\lambda_{max}=410 \text{ nm}} I(\lambda) d\lambda}$$

Thus,

$$E_{av} = \left( \frac{6.63 \times 10^{-34} \text{ Js}}{3.69 \times 10^{-7} \text{ m}} \right) \left( 3 \times 10^8 \text{ m/s} \right) = 5.38 \times 10^{-19} \frac{J}{\text{photon}}$$

$$E_{av} = \left( 5.38 \times 10^{-19} \frac{J}{\text{photon}} \right) \left( 6.023 \times 10^{23} \frac{\text{photon}}{\text{mol photon}} \right) = 324.1 \frac{KJ}{\text{mol photon}}$$

Thus,

$$E_{av} = 324.1 \frac{KJ}{\text{mol photon}}$$
Curriculum Vitae

Name
Salvador Escobedo Salas

Post-secondary Education and Degrees

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Honours and Awards

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<tr>
<td>Faculty of Graduate Studies Doctoral full time Scholarship</td>
<td>2008-2013</td>
</tr>
<tr>
<td>Western University</td>
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<tr>
<td>Recipient of the best Poster design and presentation (1st Place)</td>
<td>2013</td>
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<tr>
<td>NASCRE-3, Houston, Texas, USA</td>
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<tr>
<td>Two times recipient of the Graduate Thesis Research Award</td>
<td>2012 &amp; 2013</td>
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<tr>
<td>Western University and the Chemical and Biochemical Engineering department</td>
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</tr>
<tr>
<td>2nd Place Award Oral Presentation</td>
<td>2012</td>
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<tr>
<td>3rd Research Bridges Western University Symposium, Sarnia, Ontario.</td>
<td></td>
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<tr>
<td>Nominated for the Teaching Assistant Award</td>
<td>2010</td>
</tr>
<tr>
<td>Western University in the Physical Science division</td>
<td></td>
</tr>
<tr>
<td>Dean’s Honour List with a GPA of 91/100. BESc in Chemical Engineering</td>
<td>2006</td>
</tr>
<tr>
<td>Universidad Autonoma de Zacatecas, Mexico</td>
<td></td>
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Related Work Experience

<table>
<thead>
<tr>
<th>Position</th>
<th>Years</th>
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<tr>
<td>Teaching Assistant</td>
<td>2008-2012</td>
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<tr>
<td>Western University</td>
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<tr>
<td>Research Assistant</td>
<td>2008-2013</td>
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<tr>
<td>Western University</td>
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Publications

✓ Refereed publications:


✓ Refereed Proceedings:

a) Oral Presentations


b) Poster Presentations

